

products were separated by vpc. 1-Phenyl-3,3-dimethylbutane: nmr (CDCl<sub>3</sub>) δ 0.94 (s, 9, *t*-Bu), 1.50 (m, 2, RCH<sub>2</sub>R), 2.55 (m, 2, ArCH<sub>2</sub>R), and 7.20 (s, 5, phenyl); ir (film) 1370, 1390 (*unsym* doublet, *t*-Bu), and 698, 733 cm<sup>-1</sup> (C<sub>6</sub>H<sub>5</sub>); mass spectrum (75 eV) *m/e* (relative intensity) 162 (14) (C<sub>12</sub>H<sub>18</sub><sup>+</sup>), 57 (100) (C<sub>4</sub>H<sub>9</sub><sup>+</sup>). 1-Phenyl-3,3-dimethylbutene: nmr (CDCl<sub>3</sub>) δ 0.94 (s, 9, *t*-Bu), 6.24 (s, 2, vinyl), and 7.25 (m, 5, phenyl); ir (film) 1375, 1390 (*unsym* doublet, *t*-Bu), 975 (*trans* -CH=CH-), and 747, 694 cm<sup>-1</sup> (-C<sub>6</sub>H<sub>5</sub>); mass spectrum (75 eV) *m/e* (relative intensity) 160 (27) (C<sub>12</sub>H<sub>16</sub><sup>+</sup>), 145 (100) (M<sup>+</sup> - 15), 91 (50) (C<sub>7</sub>H<sub>7</sub><sup>+</sup>), and 57 (7) (C<sub>4</sub>H<sub>9</sub><sup>+</sup>).

A repetition, using the products above in place of the β-bromostyrene, gave no change in the composition of the product, indicating that the olefin is not reduced by the organometallic.

**Reaction of Lithium Diphenylcopper with *trans*- and *cis*-β-Bromostyrenes.**—To a suspension of 5.2 g (0.027 mol) of cuprous iodide in 10 ml of ether at 0° was added 25 ml (0.055 mol) of commercial phenyllithium in 70:30 benzene-ether.<sup>5</sup> The solution was cooled to -78° and a solution of 1.0 g (0.0055 mol) of vpc-purified *trans*-β-bromostyrene in 10 ml of ether was added. The solution was stirred at -78° for 3 hr and then worked up in the usual way to give 1.0 g of a heavy oil containing large amounts of biphenyl and styrene (80% of the mixture). The stilbene fraction (20%) contained, by vpc analysis and isolation, using a 20% Apiezon L column, 16% *cis*-stilbene, mp 4-7° (lit.<sup>8</sup> mp 5-6°), and 84% *trans*-stilbene, mp 124-125 (lit.<sup>9</sup> mp 124°).

When the above reaction was repeated using vpc-purified *cis*-β-bromostyrene, the stilbene fraction contained 70% *cis*- and 30% *trans*-stilbene.

**Registry No.**—LiCuR<sub>2</sub>, R = *i*-C<sub>3</sub>H<sub>7</sub>, 24012-11-1; LiCuR<sub>2</sub>, R = *t*-C<sub>4</sub>H<sub>9</sub>, 23924-63-2; LiCuR<sub>2</sub>, R = Ph, 23402-69-9; *cis*-1, 588-73-8; *trans*-1, 588-72-7.

(8) D. S. Brackman and P. H. Plesch, *J. Chem. Soc.*, 2188 (1952).

(9) J. C. Irvine and J. Weir, *ibid.*, 91, 1384 (1907).

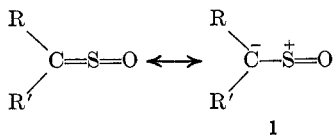
## Diphenylcyclopropenethione S-Oxide<sup>1</sup>

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The S-oxides of thiocarbonyl compounds have recently attracted considerable attention. Sulfines have been synthesized by Sheppard and Dieckmann,<sup>2</sup> and by Strating and coworkers<sup>3</sup> by dehydrochlorination of sulfinyl chlorides and the oxidation of thio ketones. *syn* and *anti* isomerism in sulfines has been detected by nmr spectroscopy.<sup>2,4</sup> Cycloaddition of enamines occurs across the C=S double bond of sulfines and the related sulfenes by nucleophilic attack at the sulfur,<sup>2,3c</sup> and Ulrich has pointed out that the products obtained are consistent with a bond polarization of the following type.<sup>5</sup>



(1) Supported by Grant-A-2305 from the National Research Council of Canada. This support is gratefully acknowledged.

(2) W. A. Sheppard and J. Dieckmann, *J. Amer. Chem. Soc.*, **86**, 1891 (1964).

(3) (a) B. Zwanenberg, L. Thijs, and J. Strating, *Tetrahedron Lett.*, 2871 (1968). (b) B. Zwanenberg, L. Thijs, and J. Strating, *ibid.*, 3453 (1967). (c) J. Strating, L. Thijs, and B. Zwanenberg, *ibid.*, 65 (1966); J. Strating, L. Thijs, and B. Zwanenberg, *Rec. Trav. Chim. Pays-Bas*, **83**, 631 (1964).

(4) S. Ghersetti, L. Lunazzi, G. Maccagnani, and A. Mangini, *Chem. Commun.*, 834 (1962).

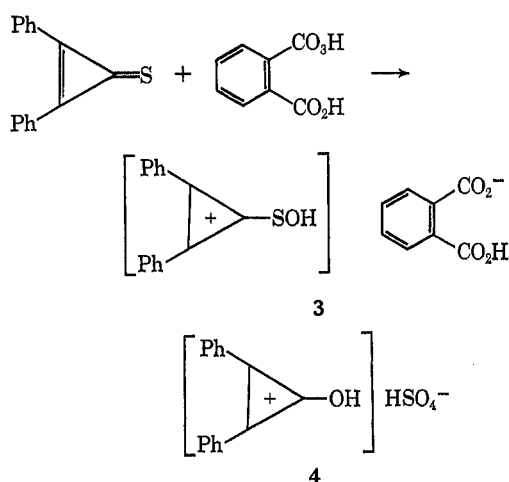
The range of known S-oxides has been extended to include those of thioamides 1 (R' = NR''),<sup>6</sup> thioacid chlorides 1 (R' = Cl),<sup>7</sup> dithiocarboxylic esters,<sup>3b</sup> and sulfinyl and sulfonyl sulfines.<sup>3a</sup>

Diphenylcyclopropenethione S-oxide was prepared in anticipation of chemical properties quite different from that of S-oxides prepared hitherto.

In the initial experiments direct oxidation of diphenylcyclopropenethione (2) with lead tetraacetate, following a procedure of Owen,<sup>8</sup> gave diphenylcyclopropenone, elemental sulfur, and lead acetate. Scheme I represents a possible mechanism for this conversion.

The products of the reaction demand attack by the oxidant at the thione carbon rather than at the sulfur. Similar results were obtained with *m*-chloroperbenzoic acid.

A successful route to the S-oxide involved reaction with monopero-phthalic acid at low temperature with very rapid work-up of the product. The initial product of the reaction proved to be the salt of the S-oxide with phthalic acid 3 obtained in nearly quantitative yield, analogous to the hydrosulfate of diphenylcyclopropenone (4).<sup>9</sup>



Compound 3 was completely insoluble in nonpolar solvents, but the orange solution in acetonitrile allowed determination of the absorption spectrum. This showed maxima at 225, 270, 295, and 310 mμ, consistent with the presence of a diphenylcyclopropene moiety,<sup>9</sup> while the visible absorption maxima at 333 and 438 mμ were tentatively assigned to the S-oxide absorption.<sup>3c</sup> A potassium bromide disk infrared spectrum showed bands at 1685 and 1695 (carboxylate carbonyl), 1842 (cyclopropene C=C stretch<sup>10</sup>), and 3420 cm<sup>-1</sup> (hydroxyl) consistent with the structure proposed for 3. The salt 3 was hygroscopic, and, while it was somewhat more stable than the free S-oxide 5, decomposed slowly at room temperature with the evolution of sulfur dioxide. Owing to the antiaro-

(5) H. Ulrich, "Cycloaddition Reactions of Heterocumulenes," Academic Press, New York, N. Y., 1967, p 188.

(6) W. Walter and K. D. Bode, *Justus Liebigs Ann. Chem.*, **681**, 64 (1965).

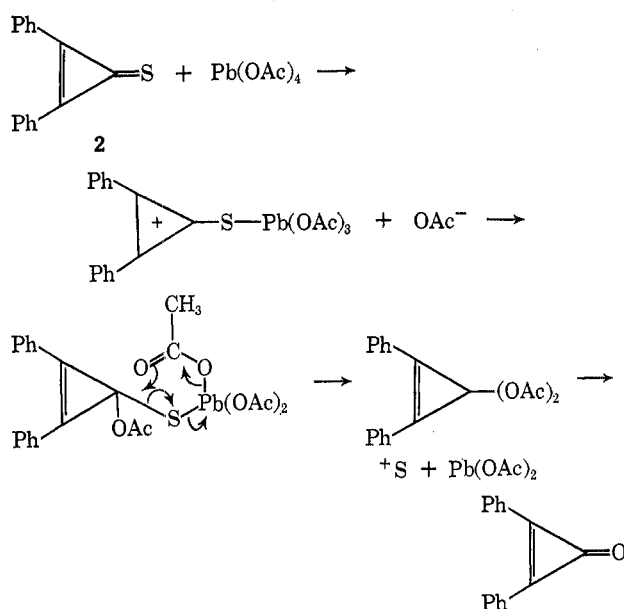
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(8) T. J. Adley, A. K. M. Anisuzzaman, and L. N. Owen, *J. Chem. Soc.*, **C**, 807 (1967).

(9) R. Breslow, T. Eicher, A. Krebs, R. A. Peterson, and J. Posner, *J. Amer. Chem. Soc.*, **87**, 1320 (1965).

(10) G. L. Closs, *Advan. Alicycl. Chem.*, **1** (1966).

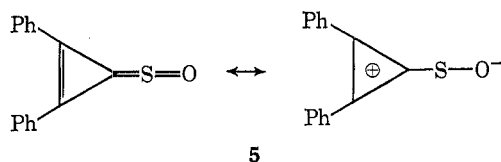
SCHEME I



matic nature of cyclopropenium anions,<sup>11</sup> the principal resonance contributor existing in the sulfines described above is precluded in 5.



Instead of this we suggest that diphenylcyclopropenethione S-oxide exists as a type of internal sulfenic acid salt.



The free S-oxide 5 could be generated by treatment of the salt with sodium bicarbonate solution and rapid extraction with chloroform. The S-oxide 5 was obtained as a very unstable, orange, crystalline solid, which decomposed violently in bulk when allowed to warm to room temperature, resulting in rapid polymerization accompanied by the evolution of hydrogen sulfide and sulfur dioxide. Fluorenylidene sulfine decomposes slowly at room temperature and rapidly at its melting point, evolving sulfur dioxide,<sup>2</sup> while isopropylidene sulfine polymerizes rapidly at ambient temperatures.<sup>2</sup> Solutions of the S-oxide 5 in methylene chloride or acetonitrile were sufficiently stable to allow determination of the absorption spectrum, which showed absorption maxima at 248 (sh), 270 (sh), 288, and 310  $\mu$  attributed to the cyclopropene moiety<sup>9</sup> and visible bands at 335 and 420  $\mu$  attributed to the S-oxide grouping.<sup>3a</sup>

Thermal decomposition of 5 in aqueous media gave some hydrogen sulfide and sulfur dioxide, diphenylacetylene (9.4%), and some as yet uncharacterized high molecular weight material. It may be noted that

(11) R. Breslow, *Chem. Eng. News*, **43**(26), 90 (1965).

diphenylcyclopropenone affords some diphenylacetylene at much higher temperatures<sup>9</sup> and that photolytic decomposition of a diphenylcyclopropenimine also gives some diphenylacetylene.<sup>12</sup>

Introduction of electron-releasing groups into the aryl rings of 5 should increase the stability of these S-oxides and allow more extensive examination of the chemical properties of these novel compounds. This aspect is currently under investigation.

#### Experimental Section<sup>13</sup>

**Diphenylcyclopropenethione (2).**<sup>14</sup>—To a solution of 2.06 g (1.01 mol) of diphenylcyclopropenone<sup>9</sup> in 10 ml of dry cyclohexane was added 2 ml of thionyl chloride and the resultant solution was heated on a steam bath for 15 min. The solvents and unreacted thionyl chloride were removed by distillation and the solid residue was redissolved in 12 ml of dry cyclohexane. To this solution was added dropwise a solution of 1.67 g (0.022 mol) of thioacetic acid in 4 ml of dry cyclohexane. The resulting yellow solid was recrystallized from 80 ml of cyclohexane as deep yellow plates: yield 1.1 g (50%); mp 122° (lit.<sup>12</sup> mp 118.5–119.6°); ir (CHCl<sub>3</sub>) 1350  $\text{cm}^{-1}$  (C=S); nmr (CDCl<sub>3</sub>)  $\delta$  7.36–8.7 (m, aromatic protons).

*Anal.* Calcd for C<sub>15</sub>H<sub>10</sub>S: C, 81.09; H, 4.50; S, 14.41; mol wt, 222.0503. Found: C, 81.05; H, 4.51; S, 14.39; mol wt, 222.0502 [mass spectrum (70 eV)].

**Oxidation of Diphenylcyclopropenethione in Attempts to Prepare the S-Oxide Derivative 1. A. Using Lead Tetraacetate.**—To a solution of 1.11 g (1.005 mol) of 2 in 25 ml of acetic acid was added over 12 min, with stirring, a solution of 4.5 g (1.01 mol) of lead tetraacetate in 190 ml of acetic acid. The solvent was removed by distillation under reduced pressure and the residue was shaken with 20 ml of water. Chloroform (20 ml) was added and the mixture was filtered to remove lead oxide and sulfur. The chloroform layer was dried (MgSO<sub>4</sub>) and evaporated to yield a red gum. The residual gum was dissolved in the minimum volume of hot cyclohexane, and when the solution was allowed to cool, yellow crystals were deposited, mp 115–119°. Crystallization of the product from cyclohexane gave diphenylcyclopropenone as a white, crystalline solid, mp 120°, identical with an authentic sample.<sup>9</sup>

**B. Using *m*-Chloroperbenzoic Acid.**—To a solution of 1.11 g (0.005 mol) of 2 in 20 ml of methylene chloride was added over 10 min, with stirring, a solution of 0.90 g (0.0052 mol) of *m*-chloroperbenzoic acid in 15 ml of methylene chloride. The mixture was stirred for 1.5 hr and then washed with a solution of 1.5 g of sodium hydrogen carbonate in 50 ml of water. The organic layer was dried (MgSO<sub>4</sub>) and the solvent was removed *in vacuo* to leave a red gum which was treated with 15 ml of hot cyclohexane. A small quantity of a yellow solid, mp 119°, separated from this solution and was identified as sulfur. The filtrate upon cooling deposited diphenylcyclopropenone (1.55 g, 53%) as a white solid, mp 115–117°, identified by comparison with an authentic sample.<sup>9</sup>

**C. Using Monoperphthalic Acid.**—A number of trial experiments were necessary using monoperphthalic acid before the optimum conditions were realized. The unsuccessful attempts were largely due to the thermal instability of diphenylcyclopropenethione S-oxide.

(12) N. Obata, A. Hamada, and T. Takizawa, *Tetrahedron Lett.*, 3917 (1969).

(13) Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Ir spectra were recorded on a Perkin-Elmer Model 421 spectrophotometer, and only the principal, sharply defined peaks are reported. Nmr spectra were recorded on Varian A-60 and A-100 analytical spectrometers. The spectra were measured on ca. 10–15% (w/v) solutions in CDCl<sub>3</sub>, with tetramethylsilane as a standard. Line positions are reported in parts per million from the reference. Absorption spectra were recorded in spectrograde solvents on a Beckman DB recording spectrophotometer. Mass spectra were determined on an Associated Electrical Industries MS-9 double-focussing, high-resolution spectrometer. The ionization energy, in general was 70 eV. Peak measurements were made by comparison with perfluorotributylamine at a resolving power of 15,000. Microanalyses were carried out by Dr. C. Daesslé, Organic Microanalysis Ltd., Montreal, Quebec, and by Mrs. D. Mahlow of this department.

(14) Diphenylcyclopropenethione has been reported previously by T. Eicher and G. Frenzel, *Z. Naturforsch.*, **20b**(3), 274 (1965), only in a preliminary communication and no experimental details were given.

A solution of 1.11 g (0.005 mol) of 2 in 50 ml of methylene chloride was cooled to  $-40^{\circ}$ . To this solution was added dropwise over 10 min, with stirring, a solution of 0.985 g (0.0054 mol) of the acid in 20 ml of ether, while the temperature was maintained below  $-30^{\circ}$ . Stirring was continued for 10 min, and after the addition had been completed, the yellow solid which had slowly separated during the addition was collected and identified as diphenylcyclopropenethione S-oxide hydrogen phthalate (3): yield 1.99 g (96%); mp  $95-98^{\circ}$ ; ir (KBr disk)  $1068\text{ cm}^{-1}$  (m, C=S=O<sup>2</sup>),  $1685$  (s),  $1695$  (s, C=O),  $1842$  (m) (cyclopropene C=C stretch<sup>10</sup>), and  $3420$  (br, OH);  $\lambda_{\text{max}}$  (CH<sub>2</sub>CN)  $225\text{ m}\mu$  (log  $\epsilon$  4.17),  $270$  (4.21),  $295$  (sh, 3.86),  $310$  (sh, 3.77),  $333$  (3.89), and  $478$  (3.37).

Anal. Calcd for C<sub>23</sub>H<sub>13</sub>SO<sub>5</sub> · 1/2H<sub>2</sub>O: C, 66.81; H, 4.14. Found: C, 66.71; H, 4.27.

The yellow salt was ground into fine particles and added in one portion to a stirred solution of 50 ml of 4% sodium hydrogen carbonate at a temperature of  $>5^{\circ}$ . A reaction ensued with the evolution of carbon dioxide, and 5 was deposited as a bright orange solid, yield 0.8 g (67.1%), mp  $40^{\circ}$  dec. The product was collected by filtration on a previously cooled apparatus, washed with ice water, and stored and dried in a vacuum desiccator containing pellets of sodium hydroxide.

Further purification was found not to be possible owing to the instability of the product. The microanalytical figures correspond to the inclusion of water in the crystals of this hygroscopic material: ir (CHCl<sub>3</sub>)  $1068$  and  $1129\text{ cm}^{-1}$  (C=S=O<sup>2</sup>); nmr (CDCl<sub>3</sub>)  $\delta$  7.0-8.3 (m, aromatic protons);  $\lambda_{\text{max}}$  (CH<sub>2</sub>Cl<sub>2</sub>)  $248$  (sh),  $270$  (sh),  $288$ ,  $310$ ,  $335$ , and  $430\text{ m}\mu$  (sh).

Anal. Calcd for C<sub>15</sub>H<sub>10</sub>SO: C, 75.60; H, 4.23; S, 13.43. Found: C, 73.16; H, 4.42; S, 12.28. Calcd: C:S, 5.63. Found: C:S, 5.96.

The S-oxide decomposed violently when the bulk material was allowed to reach room temperature and gave a polymer with the evolution of sulfur dioxide and hydrogen sulfide, which were detected by their action on acid dichromate paper and moist lead acetate paper, respectively.

**Controlled Decomposition of Diphenylcyclopropenethione S-Oxide (1).**—The S-oxide was freshly prepared exactly as described previously and decomposed by steam distillation. Hydrogen sulfide and sulfur dioxide were recognized as decomposition products by their characteristic odors and by positive reactions with lead acetate and potassium dichromate papers, respectively. When no more steam-volatile material distilled, the steam distillate (250 ml) was extracted with ether and the ether extract was dried (MgSO<sub>4</sub>). Evaporation of the solvent afforded an off-white solid, yield 0.083 g (9.4%), mp  $60^{\circ}$ , unambiguously identified as diphenylacetylene by comparison with an authentic sample (mixture melting point and superimposable infrared spectra). The residue consisted of as yet unidentified high molecular weight material.

**Registry No.**—1, 23516-87-2; 2, 2570-01-6; 3, 23516-89-4; 5, 12408-01-4.

### Correlation of the Reactivity of Thiophene Derivatives<sup>1</sup>

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We have undertaken an investigation of the solvolytic reactivity of a variety of heterocyclic systems. In a recent publication from these laboratories, we have shown<sup>3</sup> that the rates of solvolysis of a variety of

(1) Supported in part by grants from the National Science Foundation (GP-1572 and GP-6133X).

(2) National Institutes of Health Predoctoral Fellow, 1966-1968 (GM-32822).

(3) D. S. Noyce and G. V. Kaiser, *J. Org. Chem.*, **34**, 1008 (1969).

substituted furfuryl alcohol derivatives could be smoothly correlated with  $\sigma^+$  constants. An alternative approach is to examine the possibility that the heterocyclic ring system may be assigned an effective  $\sigma^+$  constant, for itself. Two additional recent studies have pursued this line of endeavor. Hill and Gross have studied the rates of solvolysis of a wide variety of heterocyclic analogs of benzyl acetate,<sup>4</sup> and Taylor has recently examined the pyrolysis of 1-aryl-2-phenylethyl acetates.<sup>5</sup>

It is the purpose of this note to present data on the rates of solvolysis of 1-(2-thienyl)ethyl *p*-nitrobenzoate and 1-(3-thienyl)ethyl *p*-nitrobenzoate and on the acid-catalyzed isomerization of *cis*-2-styrylthiophene, and to examine the correlation of these rates with other types of reactions. The relationship between benzyl systems and aromatic electrophilic substitution has been explored by several groups, including studies by Dewar,<sup>6</sup> Fierens,<sup>7</sup> and Streitwieser.<sup>8</sup> These authors have pointed out that the reactivities of benzyl systems and their analogs are useful probes for the ability of the aromatic moiety to stabilize a positive charge. Further, very good correlations are observed with  $\sigma^+$  substituent constants with a wide variety of reactions.

Our new data are summarized in Tables I and II.

TABLE I  
RATE OF SOLVOLYSIS OF SUBSTITUTED  
ETHYL *p*-NITROBENZOATES IN 80% ETHANOL

Compound	Temp, °C	<i>k</i> , sec <sup>-1</sup>
1-(2-Thienyl)ethyl <i>p</i> -nitrobenzoate	25.00	$2.27 \pm 0.04 \times 10^{-6}$
1-(3-Thienyl)ethyl <i>p</i> -nitrobenzoate	45.00	$2.61 \pm 0.05 \times 10^{-5}$
1-( <i>p</i> -Anisyl)ethyl <i>p</i> -nitrobenzoate	75.00	$9.7 \pm 0.25 \times 10^{-6}$
1-( <i>p</i> -Anisyl)ethyl <i>p</i> -nitrobenzoate <sup>a</sup>	45.00	$2.30 \times 10^{-5}$
	75.00	$5.02 \times 10^{-4}$

<sup>a</sup> From ref 3.

TABLE II  
RATE OF ISOMERIZATION OF *cis*-1-ARYL-2-PHENYLETHENES  
IN AQUEOUS SULFURIC ACID

Compound	H <sub>2</sub> SO <sub>4</sub> , wt %	H <sub>0</sub>	<i>k</i> <sub>obsd</sub> , sec <sup>-1</sup>
<i>cis</i> -2-Styrylthiophene	51.6	-3.60	$4.0 \times 10^{-3}$
<i>cis</i> -4-Methoxystilbene <sup>a</sup>	51.6	-3.60	$4.6 \times 10^{-3}$

<sup>a</sup> Interpolated from D. S. Noyce, D. R. Hartter, and F. B. Miles, *J. Amer. Chem. Soc.*, **90**, 4633 (1968).

The solvolysis rate of 1-(2-thienyl)ethyl *p*-nitrobenzoate is very similar to that of 1-(*p*-anisyl)ethyl *p*-nitrobenzoate.<sup>3</sup> The reduced reactivity of 1-(3-thienyl)ethyl *p*-nitrobenzoate is reminiscent of the reduced reactivity of the 3 position in detritiation of thiophene studied by Melander and Olsson<sup>9</sup> and the protodesilylation of thiophene derivatives, studied by Eaborn and his coworkers.<sup>10</sup>

(4) E. A. Hill and M. L. Gross, Abstracts of papers, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, p O-170.

(5) R. Taylor, *J. Chem. Soc., B*, 1397 (1968).

(6) M. J. S. Dewar and R. J. Sampson, *ibid.*, 2946 (1957).

(7) M. Planchen, P. J. C. Fierens, and R. H. Martin, *Helv. Chim. Acta*, **42**, 517 (1959).

(8) Cf. A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, N. Y., 1961, p 370.

(9) K. Halvorson and L. Melander, *Ark. Kemi*, **8**, 29 (1956); B. Ortman and S. Olsson, *ibid.*, **15**, 275 (1960).

(10) C. Eaborn and J. A. Sperry, *J. Chem. Soc.*, 4921 (1961); F. B. Deans and C. Eaborn, *ibid.*, 2299 (1959).