Electrophilic Halogenation of Octamethylnaphthalene[1,2]

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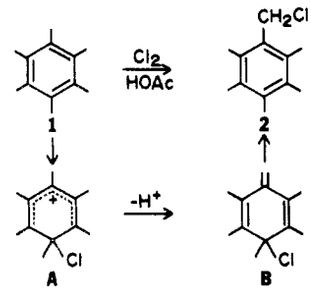
The silica gel catalyzed chlorination of hexamethylbenzene with sulfuryl chloride gives pentamethylbenzyl chloride in 96% yield. Similar chlorination of octamethylnaphthalene can be controlled to give an excellent yield of the 1-chloromethyl-, 1,8-bis(chloromethyl)-, or 1,4,5,8-tetrachloromethyl derivative, depending on the amount of sulfuryl chloride used. 1,2,3,4,5,6,7-Heptamethylnaphthalene is obtained in high yield by refluxing 1-chloromethylheptamethylnaphthalene in methanol. The reaction proceeds via the 1-methoxymethyl derivative (isolable if pyridine is present) which is rapidly dealkylated by acid. Bromination of octamethylnapthalene in carbon disulfide at −78 °C to room temperature can be controlled to give a good yield of the 1,8-bis(bromomethyl)-, 1,4,5,8-tetrabromomethyl-, or octabromomethyl derivative. The observed orientations in these successive halogenations of octamethylnaphthalene are rationalized in terms of an electrophilic aromatic substitution mechanism involving attack at a C1 position, proton loss from a methyl substituent, and rearrangement of the resulting tertiary allylic halide.

Aromatic substitution in which a group is replaced at the α position of a side chain by an electrophilic rather than free-radical mechanism is now well known.[4] A pertinent example is the reaction of hexamethylbenzene (1) with chlorine in acetic acid (in the absence of light or a catalyst) to give chloromethylpentamethylbenzene (2).[5] Although free radicals may be detected in this reaction mixture,[6] there is strong evidence[7] that the reaction proceeds by an electrophilic mechanism, as shown.[8] Attack of a chlorine electrophile at a ring carbon can give the pentadienyl cation A, which may lose a



proton from the methyl substituent para to the position attacked by the electrophile[9] to give the tertiary allylic chloride B. Rearrangement of B to 2 probably occurs by an ion-pair mechanism.[7b]

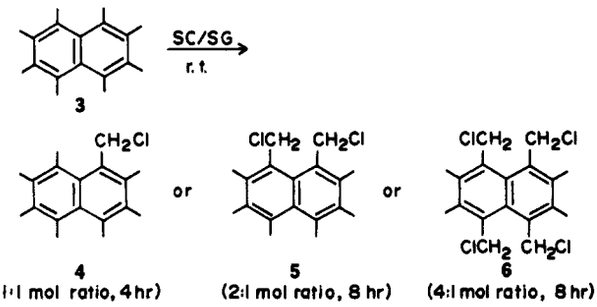
An interesting catalytic effect by silica gel on aromatic chlorinations by sulfuryl chloride was recently described.[10] Toluene, which gave only benzyl chloride when treated with sulfuryl chloride and benzoyl peroxide (free-radical mechanism),[11] gave only *o*- and *p*-chlorotoluene with sulfuryl chloride and silica gel. No trace of benzyl chloride was detected. Other chlorinations with this reagent were facilitated by electron-donating substituents and retarded by electron-withdrawing substituents on the aromatic ring, typical of an electrophilic mechanism.[10]

We decided to apply the sulfuryl chloride/silica gel reagent (SC/SG) to the chlorination of 1 with the idea that clean formation of 2 would tend to support the electrophilic mechanism for this reaction. Success with this reaction (vide infra) led us to also apply the SC/SG reagent to octamethylnaphthalene (3)[12] and, in addition, to study the bromination of 3. It is these halogenations of 3 which form the main body of this paper.

Results and Discussion

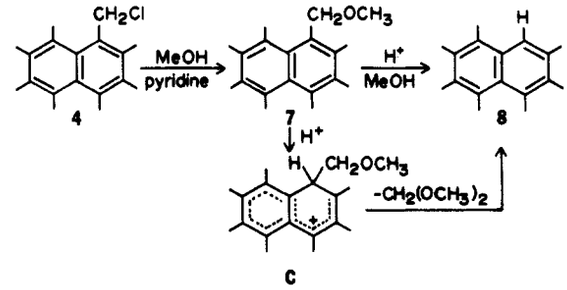
Chlorination of Hexamethylbenzene with SC/SG. Treatment of 1 in CCl_4 with an equimolar amount of sulfuryl chloride and silica gel at room temperature for 8 h gave a 96% yield of 2. When the silica gel was omitted, no chlorination occurred (<1% of 2 was formed in 72 h). Thus the catalytic effect of the silica gel is dramatic. Since the reagent is clearly electrophilic,[10] these results tend to support the Illuminati–Baciocchi mechanism[7] for the reaction.[13] The reaction is easy to work up, and constitutes an excellent synthetic method for 2. Use of excess chlorinating agent, in an attempt to obtain a high-yield synthesis of hexachloromethylbenzene,[14] gave mixtures and was not synthetically useful.

Chlorination of Octamethylnaphthalene with SC/SG. Chlorination of octamethylnaphthalene (3)[12] by SC/SG could be controlled to give an excellent yield of 1-chloromethylheptamethylnaphthalene (4), 1,8-bis(chloromethyl)hexamethylnaphthalene (5), or 1,4,5,8-tetrachloromethyltetramethylnaphthalene (6), depending on the sulfuryl chloride/3



mole ratio. All of the reactions were run at room temperature, and control experiments showed that the silica gel was catalytically effective.

Compound 4 was difficult to obtain pure. In an attempt to convert it to the corresponding methyl ether, it was refluxed for several hours in methanol. Instead of the methyl ether, a 95% yield of the known[15] 1,2,3,4,5,6,7-heptamethylnaphthalene (8) was obtained. Treatment of 4 with methanol

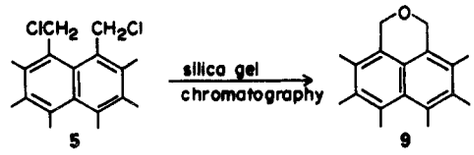


and pyridine, however, gave the desired methyl ether 7, which with a trace of acid in methanol quantitatively lost the methoxymethyl substituent. Apparently in the treatment of 4 with methanol in the absence of pyridine, the hydrogen chloride produced is sufficient to bring about dealkylation to

8. The monochlorination of 3 and dechloromethylation of 4 in refluxing methanol constitute by far the best synthetic route to 8 to date.

The ease with which 7 is converted to 8 is undoubtedly due to two factors. Considerable relief of peri strain[16] must be experienced when 7 is protonated to give C (3 itself is similarly protonated easily,[12] and indeed can be diprotonated at both peri positions[17]). The second step probably involves an S_N1 ionization of C to the stabilized methoxymethyl cation, with 8 as the leaving group. This mechanism seems more likely than an S_N2 displacement at the methylene carbon, since if this were the mechanism, 3 would also be expected to be rapidly dealkylated, whereas the reaction is much less efficient than with 7.[15b]

Compound 5 had an NMR spectrum which required a symmetric structure (three six-proton singlets for the methyl groups, and one four-proton singlet for the methylene protons). Since 5 could be prepared in high yield by the further chlorination of 4 with SC/SG, it had to have the chloromethyl groups in the 1,4, 1,5, or 1,8 positions. That the latter was the case was shown by the hydrolysis of 5 to a cyclic ether, 9.



5 9

The ^1H NMR spectrum of 6 taken at ambient temperature consisted of a sharp singlet at δ 2.50 for the four methyl groups and a broad singlet at δ 4.94 for the methylene protons.[18,19] The ^{13}C NMR spectrum of 6 consisted of only five lines, readily assigned to the methyl carbons, the methylene carbons, and three sets of aromatic carbons (see Experimental Section). Consequently 6 had to have a symmetric structure, with the chloromethyl groups either in the 1,4,5,8 or 2,3,6,7 positions. That the former was the case was shown by the high-yield synthesis of 6 by further chlorination of 5. Chromatography of 6 on silica gel converted it to the symmetric bisether 10, whose ^1H NMR spectrum showed two sharp singlets at δ 2.20 (methyls) and 4.93 (methylenes).

6 10

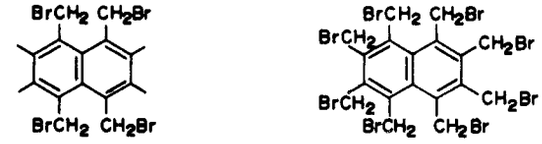
Although chlorination of 3 with a large excess of sulfuryl chloride and silica gel (mole ratios of SC/3 of 10:1) did result in chlorination beyond the tetrachloro stage, mixtures were obtained and no pure products were isolated.

Bromination of Octamethylnaphthalene. Octamethylnaphthalene is extremely susceptible to bromination. Indeed, it was not possible to limit the reaction to monobromination. For example, treatment of octamethylnaphthalene with 1 equiv of bromine in carbon disulfide at −78 °C for 1 h, followed by warming the mixture to room temperature (all of the bromine had reacted by the time the temperature reached 0 °C), gave in addition to recovered 3 a mixture of mono- (11) and di- (12) brominated products, the latter predominating. Compounds 11 and 12 could not be isolated as such from the mixture, nor could they be determined directly by NMR, owing to overlapping peaks. Therefore the mixture was analyzed as follows. One portion of the mixture was refluxed with methanol, then chromatographed on alumina to give recovered 3 and heptamethylnaphthalene 8 (derived from the dealkylation of 11). Another portion was chromatographed on silica gel, from which 9 (derived from 12) was isolated. In this way it was established that the product mixture consisted approximately of 20% recovered 3, 17% of 11, and 43% of 12.[20] Under no conditions that we tried could pure 11 be isolated.

11 12

Treatment of 3 with 2 equiv of bromine in carbon disulfide at −78 °C led to a product mixture which was predominantly the dibromide 12, although the mixture contained significant amounts of 11 and of the tetrabromo derivative 13. However, reasonably pure, crystalline 12 could be isolated by trituration with ether. The structure of 12 was clear from its NMR spectrum and its hydrolysis to 9.

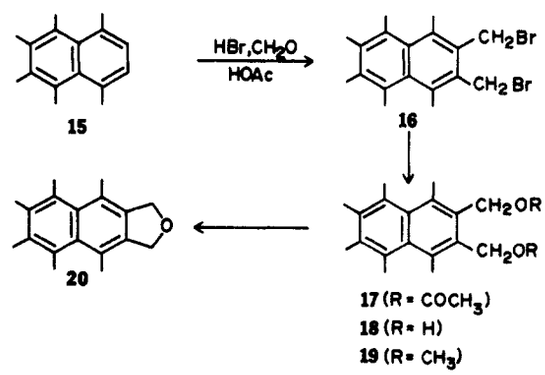
Bromination of 3 with 4 equiv of bromine in methylene chloride at 0 °C gave a good yield of the tetrabromo derivative 13. The ambient temperature ^1H NMR spectrum of 13 had a sharp singlet at δ 2.46 for the methyl groups, but the methylene protons appeared as broad singlets with equal areas at δ 4.73 and 5.10. These peaks coalesced to a sharp singlet at 80 °C, δ 4.91.[19]



13 14

Finally, treatment of 3 with excess bromine (12 equiv) at room temperature for several days gave a good yield of the octabromomethyl derivative 14 as a crystalline solid. At 100 °C, the ^1H NMR spectrum of 14 showed two sharp singlets with equal areas at δ 4.97 and 5.03 due to the two sets of methylene protons.[19] No pure compounds with more than four but fewer than eight bromines could be isolated by direct bromination of 3.

2,3-Bis(bromomethyl)hexamethylnaphthalene and Related Compounds. The structures of the 1,8-bis(halomethyl)hexamethylnaphthalenes 5 and 12 rest on symmetry arguments concerning their NMR spectra and on their hydrolysis to the pyran 9. In order to be absolutely certain about these structures, we decided to synthesize by an unambiguous route, for comparison with 9, the isomeric ether with the same symmetry, i.e., 20. Bromomethylation of 1,2,3,4,5,8-hexamethylnaphthalene(15)[12] gave the 2,3-bis(bromomethyl) derivative 16, whose NMR spectrum was very similar to but distinct from that of 12.



15 16 20

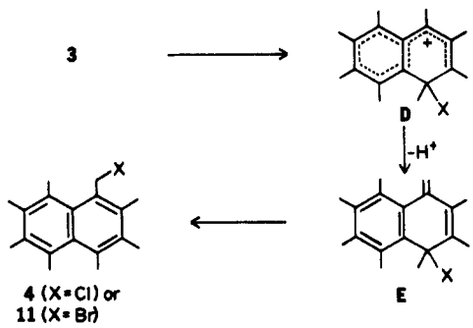
17 (R = $COCH_3$)
18 (R = H)
19 (R = CH_3)

In contrast with 5 and 12, 16 did not form a cyclic ether on direct hydrolysis, and an indirect route to 20 proved necessary.

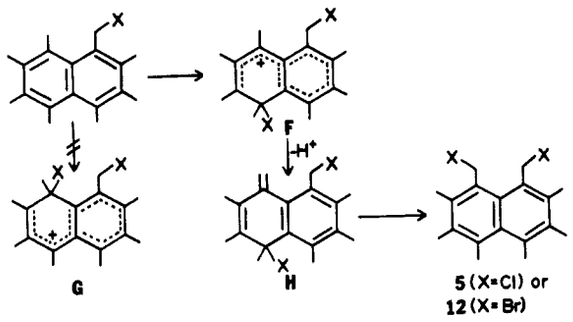
Treatment of **16** with silver acetate gave the diacetate **17** which was readily saponified to the crystalline diol **18**. Refluxing **18** in acidic methanol gave, instead of the hoped-for **20**, the crystalline bis(methoxymethyl) ether **19**. However, when **18** was heated with *p*-toluenesulfonic acid in 1,2-dichloroethane, the cyclic ether **20** was formed in modest yield. Although the properties of **9** and **20** were similar, they were not identical. In addition to a significant melting point difference, the methylene protons appeared at 0.20 ppm lower field in **20** than in **9** (the methyl protons appeared as three singlets with nearly identical chemical shifts in the two ethers).

The unequivocal structure of **20** from its synthesis, and its distinction from the ether **9** obtained from the dihalogenated octamethylnaphthalenes, clearly establish that dihalogenation of **3** occurred in the 1- and 8-methyl groups.

Mechanistic Considerations. The regiospecificity of these halogenations of octamethylnaphthalene is striking. Initial electrophilic attack at C1 is not surprising,[12,15b,21] since it is not only favored electronically but also relieves one 1,8-peri interaction in the formation of the presumed intermediate D. Of course the peri interaction is reintroduced in the substitution product, but this is compensated for by the energy gained from rearomatization of E.

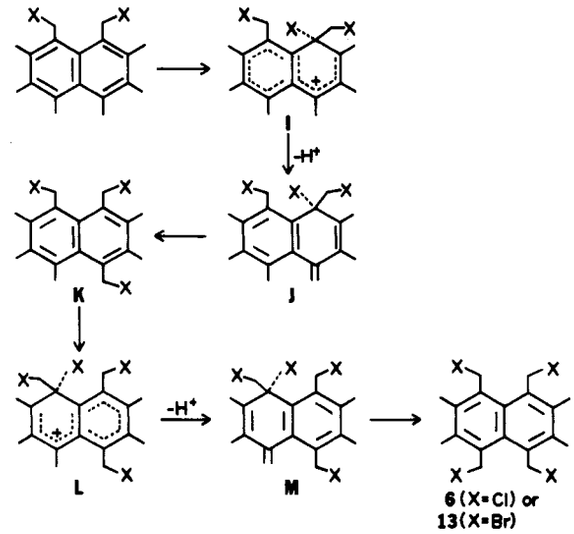


If the second substitution occurs by the same mechanism as the first, we must conclude that the first formed intermediate is F, not G. Because of the deactivating effect of the

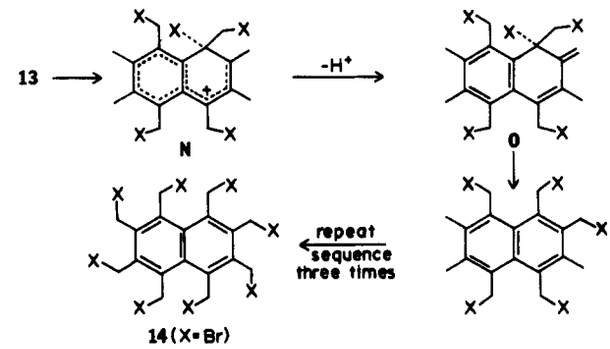


halomethyl group, the second substitution occurs in the other ring. F may be favored over G as a consequence of steric hindrance to attack at C8 or because any reasonable structure for G would involve an unfavorable interaction between the first X substituent (on the CH_2X group) and the peri X or methyl group.[22] Once the position of attack is determined and proton loss occurs (to give H), the product structure is set. In this way one can rationalize the selective formation of **5** or **12**, even though they are probably more strained than other possible dihalogenation products [such as the 1,5-bis(halomethyl) compound, which could be formed from G].

Using the same general mechanism, the tetrasubstituted products would be formed via intermediates I–M. The formation of I and L, which relieves the most severe peri interaction in their immediate precursors (**5** or **12** and K), determines the product structure.



Finally, we assume that the formation of the octabromomethyl derivative **14** occurs via intermediates analogous to I and L (i.e., electrophilic attack at a peri position) but that proton loss occurs from an *o*-methyl substituent.[23]



Although the sequence we have observed for the side-chain halogenation of octamethylnaphthalene might not have been predicted (i.e., 1; 1,8-; 1,4,5,8; 1-8), it can be adequately rationalized by an electrophilic mechanism.

The halogenated polymethylnaphthalenes which we have described here are novel compounds which promise to have considerable synthetic utility. They are readily accessible in high yield and gram quantities from octamethylnaphthalene. We are actively investigating their chemical and physical properties.

Experimental Section

^1H NMR spectra were measured at 60 MHz on a Varian T-60 or A56/60 spectrometer against tetramethylsilane as an internal standard. ^{13}C NMR spectra were determined on a Varian CFT-20 spectrometer. UV spectra were determined on a Unicam SP-800 spectrometer. IR spectra were determined on a Unicam SP-200 or Perkin-Elmer Model 167 spectrometer. Mass spectra were obtained with a Hitachi Perkin-Elmer RMU-6 spectrometer, operated by Mrs. Ralph L. Guile, to whom we are indebted. Elemental analyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich., and by Clark Microanalytical Laboratories, Urbana, Ill. Melting points are uncorrected.

Chlorination of Hexamethylbenzene (1) with Sulfuryl Chloride and Silica Gel. A solution of 1 (1.62 g, 10 mmol) in 25 mL of carbon tetrachloride to which were added in succession 0.35 g of Woelm silica gel, <0.063 mm, and 1.35 g (10 mmol) of sulfuryl chloride was stirred at room temperature for 8 h. The mixture was filtered and the organic solution was washed with saturated sodium bicarbonate solution and water and dried (Na_2SO_4). Removal of the solvent gave 1.9 g (96%) of essentially pure pentamethylbenzyl chloride (**2**), mp 79–80 °C recrystallized from hexanes.[24]

When the above procedure was followed but with the silica gel omitted, no **2** was obtained (<1% after 72 h).

1-Chloromethyl-2,3,4,5,6,7,8-heptamethylnaphthalene (4). A solution of octamethylnaphthalene[12] (3.014 g, 12.6 mmol) and sulfuryl chloride (1.72 g, 12.7 mmol) in 50 mL of carbon tetrachloride to which was added 0.69 g of silica gel (Woelm, <0.063 mm) was stirred at room temperature for 6 h. The solution was then washed with water (2 × 50 mL) and dried (Na_2CO_3). Removal of the solvent under vacuum left 3.3 g (96%) of crude **4**: mp 126–130 °C; NMR ($CDCl_3$) δ 2.28 (s, 9 H), 2.43 (s, 9 H), 2.67 (s, 3 H), 4.80 (s, 2 H, CH_2). The product decomposed slowly at room temperature, and was used without further purification.

If the silica gel was omitted from this preparation, it was necessary to heat the reaction mixture for 7 h at reflux to obtain **4**. The crude product was difficult to purify.

1-Methoxymethyl-2,3,4,5,6,7,8-heptamethylnaphthalene (7). A solution of crude **4** (1.0 g, 3.64 mmol) in 250 mL of ether containing 25 mL of methanol and 5 mL of pyridine was stirred (nitrogen atmosphere) for 24 h, then washed with 5% hydrochloric acid (2 × 50 mL) and dried (Na_2CO_3). Removal of the solvent under vacuum gave 590 mg (60%) of crude **7**, which was recrystallized from 95% ethanol: mp 90.5–92.0 °C; NMR ($CDCl_3$) δ 2.30 (s, 9 H), 2.38 (s, 3 H), 2.45 (s, 6 H), 2.60 (s, 3 H), 3.45 (s, 3 H, OCH_3), 4.40 (s, 2 H, CH_2); UV (95% EtOH) 254 nm (ε 121 000), 315 (14 300); IR (CCl_4) 2910 (br, s), 1460 (br, m), 1385 (m), 1350 (w), 1335 (m), 1150 (w), 1125 (m), 1095 (s), 995 (w), 910 cm^{-1} (w); mass spectrum (70 eV) *m/e* (rel intensity) 270 (67), 256 (64), 239 (64), 238 (100), 225 (58), 224 (95), 223 (81), 211 (40), 210 (30), 209 (84), 208 (30), 195 (25), 194 (24), 193 (39), 179 (34), 178 (22), 165 (31), 160 (47), 97 (23), 71 (51), 57 (62), 55 (42), 43 (47), 28 (60).

Anal. Calcd for $C_{19}H_{26}O$: C, 84.38; H, 9.68. Found: C, 84.26; H, 9.61.

When a solution of crude **4** (1.5 g, 5.46 mmol) in 50 mL of methanol containing 10 mL of pyridine was refluxed for 2 h, then worked up as above, only 200 mg (14%) of **7** was obtained.

1,2,3,4,5,6,7-Heptamethylnaphthalene (8). A. From 1-methoxymethyl-2,3,4,5,6,7,8-heptamethylnaphthalene. A solution of **7** (100 mg, 0.37 mmol) in methanol (10 mL) containing 1 drop of 37% aqueous hydrochloric acid was warmed for 10 min. The methanol was removed under vacuum and a solution of the residue in 20 mL of cyclohexane was filtered through alumina (a 1-in. plug of Woelm neutral alumina in a disposable pipet). The alumina was washed with cyclohexane (2 × 20 mL). Evaporation of the solvent from the combined cyclohexane solutions gave 81 mg (97%) of **8**: mp 135–136.5 °C (EtOH);[15a] NMR ($CDCl_3$) δ 2.27 (s, 9 H), 2.37 (s, 3 H), 2.50 (s, 9 H), 7.47 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 15.28, 16.21, 16.89, 17.13, 21.47, 21.97, 22.05 (methyl carbons), 122.01, 127.63, 128.76, 130.71, 131.10, 131.44, 132.86, 133.14, 133.49, 133.83 (aromatic carbons); UV (95% EtOH) λ_{max} 243 nm (ε 114 000), 303 (17 000); IR (CCl_4) 2940 (s), 1610 (w), 1590 (w), 1495 (m), 1450 (br, s), 1390 (m), 1330 (w), 1230 (w), 1135 (w), 1080 (m), 1030 (m), 1015 (s), 870 cm^{-1} (s); mass spectrum (70 eV) *m/e* (rel intensity) 226 (100), 211 (76), 181 (17), 179 (16), 165 (25), 113 (25), 89 (14), 26 (55).

Anal. Calcd for $C_{17}H_{22}$: C, 90.20; H, 9.80. Found: C, 90.26; H, 9.65.

B. From 1-Chloromethyl-2,3,4,5,6,7,8-heptamethylnaphthalene. A solution of crude **4** (1.0 g, 3.64 mmol) in 40 mL of methanol was refluxed for 3 h. The methanol was removed under vacuum and the crude residue was dissolved in 50 mL of cyclohexane. Filtration through a small alumina column (4 g, Woelm neutral) followed by elution with 100 mL of cyclohexane removed all the colored impurities. Evaporation of the solvent gave **8** (0.78 g, 95%). Further washing of the alumina with ether gave 20 mg of pyran **9**, presumably due to the presence of some **5** in the crude **4**.

1,8-Bis(chloromethyl)-2,3,4,5,6,7-hexamethylnaphthalene (5). A solution of octamethylnaphthalene[12] (240 mg, 1.0 mmol) and sulfuryl chloride (270 mg, 2.0 mmol) in 30 mL of carbon tetrachloride to which was added 27 mg of silica gel (Woelm, <0.063 mm) was stirred at room temperature for 8 h. The solution was washed with water (2 × 50 mL) and dried (Na_2CO_3). Removal of the solvent under vacuum gave 270 mg (87%) of crude **5** (light yellow crystals). Recrystallization from tetrahydrofuran gave **5** as colorless crystals: mp 184–185.5 °C; NMR ($CDCl_3$) δ 2.30 (s, 6 H), 2.42 (s, 6 H), 2.65 (s, 6 H), 4.72 (s, 4 H); UV (heptane) 256 nm (ε 112 000), 325 (16 000); IR (CCl_4) 2950 (s), 1460 (br, s), 1400 (m), 1375 (m), 1265 (s), 1240 (w), 1170 (m), 1070 cm^{-1} (m); mass spectrum 70 eV *m/e* (rel intensity) 312 (4), 310 (20), 308 (30), 275 (36), 273 (100), 234 (79), 233 (67), 221 (39), 220 (25), 219 (24), 207 (35), 206 (50), 192 (36).

Anal. Calcd for $C_{18}H_{22}Cl_2$: C, 69.90; H, 7.17. Found: C, 69.90; H, 7.22.

Compound **5** was obtained in 93% yield following a procedure exactly analogous to the above, but starting with **4** instead of **3** (reaction time 6 h).

1,4,5,8-Tetrachloromethyl-2,3,6,7-tetramethylnaphthalene (6). A solution of octamethylnaphthalene[12] (240 mg, 1 mmol) and sulfuryl chloride (540 mg, 4.0 mmol) in 30 mL of carbon tetrachloride to which was added 54 mg of silica gel (Woelm, <0.063 mm) was stirred at room temperature for 8 h. The solution was washed with water (2 × 50 mL) and dried (Na_2CO_3). Removal of the solvent under vacuum gave 340 mg (91%) of crude **6** as a light yellow solid. Recrystallization from tetrahydrofuran gave pure **6** as colorless crystals: mp 232–234 °C; NMR ($CDCl_3$) δ 2.50 (s, 12 H), 4.94 (br s, 8 H); ^{13}C NMR ($CDCl_3$) δ 16.77 (methyls), 44.74 (methylenes), 129.64 (aromatic C2,3,6,7), 133.26 (aromatic 4a,8a), 133.59 (aromatic C1,4,5,8); UV (heptane) 205 nm (ε 12 600), 257 (64 000), 331 (12 000); IR (CCl_4) 2930 (m), 1470 (br, m), 1390 (w), 1345 (w), 1260 (s), 1235 (w), 1185 (w), 1160 (w), 860 cm^{-1} (s); mass spectrum (70 eV) *m/e* (rel intensity) 384 (<1), 382 (2), 380 (10), 378 (21), 376 (17), 345 (13), 343 (35), 341 (37), 310 (12), 308 (45), 306 (67), 273 (35), 271 (100).

Anal. Calcd for $C_{18}H_{20}Cl_4$: C, 57.17; H, 5.33. Found: C, 57.28; H, 5.36.

Compound **6** was obtained in 93% yield following a procedure exactly analogous to the above, but starting with **5** instead of **3**.

4,5,6,7,8,9-Hexamethyl-1*H*,3*H*-naphtho[1,8-*cd*]pyran (9). Compound **5** (150 mg, 0.49 mmol) was subjected to preparative thin layer chromatography on silica gel (Brinkmann precoated glass plate, 2 mm) using chloroform as the solvent. A single spot was observed, R_f 0.4. The band was removed from the plate and extracted with methylene chloride to yield 120 mg (98%) of **9**: mp 194–198 °C; NMR ($CDCl_3$) δ 2.22 (s, 6 H), 2.30 (s, 6 H), 2.60 (s, 3 H), 5.00 (s, 4 H); UV (95% EtOH) 244 nm (ε 75 700), 305 (5660); IR (CCl_4) 3050 (s), 2950 (s), 2850 (m), 1470 (m), 1400 (m), 1143 (s), 1060 (m), 980 cm^{-1} (m); mass spectrum (70 eV) *m/e* (rel intensity) 254 (100), 239 (80), 225 (56), 211 (43), 195 (19), 179 (20), 165 (21).

Anal. Calcd for $C_{18}H_{22}O$: C, 84.99; H, 8.72. Found: C, 85.02; H, 8.69.

Pyran **9** was also prepared from the dibromide **12** by a similar procedure, or by column chromatography on alumina (15% chloroform in carbon tetrachloride as eluent) or by being heated at 40–70 °C for 0.5–1.0 h with aqueous base in tetrahydrofuran.

4,5,9,10-Tetramethyl-1,3,6,8-tetrahydro[2]benzopyrano[6,5,4-*def*][2]benzopyran (10). Compound **6** (150 mg, 0.40 mmol) was subjected to preparative thin layer chromatography on silica gel (Brinkmann precoated glass plate, 2 mm) using chloroform as the solvent. A single spot was observed, R_f 0.3. The band was removed from the plate and extracted with methylene chloride to yield 90 mg (84%) of **10**, which could be recrystallized from tetrahydrofuran. The sample did not melt below 310 °C but began to darken (dec) at 240 °C. NMR ($CDCl_3$) δ 2.20 (s, 12 H), 4.93 (s, 8 H); UV (95% EtOH) λ_{max} 241 nm (ε 85 000), 297 (4600); IR ($CHCl_3$) 2820 (s), 1600 (w), 1453 (m), 1397 (m), 1358 (m), 1332 (m), 1298 (m), 1120 (s), 1030 (s), 945 (s), 890 cm^{-1} (s); mass spectrum (70 eV) *m/e* (rel intensity) 268 (100), 267 (20), 253 (17), 252 (15), 239 (24), 211 (18), 210 (26).

Anal Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.53; H, 7.49.

This reaction was also accomplished on a larger scale by column chromatography of **6** on silica gel (Woelm, <0.063 mm) using chloroform as the eluent.

Attempted Monobromination of Octamethylnaphthalene. A solution of octamethylnaphthalene[12] (200 mg, 0.83 mmol) in 10 mL of carbon disulfide was cooled to −78 °C and a solution of bromine (134 mg, 0.83 mmol) in 6 mL of carbon disulfide was added dropwise with stirring. The solution was kept at −78 °C for 1 h, then was allowed to warm slowly. By the time the temperature reached 0 °C all of the bromine had reacted. The solution was diluted with 50 mL of methylene chloride, washed with saturated sodium bicarbonate solution (25 mL), and dried ($MgSO_4$). Removal of the solvents under vacuum left a residue (260 mg) which was divided into two equal parts.

One part (130 mg) was refluxed for 2 h in 15 mL of methanol. Removal of the solvent under vacuum gave a solid residue which was digested with 25 mL of hexanes and chromatographed on Woelm neutral alumina (1-in. plug in a disposable pipet) to remove any oxygen-containing products. The column was washed with another 25 mL of hexanes and the hexanes were removed under vacuum. The residue (36 mg) was analyzed by NMR (integration of the aromatic hydrogen of **8** at δ 7.47 against the aromatic methyl region). It contained 43% of **8** and 57% of recovered **3**.

The other part (130 mg) was subjected to preparative thin layer chromatography (2.0 mm Brinkmann precoated silica gel plates) using chloroform as the eluent. The band with R_f 0.4 was extracted with methylene chloride and worked up to give 45 mg of pure **9**.

These results correspond to the formation of 20% recovered **3**, 17%

of 11, and 40% of 12 in the bromination experiment.

1,8-Bis(bromomethyl)-2,3,4,5,6,7-hexamethylnaphthalene (12). A solution containing 480 mg (2 mmol) of octamethylnaphthalene[12] in 5 mL of carbon disulfide in a flask wrapped with aluminum foil was cooled to −78 °C, and a solution containing 640 mg (4 mmol) of bromine in 5 mL of carbon disulfide was added dropwise with stirring. After 2 h the reaction was stopped by quenching in aqueous sodium bisulfite. The organic layer was separated, diluted with chloroform, washed with 5% sodium bicarbonate, and dried ($MgSO_4$). Evaporation of the solvent left a viscous residue which contained approximately 20% 11, 70% 12, and 10% 13.[25] Dilution with a little ether lead to the isolation of 450 mg (57%) of 12: mp 165–170 °C; NMR ($CDCl_3$) δ 2.35 (s, 6 H), 2.50 (s, 6 H), 2.75 (s, 6 H), and 4.85 (s, 4 H); mass spectrum (70 eV) *m/e* (rel intensity) 400 (4), 398 (10), 396 (4), 320 (5), 319 (14), 318 (8), 317 (14), 316 (5), 240 (12), 239 (31), 238 (100), 237 (49), 236 (16), 223 (45), 207 (30), 193 (26).

Anal. Calcd for $C_{18}H_{22}Br_2$: C, 54.59; H, 5.60. Found: C, 54.47; H, 5.63.

1,4,5,8-Tetrabromomethyl-2,3,6,7-tetramethylnaphthalene (13). To a solution of octamethylnaphthalene[12] (240 mg, 1.0 mmol) in 30 mL of methylene chloride cooled in an ice bath was added dropwise a solution of bromine (640 mg, 4.0 mmol) in 10 mL of methylene chloride. The solution was allowed to warm to room temperature (1.5 h), then was washed with saturated aqueous sodium bicarbonate (2 × 50 mL) and dried ($MgSO_4$). Removal of the solvent under vacuum left 483 mg (87%) of 13 as a light yellow solid. Recrystallization from tetrahydrofuran gave pure 13 as a colorless solid: mp 180 °C dec; NMR ($CDCl_3$) δ 2.46 (s, 12 H), 4.73 (br s, 4 H), 5.10 (br s, 4 H); in CCl_4 at 80 °C the broad singlets coalesce to a sharp singlet at δ 4.91; UV (heptane) λ_{max} 211 nm (ε 39 000), 262 (58 000), 347 (16 000); IR (KBr) 2950 (s), 1460 (s), 1390 (m), 1210 (s), 1170 (m), 910 (w), 890 (m), 860 (s), 815 (w), 730 (m), 700 (w), 660 cm^{-1} (s); mass spectrum (70 eV) *m/e* (rel intensity) 559, 557, 555, 553, 551 (very weak, rel intensity could not be determined), 478, 476, 474, 472 (all <1%, ratio 1:2:2:1), 397 (s), 395 (10), 393 (5), 316 (35), 314 (35), 237 (25), 236 (86), 235 (30), 221 (100), 206 (37), 205 (40), 191 (30), 190 (20), 189 (26).

Anal. Calcd for $C_{18}H_{20}Br_4$: C, 38.88; H, 3.63. Found: C, 38.88; H, 3.62.

Octabromomethylnaphthalene (14). To a solution of octamethylnaphthalene[12] (100 mg, 0.42 mmol) in 30 mL of carbon disulfide cooled in an ice bath was added dropwise 810 mg (5.04 mmol) of bromine and the stirred solution was allowed to warm to room temperature. The flask was protected with a drying tube (Drierite) and the mixture was stirred for 3 days. The reaction was monitored by NMR; if a sharp peak at δ 2.46 remained (due to tetrabromide 13), more bromine (~100 mg) was added and the mixture was stirred for another day. When the singlet at δ 2.46 was absent the mixture was diluted with methylene chloride (70 mL), washed successively with saturated aqueous sodium bisulfite (2 × 100 mL) and saturated sodium bicarbonate (2 × 100 mL), and dried ($MgSO_4$). Evaporation of the solvent under vacuum left a yellow solid which was recrystallized from chloroform to give 265 mg (71%) of pure 14: mp 253–258 °C dec; NMR ($CDCl_3$, 41 °C) δ 4.90 (br s, 8 H), 5.17 (br s, 8 H); in tetrachloroethylene at 100 °C there were two sharp singlets at δ 4.97 and 5.03 (8 H each); UV (cyclohexane) λ_{max} 218 nm (ε 37 600), 292 (92 400), 354 (13 200).

Anal. Calcd for $C_{18}H_{16}Br_8$: C, 24.80; H, 1.85. Found: C, 24.72; H, 1.81.

2,3-Bis(bromomethyl)-1,4,5,6,7,8-hexamethylnaphthalene (16). Dry hydrogen bromide was bubbled through a suspension of paraformaldehyde (300 mg) in glacial acetic acid (5 mL) until the solution turned clear. To this solution was added a solution of 1,2,3,4,5,8-hexamethylnaphthalene[12] (212 mg, 1.0 mmol) in 5 mL of glacial acetic acid. The mixture was stirred for 2 h at 35 °C and for 1 h at 45 °C during which time a white solid precipitated. The mixture was poured onto ice and the solid was filtered, washed with water, and dissolved in methylene chloride. The solution was washed successively with aqueous sodium bicarbonate and water and dried ($MgSO_4$). Evaporation of the solvent and recrystallization of the residue from ether and chloroform gave 263 mg (66%) of 16: mp 182–184 °C; NMR ($CDCl_3$) δ 2.30 (s, 6 H), 2.50 (s, 6 H), 2.62 (s, 6 H), 4.90 (s, 4 H); IR (CCl_4) 3010 (m), 2920 (br, s), 1480 (m), 1442 (m), 1390 (s), 1380 (m), 1342 (m), 1210 (s), 1197 (s), 1150 (m), 985 (m), 695 (m), 625 cm^{-1} (m); UV (cyclohexane) λ_{max} 278 nm (ε 64 000), 250 (sh); mass spectrum (70 eV) *m/e* (rel intensity) 400 (6), 398 (11), 396 (6), 320 (11), 319 (43), 318 (19), 317 (43), 240 (8), 239 (30), 238 (100), 237 (25), 236 (19), 223 (43), 208 (30), 207 (25), 193 (30).

Anal. Calcd for $C_{18}H_{22}Br_2$: C, 54.59; H, 5.60. Found: C, 54.58; H, 5.67.

2,3-Bis(acetoxymethyl)-1,4,5,6,7,8-hexamethylnaphthalene (17). Silver acetate was precipitated by adding excess aqueous potassium acetate to a solution of silver nitrate (1 g). The solid was filtered, washed (three times) with glacial acetic acid, then diluted with glacial acetic acid to which acetic anhydride was added to ensure the absence of water. Dibromide 16 (800 mg, 2 mmol) was added and the mixture was kept at 100–110 °C for 7 h. The precipitated silver bromide was removed by filtration. The filtrate was concentrated under vacuum and the residue was chromatographed on alumina with ether–hexane (1:1) as eluent to give the diacetate 17 in nearly quantitative yield: NMR ($CDCl_3$) δ 2.10 (s, 6 H, acetyl methyls), 2.37 (s, 6 H), 2.50 (s, 6 H), 2.60 (s, 6 H); IR (CCl_4) 2940 (m), 1730 (s), 1380 (m), 1240 (br, s), 1030 (m), 970 cm^{-1} (w); UV (95% EtOH) λ_{max} 252 nm (ε 107 000), 315 (7900); mass spectrum (70 eV) *m/e* (rel intensity) 356 (51), 296 (39), 254 (40), 253 (40), 236 (100).

Anal. Calcd for $C_{22}H_{28}O_4$: C, 74.13; H, 7.92. Found: C, 74.25; H, 7.92.

2,3-Bis(hydroxymethyl)-1,4,5,6,7,8-hexamethylnaphthalene (18). The diacetate 17 (712 mg, 2 mmol) was dissolved in a mixture of ethanol (30 mL) and 10% aqueous sodium hydroxide (30 mL) and the solution was heated at 100 °C for 2 h. The usual saponification workup gave 450 mg (82%) of diol 18, mp 178–180 °C from chloroform–petroleum ether (bp 30–60 °C): NMR ($CDCl_3$) δ 2.37 (s, 6 H), 2.50 (s, 6 H), 2.60 (s, 6 H), and 4.97 (s, 4 H); IR (KBr) 3350 (s), 2950 (s), 1580 (w), 1490–1100 (several bands, m), 1000 cm^{-1} (s); UV (95% EtOH) λ_{max} 257 nm (ε 144 000), 315 (13 000); mass spectrum (70 eV) *m/e* (rel intensity) 272 (35), 254 (100), 239 (43), 225 (45), 211 (31), 195 (20), 179 (22), 165 (23).

Anal. Calcd for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88. Found: C, 79.36; H, 8.85.

2,3-Bis(methoxymethyl)-1,4,5,6,7,8-hexamethylnaphthalene (19). To a solution of the diol 18 (100 mg, 0.37 mmol) in 10 mL of absolute methanol was added 2 drops of concentrated hydrochloric acid, and the mixture was refluxed for 12 h. The mixture was diluted with methylene chloride, washed successively with water, dilute sodium carbonate, and water, and dried ($MgSO_4$). Chromatography on alumina with 1:1 ether–petroleum ether as eluent gave 50 mg (45%) of the dimethyl ether 19: mp 96–97 °C; NMR ($CDCl_3$) δ 2.30 (s, 6 H), 2.46 (s, 6 H), 2.60 (s, 6 H), 3.43 (s, 6 H, methoxyls), 4.66 (s, 4 H); IR (CCl_4) 2900 (br, s), 2810 (m), 1470 (m), 1443 (m), 1402 (m), 1385 (m), 1360 (w), 1340 (w), 1190 (s), 1150 (w), 1090 (br, s), 985 (m), 945 cm^{-1} (s); UV (95% EtOH) λ_{max} 256 nm (ε 80 000), 314 (6900); mass spectrum (70 eV) *m/e* (rel intensity) 300 (100), 268 (86), 253 (94), 238 (40), 225 (25), 223 (25), 207 (27).

Anal. Calcd for $C_{20}H_{28}O_2$: C, 79.95; H, 9.39. Found: C, 79.87; H. 9.39.

4,5,6,7,8,9-Hexamethyl-1,3-dihydronaphtho[2,3-*c*]furan (20). To a solution of diol 18 (100 mg, 0.37 mmol) in 10 mL of 1,2-dichloroethane was added 10 mL of a saturated solution of *p*-toluenesulfonic acid in the same solvent. The mixture was heated at 40–50 °C for 1 h, then washed with water and dried ($MgSO_4$). Evaporation of the solvent and chromatography of the residue on alumina with 30:70 ether–petroleum ether as the eluent gave 28 mg (30%) of 20, mp 180 °C dec, recrystallized from tetrahydrofuran: NMR ($CDCl_3$) δ 2.20 (s, 6 H), 2.30 (s, 6 H), 2.60 (s, 6 H), 5.20 (s, 4 H); IR (CH_2Cl_2) 2930 (m), 1390 (m), 1350 (m), 1090 (s), 1060 (s), 1000 cm^{-1} (m); uv (THF) λ_{max} 260 nm (ε 58 000), 311 (5200); mass spectrum (70 eV) *m/e* (rel intensity) 254 (1), 240 (30), 239 (54), 238 (100), 225 (14), 224 (13), 223 (50), 209 (15), 208 (30), 207 (18), 193 (35).

Anal Calcd for $C_{18}H_{22}O$: C, 84.99; H, 8.72. Found: C, 84.91; H, 8.83.

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Registry No.—1, 87-85-4; 2, 484-65-1; 3, 18623-61-5; 4, 62571-58-8; 5, 62571-59-9; 6, 62571-60-2; 7, 62571-61-3; 8, 56908-82-8; 9, 62571-62-4; 10, 62571-63-5; 12, 62571-64-6; 13, 62601-32-5; 14, 62571-65-7; 15, 36230-30-5; 16, 62571-66-8; 17, 62571-67-9; 18, 62571-68-0; 19, 62571-69-1; 20, 62571-70-4; sulfuryl chloride, 7791-25-5.

References and Notes

(1) For a brief preliminary account of a portion of the work presented here, see H. Hart and J. L. Reilly, *Tetrahedron Lett.*, 143 (1977).
(2) We acknowledge with thanks partial support of this research by the National Science Foundation (GP 43659-X) and the National Institutes of Health (GM 15997).
(3) Taken in part from the Ph.D. Thesis of J. B-C. Jiang, Michigan State University, 1975.
(4) For reviews see (a) S. R. Hartshorn, *Chem. Soc. Rev.*, 3, 167 (1974); (b)

E. Baciocchi and G. Illuminati, *Prog. Phys. Org. Chem.*, **5**, 1 (1967); (c) H. Suzuki, *Bull. Inst. Chem. Res., Kyoto Univ.*, **50**, 423 (1972).
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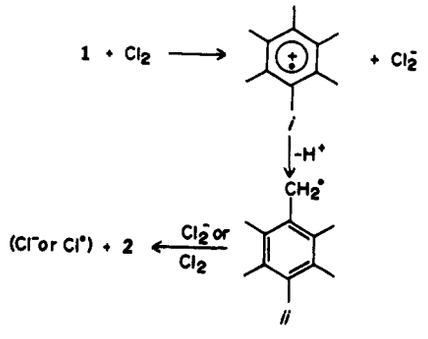
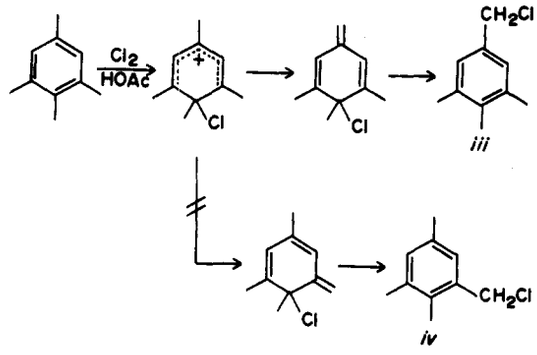
(8) In an alternative mechanism proposed by Kochi,[6] electron transfer occurs between hexamethylbenzene and chlorine to generate radical cation I and Cl_2^-. Proton loss gives the pentamethylbenzyl radical II which was detected by ESR.



Although this mechanism appears plausible, it does not readily explain the competitive formation of acetates and chlorides unless one adds a step in which II is further oxidized to a pentamethylbenzyl cation (which may then react with either acetate or chloride). Additional evidence against the radical-ion mechanism is given in ref 7.
(9) In principle, proton loss could occur from either a para or an ortho substituent. However, evidence in other cases indicates that loss from a para substituent is favored. For example, analogous chlorination of isodurene gives 3,4,5-trimethylbenzyl chloride (III) and not the 2,3,5-trimethyl isomer (IV).[7a]



(10) M. Hojo and R. Masuda, *Synth. Commun.*, **5**, 169 (1975).
(11) M. S. Kharasch and H. C. Brown, *J. Am. Chem. Soc.*, **61**, 2142, 3432 (1939); **62**, 925 (1940).
(12) H. Hart and A. Oku, *J. Org. Chem.*, **37**, 4269 (1972).
(13) The chlorination was also carried out in an ESR spectrometer. No free radicals were detected (private communication from Professor Gerald Babcock, Michigan State University).
(14) H. J. Backer, *Recl. Trav. Chim. Pays-Bas*, **55**, 591 (1936).
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(16) For reviews, see V. Balasubramaniyan, *Chem. Rev.*, **66**, 567 (1966); J. F. Liebman and A. Greenberg, *Ibid.*, **76**, 311 (1976).
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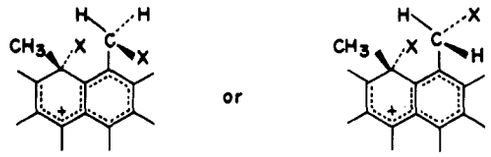
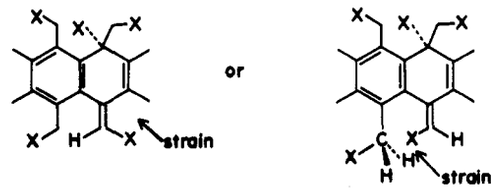
(18) The singlet at δ 4.94 sharpened when the temperature was raised to 75 °C.
(19) The ^1H NMR spectra of **4**, **5**, **6**, **7**, **12**, **13**, and **14** vary with temperature; a full discussion is reserved for a separate paper.
(20) These percentages are based on isolated, pure **3**, **8**, and **9**, respectively.
(21) H. Hart and A. Oku, *J. Org. Chem.*, **37**, 4274 (1972).
(22) For example, reasonable representations of G might be



in which the first X (in CH_2X) interacts unfavorably with either the CH_3 or X group, respectively, on the adjacent peri carbon atom. Such interactions are avoided in F.
(23) One might a priori expect proton loss to be preferred from the para position because the methylene protons of the CH_2X group should be more acidic than those of a methyl group. However, loss of a proton from the CH_2X group would give either of two products, each of which is appreciably more strained than O.



Consequently, loss of a proton from an *o*-methyl group is preferred.
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(25) The mixture, in a separate smaller scale run, was analyzed in part by NMR and in part by conversion of **12** to **9** with silica gel chromatography.

Bromovinyl Cations in Bromination. Similarity of Solvent Effects in Limiting Solvolysis and in Bromination of Olefins and Acetylenes

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Solvent effects on styrene (S) and phenylacetylene (PA) bromination have been reinvestigated. Contrary to results by previous authors, the rate-constant ratio, $k_{C=C}/k_{C\equiv C}$, does not vary significantly when the solvent passes from acetic acid to methanol, 70 and 50% aqueous methanol and water. The correlation, $\log k_{PA} = 0.95 \log k_S - 3.26$, obtained when the solvent is varied, shows that the solvent effects on bromination via bromocarbonium ions and vinyl bromocarbonium ions are very similar. The m values for styrene and phenylacetylene are 1.20 and 1.15, respectively, at 25 °C. These results suggest that the Ad_ECl mechanism of olefin bromination is also valid in acetylene bromination. In this mechanism, the role of the solvent (electrophilic assistance to the departure of the bromide ion) is consistent with the fact that m values are high and similar for styrene and phenylacetylene bromination. The differences between the reactivity ratio $k_{C=C}/k_{C\equiv C}$ in bromination (10^3) and in hydration (1) is discussed in terms of transition-state structure and of a destabilizing influence of the C_β–Br bond which is greater in the vinyl cation than in the saturated carbonium ion.

On the basis of the similarity of solvent effects on olefin bromination and on limiting solvolysis, we suggested[1] that bromination could be a convenient reaction for studying carbonium ions because solvent nucleophilic assistance is absent in free bromine additions. In the case of vinylcarbonium ions, this proposal would be of particular interest, since