[CONTRIBUTION FROM SOUTHERN REGIONAL RESEARCH LABORATORY,[1] UNITED STATES DEPARTMENT OF AGRICULTURE]

Derivatives of Unsaturated Phosphonic Acids

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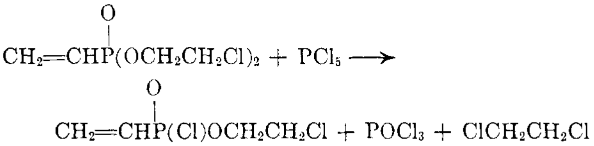
Salts of vinylphosphonic acid and derivatives of the type $CH_2{=}CHP(O)(X)OCH_2CH_2Cl$ where X = Cl, $N(CH_3)_2$ and OCH_3 have been prepared starting from the commercially available bis(2-chloroethyl) vinylphosphonate. Diethyl 1(and 2)-propynylphosphonate has been prepared from propargyl bromide and diethyl phosphonate. The molar refractions and infrared absorption spectra of several of these materials have been determined, and the significance of the spectra is discussed.

A number of esters of vinylphosphonic acid have previously been prepared by the dehydrohalogenation of the corresponding 2-chloroethylphosphonates.[2] Vinylphosphonic acid itself was unknown until recently made by the pyrolysis of 2-chloroethylphosphonic dichloride, followed by hydrolysis.[3] The vinyl group of the esters is known to be moderately reactive toward nucleophilic reagents. Addition reactions occur with alcohols,[4a] thiols,[4b] amines,[4c,g] nitroalkanes,[4d] active methylene compounds such as malonic ester,[4e] and dialkyl phosphonates[4f,g] in the presence of alkaline catalysts. Vinylphosphonates also undergo the Diels-Alder reaction with dienes,[5] and may be polymerized[6a] or copolymerized[6b] with other olefins. Certain of the esters have been used to stabilize polymers to heat and light[7] and to impart flame and shrinkage resistance to textiles.[8]

The present research has shown the readily available bis(2-chloroethyl) vinylphosphonate to be a convenient starting material for the preparation of a variety of derivatives of vinylphosphonic acid. The ester was easily saponified by 20–50% aqueous sodium hydroxide, both of the 2-chloroethyl groups being removed. A moderate amount of gas evolution occurred which may be due to the formation of acetylene, ethylene oxide or both. To facilitate product purification, the crude aqueous sodium vinylphosphonate was converted to benzylammonium hydrogen vinylphosphonate, which could be recrystallized from absolute ethanol and thus separated from inorganic salts.

When bis(2-chloroethyl) vinylphosphonate in an inert solvent was heated with phosphorus pentachloride, a rather rapid reaction occurred with removal of only one of the 2-chloroethyl groups from the ester molecule:



$$CH_2{=}CH\overset{O}{\overset{|}{P}}(OCH_2CH_2Cl)_2 + PCl_5 \longrightarrow CH_2{=}CH\overset{O}{\overset{|}{P}}(Cl)OCH_2CH_2Cl + POCl_3 + ClCH_2CH_2Cl$$

A 62% yield of 2-chloroethyl vinylphosphonochloridate resulted. Removal of the second 2-chloroethyl group proved unexpectedly difficult, even when 2-chloroethyl vinylphosphonochloridate was heated with phosphorus pentachloride in the absence of solvent, and the vinylphosphonic dichloride obtained was grossly impure.

The facile preparation of 2-chloroethyl vinylphosphonochloridate makes this compound available for the synthesis of amides and esters. Reaction with dimethylamine in the presence of triethylamine in benzene solution gave 2-chloroethyl *N*,*N*-dimethyl-*P*-vinylphosphonamidate in 66% yield. Reaction of the phosphonochloridate with methanol in the presence of triethylamine in benzene gave 2-chloroethyl methyl vinylphosphonate in 74% yield. Table I lists the density, refractive index, and molar refraction determined for the compounds. Table II gives infrared spectral data.

The reaction of sodium diethyl phosphite with propargyl bromide was studied as a means of preparing diethyl 2-propynylphosphonate:

$$CH{\equiv}CCH_2Br + NaP(O)(OC_2H_5)_2 \longrightarrow CH{\equiv}CCH_2P(O)(OC_2H_5)_2$$

The analogous reaction with allyl bromide has been described by Pudovik and Frolova.[9] The tend-

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(1) One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

(2) A. H. Ford-Moore and J. H. Williams, *J. Chem. Soc.*, 1465 (1947); M. I. Kabachnik, P. A. Rossiiskaya, and N. N. Novikova, *Bull. acad. sci. U.R.S.S., Classe sci. chim.*, 97 (1947); ref. 6a.

(3) M. I. Kabachnik and T. Ya. Medved, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 2142 (1959).

(4) (a) P. O. Tawney, U. S. Patent **2,535,172** (1950); (b) P. O. Tawney, U. S. Patent **2,535,174** (1950); (c) P. O. Tawney, U. S. Patent **2,570,503** (1951); (d) P. O. Tawney, U. S. Patent **2,535,175** (1950); (e) P. O. Tawney, U. S. Patent **2,535,173** (1950); A. N. Pudovik and O. N. Grishina, *Zhur. Obshcheĭ Khim.*, **23**, 267 (1953); (f) E. C. Ladd and M. P. Harvey, U. S. Patent **2,651,656** (1953); (g) A. N. Pudovik and G. M. Denisova, *Zhur. Obshcheĭ Khim.*, **23**, 263 (1953).

(5) J. B. Dickey, H. W. Coover, Jr., and N. H. Shearer, Jr., U. S. Patent **2,550,651** (1951); E. C. Ladd, U. S. Patent **2,622,096** (1952).

(6) (a) M. I. Kabachnik, *Bull. acad. sci. U.R.S.S., Classe sci. chim.*, 233 (1947)· (b) C. L. Arcus and R. J. S. Matthews, *J. Chem. Soc.*, 4607 (1956).

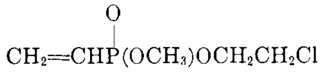
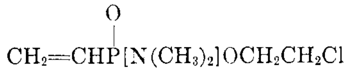
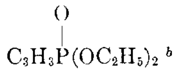
(7) D. H. Chadwick, U. S. Patent **2,784,171**, (1957); R. J. Slocombe, U. S. Patent **2,784,169** (1957); D. H. Chadwick, U. S. Patent **2,784,206** (1957).

(8) F. Ward, Brit. Patent **765,222**, Example 11 (1957).

(9) A. N. Pudovik and M. M. Frolova, *Zhur. Obshcheĭ Khim.*, **22**, 2052 (1952).

TABLE I

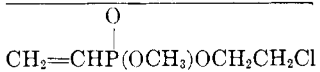
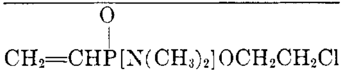
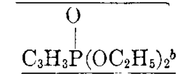
THE MOLAR REFRACTION OF UNSATURATED PHOSPHATES

Cpd.	d_{25}	n_D^{25}	Mr_d	
			Found	Calcd.[a]
 $CH_2{=}CH\overset{O}{\overset{\|}{P}}(OCH_3)OCH_2CH_2Cl$	1.239	1.4548	40.40	40.56
 $CH_2{=}CH\overset{O}{\overset{\|}{P}}[N(CH_3)_2]OCH_2CH_2Cl$	1.171	1.4723	47.19	47.08
 $C_3H_3\overset{O}{\overset{\|}{P}}(OC_2H_5)_2$[b]	1.104	1.4464	42.59	43.40

[a] Calculated from atomic refractions using 4.27 for P and 2.45 for N, as found by M. I. Kabachnik, *Bull. acad. sci. U.R.-S.S., Classe sci. chim.*, 219 (1948); and G. M. Kosolapoff and L. B. Payne, *J. Org. Chem.*, **21**, 413 (1956), respectively. [b] A mixture of diethyl 1-propynylphosphonate and 2-propynylphosphonate.

TABLE II

INFRARED ABSORPTION[a] OF UNSATURATED PHOSPHONATES

(1)		(2)		(3)	
 $CH_2{=}CH\overset{O}{\overset{\|}{P}}(OCH_3)OCH_2CH_2Cl$		 $CH_2{=}CH\overset{O}{\overset{\|}{P}}[N(CH_3)_2]OCH_2CH_2Cl$		 $C_3H_3\overset{O}{\overset{\|}{P}}(OC_2H_5)_2$[b]	
$\tilde{\nu}$ cm.$^{-1}$		$\tilde{\nu}$ cm.$^{-1}$		$\tilde{\nu}$ cm.$^{-1}$	
831	(19)	838-47	(6)	817	(4)
855	(8)[c]	855	(6)	969-76	(25)
918	(10)[c]	931	(13)	1004	(20)
932	(12)	963	(13)[c]	1055-64	(14)
965	(20)	988	(75)	1094	(14)
983	(27)	1032	(32)	1157	(12)
1031-34	(86)	1073	(28)	1258	(17)
1053	(79)[c]	1085	(28)	1370	(8)
1079	(46)	1192-1208	(17)	1391	(10)
1196	(8)	1236-45	(17)	1439	(8)
1277	(17)	1305	(30)	1475	(5)
1305	(9)	1404	(10)	1613	(3)[d]
1405	(11)	1464	(12)	1795	(1)
1458	(7)	1484	(10)	1852	(1)
1610	(4)[d]	1613	(2)[d]	1931	(1)
1869	(1)	1946	(1)	1961	(1)
1961	(1)	2475	(2)	2092	(2)
2469	(2)	2817	(6)	2208	(19)
2849	(3)	2994-3021	(19)	2445	(2)
2994	(11)	3378	(4)[d]	2950	(8)
3400	(4)[d]			3290	(2)
				3401	(3)[d]

[a] Figures in parentheses are molar absorptivities in arbitrary units. [b] A mixture of diethyl 1-propynylphosphonate and 2-propynylphosphonate. [c] Shoulder. [d] Water band.

ency of excess phosphite to react further with the initial product[9] was avoided in the present experiments by the use of inverse addition. A 36% yield of isomeric diethyl propynylphosphonates was obtained. Tests for a terminal acetylenic grouping were obtained with alkaline sodium 3,5-dinitrobenzoate[10] and with alkaline mercuric cyanide. The infrared absorption (3, Table II) shows that both isomers were present, with diethyl 1-propynylphosphonate greatly predominating. A very strong peak at 2208 cm.$^{-1}$ is clearly within the range characteristic of C≡C stretching in disubstituted acetylenes.[11] A much weaker peak at 2092 cm.$^{-1}$ corresponds to the same vibration in a terminal acetylenic group adjacent to a negatively substituted carbon atom. Weak absorption at 3290 cm.$^{-1}$ corresponds to ≡CH stretching, again attributed to small amounts of diethyl 2-propynylphosphonate. Traces of a third isomer, diethyl propadienylphosphonate, may be indicated[11] by very weak absorption at 1961 cm.$^{-1}$ characteristic of allenes.

It is evident that the triple bond in propargyl bromide shifts to a considerable extent during reaction with either sodium diethyl phosphite or

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(10) B. C. Saunders and B. P. Stark, *Tetrahedron*, **4**, 197 (1958); ref. 14.

(11) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley and Sons, Inc., New York, 1954, pp. 49-52.

with triethyl phosphite. Jacobsen *et al.*[12] obtained a 5% yield of diethyl 1-propynylphosphonate using the triethyl phosphite route. Their product failed to show infrared absorption at 2100 or 3300 cm.$^{-1}$ characteristic of a terminal acetylenic group. Failure to obtain a precipitate with ammoniacal silver nitrate was probably inconclusive, since the product obtained in the present work also failed to give the test, and other studies have shown that certain monosubstituted acetylenes having phosphonyl groups do not give an insoluble silver or copper derivative.[13]

Hunt, Saunders, and Simpson prepared several ethynylphosphonates[14] in semipurified form, and noted C≡C stretching absorption at 2075 cm.$^{-1}$ This is in good agreement with the value of liquid cyanoacetylene[15] and for diethyl 2-propynylphosphonate noted here. However, they found H—C≡ stretching absorption at 3165 cm.$^{-1}$ which is 40 cm.$^{-1}$ below that given by solid or liquid cyanoacetylene[15] and is 125 cm.$^{-1}$ lower than for diethyl 2-propynylphosphonate. The replacement of —CH_2-P(O)$(OR)_2$ by —P(O)$(OR)_2$ in the monosubstituted acetylene would not be expected to produce such a large shift.

The spectra of the vinylphosphonates studied (1 and 2, Table II) showed little similarity to spectra of alkyl acrylates[16] or of acrylonitrile.[17] A strong sharp peak at 831 cm.$^{-1}$ (12.04 μ) for methyl 2 chloroethyl vinylphosphonate could correspond to the 12.3 μ absorption noted by Walton and Hughes[16] for acrylates and acrylamides generally. The 963–965 cm.$^{-1}$ absorption given by the vinylphosphonates is probably due to P—O stretching,[18] with out-of-plane =CH_2 and =CH— deformations occurring at 983–988 cm.$^{-1}$ and 918–932 cm.$^{-1}$, respectively. The in-plane =CH— and =CH_2 deformations appear at 1305 and 1404–1405 cm.$^{-1}$

2-Chloroethyl *N,N*-dimethyl-*P*-vinylphosphonamidate (2, Table II) showed a broad and unusually intense peak at 983–988 cm.$^{-1}$ which may have been due in part to a C—N vibration.[19] Other characteristic features are a doublet at 1073 and 1085 cm.$^{-1}$, and a peak at 1484 cm.$^{-1}$ The latter peak is a part of the —CH_3 and —CH_2— deformation absorption normally at 1430–1485 cm.$^{-1}$ The integrated intensity of the entire band is an additive function of the number of such groups present.[20] The peak at 1484 cm.$^{-1}$ is missing from the spectrum of compound 1 (Table II) and so is apparently due to an *N*-methyl group. The splitting of the entire band seems more pronounced in N-methyl derivatives than in *O*-methyl derivatives.[19,21–23] However, *O*-ethyl derivatives usually show two well defined peaks, as may be seen at 1439 and 1475 cm.$^{-1}$ for diethyl propynylphosphonate.

EXPERIMENTAL

Benzylammonium hydrogen vinylphosphonate. To 56 ml. of water in a 300-ml. round bottomed one necked flask was added 24 g. (0.60 mole) of sodium hydroxide pellets. As soon as solution was complete, 23 g. (0.10 mole) of bis(2-chloroethyl) vinyl phosphonate (commercial grade)[24] was added to the warm mixture, which was then swirled. After a few minutes the two phases merged, accompanied by gas evolution. The mixture was refluxed 1 hr. and was chilled and filtered under suction to remove a brown, solid by-product. To the filtrate was added 22 ml. of concd. hydrochloric acid, giving a *p*H of about 5. The solution was evaporated to about 80 ml., cooled, and freed of salts by suction filtration. The filtrate was further evaporated to 40 ml., cooled, and 10 ml. of concd. hydrochloric acid was added. It was cooled to 5° and again filtered by suction.

The remaining salts were precipitated with 150 ml. of acetone, followed by stirring and filtration. To the filtrate was added 12 ml. (0.11 mole) of benzylamine. The solution was evaporated until its boiling temperature reached 90°. It was distilled under reduced pressure until the pot temperature reached 40–50° and the residue crystallized. The solid was dissolved in 150 ml. of hot absolute ethanol and recrystallized by cooling, followed by suction filtration at 5°. It weighed 7.2 g. and melted at 191–195°. An additional 1.8 g. of this material was obtained on evaporation of the filtrate and recrystallization of the residue. The total yield was 42%. Again recrystallized, the solid melted at 196.0–197.0° (partial immersion thermometer).

Anal. Calcd. for $C_9H_{14}NO_3P$: N, 6.51; P, 14.4. Found: N, 6.48; P, 14.1.

2-Chloroethyl vinylphosphonochloridate. To a 1-l., three-necked flask equipped with a mechanical stirrer and a reflux condenser protected with a calcium chloride tube was added 215 g. (1.03 moles) of phosphorus pentachloride and 170 ml. of 1,1,2-trichloroethane. To the stirred suspension was added 194. g. (0.83 mole) of bis(2-chloroethyl) vinylphosphonate. An exothermic reaction took place. The stirred mixture was refluxed for 1 hr. during which the remaining phosphorus pentachloride dissolved. The solvent, phosphorus oxychloride, and ethylene chloride were removed by distillation at atmospheric pressure until the head temperature reached 120°. Distillation of the volatile materials was completed under reduced pressure. The residue was distilled through a 6-in. Vigreux column at *ca.* 1 mm., giving 24 g. at 55–96°, 98 g. (62% yield) at 94–100°, and 11 g. at 100–119°. There was 16 g. of residue. The middle fraction was analyzed and used in subsequent syntheses.

Anal. Calcd. for $C_4H_7Cl_2O_2P$: P, 16.4. Found: P, 16.1.

Methyl 2-chloroethyl vinylphosphonate. To a 500-ml., three-necked flask fitted with a mechanical stirrer, reflux

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[12] H. I. Jacobson, M. J. Griffin, S. Preis, and E. V. Jensen, *J. Am. Chem. Soc.*, **79**, 2608 (1957).

[13] G. M. Kosolapoff, private communication.

[14] B. B. Hunt, B. C. Saunders, and P. Simpson, *Chem. & Ind.* (London), 47 (1960).

[15] G. C. Turrel, W. D. Jones, and A. Maki, *J. Chem. Phys.*, **26**, 1544 (1957).

[16] W. L. Walton and R. B. Hughes, *J. Am. Chem. Soc.*, **79**, 3985 (1957).

[17] F. Halverson, R. F. Stamm, and J. J. Whalen, *J. Chem. Phys.*, **16**, 808 (1948).

[18] L. J. Bellamy and L. Beecher, *J. Chem. Soc.*, 475 (1952); 728 (1953); ref. 10, p. 267.

[19] B. Holmstedt and L. Larsson, *Acta Chem. Scand.*, **5**, 1179 (1951).

[20] S. A. Francis, *J. Chem. Phys.*, **18**, 861 (1950).

[21] L. W. Daasch and D. C. Smith, *Anal. Chem.*, **23**, 853 (1951).

[22] T. S. Piper and E. G. Rochow, *J. Am. Chem. Soc.*, **76**, 4318 (1954).

[23] H. Lenormant, *Bull. Soc. Chim. France*, 36 (1948).

[24] Sample was prepared by the Monsanto Chemical Co.

condenser, and dropping funnel were added 200 ml. of benzene and 13.2 g. (0.07 mole) of 2-chloroethyl vinylphosphonochloridate. To the stirred solution were added over a period of 20 min., a solution of 6.7 g. (0.21 mole) of methanol and 7.1 g. (0.07 mole) of triethylamine in 50 ml. of benzene. The reaction was exothermic. The cooled mixture was freed of amine hydrochloride by suction filtration, the solid was washed with three 50-ml. portions of benzene, and the filtrate was shaken with solid sodium carbonate and again filtered. The solvent was removed by distillation at reduced pressure. The residue was fractionated in a 6-in. Vigreux column. The yield of liquid distilling at 82–85° (1 mm.) was 9.5 g. (74%).

Anal. Calcd. for $C_5H_{10}ClO_3P$: P, 16.8. Found: P, 16.6.

2-Chloroethyl N,N-dimethyl-P-vinylphosphonamidate. In a 1-l., three-necked flask fitted with a mechanical stirrer, reflux condenser, a calcium chloride drying tube, and dropping funnel were placed 94.5 g. (0.50 mole) of 2-chloroethyl vinylphosphonochloridate and 300 ml. of benzene. A solution of 22.5 g. (0.50 mole) of dimethylamine and 50.5 g. (0.50 mole) of triethylamine in 80 ml. of benzene was prepared by bubbling gaseous dimethylamine into a chilled mixture of the other two components. The solution of amines was added to the phosphonochloridate solution with cooling and stirring. The amine hydrochloride was removed by suction filtration, the solid being washed with benzene several times. The filtrate was stirred with solid sodium carbonate for 30 min., and then the mixture was refluxed 1 hr. After filtration, the solution was freed of solvent by distillation, first at atmospheric pressure and then under reduced pressure, keeping the pot temperature below 130°. The residue was fractionated in a 6-in. Vigreux column at 1 mm., giving 65 g. (66% yield) distilling at 107–110°, and 17 g. of residue. The product was redistilled at 118.5–119.5° (1.5 mm.).

Anal. Calcd. for $C_6H_{13}ClNO_2P$: N, 7.09; P, 15.7. Found: N, 7.04; P, 15.3.

Diethyl 1(and 2)-propynylphosphonate. Commercial grade diethyl phosphite and propargyl bromide were redistilled just prior to use. In a 200-ml., three necked flask fitted with a water bath, reflux condenser, dropping funnel, and thermometer were placed 20 ml. of tetrahydrofuran, which had been dried and redistilled over sodium, and 25 g. (0.21 mole) of propargyl bromide. In the funnel was placed a solution prepared from 4.6 g. (0.2 g.-atom) of sodium, 27.6 g. (0.2 mole) of diethyl phosphite and 26 ml. of tetrahydrofuran. The addition was carried out over a period of 20 min., the temperature of the stirred mixture rising to 40°. The suspension was refluxed 1 hr. It was then cooled, filtered under suction, the solid washed with acetone, and after 1 hr. the filtrate was refiltered. The crude dried sodium bromide weighed 15 g. (73% yield). A few crystals of hydroquinone were added to the filtrate, which was then freed of solvent by distillation at atmospheric pressure and finally at reduced pressure, keeping the pot temperature below 115°. The residue was fractionated in a 6-in. Vigreux column at 1 mm., giving 2.9 g. distilling at 45–88° and 12.7 g. (36% yield) at 99–115°. There was 13 g. of polymeric residue. Redistillation of the main fraction gave 7.9 g. coming off at 105.5–110.0° (1 mm.).

Anal. Calcd. for $C_7H_{13}O_3P$: C, 47.71; H, 7.43; P, 17.6. Found: C, 47.85; H, 7.49; P, 17.1.

The product gave a very deep wine-red color when treated with two volumes of a solution of 0.5 g. of 3,5-dinitrobenzoic acid in 10 ml. of 2% sodium hydroxide. This indicates the presence of an active hydrogen compound.[10] The material also gave a moderate quantity of a white precipitate when treated with 2–10 volumes of a half-saturated solution of mercuric cyanide in 2% sodium hydroxide. The precipitate was probably the mercury derivative of diethyl 2-propynylphosphonate. No precipitate was given by diethyl phosphite or diethyl ethylphosphonate. Previously reported constants of diethyl 1-propynylphosphonate are[12]: b.p. 108–110° (2.1 mm.) and 98–1003° (2 mm.); n_D^{25} 1.4449.

Absorption spectra. Measurements on methyl 2-chloroethyl vinylphosphonate and 2-chloroethyl N,N-dimethyl-P-vinylphosphonamidate were made with a Beckman model IR-4 spectrophotometer. With diethyl propynylphosphonate, a Perkin-Elmer Model 21 instrument was used. All data were obtained on the compounds in chloroform solution.

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NEW ORLEANS, LA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Aromatic Cyclodehydration. XLVII.[1] Pyrido[2,1-*b*]benz[*f*][1,3]oxazepinium Salts

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Through the cyclization of 1-acetonyl-2-(3-alkoxyphenoxy)pyridines the first derivatives of the new prido[2,1-*b*]benz[*f*][1,3] oxazepinium system have been prepared. The difficulty encountered in the cyclization may be explained in terms of izinium-oxonium resonance. Evidence for the existence of such resonance in the 1-methyl-2-phenoxypyridinium system has been presented.

The success met with in the cyclization of some benzylpyridinium salts (I) to the new morphanthridizinium system (II)[3] raised the question whether other groups or atoms might replace the methylene bridge connecting the aromatic rings. The 2-phenoxypyridinium salts were selected for the first study since the required 2-phenoxypyridines are readily prepared, and the final ring

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(1) For the preceding communication of this series, see *J. Org. Chem.*, **26**, 2231 (1961).

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(2) Monsanto Chemical Co. Fellow, 1959–1960. This research was supported in part by a research grant (NSF-G6215) of the National Science Foundation.

(3) K. B. Moser and C. K. Bradsher, *J. Am. Chem. Soc.*, **81**, 2547 (1959).