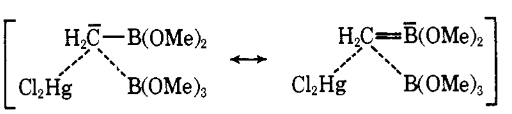

4 (unlikely)

with pK_a's (Table I), the $\Delta S^{\ddagger}$ values, a previous Hammett correlation of $ArCH_2B(OR)_2$ reaction rates,[4] failure of $HC[B(OMe)_2]_3$ and $C[B(OMe)_2]_4$ to show greatly enhanced reactivity over $CH_2[B(OMe)_2]_2$ as observed in carbanion reactions,[5,7] and failure of 10% water or 0.04 M sodium nitrate to accelerate measurably the reaction of $CH_2[B(OMe)_2]_2$. Nonpolar stabilization of loosened bonding by π delocalization ought to parallel radical stabilization, for which $B(OR)_2$ is less effective than phenyl.[8]

Previous observations which might be reinterpreted on the basis of transition states analogous to 3 include electrophilic cleavages of Me_3SiCH_2 from $(MeSiCH_2)_2SnR_2$[9] and the unusual mercuration of acetic acid, which appears to be facilitated by the carboxyl group without involving an enol.[10]

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(7) (a) D. S. Matteson and G. L. Larson, *J. Amer. Chem. Soc.*, **91**, 6541 (1969); (b) D. S. Matteson and J. R. Thomas, to be published.

(8) D. S. Matteson, *J. Amer. Chem. Soc.*, **82**, 4228 (1960).

(9) D. Seyferth, *ibid.*, **79**, 5881 (1957).

(10) W. Kitching and P. R. Wells, *Aust. J. Chem.*, **18**, 305 (1965).

(11) (a) We thank the National Science Foundation for support, Grant No. GP-9320; (b) Alfred P. Sloan Foundation Fellow, 1966–1968.

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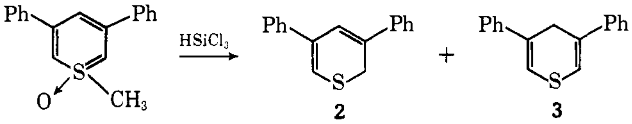
Thiabenzenes. II. Generation and Ylidic Properties of 1-Methyl-3,5-diphenylthiabenzene

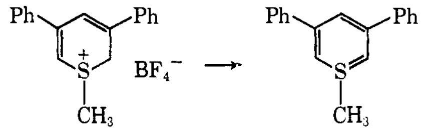
Sir:

Current interest in the type of bonding dominant in "tetravalent sulfur" heterocycles,[1] in thiabenzenes,[2-4] and in other thiacyclic systems[5] has led us to investigate the possibility of converting thiabenzene 1-oxides[4] into 1,3,5-trisubstituted thiabenzenes. We wish to describe such a synthesis of the title compound **5** *via* a novel reductive procedure, and to report some spectral and chemical properties of **5** which are consistent with an ylide-type bonding description for thiabenzenes.



1 2 3

Treatment of 1-methyl-3,5-diphenylthiabenzene 1-oxide (**1**)[4,6] with 1 mol equiv of trichlorosilane[7] in refluxing benzene (9 hr) afforded a 3:2 mixture of 2*H*- and 4*H*-3,5-diphenylthiopyrans, **2** and **3** (77% yield),[8] from which the 2*H* isomer **2** could be isolated by chromatography (Florisil) followed by recrystallization (EtOH): mp 104.6–106.1°; uv max (EtOH) 270 (ϵ 30,600) and 364 nm (ϵ 4900); nmr (CCl_4) δ 3.60 (t, 2, $J \sim 0.6$–0.9 Hz), 6.40 (q, 1, $J \sim 0.6$ Hz), 6.54 (q, 1, $J \sim 0.9$ Hz), and 7.2–7.8 (m, 10).[9] Reaction of **2** with methyl iodide–$AgBF_4$[10] gave 1-methyl-3,5-diphenyl-2*H*-thiinium tetrafluoroborate (**4**): mp 144.5–145.3° dec; uv max ($EtOH$–H_2O [2:1]) 244 (ϵ 32,300), 291 (ϵ 15,600), and 331 nm (ϵ 11,300); nmr (DMSO-d_6) δ 2.97 (s, 3), 4.78 (d, 2, $J \sim 1.0$ Hz), 6.78 (d, 1, $J \sim 0.7$ Hz), 7.28 (q, 1, $J \sim 0.9$ Hz), and 7.37–7.97 (m, 10).[9]



4 5

Treatment of **4** with base under a variety of conditions effected the generation of 1-methyl-3,5-diphenylthiabenzene (**5**). In a typical experiment, 1.24 M *t*-butyllithium (0.24 mmol) in pentane was added to a solution of 85 mg (0.24 mmol) of **4** in 0.30 ml of DMSO-d_6 under N_2 in a standard nmr tube and the two layers were mixed yielding an orange solution which showed nmr peaks attributable to **5** at δ 1.73 (s, *2.5*), 4.03 (d, 2, $J = 1.7$ Hz), 6.18 (t, 1, $J = 1.7$ Hz), and 7.21–7.82 (m, 10);[11] an increase in area at δ 2.50 corresponding to $\sim$1.7 protons as DMSO-d_x was also noted, indicating that, in addition to removal of one proton at C-2 in **4** by methylsulfinylcarbanion-d_5 (from DMSO-d_6 and *t*-butyllithium), additional base-catalyzed exchange of the S-methyl protons of **5** had occurred before complete mixing (and reaction) of **4** with the anion had taken place.[12] Addition of aqueous HBF_4 (0.24 mmol) to the solution of **5** after 1.0 hr at 35° (during which time little decomposition of **5** had occurred) led to regeneration of **4** (nmr). Treatment of the solution with water and petroleum ether yielded 39 mg (46% recovery) of **4**, obtained by slow crystallization from the aqueous layer; mp 142.6–143.9° dec; nmr (DMSO-d_6) δ 2.97 (*2.5*), 4.78 (2), 6.77 (1), 7.23 (1), and 7.40–7.97 (10); the petroleum ether layer gave 16 mg of orange oil which showed only broad absorption (nmr) in the phenyl-H region.

Thiabenzene **5** could also be generated by treatment of a degassed ethanolic solution of **4** with oxygen- and carbonate-free aqueous NaOH at room temperature and exhibited uv max (0.02 N NaOH in $EtOH$–H_2O (4:1)) at 245 (ϵ 33,700), 275 (ϵ 14,300 [sh]), and 437 nm

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(1) I. S. Ponticello and R. H. Schlessinger, *Chem. Commun.*, 1214 (1969); M. P. Cava and G. E. M. Husbands, *J. Amer. Chem. Soc.*, **91**, 3952 (1969).

(2) M. Polk, M. Siskin, and C. C. Price, *ibid.*, **91**, 1206 (1969).

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

(4) A. G. Hortmann, *J. Amer. Chem. Soc.*, **87**, 4972 (1965).

(5) W. G. Salmond, *Quart. Rev.* (London), **22**, 253 (1968).

(6) T. M. Harris, C. M. Harris, and J. C. Cleary, *Tetrahedron Lett.*, 1427 (1968).

(7) Trichlorosilane has been reported to convert phosphine oxides to phosphines (with inversion of configuration): L. Horner and W. D. Balzer, *ibid.*, 1157 (1965).

(8) Since the completion of this work, reports have appeared on the use of $HSiCl_3$ in the reduction of sulfoxides to sulfides (T. H. Chan, A. Melnyk, and D. N. Harpp, *ibid.*, 201 (1969)), and on the use of Si_2Cl_6 and Si_3Cl_8 for the deoxygenation of phosphine oxides, sulfoxides, and amine oxides (K. Naumann, G. Zon, and K. Mislow, *J. Amer. Chem. Soc.*, **91**, 2788 (1969)).

(9) Satisfactory analyses for C, H, S, and F were obtained. Melting points were determined in evacuated capillary tubes and are corrected.

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

(11) Peaks due to pentane, dissolved 2-methylpropane, and other aliphatic substances in the *t*-butyllithium solution are not listed; no other peaks (except that for DMSO-d_x) were observed.

(12) This interpretation is supported by the integrated area of the S-methyl peak at δ 1.73 which corresponded to 2.5 protons, and the further observation that, in other experiments, this area was dependent on the mode of mixing and varied over a range corresponding to 0–3 (±10%) S-methyl protons in **5**. Base-catalyzed exchange of S-methyl protons has also been observed for **1**.[4]

(ϵ 3200).[13,14] Addition of HBF_4 led to regeneration of the spectrum of **4**.

When a solution of 0.1 mmol of **5** in 0.4 ml of DMSO-d_6, obtained as described above, was treated with 10 μl of D_2O, H-2,6 and H-4 of **5** were found to undergo exchange for deuterium to the extent of *ca.* 83 and 12%, respectively, in 19 min, and 80 and 25% in 36 min, at *ca.* 35°; no exchange of the S-methyl protons was detectable.[15] The thiinium salt **4** also underwent very slow exchange of H-2,4 and 6 under similar conditions, indicating that an equilibrium between **4**, **5**, and the 4*H* isomer of **4** probably occurs.

Addition of acetic acid-d_4 to a solution of **5** in DMSO-d_6 effected rapid conversion of **5** to **4**-d_4 (δ 3.00 [s, 3] and 7.2–7.8 [m, 10]) with no detectable incorporation of deuterium in the S-methyl group; this result is in contrast to the behavior of **1** in DMSO-d_6 containing increasing amounts of acetic acid-d_4 in which exchange of the S-ring protons occurred to give **1**-d_3, but none of the corresponding 2*H*-thiinium 1-oxide-d_4 could be detected (nmr).

The nmr spectra and deuterium exchange results described above indicate especially high shielding of H-2,6 and pronounced carbanionic character for C-2,6 and C-4 in **5**. Comparison with analogous data for **1** (which are *qualitatively* similar) suggests that ylide-type bonding[4,5] predominates in both **1** *and* **5**. Our nmr results also cast some doubt on the recent claim of a synthesis of 1-phenylthiabenzene,[2] for which *all* the S-ring protons are reported to occur at δ 7.2. The only other known thiabenzene is 1,2,4,6-tetraphenylthiabenzene (**6**).[3]

The lack of evidence for any appreciable ring current effects in **5** (and **1**) lends support to the general type of bonding scheme first suggested for phosphonitrile chlorides by Dewar, and more recently extended by him to include thiabenzene derivatives;[16] thus, in **1** and **5**, two orthogonal and nonconducting hybrid d orbitals on positively charged sulfur might overlap weakly with the ends of the π system of the remaining pentadienyl carbanion.[17–19] Data (uv) in support of similar bonding in 1,1-diphenylphosphabenzene have been reported.[20]

Studies are continuing on related routes to 1-alkyl- and 1-arylthiabenzenes.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support (Grant No. 3032-A1) of this research.

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(13) The thiabenzene decomposed to the extent of ~3% in 1.1 hr under these conditions.

(14) Although thiabenzene **5** is fairly stable at room temperature in the polar media described, all attempts to extract **5** (under N_2) into less polar solvents (diethyl ether, $CHCl_3$, CCl_4), or to generate **5** in diethyl ether, led to rapid decomposition. Nmr spectra of **5** in these less-polar media showed only minor differences in the values cited above for the chemical shifts of the S-ring protons of **5** in DMSO.

(15) Similar behavior was also observed for **1** under these conditions, but exchange occurred at a considerably slower rate (R. L. Harris, unpublished results); *cf.* Y. Kishida and J. Ide, *Chem. Pharm. Bull.* (Tokyo), **15**, 360 (1967).

(16) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1969, pp 430–436, and references cited.

(17) Nmr data for pentadienyl carbanions have been reported: R. B. Bates, W. H. Deines, D. A. McCombs, and D. E. Potter, *J. Amer. Chem. Soc.*, **91**, 4608 (1969), and references cited.

(18) The observed alternation in negative charge densities in the carbanions studied by Bates, *et al.*,[17] and the fact that protons on β-carbon atoms in vinyl sulfonium salts are strongly deshielded[19] point out that ylidic character cannot necessarily be discounted for 1,2,4,6-tetraphenylthiabenzene (**6**) on the basis of the nmr data reported by Suld and Price (cited in ref 3). Also, the low dipole moment (1.88 D) of **6** might be explained as the resultant arising from a higher localization of negative charge at C-2,6 than at C-4 in the S ring of (ylidic) **6**.

(19) M. C. Caserio, R. E. Pratt, and R. J. Holland, *J. Amer. Chem. Soc.*, **88**, 5747 (1966).

(20) G. Markl, *Angew. Chem. Intern. Ed. Engl.*, **3**, 147 (1964).

(21) National Science Foundation Trainee, 1968–1969.

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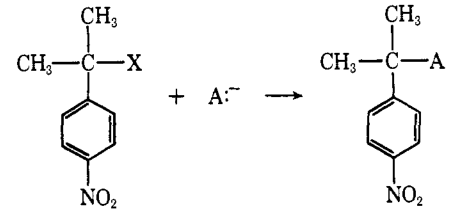
New and Facile Substitution Reactions at Tertiary Carbon. The Reactions of Amines with *p*-Nitrocumyl Chloride and α,*p*-Dinitrocumene

Sir:

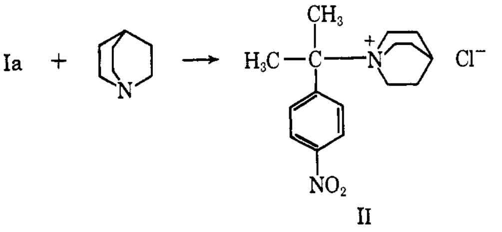
Several years ago we described a new and facile type of substitution at the tertiary carbon atom of *p*-nitrocumyl chloride (Ia) and α,*p*-dinitrocumene (Ib); in these reactions a wide variety of anions smoothly displace the chlorine of Ia, or the aliphatic nitro group of Ib, as shown in eq 1.[1a,b]



(1)

Ia, X = Cl
Ib, X = NO_2

Until now, the nucleophiles employed have always been negatively charged. We now report a set of reactions involving uncharged nucleophiles, namely, amines. Thus, when *p*-nitrocumyl chloride (Ia) is treated with quinuclidine in DMSO at room temperature for 10 hr, a 90% yield of the pure quaternary ammonium chloride (II) is isolated (eq 2). When *p*-nitrocumyl chloride is allowed to react with piperidine, a 91% yield of the pure alkylate is obtained. In the same way various other amines undergo monoalkylation on treatment with *p*-nitrocumyl chloride (Table I). In contrast, although cumyl chloride reacts with quinuclidine (and with piperidine) it gives no alkylate; instead, only α-methylstyrene and cumyl alcohol are produced.



(2)

II

The reactions of Table I might, conceivably, proceed *via* initial elimination followed by Michael addition to the olefin. But from the work of Dale and Buell[2] it is

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(1) (a) N. Kornblum, T. M. Davies, G. W. Earl, N. L. Holy, R. C. Kerber, M. T. Musser, and D. H. Snow, *J. Amer. Chem. Soc.*, **89**, 725 (1967); (b) N. Kornblum, T. M. Davies, G. W. Earl, G. S. Green, N. L. Holy, R. C. Kerber, J. W. Manthey, M. T. Musser, and D. H. Snow, *ibid.*, **89**, 5714 (1967).

(2) W. J. Dale and G. Buell, *J. Org. Chem.*, **21**, 45 (1956).