starting tributyl phosphate. A small amount of monobutyl phosphoric acid (3% of total acid) was evidenced by a second inflection in the titration curve. The aqueous layer was separated and the organic layer was washed twice with water.

Dibutyl phosphoric acid was recovered by cooling and acidifying (sulfuric acid) the aqueous solution of salts and extracting with carbon tetrachloride (two equal volume extractions). Any co-extracted monobutyl phosphoric acid was removed with a one-fourth volume water wash.[10] The dibutyl phosphoric acid, dried *in vacuo*, was identified by titration, density, and melting point of the copper salt; d_4^{25} 1.054, reported 1.057,[11] 1.054.[7]

Anal. Neut. equiv. Calcd.: 210. Found: 212. The copper salt of dibutyl phosphoric acid, $Cu(DBP)_2$, melted at 118–119° alone and when mixed with an authentic[12] specimen.

(4). *"Polymer."* The residue remaining after removal of tributyl phosphate by distillation at 1 mm. of mercury was identified as tetrabutyl pyrophosphate (TBPP). The alkali- and water-washed, dried residue (1.8 g.) contained 15.6% P (radioactive assay), had a molecular weight in benzene of 392[13] and an equivalent weight of 208 (16 hr. hydrolysis with 1*N* sodium hydroxide at room temperature, alkaline solution passed through cation resin in H^+ form, regenerated acid titrated with sodium hydroxide). Required for $(C_4H_9O)_2P(O)OP(O)(OC_4H_9)_2$: 15.4% P; m.w., 402; equivalent weight, 201. A small amount of inert (to sodium hydroxide) material was recovered and found to contain 18–20% phosphorus by radioactivity assay.

A derivative of the tetrabutyl pyrophosphate was prepared in 66% yield by heating 2 mmoles of dibenzylamine with 1 mmole of tetrabutyl pyrophosphate for 5 hr. at 100° and recrystallizing the amine salt of dibutyl phosphoric acid (precipitated by addition of petroleum ether) twice from hot *n*-hexane. Similarly, from an authentic sample of tetrabutyl pyrophosphate (prepared by the method of Toy[14] but not distilled), was derived the same amine salt. The melting point of each salt alone and mixed with an authentic specimen of $(C_6H_5CH_2)_2NH \cdot DBP$ was 109°.

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[10] D. C. Stewart and H. W. Crandall, *J. Am. Chem. Soc.* **73**, 1377 (1951).

[11] H. Adler and W. W. Woodstock, *Chem. Ind.* **51**, 516 (1942).

[12] W. H. Baldwin and C. E. Higgins, submitted to *J. Inorg. and Nuclear Chem.*

[13] F. Daniels, J. H. Mathews, and J. W. Williams, *Experimental Physical Chemistry*, 2nd ed., McGraw-Hill Book Co., Inc., New York-London, 1934, pp. 58–64.

[14] A. D. F. Toy, *J. Am. Chem. Soc.* **70**, 3882 (1948).

[Contribution from the Carothers Research Laboratory, E. I. du Pont de Nemours and Co.]

Reaction of Arylphosphinic Acids with Phosphorus Trichloride: Conversion of a Tetracovalent to a Trivalent System

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A facile method has been discovered for converting primary phosphinic acids to phosphonous dichlorides by reaction with phosphorus trichloride. The reaction provides a simple and convenient method for preparing phosphonous dichlorides of high degree of purity, and proves that the primary phosphinic acids, which are normally monobasic, are capable of reacting in their tautomeric dibasic form as phosphonous acids. An attempt to extend this reaction to the synthesis of a phosphinous chloride from a secondary phosphine oxide was not successful.

Compared to the preparation of acid chlorides from phosphonic acids (RPO_3H_2) and secondary phosphinic acids (R_2PO_2H), the conversion of primary phosphinic acids (RPO_2H_2) to the corresponding acid chlorides ($RPCl_2$) has received scant attention.[2] The probable reasons for this are twofold: The acids are usually prepared by hydrolysis of the chlorides in the first place, and this hydrolysis is accompanied by an apparently irreversible transformation in which the trivalent phosphorus atom becomes tetracovalent:

$$\underset{\text{I}}{RPCl_2} \longrightarrow \underset{\text{II}}{RP(OH)_2} \rightleftarrows \underset{\text{III}}{RPH(O)OH}$$

The product is a monobasic phosphinic acid (III) and not the expected dibasic phosphonous acid (II).

The reversal of this hydrolysis would, as pointed out by Kosolapoff,[3] be of great interest for both theoretical and practical reasons. It would prove that the phosphinic acids are capable of reacting in their tautomeric trivalent form, and would provide a simple and convenient method for the synthesis of phosphonous dichlorides of high degree of purity. The phosphinic acids, especially those of the aromatic series, are almost all well defined crystalline solids, whereas the dichlorides are usually fuming liquids. Also, several syntheses of phosphinic acids have appeared recently which do not proceed through the dichlorides as intermediates.[4]

A facile method for carrying out this reversal has now been discovered. The reaction of phenyl-

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[2] The synthesis of phosphonous dichlorides from phosphonous diesters by an exchange reaction with phosphorus trichloride according to the equation $RP(OC_2H_5)_2 + PCl_3 \rightarrow RPCl_2 + (C_2H_5O)_2PCl$ was recently described by M. Sander, *Chem. Ber.*, **93**, 1220 (1960).

[3] G. M. Kosolapoff, *Organophosphorus Compounds*, John Wiley & Sons, Inc., New York, N. Y., 1950, p. 50.

phosphinic acid (III. R = C_6H_5) with an excess of phosphorus trichloride was found to give phenylphosphonous dichloride (I. R = C_6H_5) in 70% yield. The reaction was immediate, either in the presence or absence of a solvent, and the product could be distilled at once following the removal of the phosphorous acid layer.

$$3RPO_2H_2 + 2PCl_3 \longrightarrow 3RPCl_2 + 2H_3PO_3$$

The product was a colorless, fuming liquid, b.p. 92.5°/10 mm., n_D^{25} 1.5948, and was identified as phenylphosphonous dichloride by elemental analysis, by its reaction with water or ethanol-water to regenerate the acid, and by the formation of the crystalline dipiperidide, m.p. 82–83°.

In the reaction with piperidine it was discovered that in addition to the known dipiperidide, which was formed in 67% yield, there was also produced a smaller amount (24%) of a crystalline product melting with decomposition at 125°. The same two products were obtained in roughly the same proportions when a commercial phenylphosphonous dichloride sample was employed, when the piperidine was redistilled just before use, and when the solvent was ether instead of benzene. From its elemental analysis it was established that this by-product, like the dipiperidide, had a 2:1 ratio of nitrogen to phosphorus, but its calculated molecular weight was higher (~320 *vs.* 276). It could be readily distinguished from the dipiperidide by its solubility in water and insolubility in ethyl acetate. The identity of the by-product was not established.

The effect of reducing the excess of phosphorus trichloride on the yield of phenylphosphonous dichloride is shown in Table I. The yield fell as the ratio of phosphorus trichloride to $C_6H_5PO_2H_2$ approached the stoichiometric 2:3 ratio, and at a 1:3 ratio the yield was zero. As the amount of phosphorus trichloride was reduced, there appeared more and more of a yellow undistillable solid which was unreactive toward water or ethanol.

TABLE I

EFFECT OF RATIO OF REACTANTS ON YIELD OF PHENYLPHOSPHONOUS DICHLORIDE

$C_6H_5PO_2H_2$ Moles	PCl_3, Moles	Solvent	$C_6H_5PCl_2$ Yield, %
0.09	0.03	Benzene	0
0.10	0.12	Benzene	54
0.10	1.00	Benzene	71
0.10	1.00	None	70

When the reaction was applied to *p*-tolylphosphinic acid (III. R = *p*-$CH_3C_6H_4$), the expected product, *p*-tolylphosphonous dichloride (I. R = *p*-$CH_3C_6H_4$), was obtained in even higher yield (85%).

The only previously known reaction of this type was carried out by Hatt,[5] who obtained triphenylmethylphosphonous dichloride (I. R = $(C_6H_5)_3C$) from triphenylmethylphosphinic acid (III. R = $(C_6H_5)_3C$) in 67% yield after an eight-hour reaction with phosphorus trichloride under reflux. Hydrogen chloride and free phosphorus were also produced, probably as a result of a secondary reaction between the phosphorus trichloride and the phosphorous acid. The reaction was considered to be peculiar to the triphenylmethyl system,[3] but it is evident now that it was not.

Also pertinent to this work was a much earlier investigation[6] in which it was found that phenylphosphinic acid reacts vigorously with phosphorus pentachloride giving phenylphosphonic dichloride, $C_6H_5POCl_2$. The reaction may be viewed as a redox reaction between the initially formed phenylphosphonous dichloride and the phosphorus pentachloride, though other interpretations are possible.

$$C_6H_5PO_2H_2 + 2PCl_5 \longrightarrow C_6H_5POCl_2 + POCl_3 + PCl_3 + 2HCl$$

The use of agents such as phosphorus pentachloride or thionyl chloride is therefore to be avoided because of the possibility of concomitant oxidation of the trivalent phosphorus atom.

Secondary phosphine oxides. The hydrolysis of a phosphinous chloride (IV) produces a similar situation to that described above for the phosphonous dichlorides (I); the product is not the expected phosphinous acid (V) but a neutral phosphine oxide (VI) which contains no acid function:

$$\underset{\text{IV}}{R_2PCl} \longrightarrow \underset{\text{V}}{R_2POH} \rightleftarrows \underset{\text{VI}}{R_2P(O)H}$$

It was of interest to determine whether the reversal could also be accomplished in this case by treatment with phosphorus trichloride. A single experiment with bis(2,3,5,6-tetramethylphenyl)-phosphine oxide (VI. R = 2,3,5,6-$(CH_3)_4C_6H$), however, did not give the expected phosphinous chloride. Although the oxide went into solution, there was no separation of phosphorous acid. Refluxing the mixture yielded only a glassy product which was inert toward water or ethanol. The phosphine oxide was known to be very resistant to oxidation,[7] and might also have required more severe conditions in the present reaction. Perhaps a more reactive compound such as diphenylphos-

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(4) See for example R. D. Stayner, U. S. Patents **2,686,803** (Aug. 17, 1954) and **2,693,482** (Nov. 2, 1954); H. Schmidt, *Chem. Ber.*, **81**, 477 (1948); A. R. Stiles, D. Harman, and F. F. Rust, U. S. Patent **2,724,718** (Nov. 22, 1955); C. W. Smith, U. S. Patent **2,648,695** (Aug. 11, 1953); H. C. Brown, U. S. Patent **2,584,112** (Feb. 5, 1952); ref. 2; and older methods described in ref. 3, chapter VII.

(5) H. H. Hatt, *J. Chem. Soc.*, 776 (1933).

(6) A. Michaelis and J. Ananoff, *Ber.*, **7**, 1688 (1874); A. Michaelis, *Ann.*, **181**, 265 (1876).

(7) A. W. Frank, *J. Org. Chem.*, **24**, 966 (1959).

phine oxide might undergo this reaction more readily.

In this reaction, too, the use of phosphorus pentachloride or thionyl chloride must be avoided to prevent oxidation of the trivalent phosphorus atom. Hunt and Saunders[8] found that treatment of diphenylphosphine oxide (VI, R = C_6H_5) with thionyl chloride gave diphenylphosphinic chloride, $(C_6H_5)_2P(O)Cl$. They viewed this reaction as a direct displacement of the P—H hydrogen in the phosphine oxide by a chlorine atom, since the same phosphinic chloride was produced in a reaction with *N*-chlorosuccinimide.[8] The reaction can also be interpreted as a two-step reaction via an initially formed diphenylphosphinous chloride, which then undergoes a redox reaction with the thionyl chloride.

The reported reaction[9] of 9,10-dihydro-10-phenophosphazine oxide with thionyl chloride to give a phosphinous chloride which was subsequently converted to a phosphinous ester with sodium ethoxide, with preservation of the trivalency of the phosphorus atom, seems to be an anomaly.

EXPERIMENTAL[10]

Materials. Phenylphosphonous dichloride and piperidine were purified by distillation. Phenylphosphinic acid was recrystallized from benzene; m.p. 88–88.5°. Phosphorus trichloride and benzene were used as obtained.

Phenylphosphonous dichloride (I. R = C_6H_5). (A) *With solvent.* Phosphorus trichloride, 88 ml. (1.0 mole), was added dropwise to a vigorously stirred slurry of 14.2 g. (0.1 mole) of phenylphosphinic acid in 100 ml. of benzene contained in a 500 ml. three neck flask equipped with stirrer, dropping funnel, and reflux condenser. Moisture was excluded by means of a drying tube attached to the top of the condenser. The acid gradually dissolved during the addition and an oily layer of phosphorous acid separated. The reaction mixture did not become warm, and no hydrogen chloride was evolved. At the end of the addition the solution was decanted from the phosphorous acid, concentrated to small volume, filtered to remove a yellow solid, and then distilled through a 20-cm. Vigreux column. The yield of phenylphosphonous dichloride, b.p. 92.5°/10 mm., n_D^{25} 1.5948, was 12.7 g. (71%). Buchner and Lockhart[11] give b.p. 90–92°/10 mm., n_D^{25} 1.5962 for phenylphosphonous dichloride prepared by the reaction of benzene with phosphorus trichloride and aluminum chloride. The product was a colorless, fuming liquid possessing a strong phosphine-like odor.

Anal. Calcd. for $C_6H_5PCl_2$: Cl, 39.62. Found: Cl, 39.45.

(B) *No solvent.* Phenylphosphinic acid, 14.2 g. (0.1 mole), was added in small portions to 88 ml. (1.0 mole) of vigorously stirred phosphorus trichloride contained in a 250 ml. three neck flask equipped with a stirrer and reflux condenser. Moisture was excluded by means of a drying tube attached to the top of the condenser. The acid was all added during a 10-min. period and appeared to react immediately with the separation of an oily layer of phosphorous acid. Both layers remained colorless. After 5 min. stirring, the solution was decanted from the phosphorous acid, concentrated to small volume, and then distilled through a 20-cm. Vigreux column. The yield of phenylphosphonous dichloride, b.p. 92.5°/10 mm., was 12.5 g. (70%).

Anal. Calcd. for $C_6H_5PCl_2$: Cl, 39.62. Found: Cl, 38.90.

Of the two methods, Procedure B is to be preferred for convenience and for the absence of the yellow solid.

Hydrolysis of phenylphosphonous dichloride. Hydrolysis of the phenylphosphonous dichloride obtained by Procedure A above with 10% hydrochloric acid or ethanol-water[12] gave the crystalline phenylphosphinic acid, m.p. 86–87°.

Reaction with piperidine. Phenylphosphonous dichloride, 7.17 g. (0.04 mole), was added dropwise to a vigorously stirred solution of 13.80 g. (0.162 mole) of piperidine in 100 ml. of benzene contained in a 500 ml. three neck flask equipped with mechanical stirrer, dropping funnel, and reflux condenser fitted at the top with a drying tube. Ice cooling was applied during the addition. The mixture was then stirred an additional 2 hr. at room temperature and filtered to remove the piperidine hydrochloride. After washing thoroughly with benzene and drying, the salt weighed 9.48 g. (calcd. for 0.08 mole $C_5H_{11}N.HCl$, 9.74 g.).

The filtrate and benzene washings were combined and evaporated, giving a malodorous oil which crystallized on standing to a hard mass of crystals. The crystals were triturated under water in a mortar and collected on a filter. After washing with water and drying in a vacuum desiccator, the crystals weighed 7.40 g. (67% as phenylphosphonous dipiperidide). A sample recrystallized twice from ethanol melted at 82–83°, but still possessed a piperidine-like odor as described by Michaelis.[13] The product was soluble in ether, benzene, chloroform, and ethyl acetate, and insoluble in water.

Anal. Calcd. for $C_{16}H_{25}N_2P$: C, 69.53; H, 9.12; N, 10.14; P, 11.21. Found: C, 68.67; H, 9.03; N, 10.21; P, 11.23. Previously reported melting points for phenylphosphonous dipiperidide were 78°[13] and 76°.[14]

In two other runs the filtrate from the piperidine hydrochloride only partially crystallized on evaporation. The semisolid yellow mass was slurried with ethyl acetate, which dissolved the oil but not the crystals, and filtered. Recrystallization from ethyl acetate gave 3.01 g. (24%) of white, crystalline solid, m.p. 125° dec. The product was soluble in water, benzene, and ethanol. It could readily be distinguished from phenylphosphonous dipiperidide by its solubility in water and insolubility in ethyl acetate.

Anal. Found: C, 60.85; H, 7.52; P, 9.48; N, 8.82, 8.91.

The product consumed no bromine (test for P—H or trivalent P), and gave negative tests for halogen with silver nitrate or the Beilstein test. The structure of this compound was not established.

p-Tolylphosphonous dichloride (I. R = *p*-$CH_3C_6H_4)_2$. The reaction of 15.6 g. (0.1 mole) of *p*-tolylphosphinic acid[11,15] with 88 ml. (1.0 mole) of phosphorus trichloride as described in Procedure B above gave 16.5 g. (85%) of *p*-tolylphosphonous dichloride, b.p. 110–113°/10 mm., m.p. 24–25°, n_D^{25} 1.5884. Weil, *et al.*[14] gave b.p. 116.5°/12 mm., m.p. 24°, n_D^{20} 1.591 for *p*-tolylphosphonous dichloride prepared by the reaction of phosphorus trichloride with *p*-tolylzinc bromide; the n_D values given in other references[11,16] were for mixtures of isomers. The product was a colorless, fuming liquid possessing a strong, phosphine-like odor.

Anal. Calcd. for $C_7H_7PCl_2$: Cl, 36.74. Found: Cl, 35.65.

Reaction of bis(2,3,5,6-tetramethylphenyl)phosphine oxide with phosphorus trichloride. Bis(2,3,5,6-tetramethylphenyl)-phosphine oxide[7], 15.7 g. (0.05 mole), was added in small

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(8) B. B. Hunt and B. C. Saunders, *J. Chem. Soc.*, 2414 (1957).

(9) P. G. Sergeev and D. G. Kudryashov, *Zhur. Obshchei Khim.*, **8**, 266 (1938); *Chem. Abstr.*, **32**, 5403 (1938).

(10) Melting points and boiling points are uncorrected.

(11) B. Buchner and L. B. Lockhart, Jr., *J. Am. Chem. Soc.*, **73**, 755 (1951); *Org. Syntheses*, **31**, 88 (1951).

(12) G. M. Kosolapoff and J. S. Powell, *J. Am. Chem. Soc.*, **72**, 4291 (1950).

(13) A. Michaelis, *Ber.*, **31**, 1037 (1898).

(14) T. Weil, B. Prijs, and H. Erlenmeyer, *Helv. Chim. Acta*, **35**, 1412 (1952); **36**, 1314 (1953).

(15) A. Michaelis and C. Paneck, *Ann.*, **212**, 203 (1882).

(16) Z. L. Khisamova and G. Kamai, *J. Gen. Chem. U.S.S.R.* (Eng. Transl.), **20**, 1207 (1950).

portions to 88 ml. (1.0 mole) of vigorously stirred phosphorus trichloride contained in a 250 ml. neck flask equipped with mechanical stirrer and a reflux condenser. Moisture was excluded by means of a drying tube attached to the top of the condenser. The oxide was all added during a 10 min. period, but did not appear to react although it went into solution. No phosphorous acid layer appeared. Next day the solution was heated under reflux for 1 hr., cooled, filtered to remove a viscous yellow oil, and distilled to remove the excess phosphorus trichloride. The residual viscous oil solidified on cooling to a glass which was unreactive toward water, ethanol, or piperidine, and which did not therefore contain the desired bis(2,3,5,6-tetramethylphenyl)phosphinous chloride.

WILMINGTON 98, DEL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

Phosphonic Acids and Esters. III.[1] Formation of 3-(2,5-Diphenylfuryl)phosphonic Acid in the Reaction of Dibenzoylethylene and Phosphorus Trichloride[2]

CLAIBOURNE E. GRIFFIN AND JOHN T. BROWN

Received May 31, 1960

The reaction of dibenzoylethylene and phosphorus trichloride in the presence of acetic anhydride is shown to lead to the formation of 3-(2,5-diphenylfuryl)phosphonic acid (VI) and not the product reported in the literature, 1,2-dibenzoylethylphosphonic acid (II). The structure of VI is confirmed by an examination of absorption spectra, independent synthesis, thermal dephosphonylation to 2,5-diphenylfuran, and a typical Diels-Alder reaction sequence leading to a terphenylphosphonic acid, which was independently synthesized.

Phosphonic acids in which the phosphono grouping is directly attached to a heterocyclic system have received little attention previously; heterocyclic phosphonic acids (I) incorporating the thiophene,[3] pyrazoline,[4] acridine,[5] tetrahydrofuran,[6] quinoline,[7] dihydrocoumarin,[8] pyridine,[9] and triazine[10] ring systems have been reported. In only this limited number of cases have heterocycles and their derivatives proved amenable to the introduction of the phosphono grouping by conventional procedures. An interest in the spectra of phosphonates[11] directed our attention toward an alternate synthetic mode of greater potential applicability. The variety of methods available for the synthesis of acyclic phosphonic acids suggested that ring closure of suitably substituted acids by methods common in heterocyclic chemistry might be a feasible route to I.

A particularly promising class of compounds appeared to be the phosphonic acids incorporating a 1,4-diketone structure, e.g. 1,2-dibenzoylethylphosphonic acid (II). Ring closures of 1,4-diketones are well established routes to furans, pyrroles, thiophenes, and pyridazines; application of known cyclization procedures to compound II should lead to phosphonic acids incorporating these heterocyclic systems.

Conant demonstrated that the addition of phosphorus trichloride to a variety of α,β-unsaturated ketones led to the formation of β-ketophosphonic acids by 1,4-addition.[12] In an extension of this work, Drake and Marvel reported that the addition of phosphorus trichloride to dibenzoylethylene (III) in the presence of acetic anhydride led to the formation of a cyclic adduct (IV) which was readily hydrolyzed to II.[13] The adduct was not isolated or further characterized but treatment with tetradecanol-1 led to the formation of 1-chlorotetradecane and a product formulated as V.

This experiment, employing techniques unavailable to the original investigators, led to different results in our hands; no change was made in the

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[1] Part II, C. E. Griffin, *J. Org. Chem.*, 25, 665 (1960).

[2] Presented in part before the Division of Organic Chemistry at the 137th National Meeting of the American Chemical Society, Cleveland, Ohio, April 13, 1960.

[3] H. Sachs, *Ber.*, 25, 1514 (1892).

[4] A. Michaelis and R. Pasternak, *Ber.*, 32, 2398 (1899).

[5] G. M. Kosolapoff, *J. Am. Chem. Soc.*, 69, 1002 (1947).

[6] B. A. Arbuzov and B. P. Lugovkin, *Zhur. Obshchei Khim.*, 22, 1193 (1952); *Chem. Abstr.*, 47, 4871 (1953).

[7] A. Burger, J. B. Clements, N. D. Dawson, and R. B. Henderson, *J. Org. Chem.*, 20, 1383 (1955).

[8] B. A. Arbuzov and V. M. Zoroastrova, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1955, 681; *Chem. Abstr.*, 50, 7109 (1956).

[9] R. D. Bennett, A. Burger, and W. A. Volk, *J. Org. Chem.*, 23, 940 (1958).

[10] H. Schroeder, *J. Am. Chem. Soc.*, 81, 5658 (1959). The assignment of a phosphonate structure in this study appears questionable.

[11] Examination of the ultraviolet absorption spectra of a number of substituted phenylphosphonic acids has led to the postulation of only a very weak resonance interaction between the phosphono group and the benzene ring, *cf.* L. D. Freedman and G. O. Doak, *J. Am. Chem. Soc.*, 77, 6221 (1955) and previous references. A more favorable environment for such resonance interaction is anticipated in certain of the heterocyclic phosphonic acids because of the greater electron donating ability of heterocyclic systems, notably pyrrole and thiophene, *cf.* A. R. Katritsky, *Quart. Revs.* (*London*), 13, 353 (1959).

[12] J. B. Conant and A. A. Cook, *J. Am. Chem. Soc.*, 42, 830 (1920) and previous papers.

[13] L. R. Drake and C. S. Marvel, *J. Org. Chem.*, 2, 387 (1937).