

2011

## Polyphosphate-Based Industrial Cooling Water Treatment

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POLYPHOSPHATE-BASED INDUSTRIAL  
COOLING WATER TREATMENT

BY

GEORGE THOMAS FARLEY

A DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT OF  
THE  
REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN

CHEMISTRY

UNIVERSITY OF RHODE ISLAND

2011

DOCTOR OF PHILOSOPHY  
OF  
GEORGE THOMAS FARLEY

APPROVED:

Thesis Committee:

Major Professor      William B. Euler

Brett Lucht

David R. Worthen

Brenton DeBoef

Nasser H. Zawia  
DEAN OF THE GRADUATE SCHOOL

## ABSTRACT

Condensed phosphates were first used in cooling water applications in the early 1930's. Extensive use was found for these polyphosphates because of their ability to control calcium carbonate scaling at threshold or substoichiometric dosages. Later, their ability to control the corrosion of steel in open recirculating cooling water systems and once through cooling water systems demonstrated the versatility of this class of compounds.

The use of polyphosphates began to give way to the acid chromate programs as the primary corrosion inhibitor for mild steel in open recirculating systems in the early 1960's. This preference for chromate and chromate-zinc programs was still quite prevalent in the early 1970's. The cause for this change stems from the one major disadvantage of polyphosphate treatments -hydrolytic instability which produces orthophosphate. The orthophosphate anion forms insoluble scales with all bivalent cations, the most important of which are calcium, magnesium and iron. These scales can foul heat transfer surfaces and reduce dramatically heat transfer efficiency of process heat exchangers. In addition to providing fouling problems, the orthophosphate anion fails to provide the positive effects of condensed phosphates. Orthophosphate does not show a threshold effect and is not as effective in corrosion prevention of steel as condensed phosphates.

The Clean Water Act of 1972 began a level of environmental awareness that was not seen before. One of the outcalls of this movement was the identification of hexavalent chromium (chromates) as toxic to aquatic life because of its low LD50. Chromates were also identified as potential carcinogens. Efforts to remove the chromate ion from cooling tower blowdown were hampered by the need to label any sludge from the waste treatment facility as hazardous. The need for a non chromate cooling water treatment that could provide the same or better performance as the acid-chromate-zinc treatments became a top priority for industry.

This dissertation in the form of US Patent 4,172,032 describes the development of such a cooling water treatment. It also describes the discovery of an optimum molecular weight of polyphosphate as the most critical factor in determining the performance of these programs.

The synthesis of spiro(4,4) nonanes was done in the period of 1966 to 1970. This work was completed but not defended before a Dissertation Defense Committee. It is included in Appendix A of this document in the interest of completeness

## ACKNOWLEDGEMENTS

I would like to acknowledge the faculty and staff of the University of Rhode Island 1962-1970. The knowledge and training from the educational process provided the template from which a career in industrial chemistry was born.

I would like to acknowledge the administration and staff of the University of Rhode Island 2011. The opportunity to finish the degree by defending the dissertation was provided by University President Dr. Dooley, University Provost Dr De Hayes, Graduate School Dean Dr Zawia, and Chemistry Department Chairman, Dr William Euler.

I would like to acknowledge my family and friends all of whom have provided personal support. The encouragement of Cheryl Marcum and Shawn Coyle will always be with me.

## PREFACE

The preface was written by Dr Nasser Zawia, Dean of the Graduate School.

George Farley completed his BS (1966) and MS (1971) at URI. He was then admitted to the PhD program in Chemistry and has taken all the courses required for the PhD degree in Chemistry. He has also completed the following PhD examinations: Language Exam (April 1968), Qualifying Exam (September 1968), Written Comprehensive Exam (May 1969), Oral Comprehensive (June 1969).

George also completed all the research required for his dissertation and submitted a defensible copy to the Graduate School. His Major Advisor at that time was Scott McKenzie, and Professors Clair Cheer and Charles Olney served on his committee.

In summary, George had completed all the requirements for the PhD in Chemistry except defending his dissertation because he had to abruptly leave for personal reasons.

In 2010, George Farley approached President David Dooley to see if it is possible for him to obtain his doctoral degree. President Dooley wrote the Chemistry Department to evaluate his materials. The Chair of Chemistry, Bill Euler, wrote

back confirming the above; however, Professor Euler found the draft of the dissertation harder to evaluate based on today's standards.

The matter was referred to Provost DeHayes who then consulted with the Dean of the Graduate School, Nasser Zawia. Following discussions with the Graduate School and the Department of Chemistry, the Provost wrote Mr. Farley to explain what needed to be done. The Provost requested the following:

1. Satisfactorily complete your dissertation with particular attention to enhancing the results, discussion and conclusion.
2. Make a presentation of your work and defend it to a committee of three Chemistry faculty and two external members to be appointed by the Graduate School.
3. Submit a brief written supplement, as part of your presentation, on related professional work in which you have been engaged since you left URI. This would include a summary of that work and its relevance and impact to the broad field of chemistry.
4. Enroll in any credits needed (e.g. dissertation credits) to satisfy Graduate School policy and degree requirements. Any requirement related to the need to have been a continuing registrant in the program would be waived.



A Committee of five was set up as specified above: Bill Euler (Major Professor), Brett Lucht (Chemistry), Professor Brenton DeBoef (Chemistry), Professor David Worthen (Pharmacy), The Dean of the Graduate School acted as defense Chair. The Committee then examined the requirements of the Provost and concurred with all except item 1. The Committee felt that since they did not supervise the dissertation work, and given the period of time that has passed, it would not be appropriate for them to sign on the Dissertation page. The Committee instead asked Mr. Farley to present and defend his patent work on the treatment of water to remove corrosion. Mr. Farley had developed a formula, which is in use as an industry standard for over twenty years.

On August 9, 2011, Mr. Farley successfully defended his patent work. The Committee was highly impressed by Mr. Farley and had no question that he was PhD caliber and that his patented and published work accounted for a dissertation. The Committee unanimously voted that Mr. Farley passed his oral defense satisfactorily and recommended that his past dissertation, patent and published work, and the supplemental material he had provided be accepted in lieu of a PhD dissertation.

This dissertation is written in Manuscript Format.

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Manuscript 1:

United States Patent Number 4,172,032, awarded October 23, 1979

United States Patent [19]

[11] 4,172,032

Farley

Best Available Copy

[45]

Oct. 23, 1979

[54] POLYPHOSPHATE-BASED INDUSTRIAL COOLING WATER TREATMENT

[56]

References Cited

U.S. PATENT DOCUMENTS

[75] Inventor: George T. Farley, Downers Grove, Ill.

2,742,369	4/1956	Hatch	252/391
2,941,953	6/1960	Hatch	252/389 R
3,130,152	4/1964	Fuchs	252/175
3,338,670	8/1967	Fuchs	252/175
3,728,420	4/1973	Stanford	252/89
3,751,372	8/1973	Zecher	252/181
3,873,465	3/1975	Di Simone	252/181

[73] Assignee: Nalco Chemical Company, Oak Brook, Ill.

[21] Appl. No.: 864,119

Primary Examiner—Dennis L. Albrecht

[22] Filed: Dec. 23, 1977

Attorney, Agent, or Firm—John G. Premo; Robert A. Miller

Related U.S. Application Data

[57]

ABSTRACT

[63] Continuation of Ser. No. 732,569, Oct. 15, 1976, abandoned.

When a specific condensed phosphate glass is combined with an organic phosphate ester, an improved composition is afforded for preventing scale and corrosion in industrial cooling systems. Optionally, certain azoles are combined with the phosphate glass and phosphate ester to afford corrosion protection to non-ferrous metals.

[51] Int. Cl.<sup>2</sup> ..... C02B 5/04; C02B 5/06; C23F 11/12; C23F 11/18

[52] U.S. Cl. .... 210/58; 210/57; 252/181; 252/389 A; 252/391; 422/13

[58] Field of Search ..... 252/89, 175, 181, 389 R, 252/391, 389 A; 210/55, 57, 58; 422/13

4 Claims, No Drawings

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## POLYPHOSPHATE-BASED INDUSTRIAL COOLING WATER TREATMENT

This is a continuation of application Ser. No. 732,569  
filed on Oct. 15, 1976 which is now abandoned.

### INTRODUCTION

Condensed phosphates were first used in cooling water applications in the early 1930's. Extensive use was found for these polyphosphates because of their ability to control calcium carbonate scaling at threshold or substoichiometric dosages. Later, their ability to control the corrosion of steel in open recirculating cooling water systems and once through cooling water systems demonstrated the versatility of this class of compounds.

The use of polyphosphates began to give way to the acidchromate programs as the primary corrosion inhibitor for mild steel in open recirculating systems in the early 1960's. This preference for chromate and chromate-zinc programs is still quite prevalent today. The cause for this change stems from the one major disadvantage of polyphosphate treatments—hydrolytic instability which produces orthophosphate. The orthophosphate anion forms insoluble scales with all bivalent cations, the most important of which are calcium, magnesium and iron. These scales can foul heat transfer surfaces and reduce dramatically heat transfer efficiency of process heat exchangers. In addition to providing fouling problems, the orthophosphate anion fails to provide the positive effects of condensed phosphates. Orthophosphate does not show a threshold effect<sup>1</sup> nor is it as effective in corrosion prevention of steel as condensed phosphates.

<sup>1</sup>K. F. Reilein and T. F. Bushner, J. Phys. Chem., 44 (1940) 535.

Condensed phosphates will revert to orthophosphate when dissolved in aqueous media. The kinetics of reversion may vary widely but the most important factors in determining the rate of orthophosphate production are temperature, pH, and the choice of condensed phosphate species. Control of mild steel corrosion by a cooling water treatment program based on condensed phosphate is wholly dependent on the level of performance of the particular condensed phosphate itself and the factors which affect the rate of its reversion to orthophosphate.

It is customary in the treatment of industrial cooling waters to combine inorganic polyphosphates with other materials to prevent scale and to aid in the prevention of corrosion of non-ferrous metals such as copper and copper alloys.

Useful scale inhibitors for treating industrial cooling waters are the phosphated esters of certain polyols which are described in U.S. Pat. No. 3,728,420.

In addition to using these scale inhibitors, it is often-times common to combine with the polyphosphates certain heterocyclic nitrogen compounds such as certain azoles which prevent corrosion of copper and copper alloys such as admiralty metal.

A typical prior art scale inhibitor that has been used in treating industrial cooling systems such as cooling tower waters and which is hereinafter referred to as Composition 2 has the following formula:

Composition 2	
Ingredients	% by Weight
Phosphated-Ethoxylated	

-continued

Composition 2	
Ingredients	% by Weight
Glycerine <sup>1</sup>	11.3
Benzotriazole	2.0
Potassium Pyrophosphate	21.7
Alkali, Water, Alcohol	Balance

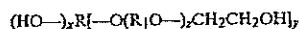
<sup>1</sup>See Example 1, U.S. 3,728,420, for general mode of preparation and Composition.

In conducting laboratory studies with this material, several conclusions were reached based upon experimental data. When this material is used to treat low hardness waters, e.g. less than 70 ppm, as calcium carbonate, the corrosion rate tends to be excessive. It was further observed that when the calcium hardness, basin temperature and holding time indexes were increased, there was an inordinate increase in deposit and scale formation. This is particularly true when the temperature of the water was in excess of 110° F. and the calcium hardness was maintained at about 250 ppm. It has also been observed and based on prior known data that conventional polyphosphates, when the extreme conditions mentioned above are employed at alkaline conditions, e.g. pH 8-9, that their reversion to orthophosphate is extremely rapid, thus rendering their use as a corrosion inhibitor quite limited as well as tending to increase the scaling tendency of the system.

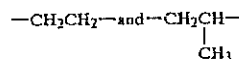
Based on the above, it would, therefore, be of benefit to the art if it were possible to provide an improved scale and corrosion inhibitor for industrial cooling waters which contained an inorganic polyphosphate in combination with other scale and corrosion inhibitors which could operate effectively under conditions of elevated temperature, high calcium hardness, and at a pH within the range of 8-9, to effectively prevent scale and corrosion.

### THE INVENTION

The invention provides a composition for preventing scale and corrosion in industrial cooling water systems which comprises (I) a water soluble alkali metal condensed phosphate glass which has an average molecular weight of about 2160 and a PO<sub>4</sub> content of 92.4% by weight, and (II) a phosphate ester of a polyol of the formula:



wherein R is a saturated, hydrocarbon radical having two to six carbon atoms, R<sub>1</sub> is a member selected from the group consisting of:



x is a number average in the range of 0-5, inclusive, y is a number average in the range of 1-6, inclusive, and the sum of x plus y equals 2-6, and z is a number average in the range of 0-30, inclusive, with the weight ratio of I:II being within the range of 1:4 to 4:1.

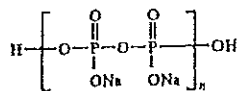
In a preferred embodiment of the invention, the ratio of I:II is about 1:1. In another preferred embodiment of the invention, the compositions contain from about 3-15% by weight of an azole from the group consisting of a member selected from the group consisting of 1,2,3-

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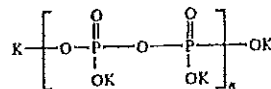
triazoles, pyrazoles, imidazoles, isoxazoles, oxazoles, isothiazoles, thiazoles and mixtures thereof.

#### The Alkali Metal Condensed Phosphate Glass

The phosphate glass has the structural formula set forth below:



In the above formula,  $n$  is 10.5. In addition, it has an average molecular weight of 2160 and a  $\text{PO}_4$  content of 92.4%. It is interesting to compare this condensed phosphate with potassium pyrophosphate which has the following structural formula:



In the above formula,  $n$  equals 1, the molecular weight is 330, and the  $\text{PO}_4$  content is 57.5%.

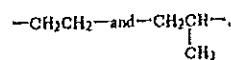
The phosphate glass is a long chain polyphosphate while pyrophosphate is the dimer of orthophosphate. The condensed phosphate in each product is responsible for the corrosion protection of mild steel. Hence, differences in mild steel corrosion rates will be directly attributable to the condensed phosphate used. The basis of comparison for these molecules must be on an equal  $\text{PO}_4$  content. This permits a measure of the amount of performance gained per phosphate grouping and thus the relative merits of each structure.

#### The Water-Soluble Phosphated Esters of Non-Surface Active Polyols

As indicated, these materials are described in U.S. Pat. No. 3,728,420, the disclosure of which is incorporated herein by reference. These esters comprise phosphate esters of a phosphated composition derived by the reaction of phosphorus pentoxide or polyphosphoric acid with a polyol composition of the formula:



wherein  $R$  is a saturated, hydrocarbon radical having two to six carbon atoms,  $R_1$  is a member selected from the group consisting of



$x$  is a number average in the range of 0-5 inclusive,  $y$  is a number average in the range of 1-6, inclusive, preferably 3-5, and the sum of  $x$  plus  $y$  equals 2-6, and  $z$  is a number average in the range of 0-30, inclusive.

Preferred embodiments include those in which said polyol is derived by oxyethylation of glycerol with 1.5 to 2.5 mols of ethylene oxide per mol of glycerol; those in which said polyol is derived by the oxyethylation of mannitol with about 2-20 mols of ethylene oxide per mol of mannitol; those in which said polyols are derived by the oxyethylation of sorbitol with about 2-20 mols of ethylene oxide per mol of sorbitol; those in which said

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polyol is derived by the oxyethylation of trimethylolpropane with 1.5 to 2.5 mols of ethylene oxide per mol of trimethylolpropane. Examples of these materials prior to reaction with either  $\text{P}_2\text{O}_5$  or polyphosphoric acid are set forth in Table I, A, of U.S. Pat. No. 3,728,420.

Example 1 of this patent shows the preparation of an ester composition that is extremely satisfactory as a scale preventative.

#### The Azoles

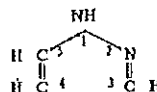
Azoles are nitrogen containing heterocyclic 5-membered ring compounds, and azoles which are suitable in the composition of this invention include triazoles, pyrazoles, imidazoles, isoxazoles, oxazoles, isothiazoles, thiazoles and mixtures thereof as disclosed in U.S. Pat. Nos. 2,618,602; 2,742,369; and 2,941,953.

The triazoles which can be employed in the composition of this invention are any water-soluble 1,2,3-triazoles such as 1,2,3-triazole itself or a substituted 1,2,3-triazole where the substitution takes place in either the 4 or 5 position (or both) of the triazole ring as shown here by the structural formula:



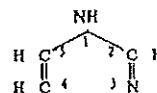
Suitable triazoles include benzotriazole (the preferred triazole); 4-phenyl-1,2,3-triazole; 1,2-naphthotriazole; and 4-nitrobenzotriazole, tolyl triazole and the like.

The pyrazoles which can be used in the composition of this invention include any water-soluble pyrazoles such as pyrazole itself or a substituted pyrazole where the substitution takes place in the 3, 4, or 5 position (or several of these positions) of the pyrazole ring as shown by the structural formula:



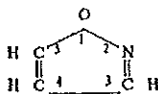
Suitable pyrazoles include pyrazole, 3,5-dimethyl pyrazole, 6-nitroindazole; 4-benzyl pyrazole; 4,5-dimethyl pyrazole, and 3-allyl pyrazole, and the like.

The imidazoles which can be used in the composition of this invention include any water-soluble imidazoles such as imidazole itself or a substituted imidazole where the substitution takes place in the 2, 4 or 5 position (or several of these positions) of the imidazole ring as shown here by the structural formula:



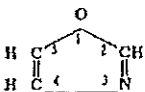
Suitable imidazoles which can be employed in the composition of this invention include imidazole; adenine, guanine, benzimidazole; 5-methyl benzimidazole; 2-phenyl imidazole, 2-benzyl imidazole, 4-allyl imidazole, 4-(beta-hydroxy ethyl)-imidazole, purine, 4-methyl imidazole, xanthine, hypoxanthene, 2-methyl imidazole, and the like.

Isoxazoles which can be employed in the composition of this invention include any water-soluble isoxazole such as isoxazole itself or a substituted isoxazole where the substitution takes place in the 3, 4 or 5 position (or several of these positions) of the isoxazole ring as shown here by the structural formula:



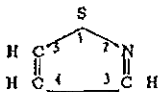
Suitable isoxazoles include isoxazole, 3-mercaptisoxazole, 3-mercaptobenzisoxazole, benzisoxazole, and the like.

The oxazoles which can be employed in the composition of this invention include any water-soluble oxazoles such as oxazole itself or a substituted oxazole where the substitution takes place in the 2, 4 or 5 position (or several of these positions) of the oxazole ring as shown here by the structural formula:



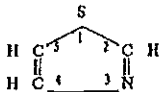
Suitable oxazoles include oxazole, 2-mercaptioxazole, 2-mercaptobenzoxazole, and the like.

The isothiazoles which can be employed in the process of this invention include any water-soluble isothiazoles such as isothiazole itself or a substituted isothiazole where the substitution takes place in either the 3, 4 or 5 position (or several of these positions) of the isothiazole ring as shown here by the structural formula:



Suitable isothiazoles include isothiazole, 3-mercaptisothiazole, 3-mercaptobenzisothiazole, benzisothiazole, and the like.

The thiazoles which can be used in the composition of this invention include any water-soluble thiazole such as thiazole itself or a substituted thiazole where the substitution takes place in the 2, 4 or 5 position (or several of these positions) of the thiazole ring as shown here by the structural formula:



Suitable thiazoles include thiazole, 2-mercaptiothiazole, 2-mercaptobenzothiazole, benzothiazole, and the like.

In the above azole compounds, the constituents substituted in the azole rings can be alkyl, aryl, aralkyl, alkylol, and alkenyl radicals so long as the substituted azole is water-soluble.

To illustrate a typical formula of the invention, Composition 1 is set forth below:

Composition 1	
Ingredients	% by Weight
Phosphated-Ethoxylated Glycerine <sup>1</sup>	6.0
Tolyl Triazole	1.0
Polyphosphate Glass	6.25
Alkali water, alcohol	82.15

<sup>1</sup>See Example 1, U.S. 3,771,420, for general mode of preparation and Composition

Compositions such as Composition 1 are effective as scale and corrosion inhibitors under the conditions previously described when used at dosages as low as 0.1 up to as high as 100 ppm based on the active ingredients contained therein. In most cases, good results are achieved when the dosage is within the range of 1-10 ppm. These dosages may be varied. For instance, when the treatments are initially started, higher dosages are sometimes used to initially form protective films and the like and are then reduced to provide a so-called maintenance level, which are the dosages previously described above.

The test apparatus used in all the examples set forth hereinafter is a pilot cooling tower laboratory unit.

The pilot cooling tower (PCT) is quite flexible in its operation. The variables of heat flux, metallurgy, flow rate, pH, chemical feed rate, bleed program, holding time index, cycles of concentration, and make-up water analysis contribute to making this unit extremely valuable for many kinds of testing. Water is pumped from the tower basin by a variable speed pump through PVC piping from which a side stream is taken and passed through an electrical conductivity cell (sensor cell) and returned to the tower basin. The conductivity of the recirculating water as measured by the conductivity cell is compared to a set point. If the conductivity of the water is too high, the blowdown pump begins removing tower basin water at the rate of 70 ml/min. The chemical feed pump is activated simultaneous to the blowdown pump and begins adding fresh chemical at such a rate to provide the desired dosage based on blowdown water removed. Since the tower basin level is being lowered, a level controller activates the make-up selenoid and fresh make-up replaces the concentrated blowdown water thus reducing the overall conductivity of the recirculating water. The above explained mechanism accounts for the basic cooling tower variables of make-up, cycles of concentration, holding capacity, holding time index and calculated continuous blowdown rate.

Beyond the conductivity cell lies an in-line metallo thermometer which basically indicates the basin temperature. The basin temperature, however, can be regulated by an adjustable screw on the outside of a thermal sensor which protrudes into the tower basin. Beyond a given water temperature this sensor activates the exhaust fan at the top of the tower and the counterflow induced draft provides the extra cooling needed to provide the desired basin temperature. With no fan cooling standard heat load, and normal recirculation rate, the basin temperature can reach 118° F.

An in-line rotometer indicates flow in gpm. This flow can be regulated at the variable speed pump which has a range of 0-3 gpm.

The pH of the system is monitored by pH electrodes which are in series with a Great Lakes pH analyzer. The pH analyzer has high set point capability. Beyond

this high set point, the acid selenoid is activated and a dilute solution of sulfuric acid is fed until the pH becomes lower than the set point pH. Hysteresis can also be regulated.

After having seen pH electrodes, the water travels shellside on three heat transfer surfaces which can be of varying metallurgy. These tube specimens are generally admiralty brass unless corrosion of mild steel heat transfer surfaces is an objective of the test. The heat flux is provided by cartridge heaters of a given wattage. The desired heat flux may be gained by rheostating the heaters to the desired power output. Mild steel corrosion coupons sit mounted in Lucite blocks beyond the heat transfer tubes. These latter specimens provide non-heat transfer corrosion and deposit results. Again, these coupons can be of various metallurgies but mild steel is most commonly employed since the majority of metal transmission lines are mild steel. The water then passes a magna corrater probe which can provide daily read-out. The above discussed section of the unit provides the necessary information for performance on the metal surfaces for a given program.

The water then moves to a water distribution (closed deck) system and falls down honey combed PVC tower fill and into the basin where the recirculation process recurs.

#### EXAMPLES

In each test sequence, a high level dosage is maintained for two days. During this high level dosage, 25 ppm polyphosphate as  $PO_4$  (200 ppm Composition 2 or 420 ppm Composition 1) are fed, pH control is maintained at 8.0 and cycles of concentration are maintained near 2.0. This is done to establish maximum polyphosphate corrosion protection while minimizing the possibility of calcium phosphate deposition. Maintaining pH=8.0 keeps orthophosphate mainly in the more soluble  $HPO_4$  form and maintaining low cycles of concentration keeps a high chemical turnover. Collectively, these two methods of operation can reduce or eliminate scaling due to hydrolytic reversion of the polyphosphate to orthophosphate. The mode of operation changes slightly for the intermediate high level dosage of 12.5 ppm polyphosphate as  $PO_4$  (100 ppm Composition 2 or 210 ppm Composition 1). Generally, no pH control is used and 2.5 cycles of concentration are maintained. The low level dosage (40 ppm Composition 2 and 84 ppm Composition 1) is fed for the ten to twelve days following high level. This is considered more than enough time for the high level effects to wear off. The evaluation, therefore, truly reflects the performance of a low level dosage operation after effective high-leveling.

When testing both Composition 2 and Composition 1, analysis of the recirculating water is quite important. Water variables such as calcium hardness, total hardness, phenolphthalein alkalinity, methyl orange alkalinity, conductivity and pH are done on a daily basis. In addition, the levels of soluble orthophosphate, soluble polyphosphate and soluble organic phosphate are monitored by spectrophotometric techniques. The amount of analyzed organic phosphate is related back to the amount of polyol ester (POE) in the formula composition and is recorded in terms of ppm Composition 2 or ppm Composition 1. The test sequences described in this report discuss the parameters of pH, calcium hardness, holding time index, and basin temperature in a specific manner. Other factors which are held constant

or which are not believed to significantly affect the overall comparison are flow velocity, conductivity, suspended solids, total microbiological count, silica concentration, time required to recirculate a volume of water equal to the holding capacity, extensive use of PVC piping rather than metal, and the use of synthetic tower fill. Fouling due to suspended solids absorption and micro-organism absorption can confuse the evaluation of corrosion and deposit control. An effort is made to factor out their influence by using make-up water with essentially no turbidity and in the case of microorganisms by adding enough bleach to maintain total counts below  $1 \times 10^6$  organisms/ml (normally a 10 ppm NaOCl slug per day). Flow velocity is 2.5-3.0 ft/sec in every test sequence and, therefore, exerts no influence when comparing one test sequence to another.

All metal specimens are dry-weighted prior to the test, after the test is completed and after all deposit is removed by inhibited hydrochloric acid. The results of each test are computed as follows:

$$\begin{aligned} \text{Corrosion weight} &= \text{initial weight} - \text{final weight} \\ \text{Deposit weight} &= \text{pre-clean weight} - \text{final weight} \\ \text{Corrosion rate (MPY)} &= \frac{\text{area factor for metal} \times \text{corrosion weight}}{\text{days exposure}} \end{aligned}$$

The corrosion weights and deposit weights are reported in milligrams. When two metal specimens are used, the weight is reported as the average. Corrosion rate is in mils per year and is also reported as an average when two specimens are used.

The desired maintenance level of a condensed phosphate is 5 ppm as  $PO_4$ . A dosage of 40 ppm of Composition 2 will feed 8.68 ppm of potassium pyrophosphate or 5.0 ppm as  $PO_4$ . Similarly, 84 ppm of Composition 1 will feed 5.735 ppm of the phosphate glass or 4.9 ppm as  $PO_4$ . In both compositions, essentially the same amount of polyol ester (8.5 ppm) will be fed by each composition at use level. The polyol ester (POE) is included for  $CaCO_3$  scale control. It has some benefit as a mild steel corrosion inhibitor but not enough to where the POE could be used singularly to control mild steel corrosion. The benzotriazole (BZT) and tolyltriazole (TT) are copper corrosion inhibitors. They are both effective in controlling corrosion of copper and its alloys at levels of 0.7 ppm to 0.8 ppm in open recirculating systems.

The standard PCT test (Test Sequence A) is conducted under what would be considered mild conditions for these critical cooling water parameters: basin temperature=100° F; holding time index=10 hours; calcium hardness=250 in the recirculating water; pH=8.8 at maintenance level. Changing these parameters to a more stressed operating condition in later test sequences can easily be related back to Sequence A.

#### Test Sequence A: Standard Conditions

Both Composition 2 and Composition 1 give good results under the standard test conditions. Experience in operating PCT's would suggest that a 14 day mild steel heat transfer (tube specimen) corrosion rate of 3.0 or lower is quite good. Mild steel deposit weights in the 350 mg to 500 mg range would be rated as good deposit control. Any measurement below 350 mg would be considered excellent. For admiralty brass heat transfer surfaces, a deposit weight of 75 mg to 100 mg would be considered good. Any deposit weight below 75 mg would, of course, be considered excellent.



Table I shows a tabulation of the actual PCT operating conditions for Test Sequence A and the Corrosion and Deposit Results from this sequence.

scription indicates that both scale and corrosion product were on the heat transfer surfaces. Composition 1, however, gave excellent results on both mild steel and

TABLE I

TEST SEQUENCE A PCT OPERATING CONDITIONS										
	Make-up Water	High Level Dose PPM	Low Level Dose PPM	Disinfectant	Basin Temp °F.	Avg. System pH	Avg. Calcium Hardness	Avg. Magnesium Hardness	Avg. Conc. Ratio	Calculated Holding Time Index
COMP. 2	Chicago Tap	100	40	bleach	100° F.	8.8	243	141	2.7	9.4
COMP. 1	Chicago Tap	210	84	bleach	100° F.	8.8	217	126	2.4	8.0

CORROSION AND DEPOSIT RESULTS										
Test Duration	Mild Steel Heat flux	Avg. ms Tube Corr. Rate	Avg. ms Tube Corr. mg.	Avg. ms Tube Dep. mg.	Admiralty Heat flux	ADM Corr. Rate	ADM Corr. mg.	ADM Dep. mg.	Avg. ms coupon Corr. Rate	Heat trans. Tube desc.
COMP. 2 14 days	10,000	2.44	325	541	10,000	0.34	46	124	3.6	scale, local attack ADM dezincification.
COMP. 1 14 days	10,000	1.23	165	171	10,000	0.40	54	60	0.73	No scale, surface etch.

The average system pH, for example, is calculated by averaging the daily pH from day 4 to the end of the test or day 14 in this case. Average calcium hardness and average magnesium hardness are calculated in the same way. The average concentration ratio is computed by dividing the average magnesium hardness by the magnesium hardness in the make-up water. Make-up water analyses can also be found in the Appendix. The holding time index is calculated using standard cooling water calculations.

It can be seen from Table I that both Composition 2 and Composition 1 give mild steel heat transfer corrosion rates of less than 3.0. Using the performance guidelines set down in this section, these results would be considered quite good.

The deposit weight on mild steel surfaces is the sum of iron oxide corrosion product, plus mineral salt scales. The suspended solids level in all test sequences is very low and, therefore, does not contribute to deposit weight. Admiralty heat transfer deposit weights are composed only of mineral salt scales. Rarely will corrosion product ever make up a significant percentage of the admiralty deposit weight. The deposit control of Composition 2 is only fair on both mild steel and admiralty heat transfer surfaces. The heat transfer tube de-

scribed the absence of any scale with Composition 1. Admiralty corrosion rates are not considered a criterion for success or failure in this study. High admiralty corrosion rates will result from heat transfer surface scaling. The presence of scale is accounted for by the tube description and deposit weight. The corrosion rate of the admiralty heat transfer surface, therefore, provides little added information in comparing the performance of the two treatments. The admiralty brass corrosion rate will be reported but will not be discussed. The overall performance of Composition 1 is better than Composition 2 under standard conditions since it is rated excellent in both corrosion and deposit control. The Composition 2 deposit control is marginal.

Test Sequence B: pH Control at 8.0

Controlling the recirculating water pH at 8.0 eliminates the possibility of calcium carbonate and calcium phosphate scaling, but at the same time increases the corrosivity of the recirculating water. Test Sequence B then is a direct comparison of the phosphate glass and potassium pyrophosphate (KPP) in their ability to inhibit mild steel corrosion. Table II shows the results of this comparison.

TABLE II

TEST SEQUENCE B PCT OPERATING CONDITIONS										
	Make-up Water	High Level Dose PPM	Low Level Dose PPM	Disinfectant	Basin Temp °F.	Avg. System pH	Avg. Calcium Hardness	Avg. Magnesium Hardness	Avg. Conc. Ratio	Calculated Holding Time Index
COMP. 2	Chicago Tap	200/100	40	bleach	100° F.	8.0	250	139	2.8	10.0
COMP. 1	Chicago Tap	420/210	84	bleach	100° F.	8.0	278	154	3.1	11.5

CORROSION AND DEPOSIT RESULTS											
Test	Mild Steel	Avg. ms Tube Corr.	Avg. ms Tube Corr.	Avg. ms Tube Corr.	Admiralty	ADM Corr.	ADM Corr.	ADM Corr.	ADM	Avg. ms coupon	Heat trans.
COMP. 2											
COMP. 1											

TABLE II-continued

	Duration	Heat flux	Rate	Corr. mg	Dep. mg.	Heat flux	Rate	mg.	Dep mg	Corr Rate	Tube desc.
COMP. 2	14 days	10,000	9.62	1301	1731	10,000	1.74	226	281	9.8	Moderate surface etch
COMP. 1	16 days	10,000	4.54	701	742	10,000	0.68	102	74	1.67	No scale, spot attack w/depth

The phosphate glass is a much better mild steel corrosion inhibitor than potassium pyrophosphate. The cor-

rosion rate on mild steel heat transfer surfaces increased for both treatments by a factor of ~3.5. The increase in corrosion rate may be due to increased reversion rate to ineffective orthophosphate, loss of bicarbonate buffering capacity, and the loss of any corrosion inhibition assistance from polyal ester which is known to be of little or no value below pH=8.5. Despite the fact that a double dose/double time high level start-up was used, there is evidence of slight under-dosage with Composition 1. The tube description indicates local attack, and the corrosion rate is somewhat higher than 3.0 mils per year (MPY). This is normally an indication that the critical potential for passivation is approached but not exceeded because of insufficient passivator<sup>1</sup>. Since good high levelling was achieved, a maintenance dosage greater than 84 ppm will be needed to achieve a 14 day corrosion rate <3.0 MPY on mild steel with Composition 1 under these conditions. Composition 2 mild steel tubes show a more general attack accompanied by a very high corrosion rate. This ~9.8 MPY result indicates gross under-dosage at maintenance level for Composition 2.

<sup>1</sup>Principles of Corrosion and Protection, D. Stewart and D. S. S. Tullock, MacMillan (1968) p.81-82.

In summary, the use of Composition 1 in lieu of Composition 2 under pH=8.0 control conditions is advantageous because less chemical will be required to achieve best results.

Test Sequence C: High Temperature; Longer Holding Time

Increasing the basin temperature and lengthening the holding time index will accentuate the hydrolytic insta-

TABLE III

TEST SEQUENCE C PCT OPERATING CONDITIONS										
	Make-up Water	High Level Dose PPM	Low Level Dose PPM	Biocide	Basin Temp 'F.	Avg. System pH	Avg. Calcium Hardness	Avg. Magnesium Hardness	Avg. Conc. Ratio	Calculated Holding Time Index
COMP. 2	Chicago Tap	200/100	40	bleach	113' F.	8.8	225	170	2.8	20.0
COMP. 1	Chicago Tap	420/210	84	bleach	116' F.	8.8	250	145	2.8	20.0

CORROSION AND DEPOSIT RESULTS

	Test Duration	Mild Steel Heat flux	Avg. ms Tube Corr. Rate	Avg. ms Tube Corr. mg.	Avg. ms Tube Dep. mg.	Admiralty Heat flux	ADM Heat Rate	ADM Corr. mg.	ADM Dep mg	Avg ms coupon Corr Rate	Heat trans. Tube desc.
COMP. 2	16 days	10,000	3.07	473	1340	10,000	0.36	60	236	3.9	brown scale, general attack
COMP. 1	16 days	10,000	0.77	120	182	10,000	0.18	30	51	0.7	No scale, light spot attack

This is largely a function of the startup procedure which holds pH=8.0 and the concentration ratio at 2.0 cycles. The increased solubility of the orthophosphate anion at pH=8.0 reduces the driving reaction force caused by calcium orthophosphate precipitation and lower cycles of concentration reduce the exposure time. These account for the higher polyphosphate residuals seen for Composition 1 during the first six days of the test and ultimately for the better corrosion protection. Table III is a summary of conditions and the results of this testing. Composition 1 is superior with respect to both corrosion protection and deposit control. A deposit weight of 1340 mg on the mild steel tube and 238 mg on the admiralty tube for the Composition 2 test, however, is quite poor. This deposit is largely a result of losing chemical mass balance based on cycles of calcium hardness and cycles of M alkalinity relative to cycles of magnesium hardness. This ion imbalance was not seen for Composition 1 in Test Sequence A despite a similar concentration ratio. This loss of calcium carbonate stabilization is probably related to the increased basin temperature. Composition 1 does not experience this loss of activity and as a result gives excellent deposit control.

Test Sequence D:

High Temperature; Longer Holding Time; High Calcium

Test Sequence D is very similar to Test Sequence C. The basin temperature is lowered somewhat: 113' F. to 110' F. and 116' F. to 111' F. The major difference, however, is the amount of calcium hardness in the recir-

oulating water. In Test Sequence D, it is in the 650 ppm to 700 ppm range while Test Sequence C had the standard 225 ppm to 250 ppm. Table IV summarizes the conditions and results.

sition 1. The effect of lignosulfonate is not known. Some preliminary work should be done to determine if any benefits can be derived from the combination of lignosulfonate, Composition 2 and Composition 1.

TABLE IV  
TEST SEQUENCE D  
PCT OPERATING CONDITIONS

	Make-up Water	High Level Dose PPM	Low Level Dose PPM	Blockde	Basin Temp 'F.	Avg. System pH	Avg. Calcium Hardness	Avg. Magnesium Hardness	Avg. Conc. Ratio	Calculated Holding Time Index
COMP. 2/ Lignosulfonate	Water A	110 21	45 21	bleach	110° F.	8.6	703	248	4.2	20.5
COMP. 1/ Lignosulfonate	Water A	420/210 - 29	84 21	bleach	111° F.	8.2	638	244	3.8	18.0

CORROSION AND DEPOSIT RESULTS

	Test Duration	Mild Steel Heat flux	Avg. ms Tube Corr. Rate	Avg. ms Tube Corr. mg.	Avg. ms Tube Dep. mg.	Adm. Heat flux	ADM Corr. Rate	ADM Corr. mg.	ADM Dep mg	Avg ms coupon Corr Rate	Heat trans. Tube desc.
COMP. 2	14 days	10,000	8.8	1170	1830	10,000	0.38	52	200	11.2	scale, severe local attack; dezincification.
COMP. 1	12 days	10,000	1.53	170	220	10,000	0.31	39	55	1.13	light spot attack, no scale.

The comparison is not as clear as in other test sequences. Composition 2 did not see a 25 ppm polyphosphate high level and the Composition 2 program was operated at an average pH=8.6 causing the M alkalinity to be an average of 75 ppm higher than in the Composition 1 experiment. There are some interesting observations nevertheless. The average polyphosphate residual at maintenance level is higher for both products than in test Sequence C averaging 1.9 ppm as PO<sub>4</sub> for Composition 2 and 2.2 ppm as PO<sub>4</sub> for Composition 1. This higher residual is attributed to a lower basin temperature. The holding time indices were the same in Test Sequence C as they were in Test Sequence D.

The corrosion protection and deposit control of Composition 1 are both excellent. This further demonstrated the excellent performance of Composition 1 under conditions that would be expected to degrade the performance of an alkaline polyphosphate program. Composition 2 does poorly in corrosion protection and deposit control. This may be partially a result of failure to high-level at both 200 ppm and 100 ppm, but in consideration of Test Sequence C, Composition 2 would still be expected to be much less effective than Compo-

Test Sequence E:

Higher Temperature; Longer Holding Time; High Calcium

This Test Sequence is similar to both Sequences C and D. The observation that average polyphosphate residual is a function of basin temperature appears to apply to this sequence as well: Polyphosphate Residuals vs. Basin Temperature.

	A 100° F.	D 110° F.	C 113°	E 117°
Composition 2	2.9 ppm	1.9 ppm	1.6 ppm	—
Composition 1	4.8 ppm	2.2 ppm	1.3 ppm (116°)	0.3 ppm

\*not enough data

Unlike Sequences C and D, Composition 1 shows a mild steel tube corrosion rate above the 3.0 MPY (Table V).

TABLE V

TEST SEQUENCE E  
PCT OPERATING CONDITIONS

	Make-up Water	High Level Dose PPM	Low Level Dose PPM	Blockde	Basin Temp 'F.	Avg. System pH	Avg. Calcium Hardness	Avg. Magnesium Hardness	Avg. Conc. Ratio	Calculated Holding Time Index
COMP. 2	Water B	200	40	bleach	117° F.	8.4	566	232	3.3	15.0
COMP. 1	Water B	420	84	bleach	117° F.	8.7	656	308	4.6	24.0

CORROSION AND DEPOSIT RESULTS

	Test Duration	Mild Steel Heat flux	Avg. ms Tube Corr. Rate	Avg. ms Tube Corr. mg.	Avg. ms Tube Dep. mg.	Adm. Heat flux	ADM Corr. Rate	ADM Corr. mg.	ADM Dep mg	Avg ms coupon Corr Rate	Heat trans. Tube desc.
COMP. 2	14 days	10,000	8.8	1170	1830	10,000	0.38	52	200	11.2	scale, severe local attack; dezincification.
COMP. 1	12 days	10,000	1.53	170	220	10,000	0.31	39	55	1.13	light spot attack, no scale.

TABLE V-continued

COMP. 2	8 days	5,000	18.4	1228	2760	15,000	3.2	213	164	—	scale, gen corrosion
COMP. 1	14 days	5,000	4.0	535	1053	15,000	0.45	59	846	2.3	soft scale, light surface attack.

The combination of operating conditions that caused this deviation from previously seen excellent results is 24 hours holding time index, 117° F. basin temperature, and an average of 650 ppm calcium hardness in the recirculating water. The deposit weight increased along with the corrosion rate. The scale is composed of calcium phosphate scale and iron oxide. The presence of scale is caused by reversion by the polyphosphate to the ineffective orthophosphate ion. The results for Composition 2 are poor. Deposit weights averaging 2760 mg in only eight days are beyond explanation. The corrosion rate of 18.4 MPY after eight days would be less after 14 days but still three to four-fold higher than with Composition 1.

Test Sequence F:

Longer Holding Time; Very Low Calcium

A very soft water was used in this sequence. When concentrated, this water produced calcium hardnesses in the 35-45 ppm range. This change produced the largest increase in mild steel corrosion rate of any of the variables tested. Since the P alkalinity was normally 10 or below (see Table VI), the potential for scale formation was nil.

dosage to maintenance levels caused a dramatic rise in corrosion rate. Obviously, the maintenance dosage must be higher for both products. The Composition 1 test would be visually rated as excellent at 400 ppm and 200 ppm product fed. The Composition 2 test would be rated visually as fair at 100 ppm product fed.

Having thus described my invention, it is claimed as follows:

1. A composition for preventing scale and corrosion in industrial cooling water systems which comprises (I) a water-soluble alkali metal condensed phosphate glass which has an average molecular weight of about 2160 and a PO<sub>4</sub> content of 92.4% by weight and (II) a phosphated glycerol which has been reacted with from 1.5-2.5 moles of ethylene oxide per mole of glycerol, with the weight ratio of (II) being about 1:1.
2. The composition of claim 1 wherein it additionally contains from 3-15% by weight of a water-soluble azole from the group consisting of 1,2,3-triazoles, pyrazoles, imidazoles, isoxazoles, oxazoles, isothiazoles, thiazoles and mixtures thereof.
3. A method of inhibiting scale and corrosion in industrial cooling waters which comprises treating said

TABLE VI

TEST SEQUENCE F PCT OPERATING CONDITIONS											
	Make-up Water	High Level Dose PPM	Low Level Dose PPM	Blockdo	Basin Temp °F.	Avg. System pH	Avg. Calcium Hardness	Avg. Magnesium Hardness	Avg. Conc. Ratio	Calculated Holding Time Index	
COMP. 2	Water C	100	40	R & H 886	100° F.	8.5	32	19	4.5	19.0	
COMP. 1	Water C	420/210	84	R & H 886	100° F.	8.5	47	22	4.7	20.0	

CORROSION AND DEPOSIT RESULTS											
	Test Duration	Mild Steel Heat Flux	Avg. ms Tube Corr. Rate	Avg. ms Tube Corr. mg.	Avg. ms Tube Dep. mg.	Adm. Heat flux	ADM Corr. Rate	ADM Corr. mg.	Avg ADM Dep. mg	ms coupon Corr Rate	Heat trans. Tube deso.
COMP. 2	14 days	10,000	54.8	7522	7856	10,000	4.6	611	246	55.5	severe surface attack.
COMP. 1	14 days	10,000	22.2	2940	4035	10,000	0.38	42	50	17.6	severe general attack

Both products showed severe general corrosion attack. The corrosion rates observed were approximately a twelve-fold increase over that observed for standard conditions. Despite the poor results for both products, the daily tube observations indicated that both products had fair to excellent control at high level. Reduction of

waters with at least 0.1 ppm of the composition of claim 1.

4. The method of claim 3 wherein the industrial cooling water has a pH of 8-9 and an average temperature greater than 110° F.

\* \* \* \* \*

APPENDIX A  
SYNTHESIS OF SPIRO (4,4) NONANES

LABORATORY RESEARCH BY  
GEORGE THOMAS FARLEY

MAJOR PROFESSOR  
DR SCOTT MCKENZIE

1966-1970

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## LITERATURE SURVEY

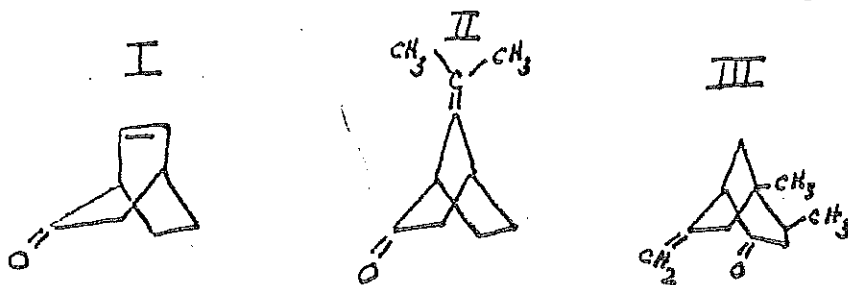
The literature section is presented to provide a basic or *raison d'être* for the series of reactions in the synthetic scheme. The reactions are directed toward the synthesis of the spiro(4,4)nonane system with two chromophoric groups. This section will be divided into three parts. The first part will elucidate the value of the spiro(4,4)nonane system contemplated, the second will reflect on past syntheses of spiro(4,4)nonanes and the third will briefly review reasons for the selection of the synthesis.

### A. SPIRO(4,4)NONANE SYSTEM

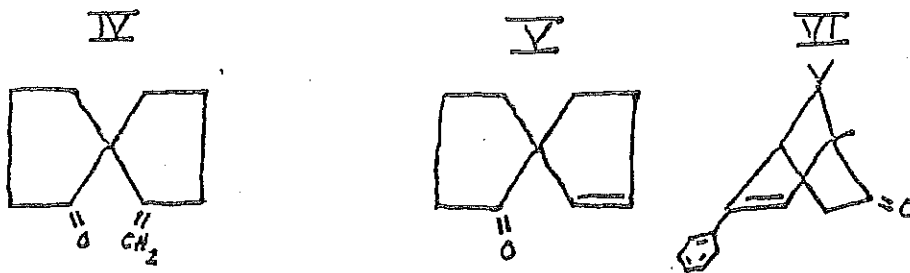
The ketone absorption in the ultraviolet is known to be a low intensity absorption showing extinction coefficients in the order of 5-25. However, certain unsaturated or aromatic, but non-conjugated ketones have been observed to show unusually high extinction coefficients. Cookson<sup>1</sup> chose to explain this phenomenon by citing the interaction of the p-orbital of the carbonyl carbon with the p-orbital of the neighboring unsaturated system. Labhart and Wagniere<sup>2</sup> suggested that the interaction between the non-bonding orbital of the carbonyl and the p-orbital of the unconjugated system is responsible for the exaltation of the ketone band. The work of Mac Kenzie<sup>3,4</sup> and Dooley<sup>5</sup> were set forth to provide a better understanding with eventual correlation between the theoretically calculated extinction coefficients

and the observed values.

Most notable among the ketones showing the exhaltation is the bicyclo system. Three compounds, bicyclo(2,2,2)octan-4-en-1-one (I), 7-(1',1'-dimethylmethenyl)-bicyclo(2,2,1)-heptanone-1 (II), and 3,4-dimethyl-6-methenylbicyclo(3,2,1)-octanone-1 (III), are known. Here a system of rigid geometry



is present which fixes the chromophoric groups in the molecule providing the necessary information for calculation of orbital overlap. Dooley<sup>5</sup> prepared two new, non-strained, unsaturated ketones (IV and V) in a study directed toward understanding



the effect of geometry on the ultraviolet spectrum. This work established the effects seen by varying the  $\gamma$ -orbital in a  $\beta,\gamma$ -unsaturated ketone. Since simple olefinic ketones normally exhibit low extinction coefficients, the effects observed are not always clear. Consequently, the desirability

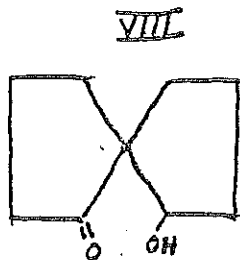


of compounds with strong ultraviolet absorptions is present, in particular the interaction between the styrene chromophore and the carbonyl. This combination produced the most extreme case of the ketone exaltation ever demonstrated<sup>6</sup>, VI. The purpose of the synthetic work set forth in this report was to study methods which might lead to novel geometric orientations of the two chromophoric groups. The work of Dooley suggested the use of the styrene absorption group in the spiro(4,4)nonane system.

#### B. PAST SYNTHETIC ROUTES TO THE SPIRO(4,4)NONANES

As early as 1913, Lebedev and Merezchkovski<sup>7</sup> proposed diketohexamethylspiro(4,4)nonane as one of the degradation products from the trimer of dimethyl allene. Zelinsky and Schuikin<sup>8</sup> cited a platinum catalyzed ring rearrangement of spiro(4,5)decane to 1-methylspiro(4,4)nonane. Indian workers<sup>9,10,11</sup> reported successful syntheses of 1-ketospiro(4,4)nonane, 1-keto-6-methyl-2,4-dicarboxyspiro(4,4)nonane and spiro(4,4)nonane. Manich<sup>12</sup> used the pyrolysis of the calcium salt of di-1-(1-cyclopentanecarboxylic acid)-1,2-ethane to prepare 1-ketospiro(4,4)nonane. Zelinski and Elagina<sup>13</sup> opened 6-ketospiro(4,5)decane to the diacid and then condensed with barium hydroxide at 295-300°C. to yield 1-ketospiro(4,4)nonane. The ketone was reduced to the parent hydrocarbon via a Wolf-Kischner reduction.

Horeau<sup>14</sup> converted 1,4,4,7-tetracarboxyheptane to 1,6-diketospiro(4,4)nonane by preparing the anhydride and then pyrolyzing. Levina and Tantsayeva<sup>15</sup> reacted 1,4-dibromobutane with an excess of sodium cyclopentadienate to yield spiro(4,4)nona-1,3-diene. Cram and coworkers<sup>16,17</sup> attempted to produce spiro(4,4)nona-1,3,6,8-tetraene. 1-Ketospiro(4,4)nonane was synthesized using the method of Zelinskii and Elagina. The ketone was then converted into the analogus alcohol and amine. Employing the reaction path of Horeau, Cram prepared the 1,6-diketone and subsequently reduced it to the corresponding dihydroxy compound with the use of lithium aluminum hydride or hydrogen gas over Raney nickel. Starting with diethyl adipate, 1-keto-6-hydroxy-spiro(4,4)nonane (VIII) was prepared. The diester was



cyclized via a Dieckmann condensation to 2-carbethoxy-cyclopentanone. The keto-ester was then subjected to metallic sodium forming the alpha anion. The anion was alkylated using ethyl  $\delta$ -bromobutyrate to ethyl  $\delta$ -(1-carbethoxy-2-keto-1-cyclopentyl)-butyrate. This compound was reduced to the corresponding hydroxy compound with the use of sodium

borohydride. The alcohol was cyclized by sodium hydride, saponified, and decarboxylated to yield 6-hydroxyspiro(4,4)-nonan-1-one. Cram<sup>17</sup> continued the work with the preparation of olefinic spiranes, 1-spiro(4,4)nonene, 1,3-spiro(4,4)-nonadiene and 1,6-spiro(4,4)nonadiene. These unsaturated spiranes were prepared by conversion of the ketone to the amine followed by Hoffmann elimination or an amine oxide pyrolysis. Attempts to prepare the olefins from 1-hydroxyspiro(4,4)nonane and 1,6-dihydroxyspiro(4,4)nonane by base-catalyzed elimination of the para-toluenesulfonates failed.

French workers<sup>18</sup> found that 1-hydroxyspiro(4,4)nonane rearranged upon treatment with polyphosphoric acid to yield 4,5,6,7-tetrahydroindane. Treatment of 1,3-spiro(4,4)-nonadiene with iron pentacarbonyl produced ring rearrangement to bistetrahydroindenyl-di-iron tetracarbonyl<sup>19</sup>. Trans-hydrindandiol-(8,9) was found to rearrange in concentrated sulfuric acid to 1-ketospiro(4,4)nonane<sup>20</sup>. Conley and coworkers<sup>21,22,23</sup> found 1-ketospiro(4,4)nonane to undergo an abnormal Schmidt reaction in polyphosphoric acid. From this reaction and the Beckmann rearrangement, the intermediate nitrile and indandienone were isolated.

Mayer and coworkers<sup>24</sup> were able to prepare 1-ketospiro(4,4)nonane from the reaction of 1-( -bromobutyl)-cyclopentanone-2 with potassium hydroxide, 35% solution.

Krapcho and Benson<sup>25</sup> studied the acetolysis of spirane systems in which a tosyl group was alpha to the spiro carbon.

The tosyl containing ring was always five-membered while the other ring varied in size from four to six members. The main reaction product was rearranged olefin with a small amount of rearranged acetate also being recovered. They observed an acceleration of reaction rate for the spiro compound in comparison to its cycloalkane analogue. This reaction acceleration was attributed to the relief of ring strain occurring presumably by neighboring group participation in the bridged ion intermediate.

Krapcho and Donn<sup>26</sup> prepared spirenes as products from the decomposition of the corresponding tosylhydrazones. Their method of synthesis produced yields in the 75-90% range for spiro(4,5), spiro(5,5), and spiro(5,4) systems, but the yield was found to be only 53% in the case of the spiro(4,4)nonane system.

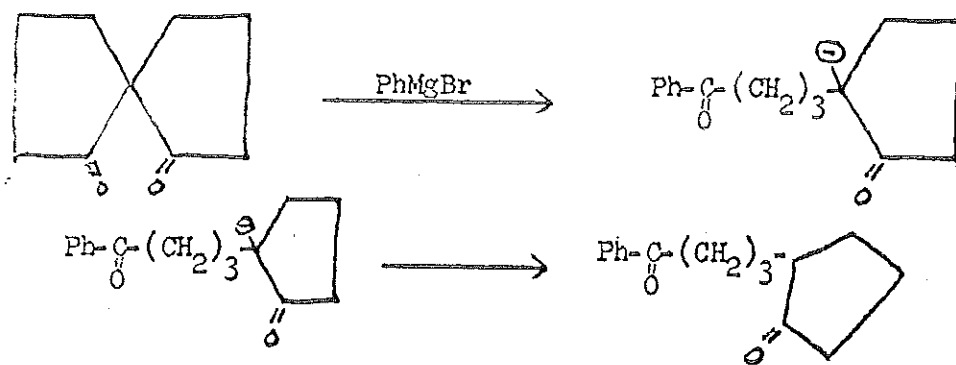
Criegee and coworkers<sup>27</sup> synthesized 1,2,3,4-tetramethylspiro(4,4)nona-1,3,6-triene. This was accomplished by condensing the nickel chloride complex of tetramethylcyclobutane with sodium cyclopentadienate and then producing rearrangement with acid to form the spiro(4,)nonane system.

Krieger and coworkers<sup>28</sup> were able to prepare spiro(4,4)nonan-1-one by condensing 1-pyrrolidinocyclopentene with 1,4-diiodobutane. In 1968, Christol and Vanel<sup>29</sup> prepared 1-methylspiro(4,4)nonanol-1. by addition of methyl magnesium

bormide in a Grignard reaction. In the same work, they successfully added triphenylmethylenephosphorane to spiro-(4,4)nonan-1-one to produce 1-methylenespiro(4,4)nonane.

### C. SELECTION OF SYNTHESIS

The series of reactions followed the course used by Dooley<sup>5</sup> and Cram<sup>16,17</sup>. It would seem from the literature that the most logical starting material for the spiranes contemplated could be spiro(4,4)nonan-1,6-dione, a known compound. Christol and Vanel<sup>29</sup> demonstrated the use of the Wittig reagent and the Grignard reagent, both strong bases, to the spirane system in tact. Dooley, however, found that spiro(4,4)nonan-1,6-dione was sensitive to base and instead of addition underwent reverse aldol condensation. The favorability of this over addition is supported by the stability of the cyclopentyl anion adjacent to the carbonyl or other electron withdrawing group. The stepwise series is shown on the next page for the addition of phenyl magnesium bromide to the diketone. From this information, ethyl  $\gamma$ -(1-carbethoxy-2-keto-1-cyclopentyl)-butyrate was synthesized and addition reactions were run on this compound. If addition was successful, the adduct would be cyclized via a Dieckmann condensation, saponified, and finally decarboxylated to the desired product.



## DISCUSSION AND RESULTS

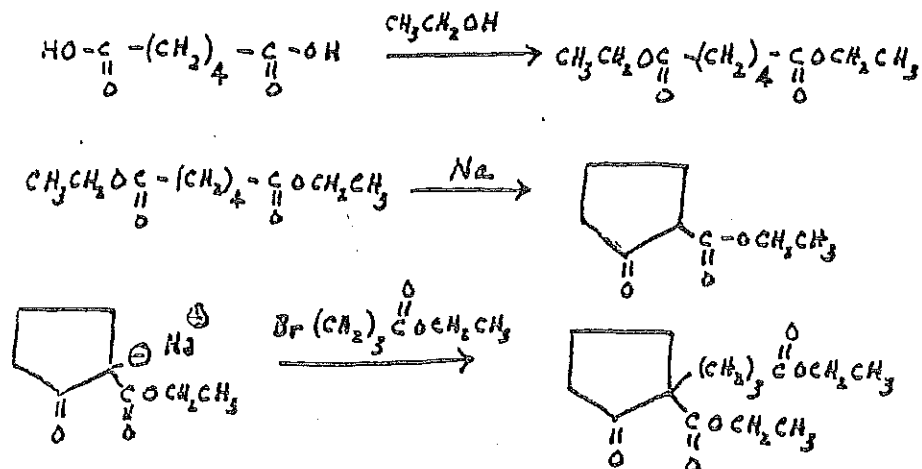
The esterification of adipic acid gave virtually quantitative yields. The reaction equilibrium was forced to product by the use of azeotropic distillation. The crucial portion of the procedure was the redistillation of the azeotropic mixture after having been dried over potassium carbonate. Best yields were obtained when the azeotrope was distilled over for the third time.

The Dieckmann condensation of diethyl adipate to 2-carbethoxycyclopentanone was found to give yields below that reported by Organic Synthesis<sup>31</sup>. The formation of sodium ethoxide during the reaction makes the reaction conditions very difficult unless the reaction is run more dilute. For this reason, it was found to be more advantageous to use a three-liter volume for the reaction of 1.0 moles instead of the 1.5 moles recommended by Organic Synthesis. The product is very pure and vacuum distillation of the material goes very smoothly.

The gas addition of HBr to  $\gamma$ -butyrolactone was found to be nearly quantitative as evidenced by the weight gain of the reaction flask. The esterification step, however, is more difficult than that seen in the preparation of diethyl adipate. Here also, it is assumed that redistillation of the azeotropic mixture is the key to the reaction.

Preparation of ethyl  $\gamma$ -(1-carbethoxy-2-keto-1-cyclopentyl)-butyrate was found to give yields higher than those

reported by Cram and Steinberg<sup>16</sup>, Bachmann and Struve<sup>34</sup> or Dooley<sup>5</sup>. The success of the reaction is attributable to the use of sodium hydride rather than sodium sand or a sodium amalgam. The synthesis to this compound is shown below.



Attempts to add diphenyl cadmium or triphenylmethylene-phosphorane to ethyl  $\delta$ -(1-carbethoxy-2-keto-1-cyclopentyl)-butyrate were equally unsuccessful. Eastham and Feeney<sup>38</sup> pointed out the rarity of adding diphenyl cadmium to carbonyl compounds and were only successful with highly reactive aldehydes. The reasoning underlying the attempt was the hope that the lower reactivity or higher selectivity of the organocadmium compound would assist reaction only to the more reactive ketone with little or no reaction to the two ester groups present. The addition of the ketone inversely immediately produced a white precipitate later identified as biphenyl. The attempts to add the Wittig



reagent to the ketone were unsuccessful producing no reaction in all cases. Dooley has shown that the addition can be done as evidenced by NMR spectra of the products.

Inverse addition of Grignard reagent with a lower than 2:1 ratio of Grignard reagent to ketone was also tried. It was hoped that since two moles of Grignard are needed to effect the addition, the alkylating agent would act in selectivity and produce adducts to the ketone alone. An adduct was recovered from this reaction, but was never identified. The adduct was cyclized, saponified and placed under decarboxylating conditions. The product boiling points seem to fit a retrograde to former reagents.

## EXPERIMENTAL SECTION

### PREPARATION OF DIETHYL ADIPATE

The procedure followed was that found in Organic Synthesis<sup>30</sup>. A three-liter flask with a downward water-jacketed condenser was heated on an oil bath. A mixture of 438.4 grams of adipic acid, 1080 ml of absolute ethanol, 540 ml of toluene dried over sodium and 2.5 ml of concentrated sulfuric acid was added. As the mixture was heated, the solid acid slowly dissolved. The azeotrope of toluene, ethanol and water began to distil at 75°C., but the reaction was allowed to proceed until a temperature of 78°C. had been reached.

The azeotropic mixture was collected in a two-liter flask containing 450.0 grams of anhydrous potassium carbonate. The slurry was stirred vigorously and then the solids were filtered by the use of a Buchner funnel. The dry toluene-ethanol mixture was returned to the distilling flask and the solution was distilled as before. After distillation reached a temperature of 78-80°C., the residual oil was transferred to a one-liter flask and connected to a flash evaporator. The remaining solvent was removed under water-aspirated suction. The crude ester was now distilled under high vacuum to yield a pure product distilling at 85-86°C./ 0.5 mm. The yield was 598.0 grams or 98.7%. Organic Synthesis reported a yield of 580-588 grams of product distilling at 138°C/ 20 mm.

### PREPARATION OF 2-CARBETHOXY CYCLOPENTANONE

The method of preparation was the alternate method found in Organic Synthesis<sup>31</sup>, making use of sodium sand. The use of smaller particles of molecular sodium is crucial to the overall yield of the reaction. The sodium sand was prepared in the following way. Placed in a 250 ml Erlenmeyer flask were 10.0 grams of metallic sodium, cut into small pieces and 100 ml of xylene. The flask was then fitted with a one-hole rubber stopper containing glass tubing with a stopcock. The stopcock was partially vented and the flask was allowed to heat in an oil bath which was held between 125-130°C.. The sodium melted at 97°C.. When the sodium had just melted, the flask was taken from the oil bath and first swirled and then shaken vigorously to produce sodium sand. If the sodium was overheated after melting, the shaking would initially have produced particles but these would coalesce since the temperature drop was not sufficient to form individual particles. After successful preparation of the sand, the solution was allowed to stand. Prior to the use of sodium sand in the reaction, the xylene was decanted and fresh portions of dry benzene to be used in the reaction were added to effect the transfer. In a three-liter three-necked flask were placed 1250 ml of benzene, carefully dried over sodium, and 51.5 grams of sodium sand. Benzene was used to

transfer the sodium. Diethyl adipate was added in one portion to this mixture until 202.0 grams (1.0 moles) had been added and then 3 ml of absolute ethanol was placed in with the mixture. The flask was placed on a steam bath and swirled until a vigorous effervescence occurred. The reaction was allowed to remain on the steam bath for an additional five minutes. One neck was then fitted with an addition funnel equipped with a pressure arm and another neck with a water-jacketed condenser having a calcium chloride drying tube in place. The middle joint was fitted with a motor-driven blade stirrer guided by a stirring shaft. The stirring action was begun and the reaction was allowed to reflux for twenty-four hours on a steam bath or a heating pad controlled by rheostat. During this period, the mixture became very thick with a copious white precipitate. The mixture sometimes became thick enough to stop the action of the stirrer. In such an instance, additional portions of benzene were added to keep the mixture fluid. At the end of the period of reflux, a large white mass had formed in a volume of yellowish-orange liquid. With cooling, 75 ml of absolute alcohol was added. After the excess sodium had been decomposed, added cautiously with swirling were alternate portions of crushed ice and 6N HCl until the mixture was sufficiently acid to render Congo red paper blue. The liquid portion was decanted leaving the

solid mass behind. This solid was dissolved by breaking and swirling three times with a mixture of 250 ml of ice water, 75 ml of water and 150 ml of crushed ice. This action rendered the mixture into a semi-solid mass. All parts of the reaction were now combined and the aqueous phase was separated. The aqueous phase was extracted twice with 300 ml portions of 1:1 (v/v) benzene:ether solution. The organic layers were then combined and were washed twice with 300 ml portions of 5% sodium carbonate solution and twice with 300 ml portions of water. The organic portion was now transferred to a 500 ml flask and the solvent removed by flash evaporation. The orange oil remaining was transferred to a smaller flask and distilled under high vacuum. The product distilled at 56°C./ 0.35 mm and the yield was 106.2 grams or 68.20%. The boiling point reported in Organic Synthesis is 108-111°C/ 15 mm with a yield of 79-82%.

#### PREPARATION OF ETHYL $\gamma$ -BROMOBUTYRATE

The preparation described is that suggested by Cram and Steinberg<sup>16</sup>. Additional information was obtained from Tinker<sup>32</sup>, and Organic Synthesis<sup>33</sup>. A 500 ml three-necked flask, one neck fitted with a water-jacketed condenser having rubber tubing extending to a six inch funnel inverted slightly above water in a 600 ml beaker, was set up. Another neck was stoppered while the third neck was fitted with a

gas inlet tube having a fritted tip. A tank of hydrogen bromide was connected to the reaction flask via a 500 ml suction flask serving as a trap. Added to the flask was 258.3 grams (3.0 moles) or 228 ml of  $\gamma$ -butyrolactone. The solution was magnetically stirred while the hydrogen bromide valve was opened. The reaction proceeded very rapidly and exothermically. Crushed ice was kept at hand for cooling if the reaction became too violent. The gas addition was allowed to continue for four hours and during this time the solution turned to a burnt orange and finally to black. When gas addition was complete, the vessel was flushed with nitrogen gas for thirty minutes to remove any residual hydrogen bromide.

The crude acid was then transferred to a three-liter one-necked flask for esterification. The neck was equipped with a Barrett distilling receiver and a water-jacketed condenser with a calcium chloride drying tube in place. After 350 ml of absolute ethanol (6.0 moles) and 750 ml of benzene dried over sodium were added, 10 ml of concentrated sulfuric acid was slowly poured down the side of the flask. The mixture was refluxed for twelve hours, water formed being drawn off intermittently. After the period of reflux, the flask was equipped with a downward water-jacketed condenser and the azeotropic mixture of benzene-ethanol-water was distilled off. The remaining oil

was then mixed with 500 ml of anhydrous ether and separated into two parts. Each portion was washed three times with 125 ml portions of 5% sodium bicarbonate solution and three times with 125 ml portions of water. The organic layer was dried with anhydrous magnesium sulfate and filtered. Product absorbed was removed by washing and combined with the filtrate and both were subjected to a flash evaporator where the solvent was removed. The product was then distilled under high vacuum giving 446.8 grams of pure ester distilling at 36°C./ 0.3 mm. The yield was 72.5%. The yield could be improved by redistilling the azeotrope in the esterification process, since conversion to the bromo acid was nearly quantitative as evidenced by weight gain. Cram reported a yield of 93% while Tinker reported 68-70%.

#### PREPARATION OF

#### ETHYL $\delta$ -(1-CARBETHOXY-2-KETO-1-CYCLOPENTYL)-BUTYRATE

The method of Bachmann and Struve<sup>34</sup> was modified by Cram and Steinberg<sup>16</sup> to give better yields by replacing potassium with sodium and the use of vigorous stirring inside the vessel itself to effect a metallic dispersion. The procedure presented here is basically that of Cram and Steinberg except that yields were improved by the use of sodium hydride-mineral oil dispersion.

The reaction vessel was a three-necked flask with a three-liter volume. The necks were fitted with a water-

jacketed condenser, an addition funnel with a side pressure arm and a motor-driven blade stirrer guided by a stirring shaft. The top of the condenser was fitted with a one-hole rubber stopper having glass tubing leading to a three-way stopcock. One inlet of the stopcock was connected to a water aspirator while the other was connected to a tank of nitrogen gas via a calcium chloride drying tube. Sodium hydride (61% in mineral oil dispersion), 52.0 grams (1.32 moles), was placed in the flask along with enough petroleum ether to sufficiently cover the solid. The dispersion was stirred magnetically and the flask was filled with nitrogen atmosphere. The petroleum ether was drawn off by water-aspirated suction and the flask was again filled with nitrogen. More petroleum ether was added as before and the process was repeated two more times. Following the third repetition, 1050 ml of toluene, carefully dried over sodium, was added and the flask was cooled to 6-8°C. by a cold benzene bath. 2-Carboethoxycyclopentanone was added dropwise over a period of thirty minutes until 190.0 ml or 205.16 grams (1.315 moles) had been added. The mixture solidified. More toluene was added to rinse the addition funnel and keep the mixture fluid. The benzene cold bath was now removed and a heating pad was placed under the vessel. The mixture was now chalky-white in appearance.

Ethyl  $\gamma$ -bromobutyrate was added through the addition



runnel over a period of fifteen minutes with good stirring. A total of 194.0 ml was used (1.321 moles). The reactants and the solvent solution were allowed to heat and reflux for a period of twenty-four hours. After cooling, the mixture was rendered acid to litmus paper by the addition of cold 1N HCl. The acid was added cautiously with swirling to allow any excess sodium hydride to fully react. The aqueous and organic layers were separated and the aqueous phase was extracted three times with 250 ml portions of toluene. The organic layers were collected and divided in half. Each half was then washed with 250 ml portions of water until the phase was neutral to pH paper. The organic layers were then combined, dried with anhydrous magnesium sulfate, and filtered. Crude product absorbed by the dessicant was collected by washing and the solvent was removed by flash evaporation. The residual oil was distilled under high vacuum. The product distilled at 117°C./ 0.05 mm giving product weighing 294.4 grams for a yield of 82.5%. Cram and Steinberg reported a yield of 70% of product redistilled over 136-142°C./ 0.20 mm. Bachmann and Struve reported 79% with the product boiling at 140-145°C./ 0.4 mm.

PREPARATION OF TRIPHENYLMETHYLPHOSPHONIUM BROMIDE

This crystalline material was prepared according to Organic Synthesis<sup>35</sup>. Pressure bottles were used which were stoppered with a glass top fitted by a rubber washer and held in place by wire clamps. Five pressure bottles were used and each contained an equal amount of 203.7 grams as total weight of triphenylphosphine. The triphenylphosphine in each of the bottles was dissolved by heating on a steam bath with 30-35 ml of benzene. After cooling in an ice-salt bath, each bottle received approximately 50.0 grams or 29 ml of cold methyl bromide liquid. Shortly after stoppering the bottles, a copious white solid began to precipitate. Initially, the reaction evolved a large amount of heat and the bottles were cooled for one hour in an ice-salt bath. After six hours, all flasks were solid with white crystalline material. The bottles were again cooled and the stoppers were removed carefully. The solids were collected, lumps were crushed and the product was placed on a Buchner funnel using benzene to effect the transfer of residual material. The solid was washed twice with 250 ml portions of hot benzene. The total dry product obtained amounted to 200.2 grams for a yield of 88.0%. Shortly after stoppering, following methyl bromide addition, one bottle burst under pressure and considerable product was lost. Organic Synthesis reported a yield of 99% with product melting at 232-233°C.

ATTEMPTED PREPARATION OF

ETHYL  $\delta$ -(1-CARBETHOXY-2-METHYLENE-1-CYCLOPENTYL)-BUTYRATE

Extensive study of the Wittig reaction and in particular the preparation of the Wittig products of cyclopentanones including this one was done by T.J. Dooley<sup>36</sup>. The procedure described here was the most successful preparation encountered.

Production of the methyl sulfinyl carbanion followed the report of Corey and Chaykovsky<sup>37</sup>. A 500 ml three-necked flask was fitted with a water-jacketed condenser having glass tubing extending to a three-way stopcock affording water aspirated suction and a nitrogen-gas inlet. Placed in the flask was 1.7 grams of 61% sodium hydride in a dispersion of mineral oil. The mineral oil was removed by adding petroleum ether, drawing off the petroleum ether and flushing with nitrogen. The process was repeated exactly as in the preparation of ethyl  $\delta$ -(1-carbethoxy-2-keto-1-cyclopentyl)-butyrate. Dimethyl sulfoxide which had been dried over calcium hydride was now added to 70 ml or 77 grams (0.935 moles). The solution was heated at 75-80°C. for a period of forty-five minutes and then cooled until solid formed. The solution at this point had taken on a greenish cast. Triphenylmethylphosphonium bromide was dissolved in 100 ml of dimethyl sulfoxide. A total of 46.3 grams (0.130 moles) was used. The solution was allowed to stand for a period fifteen minutes and then

cooled. The other two necks of the flask were then fitted with an addition funnel and a motor-driven blade stirrer adapted by a stirring shaft. Added to this solution was 11.0 grams of ethyl  $\gamma$ -(1-carbethoxy-2-keto-1-cyclopentyl)-butyrate (0.041 moles) and the mixture was heated by the use of a heating pad for eight hours at 100°C.. The reaction mixture was poured onto crushed ice and extracted four times with 250 ml portions of 1:1 (v/v) benzene:ether solution. The organic layer was further washed with 250 ml portions of 1:1 (v/v) dimethyl sulfoxide:water four times or until the wash layer was neutral to pH paper. The oil was dried by anhydrous magnesium sulfate and filtered, care being taken not to lose product in the dessicant. The solution was now subjected to flash evaporation and the residual oil was distilled under high vacuum. The distillate was found by NMR analysis not to show the presence of vinyl hydrogens. Since the pure oil distilled at 117°C./ 0.05 mm with no distillable liquid remaining, it was concluded that starting was obtained. Dooley reports a yield of 31% product based upon percentage of a mixture having vinyl hydrogens in the NMR.

ATTEMPTED PREPARATION OF  
ETHYL  $\gamma$ -(1-CARBETHOXY-1-CYCLOPENTYL-2-PHENYL-2-HYDROXY)-  
BUTYRATE BY ADDITION OF DIPHENYL CADMIUM

The procedure used was that of Eastham and Feeney<sup>38</sup>. Phenyl magnesium bromide was prepared from 3.3 grams of magnesium shavings (0.137 moles) and 20.0 ml or 30.4 grams (0.191 moles) according to the preparation described later. The Grignard reagent was prepared in a 250 ml three-necked flask. One neck was fitted with a water-jacketed condenser, another with an addition funnel equipped with a pressure arm, and the last with a motor-driven blade stirrer guided by a stirring shaft. From the top of the condenser, glass tubing having a three-way stopcock extended to a nitrogen tank via a calcium chloride drying tube and to a U-tube half filled with mercury loosely stoppered with glass wool to avoid splashing. To the ethereal solution of Grignard reagent was added 11.0 grams of cadmium chloride which had been dried under vacuum at 100°C. for twenty-four hours. The reaction took place immediately but the solution was let to stir for fifteen minutes. The condenser was now replaced with a distilling head connected to a downward water-jacketed condenser. The ether was distilled off under nitrogen atmosphere and, during distillation, two portions of 50 ml of dry benzene were added through the addition funnel. After the solvent replacement was complete,

the condenser is again set into place and 8.2 grams (0.022 moles) of ethyl  $\gamma$ -(1-carbethoxy-2-keto-1-cyclopentyl)-butyrate was added rapidly through the addition funnel. The mixture was refluxed for thirty minutes and then poured onto 200 grams of crushed ice. A 20% sulfuric acid solution was added until both phases were clear. The organic layer was separated and washed with 50 ml of water. The organic layer was then extracted twice with 50 ml portions of benzene. The organic solution was dried by anhydrous magnesium sulfate and filtered. Two 50 ml portions of benzene were passed through the dessicant to recover any product loss to the solid. The benzene was removed by flash evaporation and the remaining oil was distilled under high vacuum. Four fractions were collected. The first fraction was collected at 55-72°C./ 0.05 mm, the second from 72-95°C./ 0.03 mm, the third from 95-97°C./ 0.02 mm and the last from 95-97°C./ 0.02 mm. The last two fractions accounted for approximately 80% by weight. These two were subsequently redistilled and shown to be starting material by physical constants and IR spectra. The first two fractions were too small to identify but it was noted that both solidified while entering the flask.

ATTEMPTED PREPARATION OF

ETHYL  $\gamma$ -(1-CARBETHOXY-1-CYCLOPENTYL-2-PHENYL-2-HYDROXY)-  
BUTYRATE BY ADDITION OF PHENYL MAGNESIUM BROMIDE INVERSELY

The procedure presented here is based on the preparation of phenyl magnesium bromide and its work-up found in Organic Synthesis<sup>39</sup>. A 500 ml three-necked flask was set up with an addition funnel, a motor-driven blade stirrer, guided by a stirring shaft, and a water-jacketed condenser. Extending from the top of the condenser was glass tubing with a three-way stopcock allowing for an inlet of nitrogen gas and a U-tube half filled with mercury loosely stoppered with glass wool. The whole apparatus was heated in a stream of nitrogen to remove any moisture or oxygen. Twenty grams (0.833 moles) of magnesium turnings, 150 ml of dry ether and 2 ml of redistilled bromobenzene were combined in the flask. The mixture was stirred until the reaction begins. Initially, the flask had a cold water bath surrounding it, but this was removed when the reaction began to give off heat. When the reaction had started, the remainder of 78.5 grams of bromobenzene (0.500 moles) was added in a solution of 300 ml of ether over a period of one-half hour. If the reaction failed to begin with the initial 3.0 grams of bromobenzene, the ethereal solution was added at about 15 ml intervals not to exceed 60 ml. When the reaction was complete, evidenced by ether no longer refluxing,

the flask was cooled and stoppered in a nitrogen atmosphere. In a 250 ml flask, having three necks identically equipped to that used in the preparation of phenyl magnesium bromide and heated in the same way, was placed 14.0 grams (0.05 moles) of ethyl -(1-carbethoxy-2-keto-1-cyclopentyl)-butyrate and 150 ml of dry ether. The mixture is cooled to 5°C. by the use of a salt-ice bath. Under vigorous stirring, 30.0 ml of 1.45 N phenyl magnesium bromide was added dropwise over forty-five minutes. The ice bath was removed and the mixture allowed to stir for an additional forty-five minutes. The whole reaction was added to 200 ml of cold 10% HCl solution. The aqueous phase was separated and was extracted twice with 50 ml portions of ether. The organic layers were combined and were washed with 200 ml of water, 200 ml of 5% sodium carbonate solution, 200 ml of water and 200 ml of saturated sodium chloride solution. The ether was removed on a rotary evaporator and the orangish oil was distilled under high vacuum. Initially, starting material distilled, but over the range 162-172°C./ 0.10 mm, a thick orange liquid distilled. A white solid found in the first fraction was identified by NMR spectrum, IR spectrum and melting point to be biphenyl. The IR spectrum of the thick liquid showed the presence of an -OH band and aromatic hydrogens. This was interpreted to mean successful addition and this liquid was put to cyclization and decarboxylation



conditions without further identification.

#### CYCLIZATION OF THE GRIGNARD ADDUCT

The procedure described here is that followed by Dooley<sup>40</sup>. A 500 ml three-necked flask was equipped with an addition funnel, a motor-driven stirrer adapted by a stirring shaft and a water-jacketed condenser. From the top of the condenser extended glass tubing having a three-way stopcock affording nitrogen-gas inlet and water aspirated suction. Sodium hydride (61% in mineral oil dispersion) was placed in the flask (5.0 grams) and was covered with petroleum ether. It was washed three times as in the preparation of ethyl -(1-carbethoxy-2-keto-1-cyclopentyl)-butyrate. The action of the stirrer was begun and 250 ml of benzene dried over sodium was added. Ten milliliters of absolute methanol was added to start the reaction and the solution was brought to reflux by the use of a heating pad. Over the course of one hour was added 5.0 grams of the adduct in 80 ml of benzene. The reaction was allowed to continue at reflux for an additional ten hours. During cooling, 5 ml of n-butyl ether and 20 ml of toluene were added in one portion. The reaction was cooled to 0-5°C. by the use of an ice-salt bath and when the reaction had thoroughly cooled, 15 ml of absolute methanol was added to decompose the excess sodium hydride. The mixture was then poured into 150 ml of ice water and was refluxed for two hours and then cooled

as before. The solution was then rendered to pH 7-8 with the use of pH paper by the addition of a saturated solution of ammonium chloride and then let stand in a cold box overnight. The mixture was then refluxed for an additional two hours. After allowing the mixture to cool to room temperature, the layers were separated and the organic layer was extracted three times with 250 ml portions of ether. All organic layers were combined and were washed with 300 ml portions of water until the wash was neutral to pH paper. The ether was removed on a flash evaporator and the remainder was distilled under high vacuum. N-butyl ether distilled very early then two products distilled at 35-50°C./ 0.30 mm and then still another at 132-140°C./ 0.30 mm. The first fraction was presumed to be two products since that would fit a reversal to known products in the synthesis..

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