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PHOSPHORIC ACID AS A CATALYTIC MEDIUM
FOR ORGANIC REACTIONS^{1/}

by

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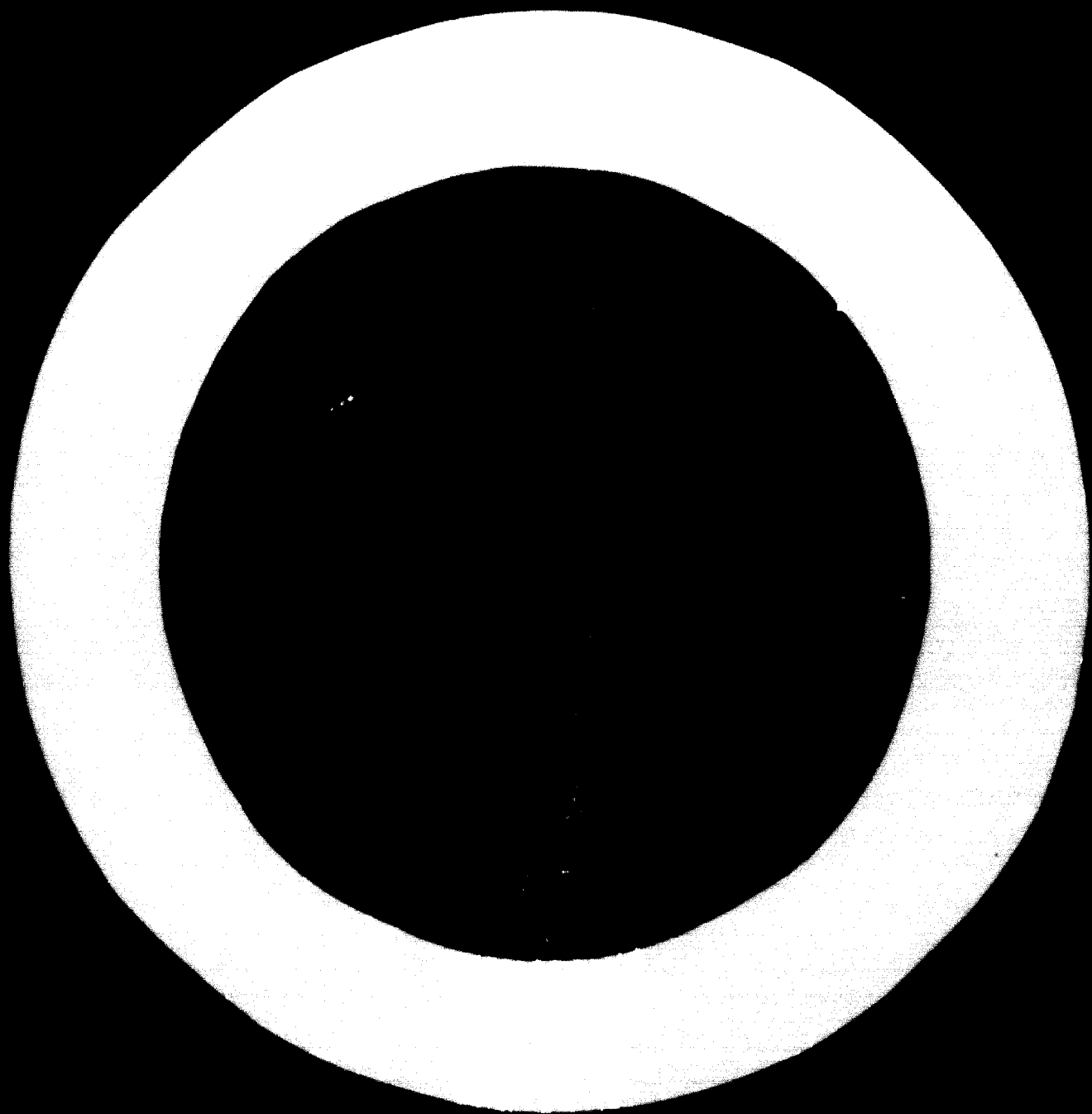
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I. INTRODUCTION

Chemical Transformations in Sulfuric Acid. The Co-product Ammonium Sulfate Problem

1. Liquid concentrated sulfuric acid serves as a catalytic medium for a number of commercially important reactions. Oxime derived caprolactam and methyl methacrylate produced from acetone cyanohydrin are among the better known. At the conclusion of these transformations, the acid is commonly neutralized with ammonia to produce ammonium sulfate as co-product. In some instances, neutralization is indispensable for the liberation and recovery of the organic compound produced. In many of these processes, the acid is present in large excess. It serves both as catalyst and solvent or liquid medium for the efficient transfer of the sometimes very considerable heat generated by the reaction. Therefore, several tons of the co-product salt are often obtained for each ton of primary product.
2. In 1968, about six million tons of the sulfate were recovered from world caprolactam manufacture alone, and the figure has grown considerably since. Co-product ammonium sulfate has been the major source of this material in the United States in recent years. The total world consumption of the salt in 1966/67 was less than ten million tons. The market trend is towards a reduction in consumption of this compound as a fertilizer, especially in developing countries where ammonium sulfate (20.5% N) is being replaced by urea (46% N). Not only has an over-capacity for ammonium sulfate thus developed, but a waste disposal problem may even be encountered in certain geographic areas.

Efforts to Limit Ammonium Sulfate Co-Production

3. There has been a considerable development effort in recent years to find alternate routes to these organic products which avoid, or at least decrease the amounts of co-product ammonium sulfate. To accomplish this end, both new chemistries have been proposed and known routes have been modified. The photo-nitrosation of cyclohexane and the Union Carbide caprolactone route to caprolactam are examples of the former approach. The Stamicarbon nitrophosphate

process, which halves ammonium sulfate production, is an example of the latter.

4. But these are at best only a partial solution to a general problem embracing many chemical reactions. Efforts to effect some of these transformations with catalytic quantities of acidic materials have so far not borne fruit. Raw material costs are generally the major cost component; very high if not essentially quantitative conversions are required, and these have not been achieved by conventional catalysis.
5. Polyphosphoric acid has been extensively studied as an acid catalyst in a wide variety of organic reactions⁽¹⁾. It has also been applied to the Beckmann rearrangement⁽²⁻⁵⁾. Acids of concentrations equivalent to 110% H_3PO_4 or higher have been used, the impression being held that lower lactam yields were a necessary corollary to lower acid concentrations. However, the industrial application of polyphosphoric acid is seriously impeded by its high viscosity (see Table I).

Chemical Transformations in Phosphoric Acid

6. Studies in our laboratories have shown that contrary to the prior contention, excellent yields of caprolactam can be achieved in 100% H_3PO_4 . In fact, many of the subject transformations can be efficiently catalysed by concentrated phosphoric acid. Its substitution for sulfuric acid allows for the co-production of mineral acid derivatives, such as ammonium phosphate, of higher value than those obtained with sulfuric acid. However, it should not be assumed that this advantage can be realized by a one to one translation from sulfuric acid based processes. The chemical characteristics of the two acids are not identical, and the optimal process conditions using the one are not necessarily those when using the other.
7. There have been two significant deterrents to the application of phosphoric acid for such purposes in the past. Clean acid must be used lest impurities emanating from the catalytic medium contaminate the product. Pure, furnace acid is too expensive to serve in this capacity; wet process acid is too impure. Technologies developed by IMI⁽⁶⁾ for

Table I

Kinematic Viscosity of Phosphoric Acid Solutions

<u>Temp. (°C)</u>	<u>100% H₃PO₄</u>	<u>110% H₃PO₄</u>	<u>115% H₃PO₄</u>
25	100	2200	
30	81	1600	
40	53	810	
50	36	410	
60	25	270	
80	14	100	1500
100	9.2	50	600
120	6.2	29	250
140	4.5	18	120
160	3.5	13	68
			41

Viscosities expressed in centistokes

From "Phosphoric Acid" by Monsanto

- a) the production of phosphoric acid using hydrochloric acid as the primary acidulant, and
- b) the purification of wet process phosphoric acid

overcome these drawbacks and provide clean acid of the necessary characteristics at an economically viable price, being particularly attractive for developing countries.

8. Let us assume that an equal weight of phosphoric acid is substituted for sulfuric acid in a given application, all other process parameters being taken as equal. The cost data given in Table II show the advantage of the substitution, even assuming the marketability of ammonium sulfate at \$ 15 per ton. A process charge of \$ 13.70 can be converted to a \$ 10.40 credit per ton of acid employed.
9. This approach to better economics is applicable to a wide variety of chemical processes which include aromatic nitration and hydrocarbon separations. Of these, the Beckmann rearrangement for caprolactam production and the Ritter reaction used in the synthesis of N-substituted amides have been selected for illustration.

II. BECKMANN REARRANGEMENT

Formulation of the Problem

10. The Beckmann rearrangement of cyclohexanone oxime to caprolactam :



entails two major technological hurdles: its high exothermicity and the basic character of the product lactam.

11. The calculated reaction enthalpy of the transformation is -45 Kcal/mol. This is one reason why it has been difficult to apply heterogeneous catalysis to this transformation. In commercial practice, a weight ratio of sulfuric acid to oxime of 4:1 is commonly used. The excess acid serves to ensure efficient heat dissipation, minimizing by-product formation.

Table II

Prices of Inorganic Chemicals (\$/ton)

H_2SO_4	20
H_3PO_4 (100%)	70
NH_3	40
$(NH_4)_2SO_4$	15 (?)
$(NH_4)_2HPO_4$	70

Inorganic Reagent Economics (per ton of acid)

Sulfuric Acid Route :	\$ 13.70 cost
Phosphoric Acid Route :	\$ 10.40 credit

12. Since the lactam is a weak base, it is bound by the acidic medium and can be liberated only by neutralizing all the acid present. This leads to the co-product problem.

Beckmann Rearrangement in Phosphoric Acid

13. A comparison of the viscosity data for 100% and 115% H_3PO_4 (Table I) shows the marked technological advantage to be gained by the use of the more dilute reaction medium. On the other hand, hydrolysis of both the oxime and the amide is sensitive to the concentration of the acid. However, with good control of the reaction parameters, efficient conversions are achievable. Two modes of operation on a laboratory scale were examined - batch reaction and in a continuous manner.

Batch Reactions

14. Similar to the Beckmann rearrangement with concentrated sulfuric acid, an excess of phosphoric acid is needed to achieve high yields of caprolactam. Quantitative conversions and yields of 95% and higher can be obtained when 100% H_3PO_4 is used in a system containing weight ratios of acid to oxime between 4.5 : 1 and 8 : 1.
15. Reactions were performed by immersing stirred solutions of the oxime in the acid into a bath maintained at approximately 140°C for a period of 5-6 minutes. Even on a small laboratory scale, the high rearrangement enthalpy could not be efficiently dissipated and temperatures developed in the reaction mixture which were five to ten degrees higher than that of the bath. In view of the short reaction times required, a continuous process was indicated.

Continuous Reactions

16. The bench reactor was a stirred 35 ml jacketed chamber heated by pumping hot glycerine (140 - 150°C) through the jacket. The feed solutions of oxime in phosphoric acid were introduced through a 60 ml. preheater maintained at 70-75°C by a hot water jacket. The residence time was regulated by the flow rate of the feed, while the reaction volume was maintained at 17 ml. by regulating a reactor bleed-off system.

17. By operating in this manner, the temperature within the reactor remained constant at 20° above that of the bath and the residence time was only six minutes. In this apparatus quantitative yields of lactams were obtained at 97% conversion using an acid to oxime ratio of 5 : 1. With half this amount of acid, 94% yields were had at 97% conversion.

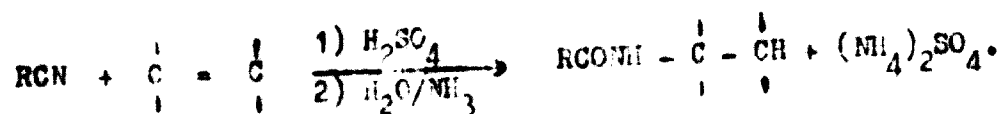
Product Recovery

18. Caprolactam can be separated from the reaction mixture by dilution with water and ammoniation of the phosphoric acid to pH 7. The behaviour of this system parallels that of solutions of caprolactam in sulfuric acid. The choice of ammoniation conditions is based on the phase diagram for the system $(\text{NH}_4)_2\text{O} - \text{P}_2\text{O}_5 - \text{H}_2\text{O}$ (7), being selected to cause ammonium phosphate to precipitate directly as a solid phase. At temperatures below 40°C and pH up to 7, an upper phase of caprolactam, water and traces of phosphoric acid is obtained. The lower liquid phase is a phosphate brine saturated with respect to the solid phase. The caprolactam can be extracted from the upper phase with a solvent such as chloroform.

III. RITTER REACTION

Background

19. A number of methods are known for the preparation of N-substituted amides. Thus, for example, carboxylic acids, as such or in the form of their acid halides or anhydrides, can be reacted with amines; unsubstituted amides can be alkylated on the nitrogen atom; oximes can be rearranged in the presence of acidic reagents; etc. A versatile procedure, and one which could lend itself well to industrial application because of its applicability to basic, relatively inexpensive industrial raw materials has been advanced by Ritter (8). In this method, nitriles interact with olefins or hydrated olefins (secondary or tertiary alcohols) in the presence of large quantities of concentrated sulfuric acid. The N-substituted amide is separated from the hydrolysed product after neutralization :

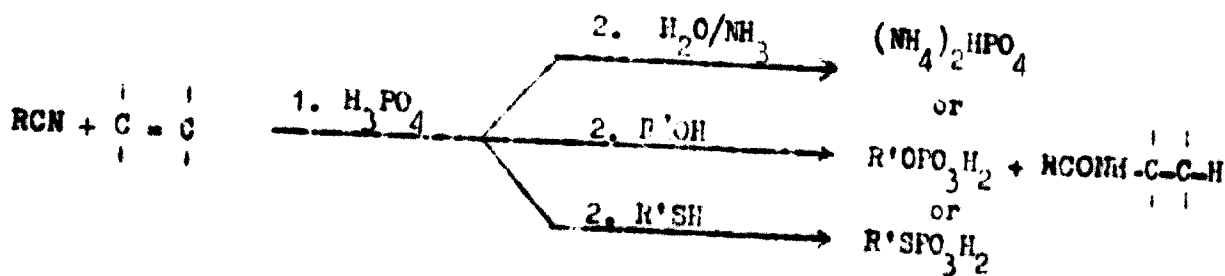


20. The co-product sulfate problem presents itself once again. Furthermore, the use of sulfuric acid in the application of this reaction to sensitive compounds is somewhat limited. For example, benzene sulfonic acid has been preferred to sulfuric acid when aromatic compounds are employed. Easily polymerizable substrates, such as acrylonitrile, have also proved to be troublesome in sulfuric acid media.
21. Attempts have been made to substitute the sulfuric acid use in the Ritter reaction by polyphosphoric acid. However, the poor yields obtained forced the conclusion that the application of polyphosphoric acid in this transformation is impractical^(1b).

Ritter Reaction in Phosphoric Acid

22. Only one attempt appears to have been made previously to use phosphoric acid for this purpose⁽⁹⁾. A yield of only 4.2% of wide was obtained.
23. It has been found in our laboratories that essentially quantitative yields can nevertheless be obtained using 100% phosphoric acid, instead of concentrated sulfuric acid, although H_3PO_4 of still lower concentration (85%) can be applied with reasonably good results. Advantages are thereby provided in that: 1) alkali and/or ammonium phosphates are obtained as co-product 2) aromatic and other sensitive materials present in this reaction medium are inert.
24. It has also been found that treatment of the olefin-nitrile reaction product with compounds containing the hydroxyl or sulfhydryl group prior to the introduction of water or neutralisation, produces the corresponding mono-substituted phosphoric acid derivatives as by-product.

25. The following outline represents three alternatives when using phosphoric acid:



The substituted phosphoric acid derivatives have found application as: lubricant additives, components in corrosion resistant coatings, in leather tanning and water proofing, as insecticides and larvacides, as emulsifiers, and as components in plastics to impart fire resistance and plasticity.

26. To effect these reactions it is only necessary to contact the olefin, nitrile, and acid in a liquid mixture at ambient temperature for approximately one hour and then add the second component, the alcohol, thiophenol, etc.
27. It is important to note that when using phosphoric acid, under preferred conditions for reaction, i.e. ambient temperature and absence of additional solvent or diluents, the molar ratio of acid to nitrile should be at least 2 : 1 to produce maximum yields, which in most cases are quantitative with respect to the organic reagents.
28. The nitrile and olefinic (or hydrated olefinic) component may be any of a wide range of aliphatic or aromatic compounds. Some of these are listed below :

<u>RCN</u> <u>R =</u>	<u>Olefin or</u> <u>Hydrated Olefin</u>
CH ₃ -	i-Butene
n-C ₁₇ H ₃₅ -	i-Butanol
C ₆ H ₅ -	i-Propanol
C ₆ H ₅ CH ₂ -	Di-isobutene
ClCH ₂ -	Camphene
CH ₂ = C(CH ₃) -	Cyclohexanol
p-NO ₂ -C ₆ H ₄ CH ₂ -	Styrene
NC(CH ₂) ₃ -	2-Methyl butene-2
CH ₂ = CH -	

29. The hydroxy or sulfhydryl component added at the termination of the primary reaction, and used to produce the substituted phosphoric acid, can be an unsubstituted or substituted primary, secondary or tertiary alcohol or thioalcohol, phenol or thiophenol. The reaction is very rapid and so mild that inorganic acid esters difficult to prepare by other means (e.g. t-butoxy derivatives of phosphoric acid) can be obtained in this manner.
30. The product amides may find use as such, or be converted to amines by hydrogenation or hydrolysis. Thus, alkyl acrylamides, useful monomers in acrylic resins, can be synthesized by this route from organic raw materials costing less than 10 £/lb. In an additional example, t-butylamine can be prepared from inexpensive isobutylene and acetonitrile.

IV. SUMMARY AND RECOMMENDATION

31. Sulfuric acid is frequently applied in the petrochemical industry as a catalytic medium and solvent. Spent acid is subsequently transformed into a chemical fertilizer, usually ammonium sulfate. Markets for this commodity are reaching saturation, though the number of commercial processes and installations which are potential producers of the salt is on the increase. Many of the new petrochemical installations are scheduled for developing countries. These countries are also major markets for chemical fertilizers.
32. It is possible to replace sulfuric acid by phosphoric acid in many of these applications. New processes for phosphoric acid manufacture and purification make this substitution both technologically and economically viable.
33. The use of phosphoric acid in the Beckmann rearrangement for caprolactam production and in the Ritter reaction for the synthesis of N-substituted amides has been described. In addition to these, phosphoric acid can be used in aromatic nitrations, in hydrocarbon separations, etc. Spent acid can be transformed into phosphates which are more valuable and marketable co-products. This substitution should be considered for examination when concentrated mineral acid media are called for.

V. ACKNOWLEDGEMENTS

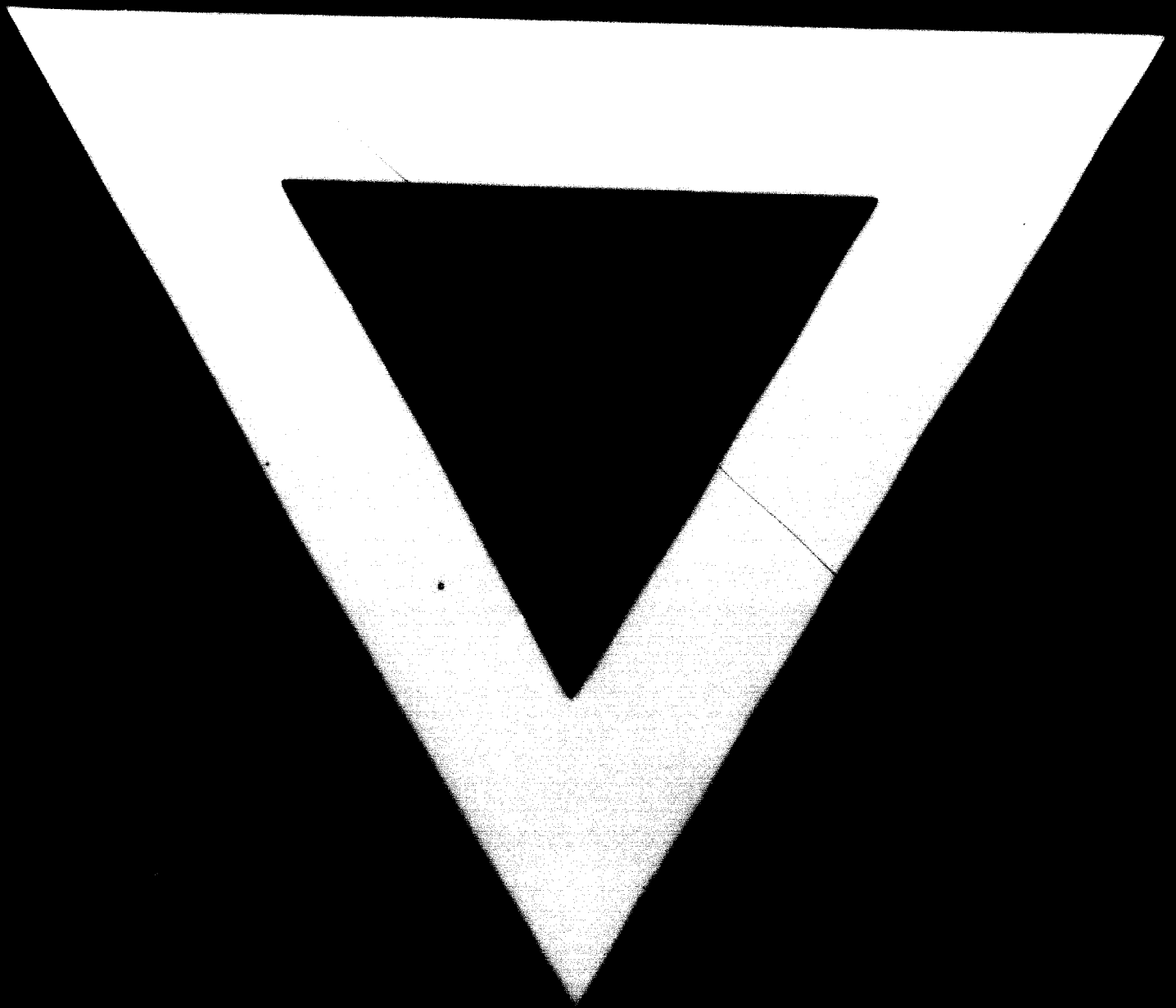
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VI. BIBLIOGRAPHY

35. 1. a) F. Popp, et al.
Trans. Kansas Acad. Sci. 63, No. 3, 169 (1960)
- b) C. T. Elston
Ph.D. Dissertation, Univ. of Ill., June 1964
2. E. C. Horning and V.L. Stromberg
J. Am. Chem. Soc. 74, 2680-81 (1952)
3. D. E. Pearson and R. M. Stone
ibid. 83, 1715-17 (1961)
4. T. R. Hopkins et al.
U. S. Pat. 3,016,375 (9.1.1962)
5. Organico
a) French Pat. 1,357,789 (2.3.1964)
b) British Pat. 1,021,197 (2.3.1966)
6. a) A. Baniel, et al.
Br. Chem. Engng. 4, 223 (1959)
b) Israel Pat. 21,247 (1967)
c) Israel Pat. 21,071 (1967)
7. B. Wendrow and K. A. Kobe
Chem. Reviews 54, 890 (1954)
8. J. J. Ritter and P. Minieri
J. Am. Chem. Soc. 70, 4045 (1948)
9. G. Glikmans, et al.
Bull. Soc. Chim. France 1376 (1966)





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