preheated oil bath (140°) and the salt was added rapidly in portions such that a rapid evolution of phosphorus pentafluoride was observed. When gas evolution ceased (15 min. over-all), the flask was cooled and the *p*-fluorobenzoic acid was recovered by extraction with a 5% sodium carbonate solution (150 ml.). The acid was precipitated when the basic solution was poured slowly with stirring into a mixture of ice and concentrated hydrochloric acid. After suction filtration and air-drying, the acid was recrystallized from a chloroform–petroleum ether (b.p. 30–60°) solvent pair. A yield of 64% (10 g.) of *p*-fluorobenzoic acid was obtained, m.p. 184–186°. A slight coloration can be removed by treating a chloroform solution of the acid with Norit.

WINDSOR, ONTARIO, CANADA

[CONTRIBUTION FROM THE CHEMICAL RESEARCH DEPARTMENT, CENTRAL RESEARCH DIVISION, AMERICAN CYANAMID CO.]

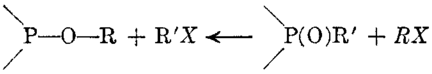
Phosphorus-Containing Monomers. II. The Synthesis and Polymerization of Dialkyl 2-Vinyloxyethylphosphonates [$CH_2{=}CHOCH_2CH_2P(O)(OR)_2$]

ROBERT RABINOWITZ

Received March 24, 1961

Synthetic routes to diethyl- and diisopropyl 2-vinyloxyethylphosphonate are described. These involve reaction of 2-chloroethyl vinyl ether with the corresponding tertiary phosphite. Low molecular weight polymers are obtained from these dialkyl 2-vinyloxyethylphosphonates using free radical techniques. Cationic polymerization failed completely.

Synthesis. The Michaelis-Arbuzov reaction is a classical method of forming a carbon-phosphorus bond.[1] Generally the tertiary phosphorus ester is heated with the alkyl halide between 100–150°, depending on the alkyl halide. A mixture of 2-chloroethyl vinyl ether and a small excess of triethyl phosphate was refluxed for ten days. Although no sign of reaction was apparent until the fifth day, a 50% yield of diethyl 2-vinyloxyethylphosphonate was obtained. No unchanged triethyl phosphite was recovered; instead diethyl ethylphosphonate, $C_2H_5P(O)(OC_2H_5)_2$ was found. It appeared that little reaction took place initially because the temperature was too low. As the low-boiling 2-chloroethyl vinyl ether was slowly consumed, the reflux temperature rose, increasing the rate. Also a factor in increasing the reflux temperature is the probable early formation of diethyl ethylphosphonate, either by thermal isomerization of the triethyl phosphite and/or by the reaction of ethyl chloride, prior to its escape as a gas, with triethyl phosphite. The reaction between triethyl phosphite and 2-chloroethyl vinyl ether in the presence of a large excess of tetralin, a high-boiling inert material, started immediately and was virtually completed in four days. A 74% yield of diethyl 2-vinyloxyethylphosphonate was obtained.



R and R′ = alkyl

It appeared likely that, as triisopropyl phosphite was higher-boiling than triethyl phosphite, it could react with 2-chloroethyl vinyl ether in a reasonable amount of time without the use of a high-boiling inert solvent. Thus, by gradually adding the 2-chloroethyl vinyl ether to the refluxing phosphite, a 76% conversion to diisopropyl 2-vinyloxyethylphosphonate was obtained after four days.

Another well known procedure to prepare phosphonates is the reaction of the sodium salt of a dialkyl hydrogen phosphonate with a primary alkyl halide.[2,3] When diethyl sodium phosphonate

$$(RO)_2P(O)Na + R'CH_2X \longrightarrow NaX + (RO)_2P(O)R'$$

was mixed with 2-chloroethyl vinyl ether at 0° no reaction occurred. Refluxing overnight gave the expected sodium chloride. However, the only product noted was divinyl ether. Apparently the base,

$$NaP(O)(OC_2H_5)_2 + ClCH_2CH_2OCH{=}CH_2 \longrightarrow NaCl + HP(O)(OC_2H_5)_2 + (CH_2{=}CH)_2O$$

diethyl sodium phosphonate, dehydrochlorinates the ether at a rate much faster than that of the displacement reaction.

Hydrolysis. An effort was made to prepare the monoester of diethyl 2-vinyloxyethylphosphonate by the following hydrolytic reaction. The reaction had previously been demonstrated as a simple route to these monoesters when working with nonolefinic phosphonates.[4] Under either reflux

$$CH_2{=}CHOCH_2CH_2P(O)(OC_2H_5)_2 + OH^- \xrightarrow[\text{ethanol}]{H_2O\text{ or}} CH_2{=}CHOCH_2CH_2P(O)(OC_2H_5)O^-$$

or room temperature aqueous conditions, *no* monoester was noted.

Polymerization studies. Only a relatively small amount of information exists on the free radical

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[1] G. M. Kosolapoff, *Organophosphorus Compounds*, Wiley, New York, 1950, p. 121.

(2) B. C. Saunders, G. F. Stacey, F. Wild, and I. G. E. Wilding, *J. Chem. Soc.*, 699 (1948).

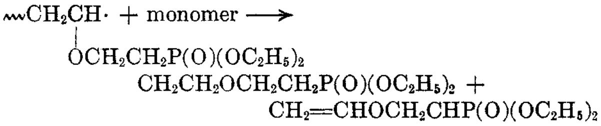
(3) G. M. Kosolapoff, *J. Am. Chem. Soc.*, **67**, 2259 (1945).

(4) R. Rabinowitz, *J. Am. Chem. Soc.*, **82**, 4564 (1960).

polymerization of vinyl ethers; they homopolymerize very poorly under thermal or peroxidic conditions.[5–9]

An attempt to polymerize diethyl 2-vinyloxyethylphosphonate at 60° using azobisisobutyronitrile failed in that no polymerization occurred. Either the radical from azobisisobutyronitrile, $(CH_3)_2\dot{C}CN$, is too stable to add to the vinyl ether and therefore disappears by dimerization or the energy of activation for addition polymerization is too high to allow the reaction to proceed at 60°.

Diethyl 2-vinyloxyethylphosphonate polymerizes quantitatively when heated with di-*t*-butyl peroxide (DTBP) at 135°. The product is a viscous oil. It was interesting to note that whereas in the usual polymerizations of vinyl monomers the molecular weight is inversely proportional to the square root of the initiator concentration, in this case varying the di-*t*-butyl peroxide concentration over a fifty-fold range had practically no effect on the molecular weight. Thus at 0.2%, 1%, 2%, and 10% di-*t*-butyl peroxide the molecular weight of the polymers obtained varied between 1300–1600. This observation suggests that a nondegradative chain transfer process is responsible for the control of the molecular weight. Another explanation for the independence of molecular weight of initiator concentration is to assume a nondegradative decomposition of the chain propagating radical.



$$\sim CH_2\underset{OCH_2CH_2P(O)(OC_2H_5)_2}{CH\cdot} + \text{monomer} \longrightarrow CH_2CH_2OCH_2CH_2P(O)(OC_2H_5)_2 + CH_2{=}CHOCH_2CHP(O)(OC_2H_5)_2$$

$$\sim CH_2\dot{C}HOCH_2CH_2P(O)(OC_2H_5)_2 \longrightarrow \sim CH_2CHO + \cdot CH_2CH_2P(O)(OC_2H_5)_2$$

This type of decomposition has been observed in the past in non-polymer system.[10] However, the infrared spectra revealed no absorption in the aliphatic aldehyde region.

A sample of diisopropyl 2-vinyloxyethylphosphonate was polymerized to a molecular weight of 954 using di-*t*-butyl peroxide at 135°. No further polymerization work was done on this material since there was no reason to doubt that its behavior would parallel that of diethyl 2-vinyloxyethylphosphonate.

The bulk of the work done in vinyl ether polymerization has been with cationic catalysts (Friedel-Crafts agents and related electrophilic substances).[11–16] All attempts to polymerize diethyl 2-vinyloxyethylphosphonate using a series of these acidic catalysts failed. These same catalysts were effective in polymerizing 2-chloroethyl vinyl ether. A possible reason for the ineffectiveness of acidic catalysts to polymerize diethyl 2-vinyloxyethylphosphonate is that the ester linkages of the monomer are susceptible to acid attack. The marked difference in polymerization behavior of diethyl 2-vinyloxyethylphosphonate and 2-chloroethyl vinyl ether cannot be attributed to the electrical or steric influence of the phosphonate group since in the β-position these effects must be minor.

The homopolymer of diethyl 2-vinyloxyethylphosphonate was prepared indirectly by polymerizing 2-chloroethyl vinyl ether using mercuric bromide[17] as catalyst and then reacting this polymer with triethyl phosphite. An almost immobile liquid was obtained which possessed a rather unusual property in that it was soluble in cold water but came out of solution as a gum when heated above 40°. This phenomenon was reversible in that, upon cooling, this gum redissolved. This effect may be general with water-soluble polyvinyl ethers as it has previously been observed with polymethyl vinyl ethers.[18] Perhaps the polymer prefers to associate with itself rather than with the water and upon heating it loses its solubilizing water of solvation. The homopolymer prepared directly, of lower molecular weight, was soluble in both hot and cold water.

EXPERIMENTAL

Materials. The 2-chloroethyl vinyl ether was distilled from the commercial Union Carbide material, b.p. 108–109°. The *triethyl* (b.p. 155–156°) and *triisopropyl phosphite* (b.p. 176–177°) were obtained from the Virginia-Carolina Chemical Corp. and distilled prior to use. The *diethyl hydrogen phosphonate*, also a Virginia-Carolina product, and a commercial grade of tetralin were used without further purification. The boron trifluoride–phosphoric acid was prepared by bubbling boron trifluoride through phosphoric acid until a saturated solution was obtained. The boron trifluoride–diethyl ether was prepared in an analogous manner.

Preparation of diethyl 2-vinyloxyethylphosphonate. (a) *Reaction of triethyl phosphite with 2-chloroethyl vinyl ether.* A mixture consisting of 39.7 g. (0.37 mole) of 2-chloroethyl

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[5] A. V. Bogdanova, M. F. Shostadovskii, and G. K. Krasil'nikova, *Izvestiya*, 990 (1948).

[6] A. M. Khomutov, *Izvestiya*, 521 (1959).

[7] F. R. Mayo, F. M. Lewis, and C. Walling, *J. Am. Chem. Soc.*, **70**, 1529 (1948).

[8] J. R. Tichy, *J. Polymer Sci.*, **33**, 353 (1958).

[9] C. Walling, *Free Radicals in Solution*, Wiley, New York, 1957, p. 120.

[10] L. P. Kuhn and C. Wellman, *J. Org. Chem.*, **22**, 774 (1957).

[11] W. Chalmers, *J. Am. Chem. Soc.*, **56**, 912 (1945).

[12] C. E. Schildknecht, A. O. Zoss, and C. McKinley, *Ind. Eng. Chem.*, **39**, 180 (1947).

[13] C. E. Schildknecht, *Vinyl and Related Polymers*, Wiley, New York, 1952, pp. 598–608.

[14] S. Okamuro, T. Higashumura, and H. Yamamoto, *Chemistry of High Polymers*, **16**, 45 (1959) and *J. Polymer Sci.*, **33**, 511 (1958).

[15] K. M. Roch and J. Saunders, *J. Polymer Sci.*, **38**, 555 (1959).

[16] G. Natta, G. Dall'Asta, G. Mazzanti, V. Gionnini, and S. Cesca, *Angewandte Chemie*, **71**, 205 (1959).

[17] Mercuric bromide, mercuric chloride, and the corresponding bismuth halides have been found to be catalysts for vinyl ether polymerizations, W. J. Luberoff and E. Smolin, this laboratory, unpublished work.

[18] C. E. Schildknecht, *Polymer Processes*, Interscience, New York, 1956, p. 671.

vinyl ether and 96 g. (0.58 mole) of triethyl phosphite was introduced into a reflux apparatus. The condenser was open to the atmosphere through a tared Dry Ice–trichloroethylene trap connected to an anhydrous calcium sulfate-filled tube. After 4 days of refluxing (135–40°) only a slight increase in pot temperature was observed. Furthermore, the trap was empty. However, the system was allowed to continue to reflux and a 10° increase in temperature was noted on the fifth day. Ethyl chloride was noted in the trap. The reaction mixture was refluxed for an additional 6 days, the temperature reaching 203°. Distillation of the reaction mixture gave a 50% yield of diethyl 2-vinyloxyethyl phosphonate, b.p. 138°/17 mm., n_D^{26} 1.4351. Essentially no triethyl phosphite was recovered; however, a large fraction, b.p. 95–98°/19 mm. was identified as diethyl ethylphosphonate.

(b) *Reaction of triethyl phosphite with 2-chloroethyl vinyl ether in the presence of tetralin.* The following components were mixed in a 1-1., three-neck flask equipped with a nitrogen bubbler, thermometer and condenser; 450 g. of tetralin (3.41 moles), 249.2 g. of triethyl phosphite (1.50 moles), and 107.0 g. of 2-chloroethyl vinyl ether (1.01 moles). Nitrogen was bubbled into the solution very slowly, the gases passing through a Dry Ice–trichloroethylene trap. The initial pot reflux temperature was 156°. A small amount of ethyl chloride was present in the trap after 5.5 hr. After 4 days the temperature was 189° and very little more ethyl chloride was evolving. The reaction mixture was refluxed for an additional 3 days, reaching a temperature of 199°. Distillation resulted in the recovery of a small amount of the ether and some triethyl phosphite. As observed before, the major portion of the excess triethyl phosphite had been converted to diethyl ethylphosphonate. A 74% yield of diethyl 2-vinyloxyethylphosphonate was obtained. It is water white, water-soluble,[19] and nonflammable; b.p. 162°/47 mm., n_D^{25} 1.4385.

Anal. Calcd. for $C_8H_{17}O_4P$: C, 46.20; H, 8.18; P, 14.92. Found: C, 46.53; H, 8.56; P, 14.48.

(c) *Reaction of 2-chloroethyl vinyl ether with diethyl sodium phosphonate.* Sodium (10.22 g., 0.256 mole) was dissolved in 250 ml. of absolute ethanol. The solution was cooled to 0° and during a 2-min. period, 38.1 g. (0.28 mole) of diethyl hydrogen phosphonate was added. Then 30.1 g. (0.28 mole) of 2-chloroethyl vinyl ether was introduced. No heat was evolved and no signs of sodium chloride appeared. Even after the reaction mixture was allowed to warm to room temperature, no sodium chloride was noted. Therefore, the reaction solution was heated. In 10 min. (60°), before refluxing had started, sodium chloride was noted. The solution was refluxed overnight, the vapor temperature dropping from 73° to 63° during this period. Distillation of the reaction mixture revealed only divinyl ether. The pot contained as a maximum (infrared estimate) only 0.6 g. of the desired product, diethyl 2-vinyloxyethylphosphonate.

Preparation of diisopropyl-2-vinyloxyethylphosphonate. A mixture of 65.4 g. of 2-chloroethyl vinyl ether (0.61 mole) and 375 g. of triisopropyl phosphite was refluxed below an 18-in. glass helix-packed, silvered, vacuum-jacketed column. A full reflux-partial take-off head was used so that the isopropyl chloride formed could be tapped off periodically. Nitrogen was bubbled slowly through the solution and passed through the head into a Dry Ice–trichloroethylene trap. After 48 hr. the reflux pot temperature had risen from 153° to 181°. An additional 24.5 g. of 2-chloroethyl vinyl ether (0.23 mole) was added. Six hours later with the temperature at 172° another 15.6 g. (0.146 mole) of the ether was added. After a total of 4 days the temperature was 184°. Almost the theoretical amount of isopropyl chloride had been collected. Distillation of the reaction mixture revealed small amounts of unchanged starting materials. A good conversion (130 g., 76%) to the desired product, diisopropyl-2-vinyloxyethylphosphonate, was found, b.p. 121–133°/6 mm., a clear, colorless liquid, insoluble in water and nonflammable.

Anal. Calcd. for $C_{10}H_{21}O_4P$: C, 50.85; H, 8.89; P, 13.10. Found: C, 51.04; H, 8.93; P, 12.85.

Attempts to hydrolyze diethyl 2-vinyloxyethylphosphonate. Refluxing a mixture of 13.0 g. of diethyl 2-vinyloxyethylphosphonate of 10% aqueous sodium hydroxide for 1 hr. resulted in the precipitation of an orange solid, which was soluble in chloroform, acetone, and insoluble in ethyl ether. Its infrared spectrum revealed no vinyl, ether oxygen, $P=O$, or $P—OC_2H_5$ absorption. The homogeneous filtrate was refluxed for an additional 90 min. No change occurred. It was extracted with carbontetrachloride, acidified (no precipitate formed), and extracted with chloroform. Evaporation of the chloroform gave no residue. The hydrolysis was repeated at room temperature. Essentially the same pattern was followed and nothing worthwhile was isolated from the reaction mixture.

Azobisiobutyronitrile initiation of diethyl 2-vinyloxyethylphosphonate. A mixture of 0.100 g. of azobisisobutyronitrile and 5.0 g. of diethyl 2-vinyloxyethylphosphonate was degassed by conventional means at −78° and sealed. Infrared examination of the contents of the tube after 4 days at 60° revealed that little change had occurred.

Di-t-butyl peroxide initiation of diethyl 2-vinylethylphosphonate and diisopropyl-2-vinylethyloxyphosphonate. The di-*t*-butyl peroxide and diethyl 2-vinyloxyethylphosphonate were introduced into a constricted, heavy-walled, test tube and degassed by conventional techniques at −78°. After 24 hr. at 135–140° the tubes were opened and small samples heated overnight at 100°/0.1 mm. removing all volatiles and unreacted monomer. The table below is a summary:

MOLECULAR WEIGHT *vs.* PEROXIDE CONCENTRATION

DTBP, %	Final Viscosity	Extent of Polymerization	Final Color	Molecular Weights
—	No increase	None	Colorless	—
0.1	Slight	Less than 10%	Light yellow	—
0.2	More	Less than 10%	Darker yellow	1300
1	Even more	100%	Reddish orange	1600
2	Most	100%	Red	1500
10	Same as with 1%	100%	Dark red	1300

Synthesis of the homopolymer of diethyl 2-vinyloxyethylphosphonate, prepared indirectly from poly-2-chloroethyl vinyl ether. (a) *Synthesis.* To a solution of 100 ml. of 2-chloroethyl vinyl ether in 300 ml. of ethyl ether at room temperature was added 2.00 g. of mercuric bromide. No heat was evolved. After 15 min. an additional 2.00 g. was added. After 30 min. a 10.0-ml. sample was removed, filtered, and devolatilized using the aspirator (no heating) leaving a tacky residue. One drop of water was added to the reaction mixture after 1 hr. A final 2.00 g. of mercuric bromide was added at the 2-hr. point and the stirrer was shut off. During the next 2.5 hr. a slow rise in temperature to 34° occurred. Two layers formed during this period, the lower one being slightly yellow and smaller. After standing over the weekend, the layers were separated by cooling at −78° followed by decanting. Evap-

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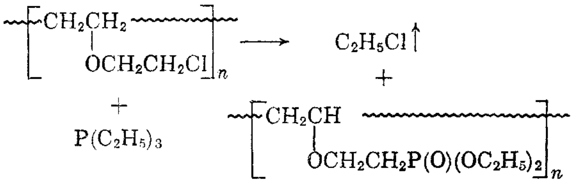
(19) It could be salted out of aqueous solution.

oration of the ethyl ether from the upper layer left a viscous oil and some salt. This was discarded. Removal of the volatiles from the lower layer left 74.5 g. of a soft, tacky, yellow polymer. This product was dissolved in 200 ml. (194 g., 1.16 moles) of triethyl phosphite and the mixture refluxed. Nitrogen was slowly bubbled into the solution and the gaseous stream passed through a Dry Ice–trichloroethylene trap. Refluxing was continued for 1 week until no further ethyl chloride evolved:



$$\left[CH_2CH_2(OCH_2CH_2Cl)\right]_n + P(C_2H_5)_3 \longrightarrow C_2H_5Cl\uparrow + \left[CH_2CH(OCH_2CH_2P(O)(OC_2H_5)_2)\right]_n$$

(b) *Isolation.* When 25.1 g. of the reaction mixture was heated *in vacuo* (1 hr. at 160° finally) 14.0 g. of polymer was recovered (96%). It still had the odor of triethyl phosphite and therefore the following isolation method was employed. A 44.5-g. portion of the reaction mixture was mixed with 100 ml. of water. The cloudy dispersion of triethyl phosphite in water clarified upon the addition of 5 drops of concd. hydrochloric acid. After standing for 24 hr. to ensure complete hydrolysis of the triethyl phosphite, the solution was extracted with two portions of dichloromethane, the extract dried, and the solvent evaporated. The residue, 23.7 g., (90%) was an orange, slightly mobile oil at room temperature and was quite tacky. It dissolved readily in cold water but precipitated as a gum above 40°. Upon cooling below 40° the gum redissolved.

STAMFORD, CONN.

[CONTRIBUTION FROM THE CENTRAL RESEARCH DIVISION, AMERICAN CYANAMID CO.]

The Polymerization of Acetylenes by Nickel-Carbonyl-Phosphine Complexes. I. Scope of the Reaction[1a]

L. S. MERIWETHER, E. C. COLTHUP, G. W. KENNERLY, AND R. N. REUSCH

Received June 5, 1961

The polymerization of thirty-five different mono- and disubstituted acetylenes with dicarbonylbis(triphenylphosphine)-nickel [$Ni(CO)_2(Ph_3P)_2$] catalyst in an inert solvent at reflux has been attempted. Primarily aromatic products were obtained from monosubstituted acetylenes with lower alkyl, aryl, vinyl, $HOCH_2$—, $C_2H_5O_2C$—, R—CO—, and R—O— substituents; monosubstituted acetylenes with higher alkyl, cyclohexyl, $HOCH_2CH_2$—, CH_3—CH(OH)—, $(CH_3)_2C(OH)$—, 1-hydroxycyclohexyl, and $(C_2H_5)_2NCH_2$—substituents yielded linear low polymers. Unreactive were most disubstituted acetylenes, disubstituted conjugated diacetylenes, and monosubstituted acetylenes with *tert*-butyl-, HO_2C—, amide, nitrile, and halogen substituents.

The trimerization of acetylenes to aromatic compounds in the presence of nickel-carbonyl-phosphine complexes was discovered by Reppe and Schweckendiek.[1b] They obtained from the reaction of acetylene with $Ni(CO)_2(Ph_3P)_2$ ($Ph = C_6H_5$) in acetonitrile a product consisting of 88% benzene and 12% styrene. With the same catalyst in refluxing benzene, propargyl alcohol gave a quantitative yield of 1,2,4- and 1,3,5-trimethylolbenzene, but 2-butyne-1,4-diol failed to aromatize, suggesting that at least one acetylenic hydrogen must be present in the monomer. Rose and Statham[2] reported the isolation of only 1,2,4-triphenylbenzene and only 1,3,5-tris(α-hydroxybenzyl)benzene from the trimerization of phenylacetylene and phenylethynylcarbinol, respectively, with the same catalyst. These authors failed to isolate products from 3-methyl-1-butyne-3-ol, 3-diethylamino-1-butyne, benzoylacetylene and phenylpropiolic acid. However, a U. S. patent issued to McKeever and Van Hook[3] describes the preparation of tris(1-methyl-1-hydroxyethyl)benzene and tris(isopropenyl)benzene from 3-methyl-1-butyne-3-ol and isopropenylacetylene, respectively, using $Ni(CO)_3(Ph_3P)$, $Ni(CO)_2(Ph_3P)_2$ or $Ni(CO)_2(Ph_3As)_2$ as catalysts. In another U. S. patent Kleinschmidt[4] describes the preparation of hexamethylolbenzene from 2-butyne-1,4-diol using $Ni(CO)_2(Ph_3P)_2$ as catalyst, and more recent patents describe the formation of 1,2,4-trivinylbenzene from vinylacetylene,[5] hexakis-(trifluoromethyl)benzene from bis(trifluoromethyl)acetylene[6] and of *o*-divinylbenzene from the copolymerization of acetylene and divinylacetylene.[7] Sauer and Cairns,[8] in attempting to test the possible formation of a cyclobutadiene intermediate, succeeded in copolymerizing acetylene and butyne-2 to *o*-xylene, but they obtained no *p*-xylene.

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(1)(a) Presented in part at the 138th Meeting of the American Chemical Society, New York, N. Y., September 11-16, 1960. (b) W. Reppe and W. J. Schweckendiek, *Ann.*, **560**, 104 (1948).

(2) J. D. Rose and F. S. Statham, *J. Chem. Soc.*, 69 (1950).

(3) C. H. McKeever and J. O. Van Hook, U. S. Patent 2,542,551 (Feb. 20, 1951).

(4) R. F. Kleinschmidt, U. S. Patent 2,542,417 (Feb. 20, 1951).

(5) Brit. Patent 824,417 (Dec. 2, 1959).

(6) J. F. Harris, Jr., U. S. Patent 2,923,746 (Feb. 2, 1960); J. F. Harris, Jr., R. J. Harder, and G. N. Sausen, *J. Org. Chem.*, **25**, 633 (1960).

(7) A. C. Cope and C. T. Handy, French Patent 1,213,148 (March 29, 1960).

(8) J. C. Sauer and T. L. Cairns, *J. Am. Chem. Soc.*, **79**, 2659 (1957).