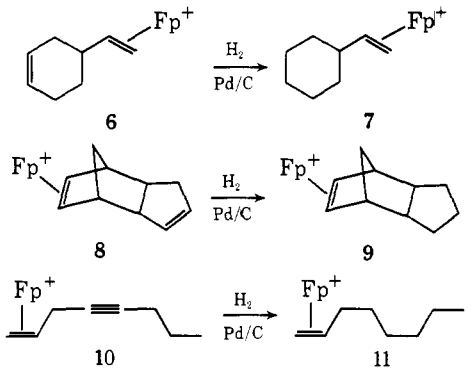
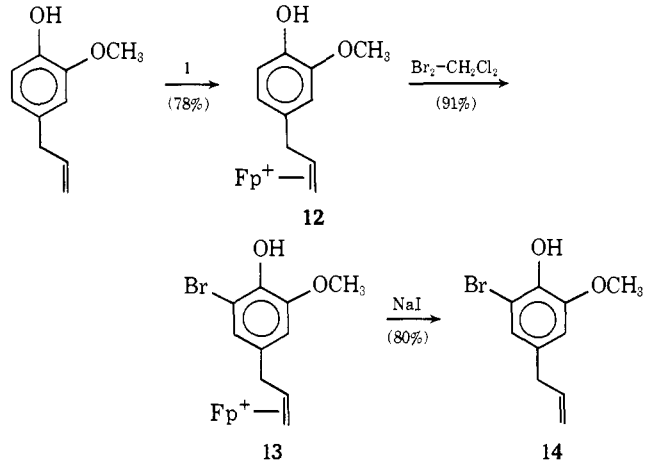


that the present protection method complements the more traditional halogenation-dehalogenation procedure since in the latter the protecting group is introduced preferentially at the more substituted double bonds.

Electrophilic addition to the carbon-carbon double bond of olefinic arenes is generally faster than electrophilic aromatic substitution. The latter process may, however, be effected if the substrate is first coordinated to the Fp^+ moiety.[12] For example, whereas bromination of eugenol (Br_2–CH_2Cl_2, 0°) proceeds faster on the olefinic side chain (followed by NMR), aromatic bromination was achieved selectively in good overall yield as shown below. The structure of



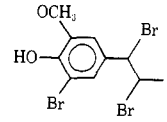
14 readily follows from its ^1H NMR spectrum: ($CDCl_3$) δ 7.2 (bs, 1 H, aromatic), 6.75 (bs, 1 H, aromatic), 5.9 (m, 1 H, olefinic), 5.65 (s, 1 H, OH), 5.2–5.0 (m, 2 H, olefinic), 3.9 (s, 3 H, OCH_3), and 3.4 (d, 2H, allylic).[13]

We are currently exploring use of the $C_5H_5Fe(CO)_2^+$ protecting group in the reactions of heterofunctional olefins.

Acknowledgment. Financial support provided by Boston College is gratefully acknowledged.

References and Notes

(1) Review: D. W. Young in "Protective Groups in Organic Chemistry", J. F. McOmie, Ed., Plenum Press, London, Chapter 8.
(2) Several isolated examples of olefin protection which lack general applicability have also been reported, e.g., argentation (G. Subbarao, G. Rao, and K. Achaya, *Tetrahedron Lett.*, 379 (1966)) and alumination (I. E. Levine, German Patent, 1,156,784 (1963)).
(3) Review: M. Rosenblum, *Acc. Chem. Res.*, **7**, 122 (1974).
(4) W. P. Giering and M. Rosenblum, *Chem. Commun.*, 441 (1971).
(5) A. M. Rosan, M. Rosenblum, and J. Tancrede, *J. Am. Chem. Soc.*, **95**, 3062 (1973).
(6) L. Schmerling, J. P. Luvisi, and R. Welch, *J. Am. Chem. Soc.*, **78**, 2819 (1956).
(7) No attempts were made to optimize yields.
(8) Satisfactory elemental analysis were obtained for the complexes **2, 6, 8, 10,** and **13.**
(9) For example, treatment of **3a–3b** with iodide produced a 3:2 mixture of *trans*-:*cis*-*exo*-5,6-dibromonorbornenes determined by comparison of the ^1H NMR spectrum with literature spectra (ref 10). The norbornene salt **5** was identical with that produced from the exchange reaction with norbornene.
(10) P. M. Subramanian, M. T. Emerson, and N. L. LeBel, *J. Org. Chem.*, **30**, 2624 (1965).
(11) P. F. Boyle and K. M. Nicholas, *J. Org. Chem.*, submitted for publication.
(12) Friedel–Crafts acylations of (diphenylacetylene)$Co_2(CO)_6$ (D. Seyferth and A. Wehman, *J. Am. Chem. Soc.*, **92**, 5520 (1970)) and of (1-phenyl-1,3-butadiene)$Fe(CO)_3$ (R. Pettit and G. F. Emerson, *Adv. Organomet. Chem.*, **1**, 1 (1964)) have been reported.
(13) Bromination of isoeugenol produces



(G. Decodts and M. Wakselman, *Bull. Chem. Soc. Fr.*, 4586 (1972).

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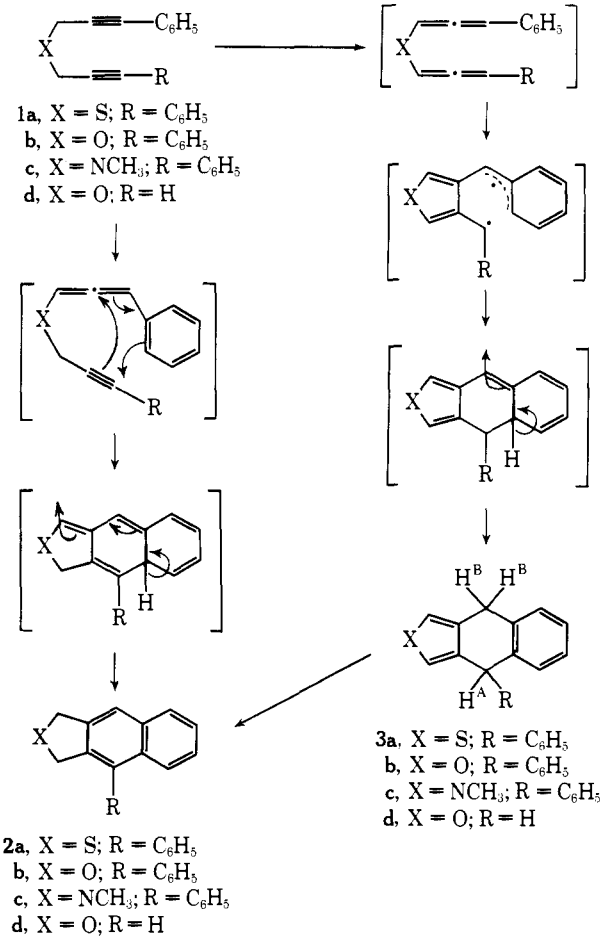
Base Catalyzed Rearrangement of Bispropargyl Sulfides, Ethers, and Amines. The Synthesis of Novel Heterocyclic Systems[1]

Sir:

Over the last 2 decades there has been a renewal of interest in the rearrangement of molecules containing acetylene groups. Both base catalyzed[2] and thermal[3] rearrangements of such systems have been studied and a variety of novel monocyclic,[3] polycyclic,[2,3] and macrocyclic compounds[2b] have been prepared. A smaller number of studies have been

Scheme I



reported on acetylenic systems containing heteroatoms.[4,5] We would now like to report some results on the base catalyzed rearrangement of bispropargyl sulfides, ethers, and amines which lead to the preparation of a number of interesting heterocyclic molecules and serve to correct the currently accepted mechanism for these reactions.

The bis(3-phenyl-2-propargyl) sulfide (**1a**), ether (**1b**) and methylamine (**1c**) had previously been investigated by Iwai and Ide.[4a] These authors found that treatment of **1a–c** with 14% KO-*t*-Bu in *tert*-butyl alcohol led to the corresponding naphthalene derivatives **2a–c**, and they proposed a mechanism involving the anionic rearrangement of one acetylene to the allene followed by cyclization and subsequent prototropic rearrangement (Scheme I).[4a,6,7] The mechanism was subsequently adopted and elaborated by Ollis and coworkers[4d] who reported that **1d** gave **2d**. We have reinvestigated these rearrangements and find that, contrary to these reports, the naphthalenic systems are not the primary reaction products.

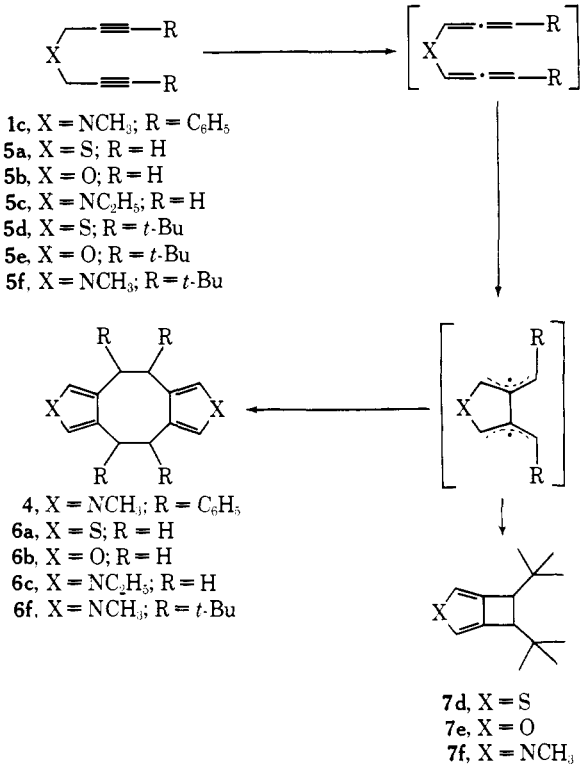
Reaction of **1a** with KO-*t*-Bu in THF at 20° for 10 min gave the thiophene **3a**, 50%, mp 46–47°.[8] The NMR spectrum ($CDCl_3$) of **3a** showed a multiplet at τ 2.82 (11 H), a singlet at τ 4.80 (1 H, H^A), and a singlet at τ 6.02 (2 H, H^B), and the electronic spectrum (EtOH) had its main maximum absorption at 247 nm (ϵ 8270). Similar rearrangement of **1b** gave **3b**, 54%, mp 58–59°,[8] and of **1d** gave **3d**, 20%, mp 79–80°,[8] the NMR[9] and electronic spectra[10] being consistent with the assigned structures. When **3a, b,** and **d** were treated with base under more vigorous conditions, or for a longer time, rearrangement to **2a, b,** and **c** occurred.[11] The rearrangement of **1c** was more complex, both **3c**, 12%, an unstable oil,[8-10] **2c**, 24%, and two isomeric dimers of gross structure **4** (**4a**, mp 248–252°;[8] **4b**, mp 209–210°[8]) being obtained (see Scheme II).

We believe that the observations are best explained by an initial rearrangement of the bisacetylene to the bisallene, which then undergoes an intramolecular allene dimerization to give the heterocyclic bismethylene diradical, or its equivalent.[12,13] This then cyclizes, and subsequent prototropic rearrangement gives **3** (Scheme I).

This scheme finds support from an examination of the products derived from the rearrangement of the unsubstituted and *tert*-butyl substituted bispropargyl compounds **5a–f**. Treatment of **5a** with KOH in methanol at 35° for 3 hr gave the dimer **6a**, 12%, mp 138–140°.[8] The NMR spectrum ($CDCl_3$) showed two signals at τ 7.05 (s, 8 H) and 3.18 (s, 4 H), consistent with the assigned structure. Rearrangement of **5b** with KO-*t*-Bu in THF at 20° gave **6b**, 16%, mp 164–165°,[8,9] and with the same base, but at 60°, **5c** gave **6c**, ca. 10%, mp 135–136°.[8,9] Reaction of **5d** with KO-*t*-Bu in *tert*-butyl alcohol at 50° gave 6,7-di-*tert*-butyl-3-thiabicyclo[3.2.0]hepta-1,4-diene (**7d**), 51% mp 44–45°.[8,14] The NMR spectrum ($CDCl_3$) showed three singlets at τ 3.25, 7.05, and 9.08 in the ratio 1:1:9. Rearrangement of **5e** with KO-*t*-Bu in THF at 50° gave **7e**, 31%, oil.[8,9] Treatment of **5f** with KO-*t*-Bu in benzene gave **7f**, 14%, mp 53–55°,[8,9] whereas with the same base in THF **5f** gave the dimer **6f**, 58%, mp 68–69°.[8] In these cases the possibility for cyclization via the benzene rings is removed,[15] and either dimerization or closure of the diradical occurs (Scheme II).

We are currently attempting to isolate the postulated allene intermediates and to verify that these reactions proceed via a diradical.[16] The synthesis of **3a–d** provides a readily accessible route to potential precursors of isonaphthoheterocycles.

Scheme II



Acknowledgment. One of us (S.B.N.) thanks University College London for the award of a Thomas Witherden Batt Scholarship.

References and Notes

(1) Part of this work was originally described at the 2nd International Symposium on Nonbenzenoid Aromatic Compounds, Lindau, Sept 23–27, 1974.
(2) See (a) G. Eglinton, R. A. Raphael, and J. A. Zabkiewicz, *J. Chem. Soc. C*, 469 (1969); (b) F. Sondheimer and R. Wolovsky, *J. Am. Chem. Soc.*, **84**, 260 (1962); F. Sondheimer, *Proc. R. Soc. London, Ser. A*, **297**, 173 (1967); (c) D. A. Ben-Efraim and F. Sondheimer, *Tetrahedron*, **25**, 2837 (1969); C. N. Bowes, D. F. Montecalvo, and F. Sondheimer, *Tetrahedron Lett.*, 3181 (1973); (d) H. Hopf, *Chem. Ber.*, **104**, 3087 (1971).
(3) See W. D. Huntsman and H. J. Wristers, *J. Am. Chem. Soc.*, **89**, 342 (1967); B. A. W. Coller, M. L. Hefferman, and A. J. Jones, *Aust. J. Chem.*, **21**, 1807 (1968); R. Criegee and R. Huber, *Chem. Ber.*, **103**, 1855 (1970); H. A. Brune, H. P. Wolff, and H. Hüther, *Tetrahedron*, **27**, 3949 (1971); T. J. Henry and R. G. Bergman, *J. Am. Chem. Soc.*, **94**, 5103 (1972); G. H. Mitchell and F. Sondheimer, *ibid.*, **91**, 7520 (1969); H. Hopf, *Chem. Ber.*, **104**, 1499 (1971).
(4) (a) I. Iwai and J. Ide, *Chem. Pharm. Bull. Jpn.*, **12**, 1094 (1964); (b) I. Iwai and T. Hiroaka, *ibid.*, **11**, 1556, 1564 (1963); (c) G. Eglinton, I. A. Lardy, R. A. Raphael, and G. A. Sim, *J. Chem. Soc.*, 1154 (1964); (d) R. W. Jemison, T. Laird, and W. D. Ollis, *J. Chem. Soc., Chem. Commun.*, 556 (1972); T. Laird and W. D. Ollis, *ibid.*, 557 (1972); A. J. Bartlett, T. Laird, and W. D. Ollis, *ibid.*, 496 (1974).
(5) See K. P. C. Vollhardt and R. G. Bergman, *J. Am. Chem. Soc.*, **95**, 7538 (1973).
(6) For a general review of the base rearrangement of acetylenes see I. Iwai in "*Mechanisms of Molecular Migrations*", Vol. 2, B. S. Thyagarajan, Ed., Interscience, New York, N.Y., 1969, p 73.
(7) Iwai[6] has elaborated his scheme to include the bisallene, but this is again considered to react by a 6 π-electron process and a subsequent prototropic shift to give the naphthalene derivative.
(8) Satisfactory microanalytical and/or high-resolution mass spectral data have been obtained for all new compounds.
(9) **3b** ($CDCl_3$) τ 2.83 (m, 11 H), 4.88 (s, 1 H), 6.13 (s, 2 H); **3c** ($CDCl_3$) τ 2.80 (m, 9 H), 3.50 (m, 1 H), 3.70 (m, 1 H), 4.80 (bs, 1 H), 6.00 (bs, 2 H), 6.40 (s, 3 H); **3d** ($CDCl_3$) τ 2.75 (m, 6 H), 6.12 (s, 4 H); **6b** ($CDCl_3$) τ 2.80 (s, 4 H), 7.30 (s, 8 H); **6c** ($CDCl_3$) τ 3.05 (s, 4 H), 6.20 (q, 4 H), 7.30 (s, 8 H), 6.85 (t, 6 H); **7e** ($CDCl_3$) τ 3.00 (s, 2 H), 6.92 (s, 2 H), 9.05 (s, 18 H); **7f** ($CDCl_3$) τ 3.82 (s, 2 H), 6.37 (s, 3 H), 6.95 (s, 2 H), 9.07 (s, 18 H).
(10) **3b** λ_{max} (EtOH) 260 sh nm (ϵ 550), 264 (600), 271 sh (425); **3c** λ_{max} (EtOH) 263 nm (ϵ 2850), 272 (1970), 348 (1120); **3d** λ_{max} (EtOH) 260 sh nm (ϵ 300), 266 (380), 272 (310).
(11) Iwai and Ide[4a] monitored the formation of **2a** and **2b** by the change in electronic spectrum, which probably accounts for their failure to observe **3a** and **3b**.
(12) See W. R. Roth and G. Erker, *Angew. Chem., Int. Ed. Engl.*, **12**, 503, 505 (1973); W. R. Roth, H. Heiber, and G. Erker, *ibid.*, **12**, 504 (1973); W. Grimme and H. J. Rother, *ibid.*, **12**, 505 (1973).

(13) Cyclization of the bisallene by a 6π-electron process followed by prototropic rearrangement to restore the benzene sextet is an alternative possibility which cannot, at present, be excluded.
(14) Hauptmann has observed the formation of a 2,4-disubstituted 6,7-di-*tert*-butyl-3-thiabicyclo[3.2.0]hepta-1,4-diene on treatment of 1,5-di-*tert*-butyl-3-bromopenta-1,4-diyne with sodium sulfide. This reaction is also suggested to proceed through a bisallene intermediate which then undergoes intramolecular dimerization. See H. Hauptmann, *Tetrahedron Lett.*, 3589 (1974).
(15) For a related example in which the benzene rings do not become involved in the cyclization see H. A. Staab and B. Draeger, *Chem. Ber.*, **105**, 2320 (1972).
(16) Attempts to trap the diradical intermediate with olefins have so far been unsuccessful.

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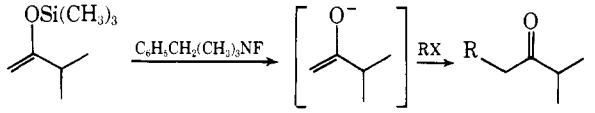
Quaternary Ammonium Enolates as Synthetic Intermediates. Regiospecific Alkylation Reaction of Ketones

Sir:

For the regiospecific alkylation of ketones[1] specific enolate anions have been generated by the aid of various precursors among which silyl enol ethers are the most versatile.[2] With all these specific enolates, some problems remain unresolved: concomitant formation of dialkylation products and loss of regiospecificity.[3] This is attributable to the low reactivities of lithium enolates toward alkyl halides. Substitution of the countercation from lithium to quaternary ammonium[4] seems to activate the enolate anion and to make the regiospecific monoalkylation more feasible.

We have examined the reactions of silyl enol ethers with benzyltrimethylammonium fluoride (BTAF) in the presence of alkyl halides under the expectation that BTAF would be a reagent to cleave the silicon–oxygen bond of silyl enol ethers to afford quaternary ammonium enolates because of high reactivity of fluoride anion in aprotic media[5] and the high value of silicon–fluorine bond energy.[6]



The regiospecific benzylation of 2-methylcyclohexanone via the trimethylsilyl enol ether **2** is illustrative. BTAF[7] (219 mg, 1.30 mmol) and 4A molecular sieves (1.0 g) were suspended in 4 ml of tetrahydrofuran (THF) and stirred overnight under an argon atmosphere.[8] A solution of the silyl enol ether **2** (213 mg, 1.16 mmol), and benzyl bromide (171 mg, 1.00 mmol) in 2 ml of THF was added to the suspension, and the reaction mixture was stirred for 1 hr at room temperature and then at 50° for 30 min. Filtration and removal of solvent afforded a pale yellow oil which by gas chromatographic (GLPC) analysis (XE-60) proved to contain little by-products. The crude reaction mixture was chromatographed on silica gel to give *cis*-6-benzyl-2-methylcyclohexanone (19 mg, 9%), and the trans isomer (161 mg, 80%).[3a,b] The NMR spectra of both compounds absolutely lacked the characteristic signals of 2-benzyl-2-methylcyclohexanone.[3a,b]

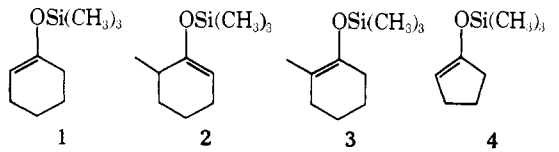


Table I. Alkylation of Ketones via Quaternary Ammonium Enolates

Silyl enol ether	RX	Molar ratio, silyl enol ether:RX[a]	React condn[b]	Yield,[c,d] %
1	Benzyl bromide	1.0:1.0	A	63
1	Methyl iodide	1.0:20	B[e]	79[f]
2	Benzyl bromide	1.2:1.0	A	89
2	Cinnamyl bromide	1.0:1.0	A	78
2	Methyl bromoacetate	1.2:1.0	B	56
2	Butyl iodide	1.0:10	B[e]	40
3	Benzyl bromide	2.0:1.0	A	59
3	Benzyl bromide	1.0:1.1	C	37
3	Methyl bromoacetate	1.2:1.0	A	42
3	Butyl iodide	1.0:3.0	A	37
4	Benzyl bromide	1.0:2.2	A	67
4	Allyl bromide	1.0:2.0	B	58

[a] BTAF was used in a little excess (1.1 equiv) to silyl enol ethers. [b] The reaction conditions are not necessarily optimum: (A) 1 hr at room temperature, 0.5 hr at 50°; (B) 14 hr at room temperature; (C) 2 hr at room temperature. [c] Isolation yield. [d] All compounds were characterized by NMR, ir, and elementary analysis. [e] No solvent was used. [f] Yield was determined by GLPC (QF-1) using tetralin as an internal standard.

The results are summarized in Table I. In every crude reaction mixture obtained after filtration of the precipitate were found the regiospecifically monoalkylated ketone, the unreacted alkyl halide, and the ketone resulting from simple hydrolysis of the starting silyl enol ether. Practically, neither dialkylation nor other by-products were detected.

The regiospecificity is lost to some extent in the alkylation reaction of the lithium enolate corresponding to the silyl enol ether **2**.[3a,b,c] On the other hand, both of the quaternary ammonium enolates formed from the silyl enol ether **2** and **3** underwent regiospecific alkylation. In addition to reactive alkyl halides, relatively less reactive alkylating agents, butyl iodide and methyl bromoacetate, also alkylated 2-methylcyclohexanone regiospecifically,[9] while the lithium enolate corresponding to the silyl enol ether **2** fails to give the desired product on butylation.[10]

With regard to the regiospecificity and the yields of monoalkylation products, the quaternary ammonium enolate described here is useful especially for the alkylation at the less highly substituted position of cyclohexanone derivatives, whereas the lithium enolate is suited for that at the highly substituted position. They appear to compensate each other.

The other features of this alkylation procedure, the preferential attack of the fluoride anion on silicon, the mild reaction conditions,[11] and the simplicity of the procedure, should also be noted.

References and Notes

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(3) (a) H. O. House, M. Gall, and H. D. Olmstead, *J. Org. Chem.*, **36**, 2361 (1971); (b) M. Gall and H. O. House, *Org. Synth.*, **52**, 39 (1972); (c) I. J. Borowitz, E. W. R. Casper, R. K. Crouch, and K. C. Yee, *J. Org. Chem.*, **37**, 3873 (1972). The reactions of lithium enolates formed from enol phosphorylated derivatives are reported. The method described therein, i.e., adding a lithium enolate to an alkyl halide, is essential for the monoalkylation of lithium enolates. (d) A highly reactive alkyl halide, γ-iodotiglate, alkylates lithium enolates regiospecifically in high yields: P. L. Stotter and K. A. Hill, *J. Am. Chem. Soc.*, **96**, 6524 (1974).
(4) For the general property of quaternary ammonium salts, see M. L. Bender, "Mechanisms of Homogeneous Catalysis from Protons to Proteins", Wiley-Interscience, New York, N.Y., 1971, pp 205–206; see also D. J. Sam and H. E. Simmons, *J. Am. Chem. Soc.*, **96**, 2252 (1974).
(5) C. L. Liotta and H. P. Harris, *J. Am. Chem. Soc.*, **96**, 2250 (1974).
(6) L. Pauling, "The Nature of Chemical Bond", 3rd ed, Cornell University Press, New York, N.Y., 1960, Chapter 3.
(7) BTAF was prepared by neutralizing commercial Triton B (40 % metha-