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# Icosahedral Carboranes. XVII.[1,2] Carboranyl Sulfoxides and Sulfones

BY ROBERT N. SCOTT, HAYWOOD HOOKS, JR., AND JOHN F. SIECKHAUS*

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Although a considerable number of divalent sulfur derivatives of the dicarba-*closo*-dodecaboranes have been reported by workers in our laboratory,[3,4] examples of sulfonyl and sulfinyl carboranes are few in number and consist almost entirely of sulfonyl halides[4] and sulfinic or sulfonic acids.[5] We now wish to report the synthesis and characterization of a series of monomeric carboranyl sulfoxides and sulfones.

$$\begin{tikzcd} m\text{-}B_{10}H_{10}C_2(SO_2Cl)_2 + 2AlCl_3 \arrow[r, "\substack{\text{in reflux}\\ ArH}"] & m\text{-}B_{10}H_{10}C_2(SO_2Cl\cdot AlCl_3)_2 \arrow[d, "\times" marking, "ArH"'] \arrow[dr, "H_2O,\ H^+"] & \\ & m\text{-}B_{10}H_{10}C_2(SO_2Ar)_2 & m\text{-}B_{10}H_{10}C_2(SO_3H)_2 \end{tikzcd} \qquad (1)$$

## Results and Discussion

The two most common synthetic procedures for diaryl and aryl alkyl sulfones involve (1) Friedel–Crafts catalyzed condensations between sulfonyl halides and suitable aromatic species and (2) oxidation of the corresponding thioethers.

A number of attempts were made to carry out Lewis acid catalyzed condensations between 1,7-bis(chlorosulfonyl)-*m*-carborane[4] and various aromatic derivatives, but the only carborane-containing product obtained was the previously unreported bis(sulfonic acid) (eq 1). Consequently, the oxidation route was adopted.

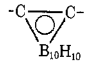
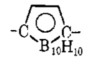
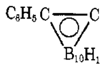
The thioethers I–V (Table I) were prepared *via* metathetical cleavage of phenyl and carboranyl disulfides (eq 2) according to the method of Smith, *et al.*[3]

$$RLi_2 + nR'SSR' \longrightarrow R(SR')_n + nR'SLi \qquad (2)$$

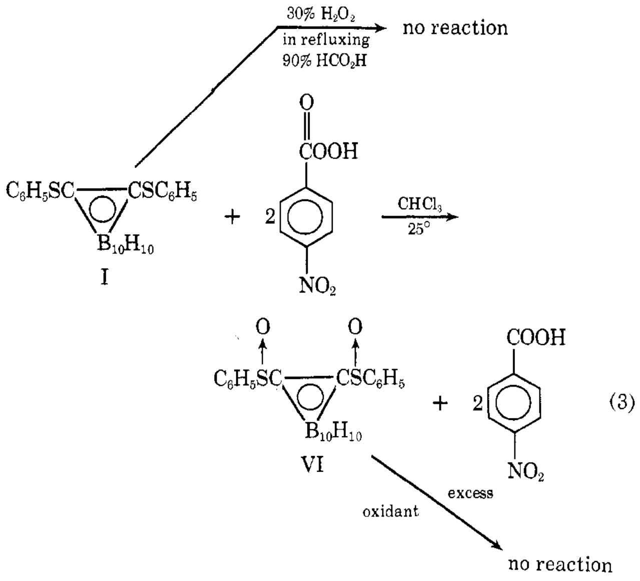
Two sets of conditions were employed in the oxidation studies: (1) 30% hydrogen peroxide in refluxing 90% formic acid and (2) *p*-nitroperbenzoic acid in chloroform at ambient temperature.

Structural variations among the sulfides were found to have significant effects on both reactivity and the nature of the reaction products.

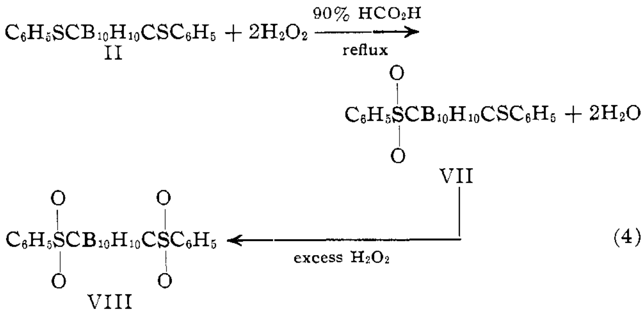
TABLE I

| No. | –R– | R′– | *n* |
|---|---|---|---|
| I |  | $C_6H_5$– | 2 |
| II | $-CB_{10}H_{10}C-$ | $C_6H_5$– | 2 |
| III |  | $C_6H_5$– | 2 |
| IV | $-CB_{10}H_{10}C-$ | $C_6H_5CB_{10}H_{10}C-$ | 2 |
| V | $-CB_{10}H_{10}C-$ |  | 1 |

Thus, the bis(phenyl thioether) of *o*-carborane (I) was found to be completely unreactive toward hydrogen peroxide in formic acid, while treatment of I with excess *p*-nitroperbenzoic acid yielded the bis sulfoxide VI (eq 3).



The corresponding *m*- and *p*-carborane derivatives II and III, on the other hand, were readily oxidized to the bis sulfones VIII and X when treated with an excess of either oxidant. Attempts to prepare bis sulfoxides analogous to VI using stoichiometric quantities of hydrogen peroxide or the peracid yielded only the monosulfones VII and IX.



$$\underset{\text{II}}{C_6H_5SCB_{10}H_{10}CSC_6H_5} + 2H_2O_2 \xrightarrow[\text{reflux}]{90\%\ HCO_2H} \underset{\text{VII}}{C_6H_5\overset{O}{\underset{O}{S}}CB_{10}H_{10}CSC_6H_5} + 2H_2O$$

$$\xrightarrow{\text{excess } H_2O_2} \underset{\text{VIII}}{C_6H_5\overset{O}{\underset{O}{S}}CB_{10}H_{10}C\overset{O}{\underset{O}{S}}C_6H_5} \qquad (4)$$

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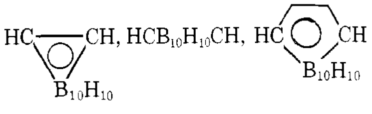
[1] Preceding communication: K. O. Knollmueller, R. N. Scott, H. Kwasnik and J. F. Sieckhaus, *J. Polym. Sci., A-1*, **9**, 1071 (1971).

[2] Nomenclature of the closo boron–carbon hydrides was discussed by R. Adams, *Inorg. Chem.*, **2**, 1087 (1963), and appropriate rules approved by the Council of the American Chemical Society were presented in *ibid.*, **7**, 1945 (1968). The terms *o*-, *m*-, and *p*-carborane are used to designate 1,2-, 1,7-, and 1,12-dicarba-*closo*-dodecaborane. In accord with current practice, the following symbols are employed for representation of these isomers in formulas, tables, etc.



[3] H. D. Smith, Jr., C. O. Obenland, and S. Papetti, *Inorg. Chem.*, **5**, 1013 (1966).

[4] N. S. Semenuk, S. Papetti, and H. Schroeder, *ibid.*, **8**, 2441 (1969).

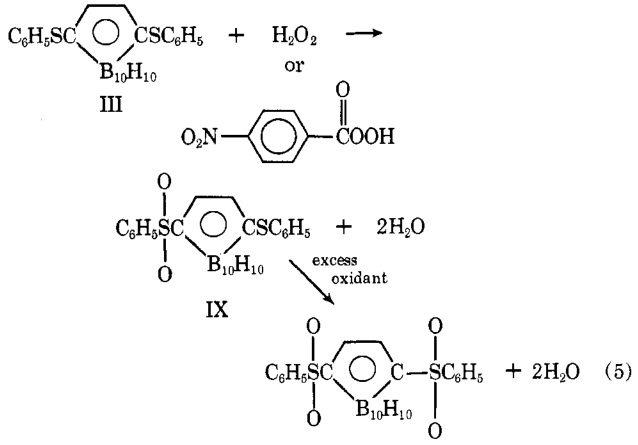
[5] L. I. Zakharkin and G. G. Zhigareva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **3**, 611 (1969).

TABLE II

PROPERTIES AND ANALYTICAL DATA OF CARBORANE-SULFUR DERIVATIVES

| Compd | Mp, °C | Reaction type[a] | Yield, % | % C Calcd | % C Found | % H Calcd | % H Found | % B Calcd | % B Found | % S Calcd | % S Found | Mol wt Calcd | Mol wt Found[b] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| I | 189–190 | A | 90 | 46.70 | 46.57 | 5.55 | 5.49 | 30.01 | 30.07 | 17.80 | 17.76 | 360 | |
| II | 99–100 | A | 41 | 46.70 | 46.38 | 5.55 | 5.56 | 30.01 | 30.00 | 17.80 | 17.90 | 360 | 350 |
| III | 157–158 | A | 27 | 46.70 | 47.37 | 5.55 | 5.81 | 30.01 | 29.71 | 17.80 | 17.79 | 360 | 345 |
| IV | 139–140 | A | 25 | 33.50 | 33.39 | 6.25 | 6.26 | 50.30 | 50.47 | | | 648 | 616 |
| V | 134–135 | A | 23 | 30.44 | 30.68 | 6.64 | 6.91 | 54.79 | 54.66 | 8.13 | 8.08 | 395 | 407 |
| VI | 172–173 | C | 64 | 42.84 | 42.94 | 5.14 | 5.27 | 27.54 | 26.78 | 16.11 | 16.11 | 392 | 387 |
| VII | 129–130 | B | | 42.84 | 42.34 | 5.14 | 5.05 | 27.54 | 27.11 | 16.11 | 15.32 | 392 | 397 |
| VIII | 193–194 | B | 88 | 39.70 | 40.68 | 4.73 | 4.73 | 25.50 | 25.00 | 15.10 | 15.17 | 424 | 433 |
| IX | 259–260 | B, C | 98 | 42.84 | 43.03 | 5.14 | 5.36 | 27.54 | 26.48 | 16.11 | 15.97 | 392 | 414 |
| X | 337–338 | B, C | 71 | 39.70 | 40.21 | 4.73 | 5.02 | 25.50 | 25.31 | 15.10 | 14.79 | 424 | 389 |
| XI | 115–116 | C | 67 | 31.94 | 31.89 | 5.95 | 6.00 | 47.91 | 47.87 | 9.47 | 9.57 | 680 | |
| XII | 172–173 | C | 58 | 29.25 | 30.01 | 6.38 | 6.70 | 52.65 | 52.79 | 7.82 | 7.55 | 411 | |

[a] A, metathetical cleavage; B, hydrogen peroxide oxidation; C, *p*-nitroperbenzoic acid oxidation. [b] By vapor pressure osmometry.

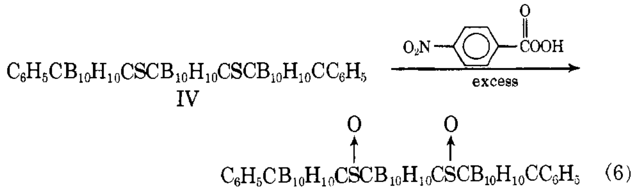


III

IX

X (5)

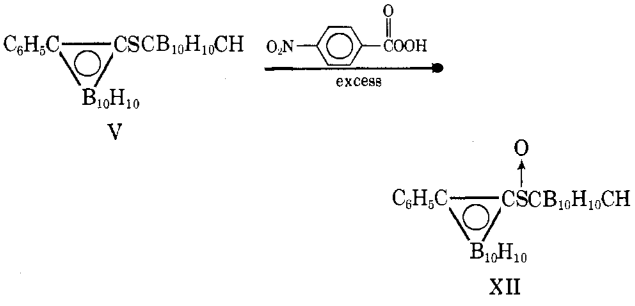
The reaction of the completely carborane substituted sulfides IV and V with excess *p*-nitroperbenzoic acid yielded the sulfoxides XI and XII.



$$\mathrm{C_6H_5CB_{10}H_{10}CSCB_{10}H_{10}CSCB_{10}H_{10}CC_6H_5} \xrightarrow[\text{excess}]{\mathrm{O_2N{-}C_6H_4{-}COOH}} \mathrm{C_6H_5CB_{10}H_{10}C\overset{O}{\overset{\uparrow}{S}}CB_{10}H_{10}C\overset{O}{\overset{\uparrow}{S}}CB_{10}H_{10}CC_6H_5} \quad (6)$$

IV

XI



V

XII

The structures proposed for the various oxidized species are consistent with the results of elemental, molecular weight, and infrared analyses (Tables II and III).

The fact that oxidations of the thioethers I and V stopped at the sulfoxide state, whereas the *m*- and *p*-carboranyl phenyl thioethers were converted totally to the corresponding bis sulfones, is probably due to a combination of steric and inductive effects.

Gasperini, Modena, and Todesco[6] have shown that ortho substituents exert a steric retardation on the rates of each of the steps in oxidation of substituted phenyl alkyl sulfides to the corresponding sulfones and that a single substituent has a greater effect upon the second (sulfoxide–sulfone) step than upon the first.

TABLE III

CHARACTERISTIC INFRARED ABSORPTION BANDS FOR CARBORANYL SULFOXIDES AND SULFONES[a,b]

| Compd | ν, cm⁻¹ | | |
|---|---|---|---|
| VI | . . . | . . . | 1099 |
| VII | 1333 | 1163 | . . . |
| VIII | 1333 | 1163 | . . . |
| IX | 1333 | 1163 | . . . |
| X | 1333 | 1163 | . . . |
| XI | . . . | . . . | 1124 |
| XII | . . . | . . . | 1114 |

[a] Only bands due to S-O vibrations are shown. [b] Spectra obtained using Nujol mulls on a Perkin-Elmer NIR 137-G Infracord.

Modena and coworkers have reported that in acid media both the oxidation of sulfides to sulfoxides[7] and the subsequent oxidation of the latter to sulfones[8] are facilitated by electron donors bonded to sulfur and retarded by electron acceptors. Studies by Hawthorne, Zakharkin, and their coworkers[9-11] have shown that the order of inductive electron withdrawal for the three isomers of carborane is ortho ≫ meta > para.

Thus, oxidations of compounds such as I and V which contain the *o*-carborane moiety are probably subject to both steric hindrance and a deactivating inductive effect.

Oxidation of compound IV which contains only *m*-carborane nuclei should not be subject to steric effects. Thus, the termination of this reaction at the bis sulfoxide stage is probably due simply to the cumulative inductive effect of two *m*-carborane nuclei bonded directly to sulfur.

## Experimental Section

All syntheses involving organolithium reagents and/or compounds bearing hydrolyzable chloro groups were performed in a nitrogen atmosphere under anhydrous conditions.

**Reagents.**—Unless specified otherwise, reagents were used as received from various commercial sources.

***p*-Nitroperbenzoic Acid.**—The peracid was prepared from *p*-nitrobenzoyl chloride as described by Vogel.[12]

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(6) G. M. Gasperini, G. Modena, and P. E. Todesco, *Gazz. Chim. Ital.*, **90**, 12 (1960).

(7) G. Modena and L. Maioli, *ibid.*, **87**, 1306 (1957).

(8) A. Cerniani and G. Modena, *ibid.*, **89**, 843 (1959).

(9) M. F. Hawthorne, T. E. Berry, and P. A. Wegner, *J. Amer. Chem. Soc.*, **87**, 4746 (1965).

(10) L. I. Zakharkin and V. N. Kalinin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1423 (1968).

(11) L. I. Zakharkin, V. N. Kalinin, and L. S. Podvisotskaya, *ibid.*, 2661 (1968).

(12) A. I. Vogel, "A Textbook of Practical Organic Chemistry," 3rd ed, Longmans, Green and Co., London, 1956, p 808.

***m*-Carborane-1,7-bis(sulfonic acid).**—A 250-ml, three-neck flask equipped with mechanical stirrer, reflux condenser, and nitrogen inlet was charged with 13.3 g (0.039 mol) of 1,7-bis(chlorosulfonyl)-*m*-carborane, 125 ml of dry benzene, and 10.7 g (0.080 mol) of aluminum chloride. The reaction mixture was heated to reflux for 3 hr and then cooled to 0° and hydrolyzed with dilute hydrochloric acid. The resulting precipitate was recrystallized from dilute hydrochloric acid to yield 13 g of the bis(sulfonic acid). *Anal.* Calcd for $B_{10}C_2H_{12}S_2O_6$: C, 7.86; H, 4.23; B, 35.5; S, 21.0; equiv wt 152; mol wt 304. Found: C, 8.28; H, 4.25; B, 36.36; S, 20.97; equiv wt 142; mol wt (osmometry) 306.

**Bis(1-phenyl-*o*-carboran-2-yl) Disulfide.**—Dropwise addition of 55 g of 1-phenyl-2-mercapto-*o*-carborane in 100 ml of diethyl ether to a solution of 62.5 g of 1-phenyl-2-chlorosulfenyl-*o*-carborane in 150 ml of diethyl ether maintained at 0.5° resulted in HCl evolution accompanied by the formation of an insoluble product. Recrystallization from hexane yielded 67 g (60.4%) of the topic compound, mp 219–220°. *Anal.* Calcd for $C_{16}H_{32}B_{20}S_2$: C, 38.2; H, 6.35; B, 43.0; S, 12.6; mol wt 504. Found: C, 38.17; H, 6.60; B, 42.19; S, 12.81, mol wt (osmometry) 491.

**Bis(1-phenyl-*m*-carboran-7-yl) Disulfide.**—Using the procedure described above for the ortho disulfide the reaction of 11.4 g of 1-phenyl-7-chlorosulfenyl-*m*-carborane with 10.0 g of 1-phenyl-7-mercapto-*m*-carborane yielded, after recrystallization from hexane, 13 g (65%) of the desired meta derivative, mp 99–100°. *Anal.* Calcd for $C_{16}H_{32}B_{20}S_2$: C, 38.2; H, 6.35; B, 43.0; S, 12.6; mol wt 504. Found: C, 38.18; H, 6.08; B, 41.73; S, 12.53, mol wt (osmometry) 492.

***o*-Carborane-1,2-bis(phenyl thioether) (I).**—Preparation was in accordance with that described by Smith, *et al.*[8] The corresponding *m*- and *p*-carboranebis(phenyl thioethers), II and III, respectively, were prepared *via* slight modifications of the above procedure.

***m*-Carborane-1,7-bis(1-phenyl-*m*-carboran-7-yl thioether) (IV).**—Dropwise addition of 2.91 × $10^{-2}$ mol of dilithio-*m*-carborane in 25 ml of anhydrous ether to a solution of 15 g (2.98 × $10^{-2}$ mol) of bis(1-phenyl-*m*-carboran-7-yl) disulfide yielded a clear solution with no detectable evolution of heat. Prolonged boiling of the reaction mixture (16 hr), followed by 24 hr of stirring at ambient temperature and acid hydrolysis, yielded 4.5 g (24.8%) of an insoluble white solid which was recrystallized from toluene.

***m*-Carborane-1-(1-phenyl-*o*-carboran-2-yl thioether) (V).**—The reaction of 0.14 mol of dilithio-*m*-carborane with 0.14 mol of bis(1-phenyl-*o*-carboran-2-yl) disulfide according to the procedure described for IV yielded 12.5 g of V which was recrystallized from hexane.

**Oxidation Reactions.**—The various carborane thioethers were oxidized by two general methods illustrated below by specific examples.

(I) **Oxidation by Hydrogen Peroxide in Formic Acid. *m*-Carborane-1,7-bis(sulfonylbenzene) (VII).**—A 1000-ml flask was charged with 5 g of II and 450 ml of 97% formic acid and the resulting dispersion was stirred rapidly at 70° with dropwise addition of 30% hydrogen peroxide. After addition of the stoichiometric quantity (6.3 g) of peroxide, a clear solution was obtained. After 30 min an additional 6.3 g of oxidant was slowly added. The resulting precipitate was filtered, washed, and recrystallized from hot toluene to yield 5.2 g of VII.

(II) **Oxidation by *p*-Nitroperbenzoic Acid. *o*-Carborane-1,2-bis(sulfinylbenzene) (VI).**—A 500-ml, three-neck flask equipped with a mechanical stirrer was charged with a solution of 13.76 g (7.53 × $10^{-2}$ mol) of *p*-nitroperbenzoic acid in 200 ml of chloroform. Then 3.6 g ($10^{-2}$ mol) of I dissolved in 50 ml of chloroform was added dropwise at ambient temperature. After the mixture had been stirred overnight, a negative test with aqueous iodide indicated that no excess peracid was present. The reaction mixture was extracted with a saturated aqueous solution of sodium bicarbonate, and the organic phase was dried over anhydrous sodium sulfate. The solvent was removed at reduced pressure to yield 2.5 g of crude product which was recrystallized from hexane.

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CONTRIBUTION FROM THE PHYSICAL CHEMISTRY DEPARTMENT,
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# A Nuclear Magnetic Resonance Study of the Ligand-Exchange Kinetics of Nickel(II) with *N*,*N*-Dimethylformamide in Mixed Solvents

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Ligand-exchange kinetics of octahedral paramagnetic transition metal complexes are usually studied in a pure solution of the ligand by nmr.[2] Recently we have reported that the ligand-exchange parameters for Co- and $Ni(DMSO)_6^{2+}$ (DMSO = dimethyl sulfoxide) in mixed solvents were independent of the composition of the solvent.[3] These results strongly support a D mechanism, which has recently been further supported by anation kinetic results.[4] To ascertain if this conclusion is applicable to other complexes of this type we wish to report data for $Ni(DMF)_6^{2+}$ (DMF = *N*,*N*-dimethylformamide) in DMF–nitromethane mixed solvents.

DMF was purified and $Ni(DMF)_6(ClO_4)_2$ prepared[5] as previously described. The mole per cent of water in the purified DMF was found to be 0.12% by integrating the residual water peak *vs.* one of the $^{13}C$ satellites of the methyl group of DMF. The nitromethane-$d_3$ utilized was identical with that previously described.[3] All data were obtained on a Varian A-60 spectrometer.

The temperature dependence of the observed transverse relaxation rate, $1/T_{2p}$, corrected for the ligand relaxation rate in the absence of the metal complex, can be analyzed using the results of Swift and Connick.[6] The limiting equation applicable in this study is $1/T_{2p} = P_M/\tau_M$, where $P_M$ is the probability that a DMF molecule is in the primary coordination sphere of the metal ion, and $1/\tau_M = k$, the ligand exchange rate. Transition state theory is used to obtain $\Delta H^*$ and $\Delta S^*$, the activation enthalpy and entropy, respectively.

A plot of $(P_M T_{2p})^{-1}$ *vs.* reciprocal temperature for $Ni(DMF)_6^{2+}$ in DMF and DMF–nitromethane mixed solvents is given in Figure 1. The compositions of the solutions utilized are also given in Figure 1. The high-temperature data, $3.90 \times 10^{-3} > T^{-1} > 3.35 \times 10^{-3}$, correspond to a large positive activation energy. In this temperature region $(P_M T_{2p})^{-1}$ is controlled by the solvent-exchange rate. At low temperatures, $T^{-1} > 4.20 \times 10^{-3}$, ligand exchange is slow and the observed relaxation time is due to second-sphere relaxation effects which will be subsequently discussed. The data in Figure 2, which have been corrected for second-sphere relaxation effects *via* extrapolation of the low-temperature data, were utilized to obtain the kinetic parameters. The data in pure DMF are almost identical with those of the mixed solvent. A least-squares treatment of the data in Figure 2 gives the following results: $\Delta H^*$ =

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[1] Present address: Rohm and Haas Co., Philadelphia Pa. 19137.

[2] T. R. Stengle and C. H. Langford, *Coord. Chem. Rev.*, **2**, 349 (1967).

[3] L. S. Frankel, *Inorg. Chem.*, **10**, 814 (1971).

[4] C. H. Langford and H. G. Tsiang, *ibid.*, **9**, 2346 (1970).

[5] R. S. Drago, D. W. Meek, M. D. Joesten, and L. LaRoche, *ibid.*, **2**, 124 (1963).

[6] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962).