hedron of sulfur atoms has been emphasized, and the ligands are indicated schematically.

The most striking feature of this structure, when the Cu_8DTS_6 cluster is compared to the $Cu_8(i\text{-MNT})_6$ and Cu_8DED_6 clusters, is that while the ligand geometry and steric requirements have changed drastically, the average copper–copper distance has not changed significantly. Table II shows pertinent molecular parameters for the

Table II. Selected Molecular Parameters of the Cu_8S_{12} Core of Cu_8DTS_6, $Cu_8(i\text{-MNT})_6$, and Cu_8DED_6 (Distances in Å, angles in degrees)

Parameter		Cu_8DTS_6	$Cu_8(i\text{-MNT})_6{}^a$	$Cu_8DED_6{}^b$
Cu–Cu	(min)	2.787 (2)^c	2.782 (3)	2.759 (6)
	(max)	2.906 (2)	2.870 (3)	2.822 (6)
	(av)	2.844 (20)	2.829 (14)	2.790 (11)
Cu–S	(min)	2.229 (4)	2.239 (4)	2.242 (10)
	(max)	2.268 (3)	2.261 (4)	2.272 (10)
	(av)	2.247 (3)	2.250 (4)	2.258 (10)
S–S (bite)	(av)	3.920 (10)	3.080 (5)	3.043 (12)
S–S (other)	(min)	3.713 (5)	3.820 (5)	3.82 (1)
	(max)	3.866 (5)	3.917 (5)	3.94 (1)
	(av)	3.814 (12)	3.870 (7)	3.88 (1)
Cu–Cu–Cu	(min)	88.7 (1)	87.4 (1)	88.1 (2)
	(max)	91.2 (1)	92.2 (1)	91.6 (2)
	(av)	90.0 (2)	90.0 (5)	90.0 (4)
S–Cu–S	(min)	111.4 (2)	116.7 (2)	116.1 (5)
	(max)	118.7 (2)	120.5 (2)	122.4 (5)
	(av)	116.2 (6)	118.6 (4)	118.4 (5)
Cu–S–Cu	(min)	76.5 (1)	76.4^d	75.0 (3)
	(max)	80.9 (1)	79.4^d	77.5 (3)
	(av)	78.6 (8)	77.9 (5)	76.3 (4)
S_3 plane to cube center	1 2^e	2.90 2.90	2.72 2.69	2.72 2.71
	3 4	2.91 2.94	2.73 2.72	2.70 2.67
	(av)	[2.91 (1)]	[2.72 (1)]	[2.70 (1)]
Cu to cube center	1 2	2.45 2.46	2.47 2.39	2.42 2.43
	3 4	2.49 2.44	2.43 2.50	2.44 2.37
	(av)	[2.46 (1)]	[2.45 (2)]	[2.42 (2)]

^{a} Parameters taken from ref 4 after further refinement from those reported in ref 3. ^{b} Parameters from ref 10. ^{c} Estimated standard deviations of the least significant digit(s) as calculated by least squares appear after the (max) and (min) entries. The standard deviations of the averages were taken as the larger of the individual standard deviations or the standard deviation of the mean. ^{d} Esd's were not available for this parameter. ^{e} The numbering of the plane and Cu distances for a given column correspond. No correspondence is implied between columns.

Cu_8S_{12} cores of the three clusters thus far studied. Note that the $S \cdots S$ "bite" distance of the DTS ligand is 0.9 Å greater than it is for the 1,1-dithiolate ligands and that the nonbite edges of the S_{12} icosahedron in the Cu_8DTS_6 cluster have actually shortened by a small amount.

The fact that the copper cube has varied insignificantly compared to the change in the ligand geometry is even clearer if we look at the distances from the center of the cube to the planes of the sulfur atoms which coordinate to each copper (e.g., S1, S3, and S6 in Figure 2). In the Cu_8DTS_6 cluster these planes are 0.2 Å further from the center of the cube than they are for the other two clusters. The copper atoms of the Cu_8DTS_6 cluster, however, are an average of only 0.01 Å further from the center than they are in the $Cu_8(i\text{-MNT})_6$ cluster and only 0.04 Å further from the center than they are in the Cu_8DED_6 cluster. The fact that the copper atoms could move further away from the center of the cube without seriously changing any of the molecular parameters other than the copper–copper distance

suggests strongly that there is an attractive interaction (bonding) between the copper atoms of the cube.[15]

The fact that the molecular orbital calculation yields no net attractive force between the copper atoms probably reflects inadequacies inherent in the assumed model, such as the assumption of idealized O_h symmetry and the inclusion of only the basic Cu_8S_{12} core in the calculation.[11]

Acknowledgment. We are grateful to the National Science Foundation and the National Institutes of Health for financial support of this research.

(15) One referee suggested that the Cu–Cu distance might be dictated by the nonbonded $S \cdots S$ interligand contacts. We feel that this hypothesis cannot explain the slight but significant (5σ) shortening of the average $S \cdots S$ distance in Cu_8DTS_6 or the apparent constancy and stability of the cubic structure.

(16) Fellow of the Alfred P. Sloan Foundation and author to whom correspondence should be addressed.
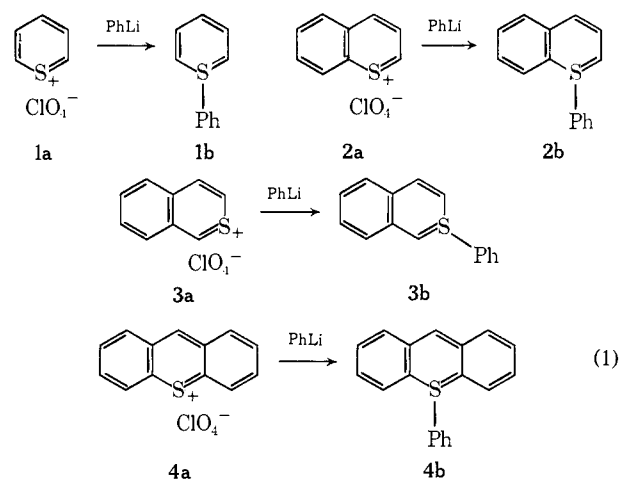
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Thiabenzenes. I. A Reinvestigation of "Stable Thiabenzenes"[1]

Sir:

The red-brown amorphous solids isolated from the reaction of phenyllithium with thiopyrylium salts, **1a–4a**, were assigned structures **1b–4b** (eq 1) on the basis of

their chemical and physical properties.[2,3] From a reinvestigation of these substances, we conclude that they are, in fact, oligomeric materials of undetermined structure, rather than the stable representatives of an interesting class of aromatic compounds, as previously claimed.[2,3]

Deprotonation of appropriately substituted sulfonium salts as a method for preparing thiabenzenes had been utilized by Price and Follweiler[4] in the synthesis of 1,2-diphenyl-2-thianaphthalene and by Hortmann and Harris in their synthesis of 1-methyl-3,5-diphenylthiabenzene (**5**).[5,6] However, it was recently noted by Hori,

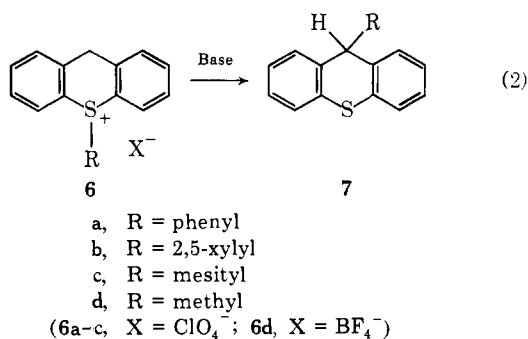(1) This work was supported by the National Science Foundation (GP-30257).

(2) M. Polk, M. Siskin, and C. C. Price, *J. Amer. Chem. Soc*, **91**, 1206 (1969).

(3) C. C. Price, M. Hori, T. Parasaran, and M. Polk, *J. Amer. Chem. Soc.*, **85**, 2278 (1963).

(4) C. C. Price and D. H. Follweiler, *J. Org. Chem.*, **34**, 3202 (1969).

(5) A. G. Hortmann and R. L. Harris, *J. Amer. Chem. Soc.*, **92**, 1803 (1970).

et al.,[7] that the deprotonation of 10-alkyl- or 10-aryl-thioxanthylium salts, **6**, does not yield 10-thiaanthracenes but affords instead the corresponding 9-alkyl- or 9-arylthioxanthenes, **7** (eq 2). Since 10-thiaanthracenes

$$\text{(structure)} \xrightarrow{\text{Base}} \text{(structure)} \quad (2)$$

6   **7**

a, R = phenyl
b, R = 2,5-xylyl
c, R = mesityl
d, R = methyl
(6a–c, X = ClO$_4^-$; 6d, X = BF$_4^-$)

had been reported to be stable species,[3] and since deprotonation of **6** might have been expected to generate a 10-thiaanthracene (*e.g.*, **6a** → **4b**),[4,5] this observation aroused our curiosity. Accordingly, we prepared[8] thioxanthylium salts, **6a–d**, and studied their deprotonation using dimsyl anion[9] (eq 2). In every case, production of the corresponding thioxanthenes, **7a–d**, was found, in agreement with the observations of Hori, *et al.*[7] Deprotonation of **6a** was expected to give **4b**, a purportedly stable species,[3] but no such substance was isolated. Further, all deprotonation reactions produced initial, intense colors[11] which could be maintained at low temperatures (<0°) and which were rapidly discharged on warming (*ca.* 25°). Indeed, the ¹H nmr spectrum at −45° of the orange reaction mixture obtained by the low temperature deprotonation[9] of **6d** in 80% toluene-d_8-20% dimethoxyethane revealed not only the resonances attributable to the methyl group of **7d** (δ 1.27 (d, $^3J_{HH}$ = 7 Hz)) but also resonances of another species at δ 6.01 (s, 1 H) and 1.05 (s, 3 H). As the reaction was allowed to warm to *ca.* 40°, the signals at δ 6.01 and 1.05 concurrently disappeared, leaving only rearrangement products.[12] This spectral evidence indicated that the highly colored species initially formed on deprotonation of **6a–d** were thiaanthracenes, which underwent rapid rearrangement to **7a–d**,[13] not unlike the rearrangements observed for 1,2,4,6-tetraphenylthiabenzene.[14a]

(6) The marked upfield chemical shift of the 2,6-protons (δ 4.03) in **5** was taken to indicate an ylide-like structure and brought into question in the alleged synthesis of **1b**[2] which reportedly featured only a single absorption (δ 7.2) for all the ring protons.

(7) M. Hori, T. Kataoka, Y. Asahi, and E. Mizuta, *Chem. Pharm. Bull.*, **21**, 1692 (1973); M. Hori, T. Kataoka, H. Shimizu, and C.-F. Hsü, *Chem. Lett.*, 391 (1973).

(8) K. K. Andersen, M. Cinquini, and N. E. Papanikolaou, *J. Org. Chem.*, **35**, 706 (1970).

(9) Reactions were carried out by treating 1.0 mol equiv of the salt in benzene-d_6 and/or toluene-d_8 with 1.0 mol equiv of dimsyl-d_5 sodium or lithium[10] under a dry nitrogen atmosphere. Techniques of deprotonation were checked by the successful repetition of previously reported deprotonation experiments.[4,5]

(10) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1345 (1965).

(11) A purple color was obtained when R = aryl and an orange color when R = methyl.

(12) Thioxanthene (**7**, R = H) was also found on the deprotonation of **6c** and **6d**.

(13) Deprotonation of a mixture of **6a** and the 2-chloro derivative of **6b** led exclusively to the formation of **7a** and the 2-chloro derivative of **7b**. The failure to detect any crossover products indicates that these rearrangements are substantially intramolecular and are best viewed as vinylogous Stevens rearrangements.

(14) (a) G. Suld and C. C. Price, *J. Amer. Chem. Soc.*, **83**, 1770 (1961); **84**, 2094 (1962). (b) G. Suld and C. C. Price, *J. Amer. Chem. Soc.*, **84**, 2090 (1962); (c) C. C. Price, J. Follweiler, H. Pirelahi, and M. Siskin, *J. Org. Chem.*, **36**, 791 (1971).

and related compounds.[14b,c] These observations were clearly inconsistent with the claim[3] that **4b** is a stable, red-brown amorphous solid.

Since our observations, and the earlier observations of Hortmann and Harris,[5,6] sharply contrasted with the claimed syntheses[2,3] of **1b** and **4b**, we attempted to repeat the reactions shown in eq 1. In each case, reaction of **1a–4a** with phenyllithium under a dry nitrogen atmosphere, followed by the described work-up,[2,3] did indeed give brown amorphous solids, whose uv, ir, and ¹H nmr spectra were consistent with published spectral characteristics.[2,3,15] However, the ¹H nmr spectra were uncharacteristic of simple monomeric species, exhibiting broad ($W_{1/2}$ = *ca.* 0.6 ppm), featureless, envelope absorptions in the aromatic region. The ¹³C nmr spectrum of the material obtained from the reaction of **4a** with phenyllithium also was uncharacteristic of a monomeric species and featured only a broad envelope absorption centered at *ca.* 126 ppm downfield from TMS. Elemental analyses of these solids were erratic, although analyses in agreement with those reported[3] could be obtained for some samples of material from the reactions of **3a** and **4a** with phenyllithium.[16] All samples of material obtained by reaction of phenyllithium with **1a–4a** were found to have molecular weights ranging from three to six times that expected for monomeric species.[16] Additional evidence, consistent with the oligomeric nature of these solids, was obtained from mass spectral analysis. Peaks with m/e values greater than the nominal molecular weights expected for **1b–4b** were observed in the fragmentation patterns of these substances.[18] High mass peaks were also observed by Price and coworkers in the mass spectra of materials which they characterized as **1b** and **4b**,[2,14c,15b] but these peaks were rationalized as arising from ion–molecule reactions.

While degradation of these oligomeric materials has yet to provide evidence on their structure, some in-

(15) (a) M. Polk, Ph.D. Thesis, University of Pennsylvania, 1964; (b) M. Siskin, Ph.D. Thesis, University of Pennsylvania, 1968.

(16) Typical analysis of the solid obtained from the reaction of **4a** with PhLi (mp 140–150° (begins softening at *ca.* 110°), lit.[3] mp 124–129°): Calcd for C$_{19}$H$_{14}$S: C, 83.17; H, 5.14; S, 11.69; mol wt, 274. Found: C, 83.07; H 5.08; S, 11.33; mol wt, 831 (osmometry in benzene). Typical analysis of the solid obtained from reaction of **3a** with PhLi (mp 120–130° (begins softening at *ca.* 105°), lit.[3] mp 121–125°): Calcd for C$_{15}$H$_{12}$S: C, 80.31; H, 5.39; S, 14.29; mol wt, 224. Found: C, 80.52; H 5.36; S, 13.65; mol wt, 919 (osmometry in benzene). Typical analysis of the solid obtained from the reaction of **2a** with PhLi (mp 130–145° (begins softening at *ca.* 120°), lit.[3] mp 106–111°): Calcd for C$_{15}$H$_{12}$S: C, 80.31; H, 5.39; S, 14.29; mol wt, 224. Found: C, 77.54; H, 4.95; S, 17.91; mol wt, 1,054 (osmometry in benzene).[17] Differential thermal analysis reveals that no phase transitions occur on heating these amorphous materials, and the data recorded above as "melting points" actually refer to the temperature range over which observable changes (shrinking, increasing fluidity) take place.

(17) All elemental analyses and molecular weight determination were performed by Schwarzkopf Microanalytical Laboratory, Inc., Woodside, N. Y.

(18) For example, the solid obtained by reaction of phenyllithium with **2a** gave the following mass spectrum (70 eV): m/e (rel intensity, %) 594 (3), 592 (3), 516 (3), 514 (3), 446 (7), 444 (10), 367 (20), 293 (12), 279 (10), 253 (10), 236 (12), 234 (12), 224 (55), 223 (85), 210 (20), 147 (100), 134 (29) (only peaks of rel intensity ≥20% are given for m/e values below 224). Literature[15b] mass spectrum for the material characterized as **2b**: m/e (rel intensity, %) 155 (15), 154 (100), 153 (33), 152 (22), 105 (12), 91 (16), 77 (26), 76 (29), 64 (12), 63 (11), 51 (19), 50 (11), 44 (58), 43 (17) (only peaks of rel intensity ≥10% are given). Mass spectrum of biphenyl:[19] m/e (rel intensity, %) 155 (13), 154 (100), 153 (26), 152 (21), 77 (10), 76 (17), 64 (7), 63 (7), 51 (10), 50 (6).

(19) E. Stenhagen, S. Abrahamsson, and F. W. McLafferty, "Atlas of Mass Spectral Data," Vol. 2, Interscience, New York, N. Y., 1969, p 928.

formation has been obtained which suggests a possible reason for their formation. Reaction of 1.0 mol equiv of p-tolyllithium[20] with 1.0 mol equiv of **3a** in C_6D_6–ether gave 33% toluene, 37% p-tolyl sulfide, 5% 1-p-tolyl-2-thiochromene,[21] and a red-brown nonvolatile material that featured a broad absorption in the aromatic region of its ¹H nmr spectrum (δ 7.5–6.5).[22,23] Production of toluene was further investigated by the reaction of 2-thianapthalenium-1,3,4-d_3 perchlorate (**8**)[24] with p-tolyllithium. In addition to the products previously noted, this reaction generated 31% toluene-d_1 (80% D).[21,26] Whether proton abstraction from **3a** occurs in an initial step[27] or whether **3b** is initially formed and proton abstraction ensues has not yet been determined. In any case, formation of both toluene and p-tolyl sulfide clearly indicates that the reaction of **3a** with aryllithium reagents results in extensive destruction of the sulfur ring system. It is not unreasonable to assume that the reactive species produced by proton abstraction and by formation of p-tolyl sulfide are responsible for the amorphous substances that are isolated.

It has been established that the stable red-brown amorphous materials which are isolated from the reactions of **1a–4a** with phenyllithium are not thiaarenes **1b–4b**. Actual properties of the class of compounds represented by **1b–4b** will be discussed in the following communication.[28]

Acknowledgment. We thank Professor Ronald H. Levin for the determination of the ¹³C nmr spectrum.

(20) M. Schlosser and V. Ladenberger, *J. Organometal. Chem.*, **8**, 193 (1967).

(21) Yields were determined by glpc and are based on p-tolyllithium. Products were identified by coinjection with authentic compounds and by glpc–mass spectral analysis.

(22) The residue was obtained by removal of all volatile material by bulb-to-bulb distillation (80°, 5 × 10⁻⁶ Torr), the progress of which was monitored by ¹H nmr.

(23) Analogous products were also found for the reactions of **1a** and **2a** with p-tolyllithium.

(24) Prepared by α-deuterium exchange of 2-thiochromanone³ with NaOD–D₂O, followed by reduction with LiAlD₄ to the alcohol and dehydration with potassium pyrosulfate to the olefin. Successive hydride abstractions with trityl perchlorate²⁵ followed by LiAlD₄ reductions gave **8** with >95% deuterium incorporation at the 1-, 3-, and 4-positions, as determined by the ¹H nmr spectrum of the olefin obtained by LiAlD₄ reduction of **8**.

(25) H. J. Dauben, Jr., L. R. Honnen, and K. M. Harmon, *J. Org. Chem.*, **25**, 1442 (1960).

(26) Control experiments ruled out deuterium abstraction from benzene-d_6.

(27) Proton abstraction by weak base is known to occur in N-substituted pyridinium salts. See J. A. Zoltewicz and L. S. Helmick, *J. Amer. Chem. Soc.*, **92**, 7547 (1970).

(28) J. Stackhouse, B. E. Maryanoff, G. H. Senkler, Jr., and K. Mislow, *J. Amer. Chem. Soc.*, **96**, 5650 (1974).

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## Thiabenzenes. II. Evidence for an Ylide Model[1]

Sir:

The preceding communication[2] presented evidence invalidating prior claims[3,4] for the syntheses of 1-

(1) This work was supported by the National Science Foundation (GP-30257).

(2) G. H. Senkler, Jr., J. Stackhouse, B. E. Maryanoff, and K. Mislow, *J. Amer. Chem. Soc.*, **96**, 5648 (1974).

phenylthiabenzene, 1-phenyl-1-thianaphthalene, 2-phenyl-2-thianaphthalene, and 10-phenyl-10-thiaanthracene. Although it had been alleged that these compounds should be much more stable than other, more highly substituted thiabenzenes,[3-6] the present work establishes the contrary: the more highly substituted thiabenzenes (*e.g.*, 1,2,4,6-tetraphenylthiabenzene (**1**),[7] 1-methyl-3,5-diphenylthiabenzene (**2**),[8] and 1,2-diphenyl-2-thianaphthalene (**4a**)[5]) are, in fact, the more stable species. We also report on some of the chemical and physical properties that are characteristic of this class of compounds.

The deprotonation of **3a** by Price and Follweiler[5] to generate **4a** suggested a convenient method for the study of substituted thiabenzenes. Sulfonium salts **3a–e**[5,9] were deprotonated (eq 1) with dimsyl-d_5 sodium or

$$\qquad\qquad (1)$$
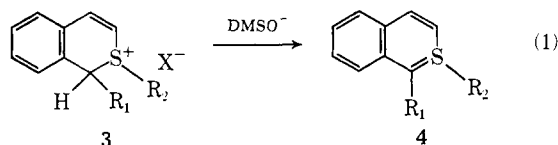
a, R_1 = phenyl; R_2 = phenyl
b, R_1 = phenyl; R_2 = methyl
c, R_1 = o-isopropylphenyl; R_2 = methyl
d, R_1 = pentafluorophenyl; R_2 = methyl
e, R_1 = H; R_2 = methyl
(**3a**, X = ClO_4^-; **3b–e**, X = BF_4^-)

lithium[12] in toluene-d_8 at $-25°$ under a dry nitrogen atmosphere. The reaction mixtures obtained from **3a–d** were intensely colored and gave the ¹H nmr spectra summarized in Table I. These spectral data are con-

Table I. 60-MHz ¹H Nmr Spectral Data for **4a–d**[a]

Compd	Aromatic H	Chemical shifts (δ) 3-H ($^3J_{HH}$, Hz)[b]	4-H[c]	S–CH₃
4a[d]	8.2–6.6 (m)	5.15 (d, 8)		
4b[e]	8.2–6.8 (m)	4.47 (d, 8)	6.72 (d)	0.92 (s)
4c[f]	7.4–6.9 (m)	4.53 (d, 8)	6.92 (d)	1.04 (s)
4d	7.3–6.7 (m)	4.76 (d, 8)	6.82 (d)	1.27 (s)

[a] Spectra run in benzene-d_6 at ambient probe temperature unless otherwise noted. [b] Assignment of the 3-H is based on the chemical shift observed for the 2,6-protons of **2** (δ 4.03, DMSO-d_6;[8] 3.91, benzene-d_6) and the assignment of the 3,5-protons of **1** (δ 7.72, benzene-d_6). [c] Assigned by irradiation of the 3-H. [d] A similar spectrum was observed for the purple solution obtained by reaction of 1-phenyl-2-thianaphthalenium perchlorate[5] with phenyllithium; it does not agree with the reported spectrum of **4a** (broad absorption at δ 7.8–6.6).[5] [e] Spectrum run at $-35°$ in toluene-d_8–benzene-d_6 (2:1). [f] Spectrum run at 5° in toluene-d_8–benzene-d_6 (2:1); isopropyl group: δ 1.09 (pr of d, J = 7 Hz, $\Delta\nu$ = 4.4 Hz), 3.25 (m).

(3) M. Polk, M. Siskin, and C. C. Price, *J. Amer. Chem. Soc.*, **91**, 1206 (1969).

(4) C. C. Price, M. Hori, T. Parasaran, and M. Polk, *J. Amer. Chem. Soc.*, **85**, 2278 (1963).

(5) C. C. Price and D. H. Follweiler, *J. Org. Chem.*, **34**, 3202 (1969); D. M. Follweiler, Ph.D. Thesis, University of Pennsylvania, 1968.

(6) C. C. Price, J. Follweiler, H. Pirelahi, and M. Siskin, *J. Org. Chem.*, **36**, 791 (1971).

(7) G. Suld and C. C. Price, *J. Amer. Chem. Soc.*, **83**, 1770 (1961); **84**, 2094 (1962).

(8) A. G. Hortmann and R. L. Harris, *J. Amer. Chem. Soc.*, **92**, 1803 (1970).

(9) **3b–e** were synthesized by reaction of the corresponding sulfide with CH_3I–$AgBF_4$.[10,11]

(10) T. E. Young and R. Lazarus, *J. Org. Chem.*, **33**, 3770 (1968).

(11) Satisfactory elemental analyses were obtained for all new compounds.

(12) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1345 (1965).