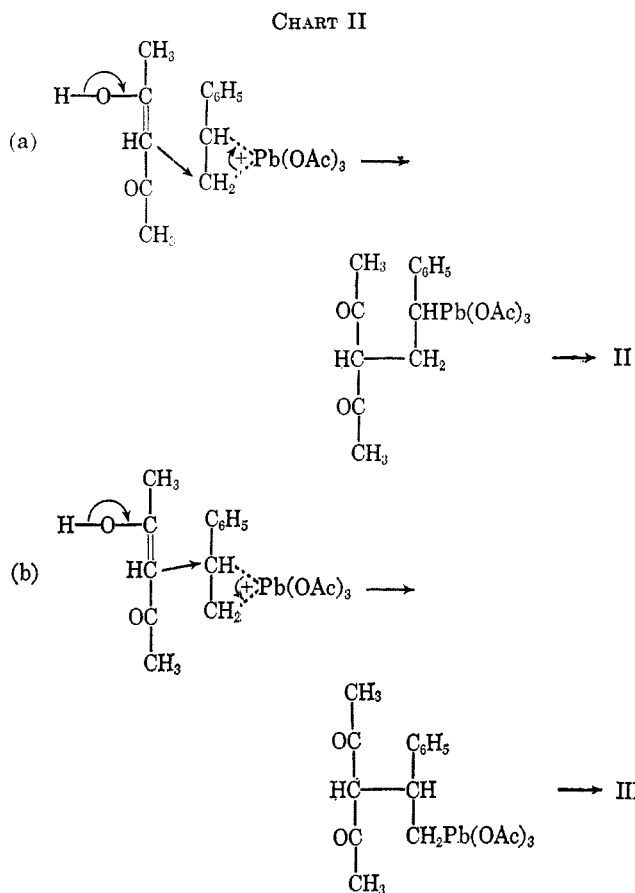
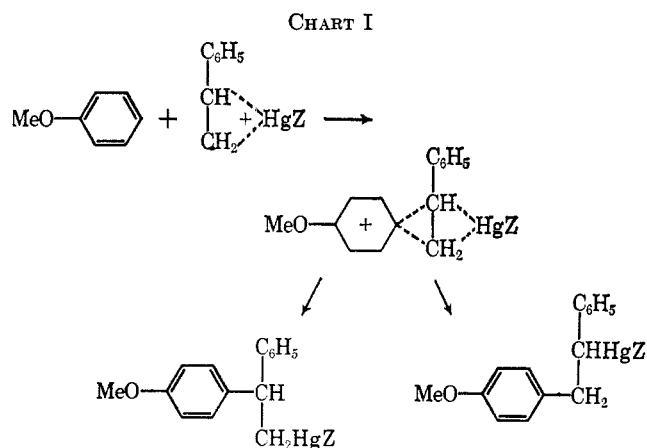


through both paths a and b in acetic acid solution, respectively. However, the question of which is the controlling factor of the possible two reaction paths remains unexplained.



The results mentioned above show that the oxyplumbation of styrene does occur and the oxyplumbate reacts with active methylene as oxymercurial and oxythallate, although the applicability might be limited because of the strong oxidative nature of lead tetraacetate.

#### Experimental Section

**Materials.**—All reagents were commercial products. Organic reagents were used after distillation.

**Spectral Measurements.**—Infrared and ultraviolet spectra were determined by JASCO IR-S and Hitachi EPS-2U, respec-

tively. The nmr spectrum was obtained on a Varian A-60 using tetramethylsilane as the internal standard in deuteriochloroform.

**Reaction of Styrene with Acetylacetone in the Presence of Lead Tetraacetate.**—The following example shows a typical experimental procedure. Into a suspension of 50 g of lead tetraacetate in 70 ml of benzene containing 7 ml of acetic acid, 25 g of styrene was added with stirring. After 3 hr, 8 g of 70% perchloric acid was added during 1 hr, followed by 20 g of acetylacetone during 0.5 hr under careful cooling. Throughout the additions, the reaction mixture was maintained at 0–3°. After 6 hr of stirring, the lead acetate formed was filtered off. The filtrate was washed with 200 ml of water, then with saturated sodium bicarbonate solution. Distillation *in vacuo* gave the following fractions: 40–50° (10 mm) (D<sub>1</sub>); 50–60° (1 mm), 3 g (D<sub>2</sub>); 60–114° (1 mm), 1.3 g (D<sub>3</sub>); 114–124° (1 mm), 2.4 g (D<sub>4</sub>); 124–154° (1 mm), 3.2 g (D<sub>5</sub>); 5.1 g of residue. These fractions were analyzed by gas chromatography. D<sub>1</sub> was a mixture of unreacted styrene and acetylacetone. D<sub>2</sub> was acetoxyacetylacetone (I). D<sub>5</sub> was a mixture of II (more than 80%) and unidentified products (less than 20%). D<sub>3</sub> and D<sub>4</sub> were the mixtures of I, II, and small amounts of unidentified products. Calculation on the basis of gas chromatograms showed that the yields of I and II were 4.3 g (22.5%) and 3.5 g (14.2%), respectively.

D<sub>2</sub> was redistilled, bp 79–80° (5.5 mm), *n*<sub>D</sub><sup>20</sup> 1.4361. The ultraviolet spectra in hexane showed λ<sub>max</sub> 283 mμ (ε 2900) and 190 mμ (ε 18,000). A grayish green copper salt was obtained, mp 250° dec.

*Anal.* Calcd for (C<sub>7</sub>H<sub>9</sub>O<sub>4</sub>)<sub>2</sub>Cu: C, 44.50; H, 4.80. Found: C, 44.56; H, 4.95.

D<sub>5</sub> was chromatographed (alumina–hexane) and distilled, bp 137–142° (2 mm), *n*<sub>D</sub><sup>20</sup> 1.5566.

*Anal.* Calcd for C<sub>13</sub>H<sub>14</sub>O<sub>2</sub>: C, 77.20; H, 6.98. Found: C, 77.25; H, 7.20.

The semicarbazone melted at 182–184°.

*Anal.* Calcd for C<sub>14</sub>H<sub>17</sub>N<sub>3</sub>O<sub>2</sub>: C, 64.84; H, 6.61; N, 16.21. Found: C, 64.66; H, 6.82; N, 15.96.

Ultraviolet absorption maxima were found at 270 mμ (ε 10,600), 191.5 (40,000), and 190 (38,000) in hexane; 280 (12,500) and 204 (12,500) in ethanol. Infrared maxima were located at 2950 (w), 2850 (w), 1740 (w), 1670 (s), 1605 (s), 1485 (w), 1440 (w), 1415 (w), 1380 (m), 1360 (m), 1320 (w), 1225 (s), 1140 (w), 1060 (w), 1025 (w), 985 (w), 965 (w), 940 (m), 765 (m), 700 (s), 630 (m), and 605 (w) cm<sup>-1</sup>.

**Acknowledgment.**—The authors are indebted to Dr. T. Shingu, Department of Pharmacy, for determining the nmr spectra.

#### Reactions of Methyl β-Naphthyl Sulfides with N-Halosuccinimides

D. L. TULEEN AND D. N. BUCHANAN

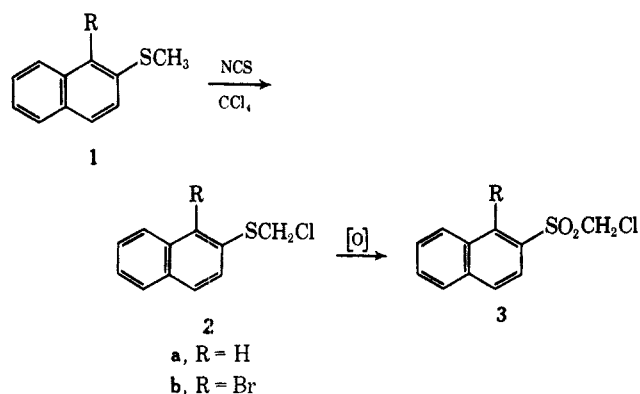
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We have previously reported the efficacy of N-chlorosuccinimide (NCS) for the preparation of α-chloro sulfides.<sup>1</sup> It seemed of interest, as part of a program examining the reactions of sulfides with various halogenating agents, to compare the behavior of representative sulfides toward NCS and N-bromosuccinimide (NBS).

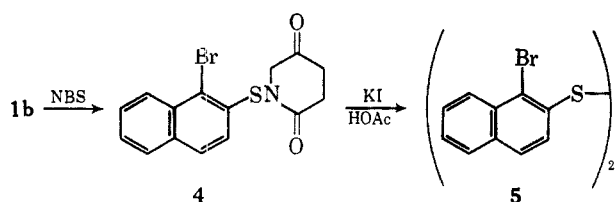
Sulfides 1 in carbon tetrachloride at 25° have been cleanly converted by NCS to α-chloro sulfides (2). Isolation of the chloro sulfides was not attempted; their identification was made using nmr. The downfield shifts of the methylene singlets of 2a,b compared with the methyl singlets of 1a,b are 2.43 and 2.50 ppm.

(1) D. L. Tuleen and T. B. Stephens, *Chem. Ind. (London)*, 1555 (1966).



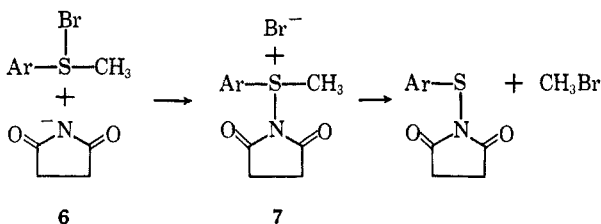
These values compare favorably with the reported shielding constant of 2.53 for chlorine in disubstituted methylenes.<sup>2</sup> Further structural proof was effected by the *m*-chloroperbenzoic acid oxidation<sup>3</sup> of the chloro sulfides to the corresponding  $\alpha$ -chloro sulfones, **3**.

Nuclear bromination occurred in the reaction of methyl 2-naphthyl sulfide (**1a**) with NBS. An excellent yield of 1-bromo-2-naphthyl methyl sulfide (**1b**) resulted from reaction in carbon tetrachloride at room temperature or at reflux. Bromination of **1b** with NBS could not be effected at room temperature; N-(1-bromo-2-naphthylthio)succinimide (**4**) was formed in refluxing carbon tetrachloride. Structural elucidation of **4** was aided by iodometric titration,<sup>4</sup> which proceeds with the formation of the known bis(1-bromo-2-naphthyl) disulfide (**5**).



Analogous bromination of the aromatic ring and N-arythiosuccinimide formation has been observed in the reactions of substituted thioanisoles with NBS.<sup>4-6</sup> When the substituent is in the *para* position (the site most susceptible to ring bromination) the formation of N-arythiosuccinimide is the predominant course of the reaction.

Groebel has postulated the intermediacy of free radicals in the reaction of methyl aryl sulfides with NBS which produces N-arythiosuccinimides.<sup>4</sup> We feel that an ionic path is more likely, perhaps involving displacement of the N-arythiosuccinimide from intermediate **7**



(2) R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1964, p 87.

(3) L. A. Paquette, *J. Am. Chem. Soc.*, **86**, 4085 (1964).

(4) W. Groebel, *Chem. Ber.*, **92**, 2887 (1959).

(5) A. Arcorio and G. Scarlata, *Ann. Chim. (Rome)*, **54**, 139 (1964); *Chem. Abstr.*, **61**, 11919 (1964).

(6) N. P. Buu-Hoi, *Ann.*, **556**, 1 (1944).

by bromide ion. The displacement of bromide ion by the succinimidyl anion in the formation of **7** and **6** is analogous to other anionic displacements on sulfonium ions.<sup>7</sup> This route is mechanistically identical with the path proposed for the formation of N-(dialkylphosphoro)succinimides in the reaction of trialkyl phosphites with NBS.<sup>8</sup> Diversion of intermediates analogous to **6** accounts for the  $\alpha$ -bromo sulfides<sup>9</sup> and arylsulfenyl bromides<sup>10</sup> which have been observed in reactions of other sulfides with NBS in carbon tetrachloride.

#### Experimental Section<sup>11</sup>

**Reagents.**—N-Chlorosuccinimide and N-bromosuccinimide were purified by recrystallization from hot water. Spectrograde carbon tetrachloride, obtained from Matheson Coleman and Bell, was used without further purification. F. M. C. Corp. *m*-chloroperbenzoic acid was used as received.

**Methyl 2-Naphthyl Sulfide (1a).**—Methylation of 2-naphthalenethiol with dimethyl sulfate afforded the sulfide (90%) which was recrystallized from hexane, mp 61–62° (lit.<sup>12</sup> mp 60–61°); nmr (CCl<sub>4</sub>) showed 2.45 (singlet) and 7.2–7.8 ppm (multiplet).

**1-Bromo-2-naphthyl Methyl Sulfide (1b).**—To a solution of **1a** (5.0 g, 0.029 mole) in 15 ml of carbon tetrachloride was added NBS (5.34 g, 0.03 mole). The mixture was refluxed for 3 hr. Evaporation of the solvent after cooling and removal of succinimide by filtration left the crude sulfide. Recrystallization from hexane afforded 6.04 g (83%) of **1b**, mp 79.5–80.5° (lit.<sup>13</sup> mp 78–79°); nmr (CCl<sub>4</sub>) showed 2.53 (singlet) and 7.1–8.3 ppm (multiplet). An 84% yield of this product was realized when the reaction was allowed to proceed at room temperature overnight.

*Anal.* Calcd for C<sub>11</sub>H<sub>9</sub>BrS: C, 52.18; H, 3.56. Found: C, 52.22; H, 3.79.

**Chloromethyl 2-Naphthyl Sulfide (2a).**—To a solution of **1a** (1.0 g, 0.0057 mole) in 10 ml of carbon tetrachloride was added NCS (0.80 g, 0.006 mole). The mixture was stirred magnetically at 20–25° for several hours. Succinimide was removed by filtration. An nmr spectrum of the filtrate displayed, in addition to the aromatic multiplet at 7.3–8.0 ppm, a singlet at 4.88 ppm.

**Chloromethyl 2-Naphthyl Sulfone (3a).**—Carbon tetrachloride was removed from the chlorosulfide solution. The residue was dissolved in 40 ml of chloroform, oxidized with *m*-chloroperbenzoic acid by the method of Paquette,<sup>3</sup> and recrystallized from ethanol to afford 1.07 g (77%) of the sulfone, mp 109.5–111°; infrared indicated  $\nu_{\text{max}}^{\text{KBr}}$  1320, 1155, and 1120 cm<sup>-1</sup> (SO<sub>2</sub>); nmr (CDCl<sub>3</sub>) showed 4.60 (singlet) and 7.5–8.5 ppm (multiplet).

*Anal.* Calcd for C<sub>11</sub>H<sub>9</sub>ClO<sub>2</sub>S: C, 54.90; H, 3.74. Found: C, 54.52; H, 3.83.

**1-Bromo-2-naphthyl Chloromethyl Sulfide (2b).**—The preparation of this compound was similar to that described for **2a**; nmr (CCl<sub>4</sub>) showed 5.03 (singlet) and 7.3–8.4 ppm (multiplet).

**1-Bromo-2-naphthyl Chloromethyl Sulfone (3b).**—Oxidation of **2b** with *m*-chloroperbenzoic acid and recrystallization from ethanol afforded the sulfone (78% based on starting sulfide, **1b**), mp 129.5–130.5°; infrared indicated  $\nu_{\text{max}}^{\text{KBr}}$  1320, 1150, and 1130 cm<sup>-1</sup> (SO<sub>2</sub>); nmr (CDCl<sub>3</sub>) showed 4.95 (singlet) and 7.5–8.4 ppm (multiplet).

*Anal.* Calcd for C<sub>11</sub>H<sub>9</sub>BrClO<sub>2</sub>S: C, 41.31; H, 2.50. Found: C, 41.69; H, 2.70.

**N-(1-Bromo-2-naphthylthio)succinimide (4).**—To a solution of 1-bromo-2-naphthyl methyl sulfide (2.0 g, 0.0079 mole) in 8

(7) For example, C. R. Johnson and W. G. Phillips, *Tetrahedron Letters*, 2101 (1965).

(8) A. K. Tsolis, W. E. McEwen, and C. A. Vanderwerf, *ibid.*, 3217 (1964).

(9) W. Tagaki, K. Kikukawa, K. Ando, and S. Oae, *Chem. Ind. (London)*, 1624 (1964).

(10) K. C. Shreiber and V. P. Fernandez, *J. Org. Chem.*, **26**, 2478 (1961).

(11) Melting points are corrected. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were obtained with a Beckman IR-10 spectrophotometer. Nmr spectra were recorded on a Varian Associates A-60 spectrometer, employing tetramethylsilane as an internal reference. The nmr spectrometer was purchased with a grant from the National Science Foundation (GP 1883).

(12) J. Jacques, *Bull. Soc. Chim. France*, 231 (1955).

(13) M. Janczewski and S. Egier, *Roczniki Chem.*, **37**, 647 (1963); *Chem. Abstr.*, **60**, 4072 (1964).

ml of carbon tetrachloride was added NBS (1.43 g, 0.008 mole). The mixture was refluxed for 10 hr and cooled. Precipitate **4** was removed by filtration and recrystallized from ethanol to afford 1.22 g (46%), mp 210–212°. Further recrystallization from benzene gave material of mp 212–213°; infrared indicated  $\nu_{\text{max}}^{\text{KBr}}$  1730 (C=O), 1300 (CH<sub>2</sub>), and 1130 (C—O) cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>) showed 2.97 (singlet) and 6.7–8.1 ppm (multiplet) in the ratio 1:1.5.

*Anal.* Calcd for C<sub>14</sub>H<sub>10</sub>BrNO<sub>2</sub>S: C, 50.00; H, 2.98. Found: C, 50.02; H, 2.87.

**Titration of 4.**—According to the method of Groebel<sup>4</sup> an iodometric titration was performed on **4**. The titrated equivalent weight was 342 (calcd 336). Bis(1-bromo-2-naphthyl) disulfide (**5**) was isolated after the titration, mp 160–161° (lit.<sup>13</sup> mp 160–161°).

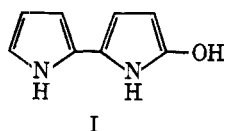
### On the Hydrogen Peroxide Oxidation Product of Pyrrole. Synthesis of 5-(2-Pyrrolyl)-2-pyrrolidone

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Received September 30, 1966

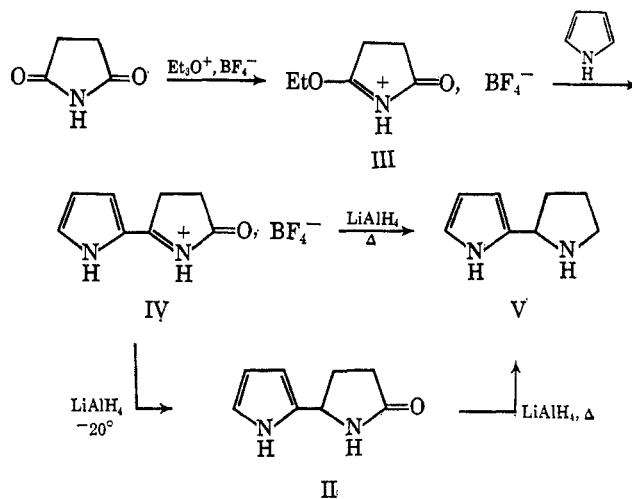
The oxidation of pyrrole by hydrogen peroxide in acetic acid produces a crystalline substance, C<sub>8</sub>H<sub>10</sub>N<sub>2</sub>O, mp 136°, which was first observed by Angeli<sup>1</sup> and later investigated by Pieroni.<sup>2</sup> This compound, one of the simplest oxidation products of pyrrole, has been of special interest as a possible intermediate in the formation of pyrrole blacks.<sup>2</sup> Pieroni's studies culminated in the assignment of I, 5-hydroxy-2,2'-bipyrrole, or a tautomer, to this so-called "oxybipyrrole."



Structure I was generally accepted until the very recent studies of Chierici and Gardini<sup>3</sup> who reinvestigated the oxidation product with the aid of infrared, ultraviolet, and nmr techniques. Based on their new spectroscopic evidence these authors concluded that II must, instead, be correct.

During studies on bipyroles related to prodigiosin<sup>4</sup> we have prepared 5-(2-pyrrolyl)-2-pyrrolidone (II) by an independent method outlined below. Our synthetic pyrrolidone is identical in every respect with the Angeli hydrogen peroxide-pyrrole oxidation product. This evidence thus confirms the structural assignment of Chierici and Gardini.

Treatment of succinimide with triethyloxonium fluoroborate<sup>5</sup> in methylene chloride for 12 hr at room temperature yielded the imino ester salt (III) which readily reacted with pyrrole to form an acidic, crystalline addition product (IV). The infrared spectrum of salt IV shows two strong bands in the double-bond



region at 1780 (carbonyl) and 1600 cm<sup>-1</sup> (protonated imino group). The molecular weight is in accord with the composition, C<sub>8</sub>H<sub>8</sub>ON<sub>2</sub>·HBF<sub>4</sub>.

Reaction of IV with lithium aluminum hydride at -20° resulted in partial reduction to the lactam II. The latter was found to be indistinguishable<sup>6</sup> (infrared, nmr, mixture melting point) from the hydrogen peroxide oxidation product of pyrrole, prepared according to the procedure reported by Chierici and Gardini.<sup>3</sup>

Reduction of salt IV at elevated temperatures, or further reduction of pyrrolylpyrrolidone II by lithium aluminum hydride yielded 2,2'-pyrrolylpyrrolidine (V), identical in all respects with the known product.<sup>7,8</sup>

#### Experimental Section<sup>9</sup>

**5-(2-Pyrrolyl)-2-pyrrolidone.**—Triethyloxonium fluoroborate (10.6 g) was prepared by the method of Meerwein<sup>9</sup> from 11.5 g of boron trifluoride etherate and 5.5 g of epichlorohydrin. The oxonium salt was dissolved in 30 ml of methylene chloride and 5.5 g (0.054 mole) of succinimide was added. Stirring of the reaction mixture was continued overnight and the solution was cooled with ice and then treated with 3.8 g of pyrrole (0.057 mole). The material which precipitated was removed by filtration after 10 min yielding 10.3 g (78%) of crystalline fluoroborate salt. A sample recrystallized three times from acetone-hexane melted at 192°, pK = 6.5. The infrared spectrum (KBr) showed peaks at 3275, 3125, 1780, 1600, and 1505 cm<sup>-1</sup>. The ultraviolet absorption spectrum had  $\lambda_{\text{max}}^{\text{EtOH}}$  335 m $\mu$ . *Anal.* Calcd: mol wt, 236. Found (titrimetric): mol wt, 232.

To a suspension of lithium aluminum hydride (1 g) in 25 ml of anhydrous ether, cooled in an ice-salt mixture, was gradually added 1 g of the above fluoroborate salt. The reaction mixture was stored for 2 hr at -20°. The excess hydride reagent was destroyed by addition of water in small portions, more ether (25 ml) was added, and after filtration, the solvent was gradually removed under vacuum. From the solution, 395 mg (62%) of lactam was obtained. After recrystallization three times from acetone-petroleum ether (bp 60–80°) the product melted at 138°. *Anal.* Calcd for C<sub>8</sub>H<sub>10</sub>N<sub>2</sub>O: C, 63.98; H, 6.71; N, 18.65. Found: C, 64.04; H, 6.83; N, 18.52. The infrared spectrum (CHCl<sub>3</sub>) showed peaks at 3475, 3430, 1690, and 1560 cm<sup>-1</sup>. This material was shown to be identical (nmr, infrared, mixture melting point) with the product obtained by the oxidation of

(6) We wish to thank Mr. Gordon Guthrie for repeating the hydrogen peroxide preparation of II<sup>3</sup> and for making the comparison of the two products.

(7) D. W. Fuhlhage and C. A. VanderWerf, *J. Am. Chem. Soc.*, **80**, 6249 (1958).

(8) J. H. Atkinson, R. Griggs, and A. W. Johnson, *J. Chem. Soc.*, 893 (1964).

(9) Melting points are uncorrected. Nmr spectra were determined with a Varian A-60 spectrometer. Infrared analyses were run on a Perkin-Elmer Model 421 spectrometer.

(1) A. Angeli and C. Lutri, *Gazz. Chim. Ital.*, **50**, 128 (1920).

(2) A. Pieroni and A. Moggio, *ibid.*, **53**, 126 (1923), and earlier papers.

(3) L. Chierici and G. P. Gardini, *Tetrahedron*, **22**, 53 (1966).

(4) H. H. Wasserman, J. E. McKeon, L. Smith, and P. Forgiione, *J. Am. Chem. Soc.*, **82**, 506 (1960).

(5) H. Meerwein, W. Florian, N. Schön, and G. Stopp, *Ann.*, **641**, 1 (1961).