Me_4Si as reference); and mass spectra on a Hitachi Perkin-Elmer RMU-6E instrument (70 eV and 170 °C). Elemental analyses were performed by Baron Consulting Co., Orange, Conn. and Micro-Tech Laboratories, Skokie, Ill. Carbon tetrachloride was dried with calcium chloride. Skelly B was extracted with concentrated H_2SO_4, washed with 10% Na_2CO_3 and water, dried with $CaCl_2$, and distilled from sodium. Other materials were used without purification.

***N*-Chloro-*N*-acetyl-1-aminoadamantane (1).** The method of Sasaki et al. was used:[2] yield 99.8%;[9] mp 69–71 °C (lit.[2] mp 69–71 °C). IR and ^1H NMR spectra were similar to those reported: IR 1660, 1450, 1370, 1250, 1065, 815, 755, 675 cm^{-1} (lit.[2] 1657, 680); ^1H NMR δ 2.20 (12 H), 1.67 (6 H) (lit.[2] 2.13 (12 H), 1.65 (6 H)). Anal. Calcd for $C_{12}H_{18}ClNO$: C, 63.24: H, 7.97; N, 6.15. Found: C, 62.90; H, 7.66; N, 6.07.

Rearrangement of *N*-Chloro-*N*-acetyl-1-aminoadamantane (1). The procedure of Sasaki et al.[2] was used except for a change in reaction time (68 h instead of 40 h). Chromatography on silica with chloroform as eluent produced **3**, mp 74–76 °C dec (lit.[2] 69.5–71.5 °C). Recrystallization from dry Skelly B afforded off-white plates, mp 85–86 °C. IR and ^1H NMR were similar to those reported: IR 1670, 1370, 1320, 1270, 1120, 1015, 850, 780, 735 cm^{-1} (lit.[2] 1671, 853, 743, 713 cm^{-1}); ^1H NMR δ 2.55 (s, NCH_2), 2.22 (s, CH_3), 2.60–1.90 (m) (lit.[2,5] δ 2.55 (d, NCH_2), 2.23 (s, CH_3), 2.50–1.45 (m)); ^{13}C NMR δ 173.92 (C=O), 66.92 (3), 64.97 (1, 8), 55.20 (5), 48.17 and 44.44 (2, 11) and (7, 10), 37.53 (9), 32.50 (6), 25.67 (CH_3); mass spectrum *m/e* (relative intensity) 91 (36), 127 (28), 128 (32), 130 (20), 148 (45), 170 (30), 186 (100), 187 (23), 188 (54), 190 (21), 210 (23), 226 (100), 227 (36), 228 (59), 261 (41), 263 (27), $M^{+\cdot}$ 295 (1), $(M^{+\cdot}+2)$ 297 (1), $(M^{+\cdot}+4)$ 299 (0.3); $(M^{+\cdot}):(M^{+\cdot}+2):(M^{+\cdot}+4)$ = 3:3:1. Anal. Calcd for $C_{12}H_{16}Cl_3NO$: C, 48.59; H, 5.44; Cl, 35.86; N, 4.72. Found: C, 48.40; H, 5.31; Cl, 35.18;[10] N, 4.92.

Acknowledgment. We gratefully acknowledge support for P.M.S. from S. C. Johnson & Son. The authors wish to thank Mr. Paul Karges for assistance in obtaining mass spectrometric data.

Registry No.—**1**, 64741-22-6; **3**, 64741-23-7; $AlCl_3$, 7446-70-0.

References and Notes

(1) Paper 27, Chemistry of *N*-Halo Compounds.
(2) T. Sasaki, S. Eguchi, T. Kiriyama, and H. Suzuki, *Synth. Commun.*, **1**, 267 (1971).
(3) P. M. Starewicz and P. Kovacic, unpublished work.
(4) R. R. Perkins and R. E. Pincok, *Org. Magn. Reson.*, **8**, 165 (1976).
(5) Further investigation of the literature product (refrigerated for 6 years) showed molecular ions at *m/e* 295, 297, and 299 in 2.8:2.6:0.8 ratio with a fragmentation pattern similar to that of **3**; elemental analysis (C, H, N) gave a figure intermediate between the theoretical values for the di- and trichloro derivatives (personal communication from Professor Sasaki). Our examination of the ^{13}C NMR spectrum of the literature sample revealed about 24 peaks (vs. 9 expected), including those characteristic of **3**. We thank Professor Sasaki for kindly supplying additional data and a sample for comparison.
(6) P. Kovacic, J.-H. Liu, E. M. Levi, and P. D. Roskos, *J. Am. Chem. Soc.*, **93**, 5801 (1971).
(7) H. Stetter, M. Krause, and W.-D. Last, *Angew. Chem., Int. Ed. Engl.*, **7**, 894 (1968); P. Kovacic and J.-H. Chen Chang, *J. Org. Chem.*, **36**, 3138 (1971).
(8) R. C. Fort, Jr., and P. v. R. Schleyer in "Advances in Alicyclic Chemistry", Vol. 1, H. Hart and G. J. Karabatsos, Ed., Academic Press, New York, N.Y., 1966, pp 335 and 336.
(9) The titration for positive chlorine gave an unexpectedly low value of 70%, possibly caused by an interfering side reaction of **1** in the acidic medium; P. Kovacic, C. T. Goralski, J. J. Hiller, J. A. Levisky, and R. M. Lange, *J. Am. Chem. Soc.*, **87**, 1262 (1965).
(10) The slightly low value for chlorine is probably due to high reactivity of the compound toward water.

Thermal Rearrangement of Halocineole to Halopinol Derivatives

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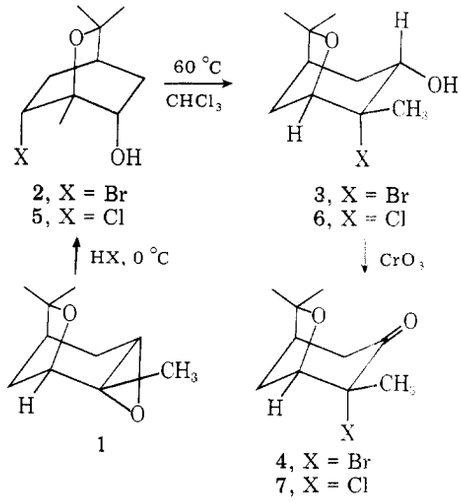
During an investigation of pinol oxide[2] (**1**) it was noted that its conversion to *endo*-6-hydroxy-*endo*-7-bromocineole (**2**) by fuming hydrobromic acid was complete after 1 h at 0 °C. Bromohydrin **2** was stable in chloroform at room temperature; however, at 60 °C it was largely transformed into pinol bromohydrin (**3**). The conversion of **2** into **3** at 60 °C was essentially complete after 20 h, at which time a mixture of 80% **3** and 20% **2** was on hand.



The structure of **3** was suggested by its NMR spectrum which showed, in part, a methyl singlet at 1.87 ppm attributed to a CH_3CBr group and a doublet at 4.22 ppm characteristic of the bridgehead proton of a pinol ring.[2] An axial C-3 proton was indicated by a broad multiplet at 3.73 ppm with a half-width of 30 Hz. Chromic acid oxidation of **3** gave the bromoketone **4**. The NMR chemical shift (1.82 ppm) of the α-methyl group in **4** was not noticeably altered on changing solvent from deuteriochloroform to benzene, while its ultraviolet spectrum showed a maximum at 307 nm requiring the presence of an equatorial methyl and axial bromine atom at C-2.

endo-6-Hydroxy-*endo*-7-chlorocineole (**5**) was recovered unchanged after refluxing in chloroform or benzene for 24 h. In refluxing toluene (110 °C) chlorohydrin **5** slowly rearranged to *cis*-pinol chlorohydrin **6**. Further change was not noted after 120 h and NMR analysis of the resulting mixture indicated the presence of 78% of **6** and 22% of **5**. In refluxing xylene (140 °C) an apparent stationary state was reached in 24 h, and severe darkening was observed on more prolonged heating. Essentially the same mixture of **6** and **5** was obtained from pure **5** when it was heated in xylene for 24 h.

The structures of *cis*-pinol chlorohydrin (**6**) and the ketone **7** obtained by chromic acid oxidation were demonstrated by spectral analysis (see the Experimental Section).

endo,endo-6,7-Dibromocineole (**8**) rearranged to pinol dibromide **9** at about the same rate that chlorohydrin **5** rearranged to **6**. Refluxing in bromobenzene (154 °C) was required for completion in 5 h and despite the formation of appreciable black tar, pinol dibromide **9** could still be isolated by column chromatography. The rearrangement of **8** to **9** was also noted on passing **8** through a GLC column at 190 °C. The structural assignment to **9** is based on its NMR spectrum and the stereochemistry is suggested by analogy with that of bromohydrin **3**.

endo,endo-6,7-Dichlorocineole (**10**) similarly rearranged to pinol dichloride **11** on refluxing in bromobenzene but much more slowly than the corresponding dibromide. A 33% conversion to **11** was noted after 18 h. Heating dichloride **10** at 280 °C for 1 h furnished **11** in good yield. The methoxy chloride **13** rearranged to **14** at a rate comparable with that of dichloride **10**.

By contrast, *endo,endo*-6,7-dihydroxycineole (**12**) and its diacetate derivative **12a**[2,3] were stable at 200 °C in refluxing tetralin.

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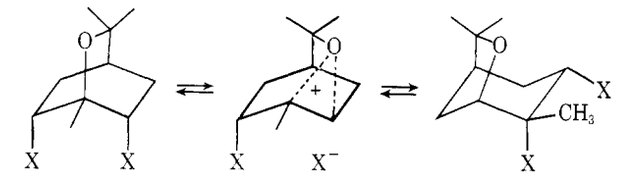
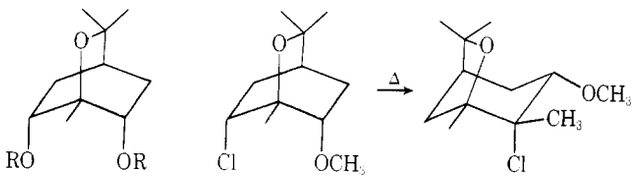


8, X = Br
10, X = Cl

8a

9, X = Br
11, X = Cl



12, R = H
12a, R = Ac

13

14

Electrophilic additions to pinol[2] involving the development of substantial positive charge in the transition state invariably proceed with oxygen migration and afford kinetically controlled cineole products derived by attack of a nucleophile at the sterically less hindered secondary carbon of the cineole (oxabicyclo[2.2.2]octane) ring system. Thermolysis of halocineole derivatives offers thefirst synthetic entry to pinol derivatives bearing a halogen at the C-4 position. The thermolysis appears to involve ionization (bromides much faster than chlorides) assisted by the favorably located neighboring oxygen atom[4,5] to form an ion pair intermediate **8a**, followed by internal return with attack of halide occurring at the more hindered tertiary position yielding the more thermodynamically stable pinol (oxabicyclo[3.2.1]octane) ring system.[6] In accord with this view is the observation that the thermolysis of dichloride **10** to **11** at 110 °C occurs 25 times faster in the more polar dimethylformamide than in toluene.

The nonrearranging substituent appears to play an important role in determining the rate of rearrangement as illustrated by the facile rearrangement of chlorohydrin **5** as compared with the dichloride **10** and methoxy chloride **13**. The accelerating effect of the hydroxyl group is most likely a consequence of intramolecular hydrogen bonding which assists in the ionization of the halide.[7]

Experimental Section

All boiling and melting points are uncorrected. Infrared spectra were measured with a Perkin-Elmer Infracord, Model 137-B. NMR spectra were recorded with Varian Associates A-60A and Perkin-Elmer R-32 spectrometers and are reported in ppm from tetramethylsilane as an internal standard. Mass spectra were determined with a Hitachi RMU-6D instrument by the Purdue University Spectral Service. Ultraviolet spectra were recorded on a Cary Model 15 spectrometer. Microanalyses were performed by Dr. C. S. Yeh and associates.

Pinol Bromohydrin (4α-Bromo-4β,7,7-trimethyl-6-oxabicyclo[3.2.1]octan-3-ol, 3). A solution of 630 mg of *endo*-6-hydroxy-*endo*-7-bromocineole (**2**) in 30 mL of chlorofrom was heated to reflux and aliquots were periodically withdrawn for NMR analysis. The ratio of the integrated areas for the 1.87-ppm singlet (CH_3CBr in **3**) and the 1.30-ppm singlet (CH_3CO in **2**) was used to determine the composition of the mixture. The proportion of **3** was ca. 35% after 6 h, reached 80% after 25 h, and remained unchanged thereafter.

A 2-g sample of **1** was refluxed in chloroform for 24 h. The solvent was removed in vacuo and the residue was chromatographed on silica gel using ether–pentane as eluant to give, after recrystallization from hexane, 940 mg of pinol bromohydrin **3**: mp 72–73 °C; NMR ($CDCl_3$) 1.19 and 1.37 (s, 6, $(CH_3)_2CO$), 1.87 (s, 3, CH_3CBr), 1.75–2.47 (m, 5), 2.51 (s, 1, OH), 3.73 (m, 1, $W_{1/2}$ = 30 Hz, CHOH), and 4.22 ppm (d, 1, J = 6 Hz, CHOC); mass spectrum (70 eV) m/e 248 (2%). Anal. Calcd for $C_{10}H_{17}BrO_2$: C, 48.19; H, 6.83; Br, 32.73. Found: C, 48.37; H, 6.65; Br, 32.68.

From 1.2 g of (−)-**2**, mp 76–77 °C, $[\alpha]^{25}D$ −9.97° (*c* 6.52, $CHCl_3$), there was obtained 760 mg of (+)-**3**, mp 50–51 °C, $[\alpha]^{25}D$ + 50.08° (*c* 4.74, $CHCl_3$).

Table I. Rate of Thermal Rearrangement of Cineol Chlorohydrin (5)

Solvent	Temp, °C	k, s^{-1}
Toluene	110	6.30×10^{-6}
Dioxane	101	4.92×10^{-6}
DMF	110	1.35×10^{-4}
DMF	90	3.50×10^{-5}

4α-Bromo-4β,7,7-trimethyl-6-oxabicyclo[3.2.1]octan-3-one (4). Approximately 2 mL of Jones reagent was added slowly to a solution of 1 g (4 mmol) of pinol bromohydrin (**3**) in 25 mL of acetone. Isopropyl alcohol (0.25 mL) was added to destroy the excess oxidant and the salts were removed by filtration and washed thoroughly with ether. The ether solution was washed with 5% sodium bicarbonate, dried (Na_2SO_4), and evaporated to leave 890 mg of light-yellow oil. The oil was chromatographed on silica gel using ether–pentane as eluant and then evaporatively distilled to yield 693 mg of pure **4**: IR 5.81 μm; UV λ_{max} (MeOH) 307 nm (E = 83); NMR 1.17 and 1.22 (s, 6, $(CH_3)_2CO$), 1.82 (s, 3, CH_3CBr), 2.32 (m, 2), 2.72 (m, 3), and 4.23 ppm (d, 1, CHO); NMR (C_6H_6) 1.02 (s, 6, $(CH_3)_2CO$), 1.83 (s, 3, CH_3CBr), 1.92–2.97 (m, 5), and 4.17 ppm (d, 1, –CHO–); mass spectrum m/e (rel intensity) 246 (33), 167 (48), and 97 (100). Anal. Calcd for $C_{10}H_{15}O_2Br$: C, 48.58; H, 6.07; Br, 32.39. Found: C, 48.43; H, 6.29; Br, 32.60.

Pinol Chlorohydrin (4α-Chloro-4β,7,7-trimethyl-6-oxabicyclo[3.2.1]octan-3α-ol, 6). A solution of 2 g of cineol chlorohydrin (**5**) in 25 mL of *p*-xylene was refluxed for 20 h and the solvent was removed under reduced pressure to leave a brown oil whose NMR indicated the presence of an 80:20 mixture of **6** and **5**. Column chromatography on silica gel using ether–pentane, followed by recrystallization from hexane, afforded 980 mg of pinol chlorohydrin **6**: mp 77–78 °C; NMR ($CDCl_3$) 1.18 and 1.35 (s, 6, $(CH_3)_2CO$), 1.63 (s, 3, CH_3CCl), 1.85–2.55 (m, 5), and 4.12 ppm (d, 1, –CHO–).

From 1.0 g of (+)-**5**, mp 72–73 °C, $[\alpha]^{25}D$ +11.14° (*c* 4.72, $CHCl_3$), there was obtained 575 mg of (+)-**6**, mp 81–82 °C, $[\alpha]^{25}D$ + 78.52° (*c* 3.1, $CHCl_3$).

The rate of rearrangement of **5** to **6** was followed by dissolving 300–400 mg of **5** in 25 mL of the appropriate solvent and the resulting solution was heated in an oil bath. Aliquots were periodically withdrawn, the solvent was evaporated under reduced pressure, and the NMR spectrum of the residue was determined in $CDCl_3$. The ratio of the area of the signal at 1.63 ppm to the area of the signal at 1.37 ppm was used to determine the composition of the mixture.

4α-Chloro-4β,7,7-trimethyl-6-oxabicyclo[3.2.1]octan-3-one (7). To a solution of 1.6 g of pinol chlorohydrin (**5**) in 25 mL of acetone was added Jones reagent until the red-orange color persisted. The mixture was worked up in the usual manner to afford 1.4 g of oil. Chromatography on silica gel followed by evaporative distillation gave 1.0 g of chloroketone **7**: IR 5.80 μm; UV λ_{max} (MeOH) 298 nm (E = 40); NMR ($CDCl_3$) 1.15 and 1.20 (s, 6, $(CH_3)_2CO$), 1.63 (s, 3, CH_3CCl), 2.0–3.0 (m, 5), and 4.20 ppm (d, 1, –CHO–); NMR (C_6H_6) 0.97 (s, 6, $(CH_3)_2CO$), 1.70 (s, 3, CH_3CCl), 1.8–2.2 (m, 5), and 4.02 ppm (d, 1, –CHO–); mass spectrum m/e 202 (39), 167 (15), 125 (22), 123 (18), and 97 (100). Anal. Calcd for $C_{10}H_{15}ClO_2$: C, 59.26; H, 7.41; Cl, 17.53. Found: C, 59.19; H, 7.52; Cl, 17.40.

***endo*-6-Methoxy-*endo*-7-chlorocineole (13).** An ethereal solution of diazomethane, prepared from 36 g of *N,N'*-dimethyl-*N,N'*-dinitrosoterephthalamide, 120 mL of 30% NaOH, 90 mL of carbitol, and 600 mL of ether, was distilled into a receiver containing 1 g of cineal chlorohydrin (**5**) and 0.3 mL of boron trifluoride etherate in 10 mL of ether. The solution was kept at ambient temperature overnight and was then washed with water and 5% sodium bicarbonate solution and dried (Na_2SO_4). The solvent was removed and the residue was chromatographed on silica gel using ether–pentane as eluant to afford 350 mg of chloro methyl ether **13**, followed by 75 mg of 4α-chloro-3α-methoxy-4β,7,7-trimethyl-6-oxabicyclo[3.2.1]octane (**14**) and 450 mg of starting cineole chlorohydrin (**5**). The analytical sample of **13** was obtained by evaporative distillation: NMR ($CDCl_3$) 1.21 (s, 6, $(CH_3)_2CO$), 1.31 (s, 3, CH_3CO), 1.4–2.1 (m, 3), 2.3–3.1 (m, 2), 3.33 (s, 3, CH_3O), 3.40 (m, 1, CHO), and 3.96 ppm (d of q, 1, CHCl); mass spectrum m/e 218 (15), 160 (12), 126 (49), 125 (78), 124 (21) and 43 (100). Anal. Calcd for $C_{11}H_{19}ClO_2$: C, 60.39; H, 8.77; Cl, 16.20. Found: C, 60.35; H, 8.88; Cl, 16.20.

Chloromethoxy pinol (**14**) was an oil and showed NMR ($CDCl_3$) 1.20 and 1.36 (s, 6, $(CH_3)_2CO$), 1.63 (s, 3, CH_3CCl), 1.8–2.6 (m, 5), 3.43 (s, 3, CH_3O), 3.62 (q, 1, $CHOCH_3$) and 4.04 ppm (d, 1, CHO).

A sample of **13** in *p*-xylene at 110 °C showed no change after 24 h. At 140 °C, 13% rearrangement to **14** had occurred in 14 h, 26% in 23 h, and 32% in 39 h.

Pinol Dibromide (3α,4α-Dibromo-4β,7,7-trimethyl-6-oxabicyclo[3.2.1]octane, 9). *endo,endo*-6,7-Dibromocineole (8) was unchanged after refluxing in toluene for 24 h. In 48 h a 10% conversion to 9 was noted. In *p*-xylene (140 °C) 45% rearrangement was observed in 8 h and 75% after 24 h. In bromobenzene (154 °C) the rearrangement of 8 to 9 was essentially complete in 5 h.

The black bromobenzene solution resulting from heating 638 mg of dibromide 8 in bromobenzene for 5 h was chromatographed on 50 g of silica gel using hexane, 2% ether–hexane, and 4% ether–hexane as eluants to give 300 mg of pinol dibromide (9). After two sublimations in vacuo, dibromide 9 displayed mp 58–60 °C: NMR ($CDCl_3$) 1.22 and 1.41 (s, 6, $(CH_3)_2CO$), 1.83 (s, 3, CH_3CBr), 2.0–2.8 (m, 8), 4.30 (d, 1, –CHOC–), and 4.40 ppm (d of d, 1, $W_{1/2}$ = 30 Hz, CHBr); mass spectrum, *m/e* 310 (2.5), 231 (100), 133 (67), 125 (56), 123 (28), 93 (56), 81 (41) and 69 (36). Anal. Calcd for $C_{10}H_{16}Br_2O$: C, 38.46; H, 5.13; Br, 51.28. Found: C, 38.54; H, 5.21; Br, 51.40.

Pinol Dichloride (3α,4α-Dichloro-4β,7,7-trimethyl-6-oxabicyclo[3.2.1]octane, 11). Aliquots were periodically withdrawn from a refluxing solution of *endo,endo*-6,7-dichlorocineole (10) in bromobenzene and analyzed by NMR. After 18 h, 33% rearrangement to 11 had occurred. The mixture darkened appreciably after 100 h and even after 134 h (60% 11) the conversion to 11 was not complete.

A 534-mg sample of dichloride 10 was heated at 260–270 °C for 1 h with considerable foaming and discoloration. The mixture was cooled and washed through a short plug of Florisil with hexane and ether. A total of 380 mg of brown oil was recovered and GLC analysis using a 10% Carbowax column at 170 °C indicated the presence of 82% of 11 (retention time 14 min) and 18% of 10 (retention time 19 min).[9] A pure sample of dichloride 11 was obtained by GLC and showed: NMR ($CDCl_3$) 1.21 and 1.39 (s, 6, $(CH_3)_2CO$), 1.65 (s, 3, CH_3CCl), 1.8–2.8 (m, 5), 4.20 (d, 1, J = 6 Hz, CHO), and 4.35 ppm (m, 1, CHCl); mass spectrum (70 eV) *m/e* (rel intensity) 222 (24), 187 (100), 180 (14), 178 (18), 171 (7), 169 (17), 151 (21), 145 (24), 143 (48), 97 (38), 93 (43), 81 (37), and 43 (45). Anal. Calcd for $C_{10}H_{16}Cl_2O$: C, 58.81; H, 7.17; Cl, 31 87. Found: C, 54.11; H, 7.15; Cl, 32.03.

Registry No.—1, 5718-71-8; (±)-2, 64665-45-8; (−)-2, 64665-46-9; (±)-3, 64611-57-0; (+)-3, 64611-58-1; 4, 64611-59-2; (±)-5, 60760-99-8; (+)-5, 64665-47-0; (±)-6, 60705-69-3; (+)-6, 64611-60-5; 7, 60705-71-7; 8, 32207-49-1; 9, 64611-61-6; 10, 32221-12-8; 11, 64611-62-7; 13, 64611-63-8; 14, 64611-64-9.

References and Notes

(1) Abstracted in part from the Ph.D. Thesis of M.K.V., Purdue University, May 1976.
(2) J. Wolinsky, R. O. Hutchins, and J. H. Thorstenson, *Tetrahedron*, **27**, 753 (1971).
(3) For the acid-catalyzed thermal rearrangement of *endo,endo*-6,7-dihydroxycineole and its acetate derivative, see R. O. Hutchins and D. Koharski, *J. Org. Chem.*, **34**, 2771 (1969).
(4) L. A. Paquette and P. C. Storm, *J. Am. Chem. Soc.*, **92**, 4295 (1970); L. A. Spurlock and R. G. Fayter, *ibid.*, **94**, 2707 (1972).
(5) See H. Kwart and P. A. Silver, *J. Org. Chem.*, **40**, 3019 (1975), for the thermolysis of an α-chloro ether.
(6) See H. L. Goering and M. F. Sloan, *J. Am. Chem. Soc.*, **83**, 1992 (1961), for the corresponding behavior of bicyclo[2.2.2]octane and bicyclo[3.2.1]-octane derivatives.
(7) For a review of intermolecular hydrogen bond assistance to ionization see A. J. Parker, *Q. Rev., Chem. Soc.*, **16**, 163 (1962), and J. March, "Advanced Organic Chemistry", McGraw-Hill, New York, N.Y., 1968, pp 293–296.
(8) J. A. Moore and D. E. Reed, "Organic Synthesis", Collect. Vol. V, Wiley, New York, N.Y., 1973 p 351.
(9) Dichlorides **10** and **11** were stable to these GLC conditions.

Carbon-13 Nuclear Magnetic Resonance Study of Iodine–Sulfide Charge-Transfer Complexes

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Charge-transfer complexes between iodine and alkyl or aryl sulfides have been known for some time now.[1b,c] Most of the studies hitherto have been concerned with the measurement of the formation constants utilizing spectrophotometric methods,[2] although one proton NMR study has been reported.[3] While these investigations have presented useful information concerning the structural features which affect the strength of the charge-transfer interaction, they have not dealt with the gross molecular reorganization in these complexes. Since carbon-13 NMR chemical shifts are sensitive to changes in electron density[4] and the stereochemical relationship of atoms in a molecule,[5] it was felt that this spectroscopic method would provide additional insight into the electronic reorganization of the sulfides. In fact, Roberts has already shown that carbon-13 NMR spectroscopy can be utilized in the study of charge-transfer complexes.[6]

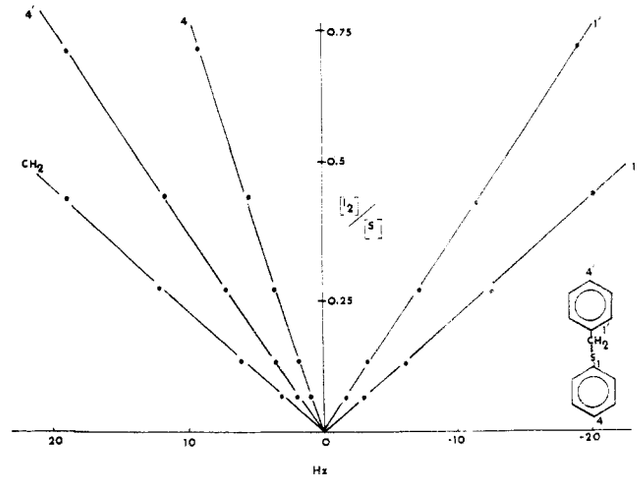

Figure 1. Plot of the ratio of iodine to sulfide concentration against the magnitude of the iodine-induced shift for benzyl phenyl sulfide.

It is generally agreed that the sulfide–iodine charge-transfer interaction is a 1:1 species[2d] and that the sulfur–iodine bonds all lie in a straight line.[7] For the purpose of this report, all other species will be ignored. It has also been shown that in aromatic sulfides only the sulfur atom is complexed by the iodine.[2d]

A typical set of data is illustrated by the plot given in Figure 1. The plot is clearly monotonic, at least to molar concentrations less than 0.75, and this is a good indication that only one complexed species is present in solution.[8] Attempts at obtaining the limiting shift of the complex were not performed due to the insolubility of iodine under the experimental conditions. Attempts at decreasing the sulfide concentration (thus increasing the accumulation time significantly) facilitated some oxidation to the corresponding sulfoxide.

Given in Figure 2 are the carbon chemical shifts and iodine-induced chemical shifts (in parentheses) for the sulfides studied. The iodine-induced shifts were obtained directly from the plotted data by extrapolation of the $\Delta\delta$ vs. concentration curve to a 1:1 ratio. The value obtained by this method should be proportional to the limiting shift of the sulfide–iodine complex.[9]

The iodine-induced shifts in the aliphatic sulfides I, V, VI, and VII appear quite unexceptional. The α-carbon resonances suffer a large downfield shift due to the increase of the electron withdrawing nature of the sulfide–iodine complex vs. that of the free sulfide. The β-carbon resonances are shifted to higher field and this most likely results from a polarization of the C–H bond, the well known γ effect.[10] For the remaining sulfides II, III, and IV, the aliphatic α-carbon resonances are also shifted to lower field but to a lesser extent than the above compounds. However, for a directly bonded aromatic α-carbon the direction of shift is to *higher* field. An upfield shift is also observed for all ipso aromatic carbon resonances β to the sulfur atom. In aromatic systems there is a good correlation between the direction of the shift and electron density at a carbon site.[4]

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