

**Reaction of Pentyl Perchlorate with Pentanol.** Pentanol (0.053 g, 0.6 mmol) and potassium carbonate (0.276 g, 2 mmol) were added to a solution of 0.6 mmol of pentyl perchlorate in 3 ml of carbon tetrachloride and the mixture was stirred at ambient temperature. Dipentyl ether was formed in 5% yield in 20 hr, 25% in 4 days, and 90% in 8 days. The reaction was monitored by nmr, and the product was identified by glpc comparison with an authentic sample.

**Reaction of Isopropyl Perchlorate with Pentanol.** Pentanol (0.026 g, 0.3 mmol) and sodium sulfate (0.142 g, 1 mmol) were added to a solution of 0.3 mmol of isopropyl perchlorate in 2 ml of carbon tetrachloride and the mixture was stirred. Isopropyl pentyl ether was formed in 25% yield in 18 hr, 50% in 3 days, and 85% in 6 days.

**Reaction of Allyl Perchlorate with 2-Fluoro-2,2-dinitroethanol.** To a solution of 0.72 mmol of allyl perchlorate in 5 ml of carbon tetrachloride was added 5 ml of methylene chloride, 0.30 g (2 mmol) of 2-fluoro-2,2-dinitroethanol,<sup>24</sup> and 0.69 g (5 mmol) of potassium

carbonate. The mixture was stirred for 48 hr. The solution was washed with water and with 5% sodium hydroxide and dried over sodium sulfate, and the solvent was removed to give 0.11 g (79%) of allyl 2-fluoro-2,2-dinitroethyl ether, identical with an authentic sample.<sup>25</sup>

**Reaction of Hexyl Perchlorate with Dimethyl Sulfoxide.** Dimethyl sulfoxide (5 ml) and 0.5 g (6 mmol) of sodium bicarbonate were added to a solution of 1.74 mmol of hexyl perchlorate in 10 ml of carbon tetrachloride. An initially exothermic reaction took place, and nmr spectra showed the immediate consumption of perchlorate and slow formation of hexaldehyde. After 24 hr the mixture was washed with water and dried. The only products detected by nmr were hexaldehyde (95% yield) and dimethyl sulfide. Vacuum distillation gave pure hexaldehyde.

(24) V. Grakauskas and K. Baum, *J. Org. Chem.*, **33**, 3080 (1968).

(25) V. Grakauskas, *J. Org. Chem.*, **35**, 3030 (1970).

## Reactions of Dichlorine Heptoxide with Amines<sup>1</sup>

Charles D. Beard and Kurt Baum\*

Contribution from Fluorochem, Incorporated, Azusa, California 91702.





Received November 15, 1973

**Abstract:** Dichlorine heptoxide in carbon tetrachloride reacts as a perchlorylating agent with secondary and primary amines. Piperidine, diethylamine, dipentylamine, and 2-ethylaziridine gave *N*-perchlorylpiperidine, *N*-perchloryldiethylamine, *N*-perchloryldipentylamine, and *N*-perchloryl-2-ethylaziridine, respectively. Hexylamine, butylamine, propylamine, isopropylamine, and *tert*-butylamine gave *N*-perchlorylhexylamine, *N*-perchlorylbutylamine, *N*-perchlorylpropylamine, *N*-perchlorylisopropylamine, and *N*-perchloryl-*tert*-butylamine, respectively. The primary perchlorylamines are acidic and form sodium salts with aqueous sodium hydroxide; the ionization constant of *N*-perchloryl-*tert*-butylamine is  $1.51 \times 10^{-7}$ . The salts of *N*-perchlorylhexylamine and *N*-perchlorylbutylamine were chlorinated with sodium hypochlorite. In carbon tetrachloride solution, primary alkyl *N*-perchlorylamines and the *N*-chloro derivatives give the corresponding carboxylic acids at ambient temperature, whereas *N*-perchlorylisopropylamine gives acetone and *N*-perchloryl-*tert*-butylamine is unchanged.

Only two compounds with nitrogen-bonded perchloryl groups have been reported, the ammonium salt of perchlorylamide<sup>2</sup> and *N*-perchlorylpiperidine,<sup>3</sup> which were prepared by reactions of perchloryl fluoride with ammonia and with piperidine. Attempts to extend this reaction to other amines gave only oxidation and fluorination products,<sup>4</sup> and perchloryl fluoride was recently used as the reagent of choice for the fluorination of an amine.<sup>5</sup> The function of dichlorine heptoxide in carbon tetrachloride solution as an effective and convenient perchlorylating agent for alcohols<sup>6</sup> suggested that its reaction with amines might provide a practical route to perchlorylamines.

Dichlorine heptoxide in carbon tetrachloride reacted with secondary amines to give high yields of perchlorylamines, as shown in Table I. Two moles of amine were used per mole of dichlorine heptoxide, with one functioning as a base, and the reactions were complete on mixing the reagents. The perchlorylamines were obtained as carbon tetrachloride solutions, with no

Table I. Perchlorylamines from Amines and Dichlorine Heptoxide

Starting material	Product	Yield, %
		73
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NH	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NClO <sub>3</sub>	77
(C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> NH	(C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> NClO <sub>3</sub>	81
		
C <sub>2</sub> H <sub>5</sub> CH—CH <sub>2</sub>	C <sub>2</sub> H <sub>5</sub> CH—CH <sub>2</sub>	83
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CH <sub>2</sub> NH <sub>2</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CH <sub>2</sub> NHClO <sub>3</sub>	63
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> NHClO <sub>3</sub>	61
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> NHClO <sub>3</sub>	61
(CH <sub>3</sub> ) <sub>2</sub> CHNH <sub>2</sub>	(CH <sub>3</sub> ) <sub>2</sub> CHNHClO <sub>3</sub>	60
(CH <sub>3</sub> ) <sub>3</sub> CNH <sub>2</sub>	(CH <sub>3</sub> ) <sub>3</sub> CNHClO <sub>3</sub>	71

impurities detectable by nmr. Thus piperidine, diethylamine, and dipentylamine gave *N*-perchlorylpiperidine, *N*-perchloryldiethylamine, and *N*-perchloryldipentylamine, respectively. This reaction was even applicable to the preparation of a strained molecule such as *N*-perchloryl-2-ethylaziridine.



Primary amines reacted similarly to give the corresponding perchlorylamines. Thus, hexylamine, butylamine, and propylamine, as well as isopropylamine

(1) This work was supported by the Office of Naval Research.  
(2) H. C. Mandell, Jr., and G. Barth-Wehrenalp, *J. Inorg. Nucl. Chem.*, **12**, 90 (1959).

(3) D. M. Gardner, R. Helitzer, and C. J. Mackley, *J. Org. Chem.*, **29**, 3738 (1964).

(4) D. M. Gardner, R. Helitzer, and D. H. Rosenblatt, *J. Org. Chem.*, **32**, 1115 (1967).

(5) J. Cantacuzene and J. Leroy, *J. Amer. Chem. Soc.*, **93**, 5263 (1971).

(6) K. Baum and C. D. Beard, *J. Amer. Chem. Soc.*, **96**, 3233 (1974).

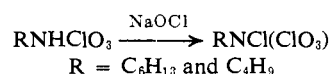
and even *tert*-butylamine, gave the corresponding perchlorylamines in yields of 60–71%.



The primary perchlorylamines comprise a new reactive organic functional group in that the hydrogens on nitrogen are acidic. The NH was exchanged with  $\text{D}_2\text{O}$  on mixing. The compounds were extracted from carbon tetrachloride by aqueous sodium hydroxide and recovered quantitatively on acidification. The ionization constant of *N*-perchloryl-*tert*-butylamine, determined by potentiometric titration, was  $1.51 \times 10^{-7}$ . The first ionization constant of the parent perchlorylamide,  $\text{H}_2\text{NClO}_3$ , was reported<sup>2</sup> to be  $3.0 \times 10^{-6}$ .



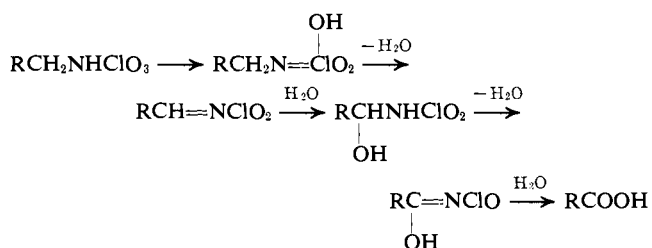
*N*-Perchlorylhexylamine and *N*-perchlorylbutylamine in carbon tetrachloride solution were chlorinated by stirring with aqueous sodium hypochlorite. The ir and nmr spectra of the products were consistent with the corresponding *N*-chloro-*N*-perchlorylamine structures and showed no evidence of NH bonds. The products were not extractable with 1 *N* sodium hydroxide. Yields were 84–87%. *N*-Perchloryl-*tert*-butylamine was not chlorinated under these conditions, probably because of steric hindrance.



Primary perchlorylamines with  $\alpha$  hydrogens were found to undergo a self-oxidation reaction at ambient temperature in carbon tetrachloride solution. Thus, *N*-perchlorylpropylamine was completely converted to propionic acid in 18 hr and *N*-perchlorylhexylamine to hexanoic acid in 3 days. Acetone was also formed from *N*-perchlorylisopropylamine under the same conditions.

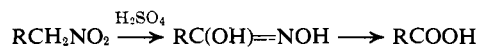
Hexanoic acid was obtained similarly from *N*-chloro-*N*-perchlorylhexylamine. On the other hand, *N*-perchloryl-*tert*-butylamine gave no detectable decomposition in a week under the same conditions, and the *N*-perchloryl derivatives of secondary amines also gave no evidence of decomposition.

The formation of carboxylic acids from primary alkyl perchlorylamines can be rationalized on the basis of a mechanism such as the following.



The acidic perchlorylamines are assumed to be in tautomeric equilibrium with their enolic isomers. The  $\alpha$  hydrogens of the latter could be sufficiently labile for isomerization to the corresponding hydroxychlorylamines by elimination and readdition of water, and repetition of this process would yield carboxylic acids. A similar route can be envisioned for the formation of ketones from secondary alkyl derivatives. Acids could

be formed similarly from *N*-chloroperchlorylamines by the initial elimination of HCl or by preliminary hydrolysis to HOCl and the *N*-perchlorylamine. This reaction path has similarities to that of the conversion of nitroalkanes to carboxylic acids, in which hydroxamic acids are intermediates.<sup>7</sup>



Other possible mechanisms for these reactions involve an initial  $\alpha$ -elimination or  $\beta$ -elimination of  $\text{HClO}_3$ , which subsequently acts as an oxidizing agent. The stability of *N*-perchloryl-*tert*-butylamine, however, argues against an  $\alpha$ -elimination route, while the stability of perchloryl derivatives of secondary amines argues against  $\beta$ -elimination routes.

The spontaneous formation of carboxylic acids from primary *N*-perchlorylamines offers an attractive synthetic method for the direct conversion of primary amines to acids. The addition of an amine to the dichlorine heptoxide-carbon tetrachloride solution of the perchlorylamine on mixing, which on standing at room temperature gives the carboxylic acid in high over-all yields.

### Experimental Section

**Caution:** Neat perchlorylamines are sensitive explosives and should be handled only with adequate protective devices. No explosions occurred in the solution reactions described, but in the primary amine reactions, errors in stoichiometry could lead to potentially dangerous precipitates of perchlorylamine salts. Precautionary comments of the preceding paper<sup>6</sup> are applicable.

**General.** Nmr spectra were recorded with a Varian T-60 spectrometer, and ir spectra were recorded with a Perkin-Elmer 700 spectrometer.

***N*-Perchlorylpiperidine.** Piperidine (0.104 g, 1.2 mmol) was added dropwise with stirring to 2 ml of 0.3 *M* dichlorine heptoxide in carbon tetrachloride<sup>6</sup> at 0°. After 5 min, the mixture was washed with dilute sulfuric acid and then with water. The carbon tetrachloride solution was dried over molecular sieves. Analysis of the solution by nmr using chlorobenzene as a quantitative internal standard showed a 73% yield of *N*-perchlorylpiperidine: nmr ( $\text{CCl}_4$ )  $\delta$  3.42 (t,  $J = 6$  Hz, 4 H,  $\text{NCH}_2$ ) and 1.85 ppm (broad m, 6 H). The ir spectrum was identical with that reported.<sup>2</sup>

***N*-Perchloryldiethylamine.** The reaction of 0.22 g (3.0 mmol) of diethylamine with 5 ml of 0.3 *M* dichlorine heptoxide in carbon tetrachloride by the above procedure gave a 77% yield of *N*-perchloryldiethylamine: nmr ( $\text{CCl}_4$ )  $\delta$  3.47 (broadened q, 4 H,  $\text{CH}_2$ ) and 1.37 ppm (t, 6 H,  $J = 6$  Hz,  $\text{CH}_3$ ); ir ( $\text{CCl}_4$ ) 1240 (vs), 1200 (vs), 1010 (s), and 680  $\text{cm}^{-1}$  (s).

***N*-Perchloryldipentylamine.** By the above procedure, *N*-perchloryldipentylamine was obtained in 81% yield: nmr ( $\text{CCl}_4$ )  $\delta$  3.27 (m, 4 H,  $\text{CH}_2\text{NClO}_3$ ), 1.47 (broad m, 12 H,  $-\text{CH}_2-$ ), and 0.93 ppm (distorted t, 6 H,  $\text{CH}_3$ ); ir ( $\text{CCl}_4$ ) 1240 (s), 1200 (s), 1020 (s), and 680  $\text{cm}^{-1}$  (m).

***N*-Perchloryl-2-ethylaziridine.** The above procedure gave an 83% yield of *N*-perchloryl-2-ethylaziridine. An analytical sample was obtained by removing solvent under vacuum and vacuum transferring the residue to a  $-78^\circ$  receiver at 0.05 mm: nmr ( $\text{CCl}_4$ )  $\delta$  2.85 (broad m, 3 H, aziridine ring H's), 1.67 (m, 2 H,  $\text{CH}_2$  of ethyl), and 1.30 ppm (distorted t, 3 H,  $\text{CH}_3$ ); ir ( $\text{CCl}_4$ ) 1245 (vs), 1210 (vs), 1020 (vs), and 680  $\text{cm}^{-1}$  (s).

**Anal.** Calcd for  $\text{C}_4\text{H}_8\text{NClO}_3$ : C, 31.28; H, 5.25; Cl, 24.08. Found: C, 30.76; H, 4.81; Cl, 23.57.

***N*-Perchlorylbutylamine.** The reaction of butylamine with dichlorine heptoxide, as above, gave a 61% yield of *N*-perchlorylbutylamine: nmr ( $\text{CCl}_4$ )  $\delta$  5.77 (broad s, 1 H, NH, disappeared on addition of  $\text{D}_2\text{O}$ ), 3.40 (t, 2 H,  $\text{CH}_2\text{N}$ ), 1.53 (m, 4 H,  $\text{CH}_2\text{CH}_2$ ), and 0.97 ppm (m, 3 H,  $\text{CH}_3$ ); ir ( $\text{CCl}_4$ ) 3280 (m, NH), 1245 (s), 1215 (vs), 1030 (s), and 670  $\text{cm}^{-1}$  (s).

***N*-Perchloryl-*tert*-butylamine.** The above procedure gave a 71% yield of *N*-perchloryl-*tert*-butylamine: nmr ( $\text{CCl}_4$ )  $\delta$  7.10 (broad s,

(7) S. B. Lippincott and H. B. Hass, *Ind. Eng. Chem.*, **31**, 118 (1939).

1 H,  $\text{NHClO}_3$ , disappeared on addition of  $\text{D}_2\text{O}$ ) and 1.32 ppm (s, 9 H,  $\text{CH}_3$ ); ir ( $\text{CCl}_4$ ) 3280 (m, NH), 1260 (s), 1210 (vs), 1020 (vs), and  $660\text{ cm}^{-1}$  (s). The carbon tetrachloride solution underwent no visible or spectral changes within one week at ambient temperature.

An analytical sample was obtained by vacuum transfer to a  $-78^\circ$  receiver at 0.02 mm.

*Anal.* Calcd for  $\text{C}_4\text{H}_{10}\text{NClO}_3$ : C, 30.86; H, 6.46; Cl, 22.87. Found: C, 29.62; H, 6.47; Cl, 22.62.

Potentiometric titration gave an equivalent weight of  $151 \pm 4$  (calcd 155) and an ionization constant of  $1.51 \times 10^{-7}$ .

***N*-Perchlorylhexylamine.** The above procedure gave a 63% yield of *N*-perchlorylhexylamine: nmr ( $\text{CCl}_4$ )  $\delta$  6.73 (broad t, 1 H,  $\text{NHClO}_3$ , disappeared on addition of  $\text{D}_2\text{O}$ ), 3.42 (q, 2 H,  $\text{CH}_2\text{N}$ ), 1.40 (m, 8 H,  $\text{CH}_2\text{CH}_2$ ), and 0.93 ppm (distorted t, 3 H,  $\text{CH}_3$ ); ir ( $\text{CCl}_4$ ) 3290 (w, OH), 1240 (sh), 1210 (vs), 1020 (s), and  $665\text{ cm}^{-1}$  (s). On standing at ambient temperature for 3 days, the compound was completely converted to hexanoic acid and an unidentified inorganic solid. Hexanoic acid was identified by ir, nmr, and glpc comparison with an authentic sample.

***N*-Perchlorylpropylamine.** The above procedure gave *N*-perchlorylpropylamine in 61% yield: nmr ( $\text{CCl}_4$ )  $\delta$  6.9 (broad, 1 H,  $\text{NHClO}_3$ ), 3.4 (m, 2 H,  $\text{CH}_2\text{N}$ ), 1.72 (m, 2 H,  $\text{CH}_2\text{CH}_3$ ), and 1.07 ppm (t,  $J = 6\text{ Hz}$ ,  $\text{CH}_3$ ); ir ( $\text{CCl}_4$ ) 3270 (m, NH), 1250 (s), 1240 (sh), 1210 (vs), 1030 (vs), and  $645\text{ cm}^{-1}$  (s). The compound was completely converted in 18 hr at ambient temperature to propionic acid and an unidentified inorganic material.

***N*-Perchlorylisopropylamine.** The above procedure gave *N*-perchlorylisopropylamine in 60% yield: nmr ( $\text{CCl}_4$ )  $\delta$  6.7 (broad, 1 H,

$\text{NHClO}_3$ ), 3.83 (m, 1 H, CH), and 1.33 ppm (d,  $J = 7\text{ Hz}$ ,  $\text{CH}_3$ ); ir ( $\text{CCl}_4$ ) 3270 (m, NH), 1230 (sh), 1205 (vs), 1020 (vs), and  $660\text{ cm}^{-1}$  (s). The compound in carbon tetrachloride was 60% converted to acetone in 1 week.

**Sodium Salts of *N*-Perchloryl Primary Amines.** Extracting the carbon tetrachloride solutions of *N*-perchloryl primary amines with 1 *N* sodium hydroxide left nothing in the carbon tetrachloride layer observable by nmr. Acidification of the aqueous layer resulted in reextraction of the starting material with no change in nmr and in ir spectra.

***N*-Chloro-*N*-perchlorylhexylamine.** A solution of 0.95 mmol of *N*-perchlorylhexylamine in 5 ml of carbon tetrachloride was stirred for 5 min with 5 ml of 5% aqueous sodium hypochlorite, and the organic layer was dried. Nmr and ir spectra of the solution showed no evidence of NH, and the product was not affected by extraction with 1 *N* sodium hydroxide. Analysis by nmr using chlorobenzene as a quantitative reference indicated an 87% yield of *N*-chloro-*N*-perchlorylhexylamine: nmr ( $\text{CCl}_4$ )  $\delta$  3.70 (t,  $J = 6\text{ Hz}$ , 2 H,  $\text{CH}_2\text{N}$ ), 1.40 (broad m, 8 H,  $-\text{CH}_2-$ ), and 0.90 ppm (distorted t, 3 H,  $\text{CH}_3$ ); ir ( $\text{CCl}_4$ ) 1250 (vs), 1220 (vs), 1020 (s), 975 (m), and  $650\text{ cm}^{-1}$  (m). The compound in carbon tetrachloride was completely converted to hexanoic acid in 20 hr.

***N*-Chloro-*N*-perchlorylbutylamine.** By the above procedure, 0.92 mmol of *N*-perchlorylbutylamine in 5 ml of carbon tetrachloride gave an 84% yield of *N*-chloro-*N*-perchlorylbutylamine: nmr ( $\text{CCl}_4$ )  $\delta$  3.65 (t,  $J = 6\text{ Hz}$ , 2 H,  $\text{CH}_2\text{N}$ ), 1.7 (broad m, 4 H,  $\text{CH}_2$ ), and 1.0 ppm (distorted t, 3 H,  $\text{CH}_3$ ); ir ( $\text{CCl}_4$ ) 1250 (vs), 1220 (vs), 1020 (vs), and  $650\text{ cm}^{-1}$  (s).

## Reactions of 1,4- and 1,5-Dihaloalkanes with Alkali Naphthalenes<sup>1,2</sup>

John F. Garst\* and John T. Barbas

Contribution from the Department of Chemistry, The University of Georgia, Athens, Georgia 30602. Received September 13, 1973

**Abstract:** Reactions of 1,4-dihalobutanes and 1,5-dihalopentanes with alkali naphthalenes give reduction products (mostly cycloalkanes and olefins) and alkylation products (alkylated naphthalene derivatives). The products do not include dimeric or polymeric residues of the dihaloalkanes. Thus, initially formed alkyl radicals do not couple. Instead, they react with alkali naphthalene to give alkyl and alkylated naphthalene anions. Therefore, alkyl dimers from reactions of monohaloalkanes with sodium naphthalene cannot arise from coupling of initially formed radicals. They must result instead from reactions of alkyl anions, probably with alkyl iodides. These are not conventional  $\text{S}_\text{N}2$  reactions; they may involve intermediate radical pairs. From the fact that the reduction-alkylation ratio from the  $\alpha,\omega$ -dihaloalkanes is halogen and chain length independent it is concluded that the intermediate  $\omega$ -haloalkyl radicals are not bridged and that they do not undergo internal  $\text{S}_\text{H}$  reactions. No definitive conclusions can be reached on the mechanisms of the reactions of intermediate  $\omega$ -haloalkylalkalies to give cycloalkanes and olefins. For the iodides, it appears that the postulate of intermediate  $\alpha,\omega$ -alkadiyls (diradicals) is consistent with available data, but for other halogens this is not easily reconciled with the fact that there is a substantial halogen effect on the distribution among the resulting cycloalkanes and olefins.

Studies of reactions of monohaloalkanes with sodium naphthalene and related compounds in DME and other ethers have led to Scheme I.<sup>2-4</sup> The least understood aspect of these reactions has persisted in being

the route to alkyl dimers, which dominate when alkyl iodides are reactants. We initiated studies of reactions of 1,4-diiodobutane with sodium naphthalene in order to test one of the theories of alkyl dimer formation that had been proposed earlier. The results are germane to additional topics of interest, and the studies were expanded to include other  $\alpha,\omega$ -dihaloalkanes and some variations in the alkali arene and the solvent. Here we consider reactions of 1,4-dihalobutanes and 1,5-dihalopentanes.

### Experimental Section

**Solvents.** 1,2-Dimethoxyethane (DME), tetrahydrofuran (THF), and 2-methyltetrahydrofuran (MeTHF) were refluxed over fresh-cut sodium for 12 hr then fractionally distilled on a spinning band

(1) Based on the Ph.D. Dissertation of John T. Barbas, The University of Georgia, Athens, Georgia, 1971.

(2) Part of this work has been published in preliminary form: (a) J. F. Garst and J. T. Barbas, *J. Amer. Chem. Soc.*, **91**, 3385 (1969); (b) *Tetrahedron Lett.*, 3125 (1969).

(3) S. Bank and J. F. Bank, *Tetrahedron Lett.*, 4533 (1969).

(4) The foundations of Scheme I have been reviewed recently from several viewpoints.<sup>5-7</sup>

(5) J. F. Garst, *Accounts Chem. Res.*, **4**, 400 (1971).

(6) J. F. Garst, "Free Radicals," J. K. Kochi, Ed., Wiley, New York, N. Y., 1973, pp 520-527.

(7) J. F. Garst, "Chemically Induced Magnetic Polarization," A. R. Lepley and G. L. Closs, Ed., Wiley, New York, N. Y., 1973, p 223 ff.