REFERENCES

1. AOCS, "Official and Tentative Methods of Analysis," 2nd ed. rev. to 1961, Chicago.
2. Bailey, A. E., and R. O. Feuge, Ind. Eng. Chem., Anal. Ed., *15*, 280–281 (1943).
3. Deutschmann, A. J., and I. S. Klaus, Anal. Chem., *32*, 1809–1810 (1960).
4. Feuge, R. O., and E. R. Cousins, JAOCS, *37*, 267–271 (1960).
5. Frankel, E. N., C. Evans, Helen A. Moser, D. G. McConnell, and J. C. Cowan, *Ibid.*, *38*, 130–134 (1961).
6. Kuck, J. C., W. A. Pons, Jr., and V. L. Frampton, *Ibid.*, *39*, 84–86 (1962).
7. Luddy, F. E., R. A. Barford, and R. W. Riemenschneider, *Ibid.*, *37*, 447–451 (1961).
8. Paul, S., and A. Roylance, *Ibid.*, *39*, 163–165 (1962).
9. Pohle, W. D., R. L. Gregory, and J. R. Taylor, *Ibid.*, *39*, 226–229 (1962).
10. Pons, W. A., Jr., J. C. Kuck, and V. L. Frampton, *Ibid.*, *37*, 671–673 (1960).
11. Pons, W. A., Jr., J. C. Kuck, and V. L. Frampton, *Ibid.*, *38*, 104–107 (1961).
12. Pons, W. A., Jr., J. C. Kuck, and V. L. Frampton, *Ibid.*, in press.
13. Stern, M. H., and J. G. Baxter, Anal. Chem., *19*, 902–905 (1947).

[Received March 18, 1963—Accepted July 15, 1963]

The Reaction of Phosphorus Trichloride with Fatty Acids

A. R. GALBRAITH, P. HALE, and J. E. ROBERTSON, Procter & Gamble Limited, Newcastle upon Tyne, England

Abstract

An investigation of the reaction of phosphorus trichloride with fatty acids has provided a reliable guide to choice of reaction conditions. Excesses of 25–100% phosphorus trichloride are required for high conversions; the shorter the chain length of the acid, the larger the excess of reagent required.

We consider the reaction path to be satisfactorily established and have shown several hypotheses made to account for the formation of hydrogen chloride as a by-product, to be unnecessary.

Two alternative mechanisms for the reaction are proposed and discussed.

Introduction

RECENT WORK in these laboratories has utilised fatty acid chlorides as intermediates, and a clean, rapid and economical method of preparation was sought. Acid chlorides may be readily prepared by a variety of reagents and Bauer (1) has made a cost comparison favouring phosphorus trichloride as the most economical reagent. A survey of the literature, however, revealed a wide variation in recommended usage (1–6). Sonntag (2) has remarked that no satisfactory account of the reaction of phosphorus trichloride with carboxylic acids is available, and that work is required to establish the contributions of the various reactions postulated. The generally accepted (2,7,8) stoichiometry of the reaction is given by equation I, with production of an upper layer of

$$3RCOOH + PCl_3 \longrightarrow 3RCOCl + H_3PO_3 \qquad [I]$$

acid chloride containing phosphorus chlorides, and a lower layer of impure phosphorus acid. We refer to this impure phosphorous acid as "phosphorous acid," to distinguish it from pure crystalline phosphorous acid. All phosphorus trichloride/carboxylic acid reactions evolve hydrogen chloride, and it is the failure of equation I to account for this by-product which has led to the confused and hesitant explanations in the current textbooks (2,7–9).

Experimental

Raw Materials. The fatty acids used were acetic (99.6% May and Baker laboratory chemicals), octanoic (98% B.D.H. laboratory reagent grade), oleic (95–100% B.D.H. laboratory reagent grade), and tallow (mw 266). Phosphorus trichloride was from Albright and Wilson, Ltd.

Infrared Spectra. IR curves were obtained in CCl_4 solution on a Perkin-Elmer "Infracord" spectrophotometer.

General Method of Reaction. A convenient sample size (100–200 g) of liquid or molten fatty acid was treated with phosphorus trichloride over a set period with or without agitation, and allowed to separate into two layers. The syrupy lower layer, essentially (3) phosphorous acid, was run off leaving a water-white layer of acid chloride, containing unreacted fatty acid and chlorides of phosphorus. All runs were carried out under anhydrous conditions, and hydrogen chloride evolved during the reaction was flushed out at the end of the reaction period with dry nitrogen. Yields were estimated from the weight of product, its analysis for free fatty acid (IR carbonyl stretching intensity using calibration curves), and phosphorus chlorides content (volumetric analysis for phosphorus). Hydrogen chloride was estimated by back titration after absorption in a caustic trap, in front of which was a solid CO_2/methanol trap to retain volatile acid chlorides.

Discussion

An examination of the reaction variables: agitation, time, temp and excess of phosphorus trichloride, adopting the stoichiometry of equation I, and confining ourselves to acetic, caprylic, and tallow acids, afforded results in Table I. The following conclusions were made on the basis of these experimental results:

1) Little reliance could be placed upon the analyses of acetyl chloride, which partly hydrolysed during the combined operational and analytical procedures (Table I, runs 24–29).
2) Reaction rate for all three acids was rapid, a period of 2 hr ensured reaction completeness and clean separation of layers. (Table I, 17,18,20).
3) Evolution of hydrogen chloride was temp-dependent (Table I, 3 and 12; 5,7, and 11; 21,22 and 23).
4) Yield of acid chloride was independent of temp over the range 70–160F, although operation at 180F or above caused drastic reductions in yield (Table I, 2,4,8 and 13).
5) The effect of agitation was insignificant compared with that of the excess of phosphorus trichloride. (Table I, 1 and 2; 6 and 7).

In later experiments, conditions were fixed at 2 hr reaction time, no agitation, and minimum temp at which the fatty acid was liquid, leaving the excess

TABLE I

Results of Initial Acid-Phosphorus Trichloride Reactions

Run no.	Acid chain length	Agit.	Temp F	Time hr	Excess PCl_3 %	Yield %	FFA %	HCl evolution moles/ mole F.A.	P in "H_3PO_3" %
1	C_{17} avg	No	110	2	0	87	13.4	0.07	32.6
2		Yes	110	2	0	90	9.7	0.14	......
3		No	110	2	100	99	0.5	0.21	36.3
4		Yes	140	2	10	90	10.0	......	......
5		Yes	140	2	60	98	1.4	0.21	......
6		Yes	160	2	60	99	1.1	0.25	......
7		No	160	2	60	99	0.9	0.27	36.0
8		Yes	160	2	10	87	11.6	......	......
9		Yes	180	2	10	86	11.7	......	......
10		Yes	180	2	10	80	9.7	......	......
11		Yes	180	2	60	97	0.7	0.30	......
12		No	180	2	100	52 small upper layer	0.5	0.56	......
13		Yes	200	2	10	no separation of layers		......	......
14		No	110	2	20	92	7.1	0.09	38.0
15		No	110	2	25	95	4.7	0.05	38.1
16		No	110	2	100	99	0.4	0.12	38.0
17	C_8	No	70	22	0	88	12.6	......	......
18		No	70	6	0	87	11.4	......	......
19		No	70	2	0	76	22.4	......	......
20		Yes	70	2	0	85	12.3	......	......
21		No	70	2	60	93	6.8	0.09	......
22		Yes	180	2	0	87	10.5	0.16	......
23		Yes	240	2	0	no separation of layers		0.35	......
24	C_2	Yes	65	2	0	70	29.0	0.01	......
25		Yes	65	2	0	90	9.8	0.06	29.9
26		Yes	65	4	0	62	37.0	0.02	......
27		Yes	65	4	0	80	19.4	0.10	......
28		Yes	65	6	0	72	27.4	0.05	......
29		Yes	65	6	0	83	16.0	0.10	......

H_3PO_3 has % P = 37.8. P_2O_3 has % P = 56.4.

of phosphorus trichloride as the only variable. The results of this investigation are expressed graphically in Figure I. The acid chlorides contain mixed phosphorus chlorides, proof of which is given in a later section of the text. For convenience, we have expressed the phosphorus content as phosphorus trichloride, and we shall discuss the effect of the assumption later. The phosphorus content is plotted as %PCl_3 by weight to allow use of the same scale as the % free fatty acid content. Both PCl_3 content curves become virtually identical as expected, if plotted as mole PCl_3/mole fatty acid chloride.

Comparison of the curve for tallow acid chloride with that of the lower acid chloride indicates the comparative economy of reagent usage when working with longer-chain acids. The sharpness of the break in the fatty acid curve for tallow acid chloride suggests an optimum at 30% excess trichloride, as little further conversion is achieved on increasing the excess used, while a rise in phosphorus chlorides content must be tolerated. With caprylic acid, the picture is less clear-cut, and the excess chosen will depend on the degree of conversion required.

The investigation has been extended to include oleic acid in order to check the above findings, and also to check the effect of phosphorus trichloride under these conditions on the *cis* double bond. The results were consistent with the general pattern, although the conversion was somewhat lower than expected: 85% conversion using 20% excess trichloride. Nevertheless, this represents an advantage over previous findings for oleoyl chloride (Table II).

It was noticeable that in all cases where a good grade of acid was used, water-white product was obtained, comparable to that produced by distillation. Thus if the chlorides of phosphorus present in the product can be tolerated, this procedure offers a high yield of good quality product. Preparations using thionyl chloride or phosphorus pentachloride afford dark products which require distillation, with consequent dimimution of yield, to achieve similar quality.

In Table II a comparison has been made of yields of acid chloride obtained in these laboratories with those reported in the literature for reactions using phosphorus trichloride. If the known levels of chlorides of phosphorus in the product can be tolerated the high yields obtained favour isolation without distillation. When phosphorus must be eliminated from the product, the patented method (4,9), of rapid treatment with water may be used without incurring reduction in yield.

Hydrogen Chloride Evolution. Hydrogen chloride is evolved in all fatty acid/phosphorus trichloride reactions. Equation I accounts for the stiochiometry observed in the reaction, but offers no explanation of the evolution of hydrogen chloride. The literature is undecided whether the evolution is part of the main reaction, or due to a side reaction. Equations II and III have been postulated (2,3) as alternative reaction

Reference		
2	$6RCOOH + 3PCl_3 \rightarrow 6RCOCl + P_2O_3 + 3HCl + H_3PO_3$	[II]
3	$3RCOOH + 2PCl_3 \rightarrow 3RCOCl + P_2O_3 + 2HCl$	[III]

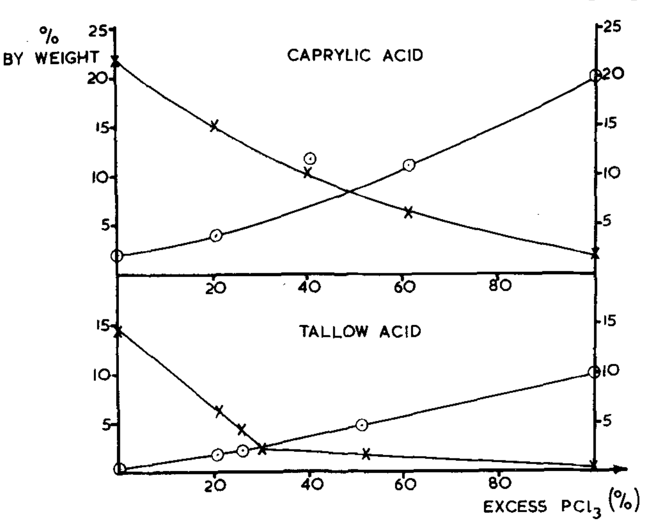


FIG. 1. Effect of excess of phosphorus trichloride reagent on yield of acid chloride. ○ = PCl_3, × = Fatty acid.

TABLE II

Comparison of Present and Literature Yields of Acid Chloride

Fatty acid	Excess PCl_3 %	Yield	Isolation procedure	Ref.
Acetic acid	0	69	Distilled	10
Acetic acid	20	84	Separated off	Present work
Acetic acid	80	79	Distilled	11
Caprylic	40	90	Separated off	Present work
Decanoic	200	97	Excess PCl_3 reagent removed at reduced pressure	3
Lauric	7	96	In solvent, lower layer separated off and solvent removed	3
Lauric	20	54–59	Distilled	1
Lauric	200	70–96	Distilled	1
Tallow	20	93	Separated off	Present work
Palmitic	200	85	Distilled	1
Oleic	20	85	Separated off	Present work
Oleic	20	37–60	Distilled	1
Oleic	30	42	Distilled	12
Oleic	450	89	Distilled	13

stoichiometries, but they can play no major part in the reaction, as the high conversions achieved on the stoichiometry of I, and the phosphorus content of the lower "phosphorous acid" layer found by both Piekarski (3) and ourselves (Table I) confirm that the reaction path is as represented by I. The reaction path of equation II is said (2) to proceed via the anhydride as an intermediate. We find this postulate difficult to accept since no evidence of anhydride formation is provided. These equations can still be used to explain hydrogen chloride evolution, but bearing in mind the temp dependence found for the evolution, we reject these equations in favour of a side reaction.

The following side reactions represented by equations IV–VII have been postulated in the literature (2,3,10,14) to account for hydrogen chloride evolution. We investigated these reactions under experimental conditions. No reaction took place between phosphorus trichloride and "phosphorous acid," contradictory to the postulation of Piekarski (3), but in agreement with Brooks (14), Partington (15) and Wolf (16). At higher temp volatilisation of trichloride and decomposition of the "phosphorous acid" took place.

Reference		
3	$PCl_3 + H_3PO_3 \longrightarrow P_2O_3 + 3HCl$	[IV]
2,14	$RCOOH + RCOCl \longrightarrow (RCO)_2O + HCl$	[V]
14	$RCOCl + H_3PO_3 \longrightarrow RCOOP(OH)_2 + HCl$	[VI]
10	$HPO(OH)Cl \longrightarrow (HPO_2) + HCl$	[VII]

We were unable to detect significant quantities of anhydride in any reaction product, or to find reliable accounts of anhydride formation and identification in the literature (4,10,14). We consider it more likely that anhydride formation would take place during distillation of the product, and cannot support Brooks' (14) postulate that acid chloride and fatty acid react to form anhydride, generating hydrogen chloride. We quote the results of runs 3,5,6,7,11, Table I as support. Sonntag (17) also doubts the validity of equation V in the case of higher fatty acids.

Brooks (14) has described the preparation of acetoxyphosphorus compounds as in equation VI, but under our reaction conditions no reaction was obtained between fatty acid chloride and "phosphorous acid"; raising the temp of the reactants only succeeded in decomposing the "phosphorous acid."

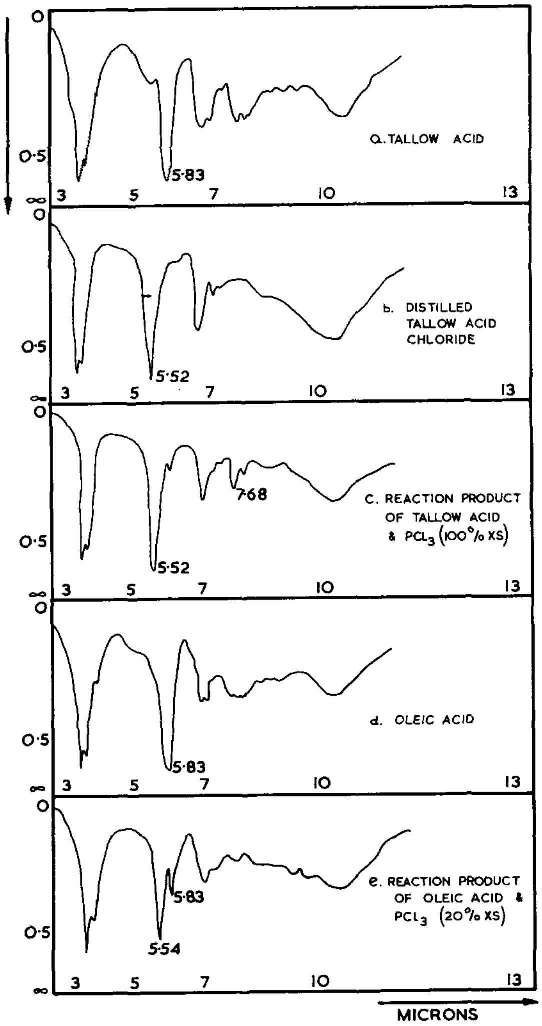


FIG. 2. Infrared spectra in CCl_4 solution.

The only credible explanation of hydrogen chloride evolution is given by Cade and Gerrard (10), who propose that the reaction proceeds by stepwise hydroxylation of phosphorus trichloride, producing two intermediates, $HPOCl_2$ and $HPO(OH)Cl$. The latter may either continue to react with another molecule of acid, or degrade to hydrogen chloride and condensed phosphorous acids as in equation VII. This degradation we would expect to be temp-dependent, and VanWazer (18) considers that these intermediates are capable of at least temporary existence. We have found evidence of their existence in tallow acid chloride containing 2% phosphorus: namely, a peak at 7.7 μ in the IR spectrum of the reaction product, attributable only to the P=O stretching frequency, as the peak is absent in the spectrum of the pure acid chloride, and the acid content of the reaction product is too low to account for it. (Fig. 2, a,b and c).

Further evidence was forthcoming from unsuccessful attempts to remove excess phosphorus trichloride from reaction products by distillation, contrary to reported claims (2,3,12,14,19). Distillation of the above tallow acid chloride below 212F afforded no phosphorus trichloride (bp 167F) and when tenfold excesses of phosphorus trichloride were used, only part of the calculated excess was recovered. It appears unlikely that phosphorus present in the reaction product exists as the trichloride.

In the lower "phosphorous acid" layer, in spite of repeated flushing with nitrogen, chlorine could not be entirely removed. We suspect the presence of the chlorophosphorous acid, rather than dissolved hydrogen chloride. We have found enough chlorine to account for 4% of the lower layer as monochlorophosphorous acid [HPO(OH)Cl]. The observed diminution in yield at increased temp (Table I, 10,12,13 and 23) may be attributed to interaction of both intermediate chlorophosphorous acids with fatty acid chloride, producing acyloxyphosphorous compounds,

$$\mathrm{RCOCl + HPO(OH)Cl \longrightarrow HPO(OCOR)Cl + HCl} \quad [\mathrm{VIII}]$$

as in equation VIII. This reaction we expect to proceed more readily that the acid chloride/phosphorous acid reaction of Brooks (14) (equation VI), as the latter reagents are immiscible. A concrete example may be found in the reaction with oleic acid. Sonntag (12) reports a 42% yield after distillation from a reaction using 30% excess phosphorous trichloride, and doubts the value of this reagent with unsaturated acids. He considers that side reactions such as isomerisation of, and hydrogen chloride addition to the double bond are extremely likely. With oleic acid we have shown that no isomerisation of the double bond takes place under mild conditions; no increase in absorption at 10.4 μ (Fig. 2, d and e). We have obtained an 85% yield using only 20% excess phosphorus trichloride. We consider that poor yields reported for phosphorus trichloride reactions with fatty acids are caused by high temp, either in the reaction or in the isolation, at which acyloxyphosphorous compounds are formed. The postulate of chlorophosphorous acids affords an explanation of observed increases in yields from stirred reactions (Table II, 1 and 2; 19 and 20), namely, better contact of unreacted fatty acid with the chlorophosphorous acids carried down to the lower layer.

The phosphorus contents were expressed as $\%\mathrm{PCl_3}$ in Figure 1. From the evidence quoted above, we must modify them to correct for the over-estimation of mol wt of the impurity, by using a correction factor intermediate between 100/137 and 119/137. This will increase the yields of acid chloride, but not enough to make a significant difference to the values quoted in Tables I and II.

The explanation of Cade and Gerrard (10) is the only one to explain all the observed facts, and we consider that no other explanation of hydrogen chloride evolution is necessary.

Catalysis of the Reaction. Reaction catalysis by neutral salts has been studied by Kraft (5). His arguments lead him to favour a mechanism proposed by Lucas and Pressman (20), but his evidence is based on the belief that rate of evolution of hydrogen chloride is a direct measure of reaction rate. On our

$$\begin{aligned}&\mathrm{RCOOH + PCl_3 \longrightarrow RCOOPCl_2 + HCl}\\&\mathrm{RCOOPCl_2 \longrightarrow RCOCl + (POCl)}\end{aligned}$$

evidence we consider that hydrogen chloride simply measures loss of available reagents, varies with temp, and is not related to the yield of acid chloride. We therefore disregard Kraft's conclusions. We have investigated catalysis of the reaction by the neutral salts (NaCl and KCl), but have found no significant gains in conversion over the 2 hr period (Table III). Rate of reaction was not studied.

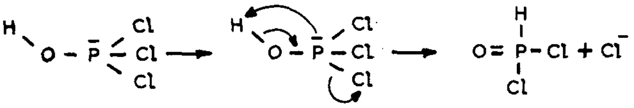
Mechanism of the Reaction. In spite of the use made of this reaction, little has been said on its mechanism. The mechanism suggested by Lucas and Pressman (20) may be ruled out since it requires one mole of hydrogen chloride to be evolved for each mole of fatty acid, and that strong acids might be expected to react faster than weak acids. Our observations of hydrogen chloride evolution were normally 0.1 mole/mole (Table II), and weak acids react much more rapidly (5) than do strong acids.

TABLE III

Comparison of Conversions from Catalysed and Uncatalysed Reactions

Run no.	Acid chain length	Catalyst 1g	Temp F	Time hr	Excess $\mathrm{PCl_3}$ %	FFA %	HCl evolution moles/mole F.A.	P in "$\mathrm{H_3PO_3}$" %
1	C_7	....	110	2	0	13.4	0.07	32.6
2		....	110	2	0	9.7	0.14	......
30		NaCl	110	2	0	4.8	0.04	34.3
31		NaCl	110	2	0	14.8	0.08	
14		....	110	2	20	7.1	0.09	38.0
32		NaCl	110	2	20	5.0	0.09	32.2
33		NaCl	110	2	20	4.3	0.14	......
19	C_8	....	70	2	0	22.4	......	......
20		....	70	2	0	12.3	......	......
34		NaCl	70	2	0	21.2	......	......
35		KCl	70	2	0	18.2	......	......
36		NaCl	70	2	40	5.2	......	......
37		NaCl	70	2	40	15.4	......	......

Cade and Gerrard (10) explain the reaction as a stepwise hydroxylation to phosphorous acid, by a four-centre transition mechanism. This explanation is acceptable, but provides no explanation of the more rapid reaction rate of weak acids, nor does it suggest a driving force for the reaction. We can also regard phosphorus trichloride as a strong acid, capable of using a weak acid to act as its conjugate base, supplying OH⁻. The driving force could be the expansion of the d orbital of phosphorus to accommodate 10 electrons, eliminating Cl⁻. With increase in acid



strength, this reaction would proceed more slowly, and with fully ionised acids, little or no reaction would take place, as is found experimentally (5). There is no evidence as yet for the existence of the intermediate ion $\mathrm{RC^{+}{=}0}$, and a kinetic investigation of the reaction is necessary to differentiate between the two mechanisms.

ACKNOWLEDGEMENTS

Special analyses by R. Brotherton and his staff. Helpful discussions with N. E. Ward and P. Robson.

REFERENCES

1. Bauer, S. T., Oil & Soap *23*, 1, (1946).
2. Markley, K. S., "Fatty Acids," 2nd Ed., Part 2, Interscience, New York, 1961, p 1127–1138.
3. Piekarski, S., Oleagineux, Vol. 13, p 749, (1958).
4. Youngs, C. C., A. Epp, B. M. Craig, and H. R. Sallens, JAOCS *34*, 107, (1957).
5. Kraft, M. Ya, and V. V. Katyshkina, J. Gen. Chem. U.S.S.R. *29*, 62, (1959).
6. Kastens, M. L., and J. J. Ayo, Ind. Eng. Chem. *42*, 1626, (1950).
7. Vogel, A. I., "Practical Organic Chemistry," 3rd Ed., Longman's, London, 1956, p 367.
8. Feiser, L. F., and M. Feiser, "Organic Chemistry," 3rd Ed., Reinhold, New York, 1956, p 180–181.
9. Ralston, A. W., M. R. McCorkle, and R. J. VanderWal (Armour & Co.), U.S. 2,262,431 (1941).
10. Cade, J. A., and W. Gerrard, J. Chem. Soc. 2030, (1954).
11. Clark, R. H., and A. Bell, Trans. Roy. Soc. Canada *27*, III, 97, (1933).
12. Sonntag, N. O. V., J. R. Trowbridge and I. J. Krems, JAOCS *31*, 151, (1954).
13. Craig, B. M., N. O. Lundberg, and W. F. Geddes, *Ibid.*, *29*, 169, (1952).
14. Brooks, B. T., J. Am. Chem. Soc., *34*, 492, (1912).
15. Chalk, L. J., and J. R. Partington, J. Chem. Soc. 1930, (1927).
16. Wolf, L., E. Kalaehne, and H. Schmager, Chem. Ber. *2*, 1441, (1929).
17. Sonntag, N. O. V., Chem. Revs. *52*, 330, (1953).
18. VanWazer, J. R., "Phosphorus and Its Compounds," Vol. I., Interscience, New York, 1958, Chapter 5.
19. Cahn, F. J. (The Emulsol Corp.), U.S. 2,282,320 (1942).
20. Lucas, H. J., and D. Pressman, "Principles and Practice in Organic Chemistry," John Wiley and Sons Inc., New York, 1949, p 267.

[Received March 28, 1963—Accepted September 13, 1963]