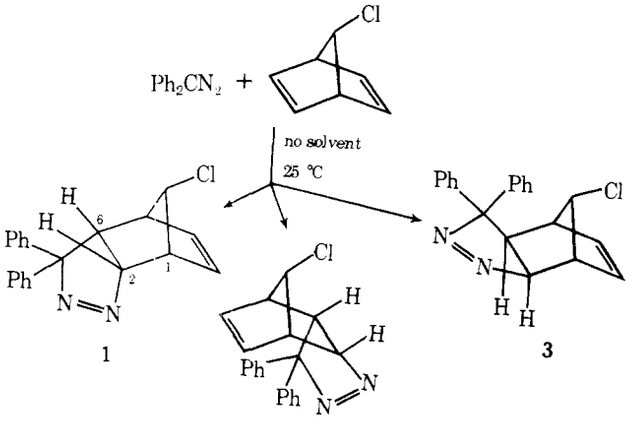
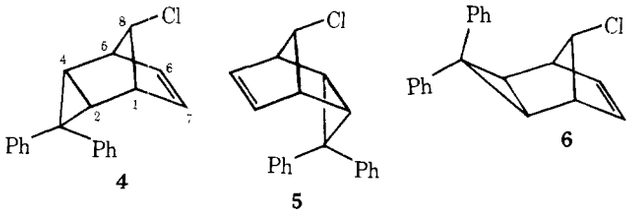
Scheme I



ride **4**, characterized by its symmetry-simplified NMR spectrum: δ (CCl_4) 6.9–7.5 (m, Ar-H), 5.07 (t, J = 2 Hz, H-6,7), 4.03 (shp m, H-8), 3.20 (six-line m, J = 2 Hz, H-1,5), 2.06 (t, J = 2 Hz, H-2,4). The syn nature of adduct **2** was demonstrated by its photolysis in benzene to chloride **5**, identical with that reported.[2a] Exo adduct **3** yielded chloride **6** upon photolysis in benzene, also readily characterized by its NMR spectrum: δ ($CDCl_3$) 7.0–7.4 (m, Ar-H), 6.37 (t, H-6,7), 3.58 (m, H-8), 3.10 (m, H-1,5), 1.75 (s, $W_{1/2}$ = 2 Hz, H-2,4).



The present results reaffirm the complexity inherent in such additions. It seems clear that the MO rationale[3] for eq 1 is not general and that it must somehow be modified to incorporate more features of the diazo component. A possible interpretation would involve a shift away from a type I cycloaddition (HOMO diazoalkane – LUMO diene control) in eq 1 toward a type II cycloaddition (all four frontier orbitals control) in Scheme I.[5] Such a shift would place less emphasis upon the LUMO of 7-chloronorbornadiene and thereby reduce the favorability of endo,anti approach. Alternatively, steric effects could be invoked, as in other comparisons of 1,3-dipolar cycloadditions of diphenyldiazomethane.[7] This seems unsatisfactory, however, in that the larger diazoethane was superior to the smaller diazomethane in its reaction in eq 1,[3] and in that the very crowded adduct **2** resulted as a significant product in Scheme I.

Experimental Section

Melting points were taken on a calibrated Fisher-Johns block. Infrared spectra were determined on a Perkin-Elmer Model 700 instrument. NMR spectra were recorded on a Varian A-60A spectrometer. Only significant absorptions for structural assignment are given for these spectra. Microanalyses were performed by Micro-Tech Laboratories, Skokie, Ill.

Addition of Diphenyldiazomethane to 7-Chloronorbornadiene. From the six additions carried out, a typical preparation is described. Diphenyldiazomethane (4.80 g, 24.7 mmol) was added to neat 7-chloronorbornadiene (used as received from Frinton Laboratories, 3.13 g, 24.7 mmol) and the homogeneous, liquid mixture was allowed to stand at room temperature for 12 weeks.[8] The dark, now solid mass was triturated with cold hexane, leaving adduct **1** [2.14 g, 27%, mp 161–162 °C dec from ether–hexane, IR ν (KBr) 1560 cm^{-1} (N=N), NMR δ ($CDCl_3$) 4.72 (dd, H-2, $J_{1,2}$ = 3.5 Hz). Anal. Calcd for $C_{20}H_{17}ClN_2$: C, 74.88; H, 5.34. Found: C, 74.68; H, 5.29]. Chromatography of the hexane-soluble material over alumina yielded upon elution (10% ether in hexane) benzophenone azine containing some adduct **2** [NMR δ ($CDCl_3$) 4.80 (dd, H-2, $J_{1,2}$ = 3.5 Hz)], followed by a mixture of **2** and **3** (Anal. Found: C, 74.83; H, 5.30), and finally pure adduct **3** [mp 164–166 °C dec from ether–hexane, NMR δ ($CDCl_3$) 5.22 (dd, H-2, $J_{1,2}$ = 1 Hz)]. Analysis of those fractions containing adducts **2** and **3** by NMR indicated a total weight of 0.61 g (8%) of the former and 0.97 g (12%) of the latter. Unidentified tarry material remained on the column.

Photolysis of the Adducts 1, 2, and 3. The appropriate adduct (200 mg) was dissolved in 5 mL of either acetone (adduct **1**) or benzene (adducts **2** and **3**) in a Pyrex test tube and irradiated at 366 nm in a small irradiation unit (Bradford Scientific, Inc., Marblehead, Mass.). After 2 h the photolyses were complete, as indicated by cessation of nitrogen evolution. The solvent was evaporated and the NMR spectrum of the crystalline residue was taken. The chlorides **4**, **5**, and **6** were fairly labile to chromatography on a variety of columns (alumina, Florisil, and silica gel), as well as thermally labile. Photolysis of **1** in benzene containing benzophenone gave only **4** also, exactly as did the use of acetone as solvent. Benzophenone appeared to be without effect in the photolyses of the other adducts.

Registry No.—**1**, 64011-10-5; **2**, 64044-01-5; **3**, 64044-02-6; **4**, 64044-03-7; **6**, 64044-04-8; diphenyldiazomethane; 883-40-9; 7-chlornorbornadiene, 1609-39-8.

References and Notes

(1) For recent treatments and leading references see: R. Sustmann, *Pure Appl. Chem.*, **40**, 569 (1974); R. Huisgen, *J. Org. Chem.*, **41**, 403 (1976); R. Sustmann, E. Wenning, and R. Huisgen, *Tetrahedron Lett.*, 877 (1977); J. Geittner, R. Huisgen, and R. Sustmann, *ibid.*, 881 (1977).
(2) (a) J. W. Wilt and D. R. Sullivan, *J. Org. Chem.*, **40**, 1036 (1975); (b) H. Taniguchi, T. Ikeda, Y. Yoshida, and E. Imoto, *Chem. Lett.*, 1139 (1976).
(3) M. Franck-Neumann and M. Sedrati, *Angew. Chem., Int. Ed. Engl.*, **13**, 606 (1974).
(4) Pyrolysis of adduct **1**, or its photolysis in benzene at 366 nm, gave chloride **4** along with other compounds not fully characterized.
(5) In a Sustmann approach,[1] the frontier orbital energy levels of 7-chloronorbornadiene would be held constant. The variables would be the position of the frontier orbitals of diazomethane and diphenyldiazomethane relative to the diene. Unfortunately, the frontier orbital energies of diazomethane are only estimates as yet,[6] and those for diphenyldiazomethane appear to be unreported.
(6) K. N. Houk, J. Sims, R. E. Duke, Jr., R. W. Strozier, and J. K. George, *J. Am. Chem. Soc.*, **95**, 7287 (1973).
(7) R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **11**, 633 (1963); K. N. Houk, J. Sims, C. R. Watts, and L. J. Luskus, *J. Am. Chem. Soc.*, **95**, 7301 (1973).
(8) This is the most convenient method if time is not critical. Reaction in benzene solvent at 50 °C over 5 days gave similar results, but more tar was formed.

Thiol Addition to Crotepoxide and Dideacetylcrotepoxide[1a,b]

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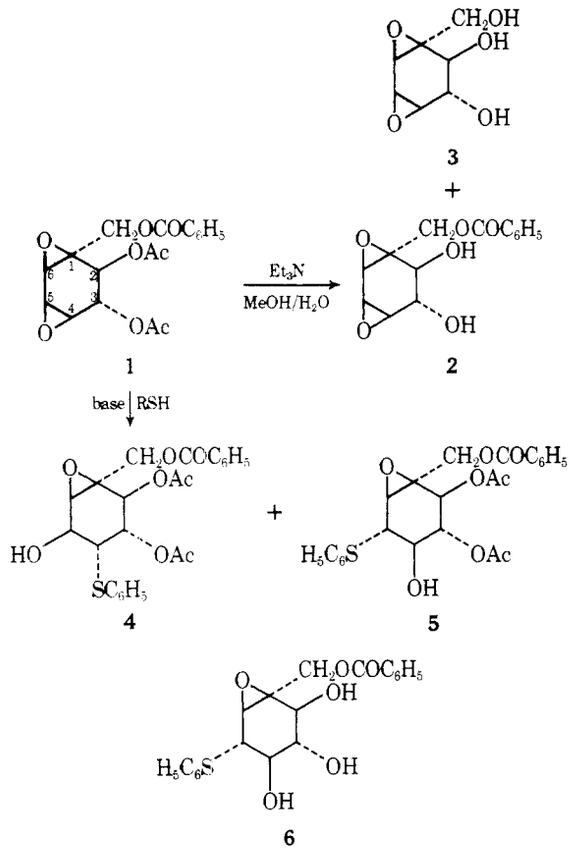
In the course of our continuing research on tumor inhibitory compounds from plant sources, we have observed a marked difference between the reactions of crotepoxide (**1**), a tumor-inhibitory cyclohexane diepoxide previously isolated from the dried fruits of *Croton macrostachys* Hochst ex A. Rich. (Euphorbiaceae),[2] and dideacetylcrotepoxide (**2**) toward thiophenol. Since a large number of the plant-derived tumor inhibitory drugs isolated in these laboratories show reactivity toward sulfhydryl-containing compounds[3–5] as a potential mode of biological action, we felt that crotepoxide (**1**) might also exhibit this reactivity.

Thiophenol reacted with **1** in methanolic solution containing 10% pyridine at 25 °C to yield the thioethers **4** and **5** in approximately equal amounts. Hydrolysis of **1** under mild conditions[6] (triethylamine–water–methanol, 1:1:8, 30 min, 25 °C) gave both dideacetylcrotepoxide (**2**) and debenzoyldideacetylcrotepoxide (**3**). The reaction of thiophenol with **2** was carried out under the same conditions employed for **1** and gave thioether **6** exclusively. Hydrolysis of either **4** or **5** using



the triethylamine–water–methanol (1:1:8) system also led exclusively to **6**.[7]

We suggest that a conformational difference between **1** and **2** would explain the differing reactivity of **1** and **2** toward thiophenoxide anion. In **1** the preferred conformation has the C-3 acetate in the equatorial position, thus allowing attack at both C-4 and C-5 and resulting in approximately equal amounts of both products. However, in **2** attack occurs exclusively at C-5. Consequently, the C-3 hydroxyl group appears to be axial and thus able to sterically hinder attack at C-4. An adverse steric interaction between diaxial C-3 and C-4 substituents is also suggested by the observation that hydrolysis of **4** leads exclusively to **6**.[8] The implication, therefore, is that hydrogen bonding between the C-2 hydroxyl group and the C-4,5 epoxide oxygen occurs in **2**, thus forcing the conformation in which the C-3 hydroxyl group is axial to be preferred and directing attack by thiophenoxide anion to C-5.

The reactivity toward thiophenol exhibited by **2** is analogous to that shown by other epoxide-containing antitumor agents[9] and may, in fact, mimic the biological mode of action.

Experimental Section

IR spectra were recorded on a Perkin-Elmer Model 257 grating infrared spectrophotometer. NMR spectra were done on a JEOL PS-100 p FT NMR spectrometer interfaced to a Texas Instruments JEOL 980A computer, with tetramethylsilane as an internal standard. UV spectra were determined on a Beckman DK-2A ratio recording spectrophotometer. Mass spectra were determined on a Hitachi Perkin-Elmer Model RMU-6E spectrometer. Optical rotations were taken on a Perkin-Elmer Model 141 automatic polarimeter. Melting points were determined on a Mettler FP2 hot stage instrument at a heating rate of 2 °C/min and are uncorrected. Microanalyses were carried out by either Spang Microanalytical Laboratory, Ann Arbor, Mich., or Micro-Tech Laboratories, Skokie, Ill. Thin-layer chromatography (TLC) was carried out on 20 × 20 cm × 0.25 mm E. Merck Silica Gel 60 F-254 plates (EM) or Mallinckrodt ChromAR 7GF plates (ChromAR); visualization was effected by either UV light, iodine spray, or cerium sulfate solution spray (0.125% cerium sulfate in 1:7 concentrated sulfuric acid–water) followed by heating.

Isolation of Crotepoxide (1). Crotepoxide (1) was obtained from roots, leaves, or dried fruits of *Croton macrostachys* in the manner previously reported.[5] Typically the plant material was placed in a Soxhlet extractor for 24 h with 95% ethanol. The concentrated material was partitioned between 90% aqueous methanol and petroleum ether (bp 60–68 °C). The methanol soluble material was further partitioned between 1-butanol and water. The 1-butanol layer was taken to dryness in vacuo and chromatographed on a large SilicAR CC-7 special (Mallinckrodt) column. The fractions eluting with 30% ether in carbon tetrachloride were retained for further chromatography. Extensive column chromatography of these fractions gave a highly enriched concentrate of **1** which crystallized from the concentrate upon addition of methanol. TLC of the mother liquors gave additional quantities of **1**. From 30 kg of plant material a yield of 2.462 g of pure, crystalline **1** (mp 147.6–148.6 °C; lit.[2] mp 150–151 °C) was obtained.

Reaction of Crotepoxide (1) with Thiophenol. To 100 mg of **1** (0.267 mmol) in 1 mL of 1:1 chloroform–methanol was added 0.1 mL of thiophenol (Aldrich, used without purification) and 0.1 mL of pyridine. The solution was stirred at 25 °C for 20 h and then subjected to PTLC on three EM plates developed with 8% methanol–chloroform. The band corresponding to unreacted **1** was crystallized from methanol to afford 47 mg of crotepoxide. A slightly lower R_f band was removed and subjected to PTLC on two ChromAR plates developed with 30% ethyl acetate–benzene. The band of highest R_f value was crystallized from carbon tetrachloride–hexane to afford 25 mg (36.2% based on recovered **1**) of **5**: mp 81.5–85 °C; $[\alpha]^{23}_D$ −78.0° (*c* 0.30, $CHCl_3$); UV (MeOH) λ_{max} (ϵ) 279 (1460), 251 (5040), 222 (18,800) nm; IR (KBr) 2.95, 5.79, 5.83, 7.03, 7.38, 8.08, 8.26, 9.07, 9.51, 9.89, 13.5, 14.3 μm; NMR ($CDCl_3$) δ 1.62 (1 H, s, OH), 2.06, 2.09, (6 H, 2s, $-OCOCH_3$), 3.43 (1 H, d, J = 9 Hz, 5-H), 3.60 (1 H, t, J = 9 Hz, 4-H), 3.64 (1 H, s, 6-H), 4.17, 4.48 (2 H, 2d, J = 12 Hz, 7-H), 5.15 (1 H, t, J = 9 Hz, 3-H), 5.54 (1 H, d, J = 8.5 Hz, 2-H), 7.26 (5 H, m, –SPh), 7.40, 7.45, 7.53, 7.62 (3 H, m, BX_2 portion of an A_2BX_2 system, *m*- and *p*-benzoate protons), 7.94, 7.95, 8.02 (2 H, m, A_2 portion of an A_2BX_2 system, *o*-benzoate protons); mass spectrum (*m/e*) 472 (M^+), 394, 352, 337, 295, 277, 235, 230, 217, 125, 110, 105, 77.

Anal. Calcd for $C_{24}H_{24}O_8S \cdot H_2O$: C, 58.77; H, 5.34; S, 6.54. Found: C, 58.82; H, 5.11; S, 6.63.

The thiophenol adduct to C-4 (**4**) was obtained from the band of lower R_f as an oil, 19 mg (27.5%): $[\alpha]^{27}_D$ −90° (*c* 0.01, MeOH); UV (MeOH) λ_{max} (ϵ) 254 (6815) nm; IR (KBr) 2.86, 3.28, 3.43, 5.70, 5.77, 6.22, 6.30, 6.76, 6.88, 6.95. 7.27, 7.58, 7.86, 8.10, 8.47, 8.98, 9.33, 9.74, 13.35, 13.95, 14.4 μm; mass spectrum M^+ at *m/e* 472.1198 (Calcd for $C_{24}H_{24}O_8S$: 472.1191), 352, 227, 295, 277, 235, 231, 230, 217, 110, 109, 105, 77, 69; NMR ($CDCl_3$) δ 1.26 (1 H, s, OH), 2.11, 2.14 (6 H, 2s, $-OCOCH_3$), 3.49 (1 H, d, J = 9.5 Hz, 4-H), 3.63 (1 H, s, 6-H), 3.80 (1 H, d, J = 9.5 Hz, 5-H), 4.15, 4.46 (2 H, 2d, J = 12 Hz, 7-H), 4.94 (1 H, t, J = 9.8 Hz, 3-H), 5.38 (1 H, d, J = 9 Hz, 2-H), 7.21–8.02 (10 H, m, aromatic protons).

Hydrolysis of Crotepoxide (1). To 675 mg (1.86 mmol) of **1** in 2 mL of chloroform was added 15 mL of (1:1:8) triethylamine–water–methanol. The solution was swirled and allowed to stand for 30 min. The volume was reduced in vacuo and the mixture was subjected to PTLC on four EM plates developed with 8% methanol–chloroform. Bands corresponding to **2** and **3** were removed and set aside; the band corresponding to unreacted **1** was recovered and resubjected to the above hydrolysis conditions, followed by TLC, etc. This process was continued until all but 9 mg of **1** had been hydrolyzed. The combined bands of **3** were eluted with chloroform–acetone, evaporated, and crystallized from methanol–ether giving debenzoyldideacetylcrotepoxide (**3**, 138 mg, 43.1%): mp 94.0–95.0 °C (lit.[2] mp 101–102 °C). The combined bands of **2** were eluted with acetone–chloroform, evaporated, and crystallized from methanol–methylene chloride giving dideacetylcrotepoxide (**2**, 104 mg, 20.3%): mp 136.0–137.0 °C; $[\alpha]^{24}_D$ +23.5 °C (*c* 0.034, MeOH); UV (MeOH) λ_{max} (ϵ) 281 (7950), 273 (985), 230 (13 850) nm; IR (KBr) 2.88, 3.11, 5.86, 6.93, 7.35, 7.49, 7.66, 7.80, 8.10, 8.16, 8.55, 8.88, 9.01, 9.22, 9.33, 9.40, 9.46, 10.2, 10.9, 11.7, 13.3, 14.3 μm; NMR (Me_2SO-d_6) δ 2.93 (1 H, br d, J = 4.5 Hz, 4-H), 3.42 (1 H, d, J = 4 Hz, 5-H), 3.64 (1 H, d, J = 2.5 Hz, 6-H), 3.86 (1 H, br d, J = 9 Hz, 3-H), 3.91 (1 H, d, J = 9 Hz, 2-H), 4.33, 4.61 (2 H, 2d, J = 12 Hz, 7-H), 5.4 (2 H, t, J = 6 Hz, OH), 7.47–8.03 (5 H, m, –OCOPh); mass spectrum *m/e* 279 $(M + 1)^+$, 218, 185, 167, 154, 149, 129, 109, 83, 82, 71, 70, 69.

Anal. Calcd for $C_{14}H_{14}O_6$: C, 60.43; H, 5.07. Found: C, 60.35; H, 5.09.

Reaction of Dideacetylcrotepoxide (2) with Thiophenol. To 65 mg (0.23 mmol) of **2** in 1 mL of 1:1 solution of methanol–chloroform was added 0.1 mL of thiophenol and 0.1 mL of pyridine. The mixture was flushed with nitrogen, stoppered, and stirred at 25 °C for 18 h.

The mixture was subjected to PTLC on two EM plates developed with 5% methanol–ethyl acetate. The band containing **6** was removed and again subjected to PTLC on four EM plates developed with 8% methanol–chloroform. Elution of the band corresponding to **2** afforded 12 mg of recovered **2**. The product band was removed and crystallized from acetone–benzene yielding 31 mg of **6** (41.9% based on recovered **2**). Recrystallization from acetone–carbon tetrachloride afforded a pure sample of **6**: mp 133.5–136.5 °C; $[\alpha]^{26}D$ −133.7° (*c* 0.155, MeOH); UV (MeOH) λ_{max} (ϵ) 280 (1550), 270 (2600), 253 (5350), 223 (16,220) nm; IR (KBr) 2.97, 5.84, 6.95, 7.01, 7.68, 7.88, 8.99, 9.20, 9.38, 9.90, 10.3, 10.7, 11.5, 12.0, 13.4, 13.7, 14.3, 14.6 μm; NMR ($CDCl_3$) δ 1.60 (3 H, s, OH), 2.86 (1 H, br s, 4-H), 3.35 (1 H, d, J = 4 Hz, 5-H), 3.57 (1 H, s, 6-H), 3.65 (1 H, m, 3-H), 3.91 (1 H, d, J = 8.5 Hz, 2-H), 4.16, 4.87 (2 H, 2d, J = 12 Hz, 7-H), 7.26–8.07 (10 H, m, aromatic protons); mass spectrum M^+ at *m/e* 388.0985 (Calcd for $C_{20}H_{20}O_6S$: 388.0980), 357, 299, 284, 248, 230, 218, 217, 195, 178, 177, 165, 163, 152, 139, 135, 123, 122, 111, 110, 109, 106, 105, 77.

Hydrolysis of 4 or 5. The hydrolysis reaction of either **4** or **5** leads to the same product **6**. For simplicity, the description of the hydrolysis of **4** is given. To a 5-mL chloroform solution containing 27 mg of **4** was added 1 mL of a solution of triethylamine–water–methanol (1:1:8). The solution was allowed to stand for 5 min, the solvent was removed in vacuo, and the residue was subjected to PTLC on two EM plates developed with 8% methanol–chloroform. The band corresponding to **6** was removed and crystallized from acetone–hexanes to afford 15 mg of **6** (68.2%) which was identical by mixture TLC, mixture melting point, IR, and NMR with an authentic sample of **6**.

Anal. Calcd for $C_{20}H_{20}O_6S \cdot \frac{1}{2}H_2O$: C, 60.44; H, 5.32; S, 8.07. Found: C, 60.68; H, 5.10; S, 8.04.

Acknowledgments. We wish to thank Dr. Gary A. Howie of the University of Virginia for helpful discussions.

Registry No.—**1**, 20421-13-0; **2**, 64011-11-6; **3**, 20421-15-2; **4**, 64011-12-7; **5**, 64011-13-8; **6**, 64011-14-9; thiophenol, 108-98-5.

References and Notes

(1) (a) Tumor Inhibitors 127. For previous paper in the series, see S. M. Kupchan, K. L. Stevens, E. A. Rohlfing, B. R. Sickles, A. T. Sneden, R. W. Miller, and R. F. Bryan, *J. Org. Chem.*, submitted for publication. (b) This work was supported by grants from the National Cancer Institute (CA-11718) and the American Cancer Society (CH-42L) and a Postdoctoral Fellowship grant to W.L.S. from the National Cancer Institute, National Institutes of Health (CA-02888-02). (c) Deceased Oct 19, 1976.
(2) S. M. Kupchan, R. J. Hemingway, and R. M. Smith, *J. Org. Chem.*, **34**, 3898 (1969).
(3) S. M. Kupchan, *Fed. Proc.*, **33**, 2288 (1974), and references therein.
(4) R. L. Hanson, H. A. Lardy, and S. M. Kupchan, *Science*, **168**, 378 (1970).
(5) S. Remillard, L. I. Rebhun, G. A. Howie, and S. M. Kupchan, *Science*, **189**, 1002 (1975).
(6) S. M. Kupchan, S. P. Ericksen, and M. Friedman, *J. Am. Chem. Soc.*, **88**, 343 (1966); S. M. Kupchan, S. P. Ericksen, and Y.-T. S. Liang, *J. Am. Chem. Soc.*, **88**, 347 (1966).
(7) The structures of **4**, **5**, and **6** were assigned based on comparisons of the NMR signals of the C-4 and C-5 protons in each compound with the NMR data for the known monochlorohydrin and monoiodohydrin of crotepoxide given in ref 2.
(8) No product corresponding to addition at C-4 was obtained. As noted by a referee, it is possible that thiol addition occurs at both C-4 and C-5 and that rapid rearrangement then occurs to afford exclusively the C-5 addition product (**6**).
(9) S. M. Kupchan and R. M. Schubert, *Science*, **185**, 791 (1974).

Preparative Carbocation Chemistry. 13.[1] Preparation of Carbocations from Hydrocarbons via Hydrogen Abstraction with Nitrosonium Hexafluorophosphate and Sodium Nitrite–Trifluoromethanesulfonic Acid

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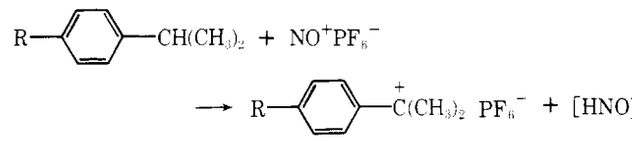
In 1966, we reported the observation that nitrosonium salts are capable of initiating the condensation reaction of cumene (cymene),[2] indicating that abstraction of a benzylic hydrogen occurs to generate the cumyl (cymyl) cation as an intermediate. The necessity of the presence of an activated, abstractable benzylic hydrogen was demonstrated in the observation that neither toluene nor *tert*-butylbenzene reacts with $NO^+PF_6^-$



under similar conditions.[2] Ring nitrosation of the alkylbenzenes was not observed. This is in accord with previous observations[3] that electrophilic aromatic nitrosation is successful only with highly activated systems such as phenol and *N,N*-dimethylaniline.

Various reactions involving NO^+ as a hydrogen-abstracting agent in the gas phase have been subsequently reported. Searles and Sieck[4] observed the reaction of normal, branched, and cyclic alkanes having three to six skeletal carbons with NO^+. Hunt and Ryan also noted that the nitrosonium ion can act as a hydrogen abstractor (or electrophile)[5] toward various organic substrates in the ion source of a mass spectrometer. Williamson and Beauchamp[6] studied the reaction of NO^+ with such simple organic molecules as acetaldehyde and isobutane by ion cyclotron resonance spectroscopy.

More recently, we have found that nitrosonium salts can also be used advantageously in synthetic reactions. Benzyl alcohols are oxidized to arylcarbonyl products and aliphatic or alicyclic secondary alcohols are converted into ketones in good yields via reaction of their trimethylsilyl or tributylstannyl derivatives with nitrosonium tetrafluoroborate.[7] Benzyl and benzhydryl esters are oxidatively cleaved to the parent carboxylic acids and benzaldehyde or benzophenone, respectively.[8] This latter reaction represents a mild procedure to deblock esters to the corresponding acids which is complementary to the existing reductive methods.[9] All these reactions include hydrogen abstraction as the initial step.

In continuation of our study of carbocation chemistry and broadening the scope of reactions initiated by nitrosonium and nitronium salts, we now wish to describe the preparation of stable carbocations by hydrogen abstraction from their hydrocarbon precursors with nitrosonium salts.

Results and Discussion

Representative hydrocarbons capable of forming stable carbocations upon hydrogen abstraction were reacted with nitrosonium hexafluorophosphate.

$$RH + NO^+PF_6^- \rightarrow R^+PF_6^- + [HNO]$$

The expected ions were cleanly formed. Nitrosonium hexafluorophosphate was used in the reactions because of its higher solubility in most of the suitable solvents than, for example, of the tetrafluoroborate salt. The reactions were carried out under a variety of conditions. Solvents used were sulfur dioxide, sulfuryl chlorofluoride, acetonitrile, and trifluoromethanesulfonic acid. Reaction of the precursor hydrocarbons with these solvents was not detectable by NMR spectroscopy within the durations normally required for their complete reaction with $NO^+PF_6^-$, although Nojima and Tokura[10] described the formation of cation radicals from electron-rich molecules in liquid sulfur dioxide. Kantner and Kreevoy[11] have, moreover, reported the disproportionation of the triphenylmethane in triflic acid. However, control experiments have indicated that such side reactions do not occur under our milder conditions, i.e., 0 °C, as neither the tri-