

TABLE I

17	18	19
8.70 (3, d, $J = 8.0$ Hz)	8.58 (3, d, $J = 7.0$ Hz)	8.62 (3, d, $J = 7.5$ Hz)
7.72 (3, s)	7.70 (3, s)	7.73 (3, s)
7.68 (3, s)		
7.58 (6, s)	7.50 (3, s)	7.57 (3, s)
7.42 (6, s)	7.35 (3, s)	7.48 (3, s)
	7.23 (3, s)	7.32 (3, s)
7.00 (3, br s)	6.92 (3, br s)	6.98 (3, br s)
5.58 (1, q, $J = 8.0$ Hz)	5.53 (1, br q)	5.50 (1, br q)
	2.43 (2, q, $J = 6$ Hz)	2.43 (1, m)
		1.72 (1, m)

*Anal.* Calcd for  $C_{20}H_{24}Br_4$ : C, 41.13; H, 4.14. Found: C, 41.37; H, 4.20.

The cyclohexane solution obtained after the removal of 14 was chromatographed on silica gel with cyclohexane eluent to give 1.95 g (59%) of 15: mp 121.5–122.5° from petroleum ether; ir 1645 (m), 1610 (m), 1460 (s), 1380 (m), 918 (vs), 680  $cm^{-1}$  (s);  $\lambda_{max}^{hexane}$  270 nm (sh, log  $\epsilon$  3.95), 267 (sh, 4.30), 245 (4.67), 218 (sh, 4.20); nmr  $\tau$  8.23 (3, d,  $J = 0.8$  Hz), 8.13 (3, d,  $J = 0.8$  Hz), 7.88 (12, br s), 7.75 (3, s), 5.17 (1, d,  $J = 1.8$  Hz), 4.90 (1, d,  $J = 1.8$  Hz).

*Anal.* Calcd for  $C_{15}H_{22}Br$ : C, 68.88; H, 6.99. Found: C, 68.91; H, 6.93.

**Protonation of Octamethylnaphthalene.**<sup>16</sup>—The nmr spectra of ions 17–19 derived from octamethylnaphthalene and the 1,2,3,4,5,8- and 1,2,3,4,5,6-hexamethylnaphthalenes in trifluoroacetic acid are shown in Table I.

The reference compound was tetramethylammonium tetrafluoroborate, assigned  $\tau$  6.87. The spectrum of 17 was unchanged after 24 hr, but that of 18 and 19 broadened and became complex after 1.5 hr at room temperature. When solutions containing ions 17–19 were quenched (the last two within 30 min) the parent hydrocarbons were recovered unchanged. The nmr spectrum of 1,2,3,4-tetramethylnaphthalene in trifluoroacetic acid, even after standing overnight, was identical with that obtained in carbon tetrachloride, except for a slight solvent shift.

**Registry No.**—1, 18623-61-5; 3, 17384-74-6; 4, 36230-30-5; 7, 17384-75-7; 8, 17384-76-8; *endo*-9, 36744-72-6; *exo*-9, 36744-73-7; 10, 36870-60-7; 11, 36794-90-8; 12, 36900-85-3; 13, 36230-32-7; 14, 36807-30-4; 15, 36794-92-0; 17, 36812-96-1; 18, 36863-00-0; 19, 36863-01-0; 20, 36794-93-1; dibromocarbene, 4371-77-1.

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## Electrophilic Oxidation of Octamethylnaphthalene

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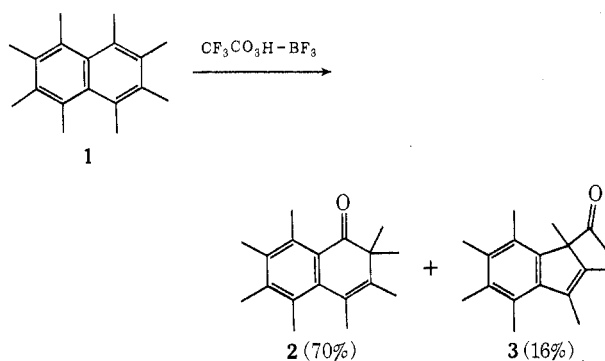
Received June 6, 1972

Oxidation of octamethylnaphthalene (1) with peroxytrifluoroacetic anhydride–boron fluoride occurred exclusively at the  $\alpha$  position, to give 2,2,3,4,5,6,7,8-octamethyl-1(2*H*)naphthalenone (2, 70%) and 1-acetyl-1,2,3,4,5,6,7-heptamethylindene (3, 16%), formed as a result of methyl and aryl migration, respectively.

In the preceding paper<sup>1</sup> we described a five-step synthesis of octamethylnaphthalene (1) from hexamethylbenzene, in an overall yield over 50%. This synthesis made possible a study of the electrophilic oxidation of 1 with peroxytrifluoroacetic acid–boron fluoride,<sup>2</sup> done for the purpose of comparing the reactivity of 1 with that of hexamethylbenzene<sup>3</sup> and 1,2,3,4-tetramethylnaphthalene.<sup>4</sup> It was anticipated that 1 would be highly susceptible to electrophilic oxidation not only because of the electron-donating effect of the methyl groups, but because the peri methyl interactions might distort the aromatic  $\pi$  system. The oxidation did have several unusual features, including the ring contraction of the naphthalene ring system to an indene.

### Results

Treatment of 1 with peroxytrifluoroacetic acid–boron fluoride gave one major and one minor product, assigned structures 2 and 3, respectively. A third product, isolated in 14% yield, is the result of reaction of a second mole of oxidant with one of the primary prod-



ucts, and its structure will be discussed separately below.

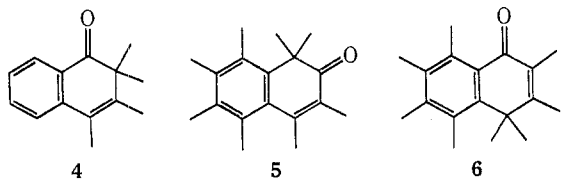
The major product (2) had ir and uv spectra which are characteristic of an unsaturated ketone and similar to those of 4, the principal electrophilic oxidation product of 1,2,3,4-tetramethylnaphthalene.<sup>4</sup> The nmr spectrum of 2 had a sharp singlet for the *gem*-dimethyl group at  $\tau$  8.88, two homoallylically coupled methyl signals at  $\tau$  8.21 and 8.02 ( $J = 1.1$  Hz), three aromatic methyl protons in a broad singlet at  $\tau$  7.78, and one sharp aromatic methyl singlet at  $\tau$  7.70, consistent with the assigned structure. The alternative structure 5 (a possible product of  $\beta$  electrophilic attack, the analog of which was a minor oxidation product of 1,2,3,4-tetramethylnaphthalene<sup>4</sup>) and 6 (a possible

(1) A. Oku, T. Kakhana, and H. Hart, *J. Amer. Chem. Soc.*, **89**, 4554 (1967); H. Hart and A. Oku, *J. Org. Chem.*, **37**, 4269 (1972).

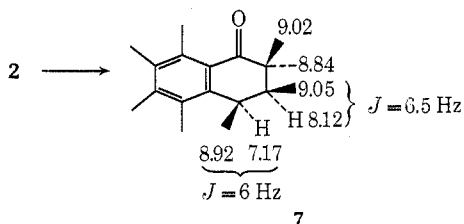
(2) For a review of oxidations with this reagent, see H. Hart, *Accounts Chem. Res.*, **4**, 337 (1971).

(3) H. Hart, P. M. Collins, and A. J. Waring, *J. Amer. Chem. Soc.*, **88**, 1005 (1966).

(4) H. Hart and R. K. Murray, Jr., *J. Org. Chem.*, **32**, 2448 (1967).

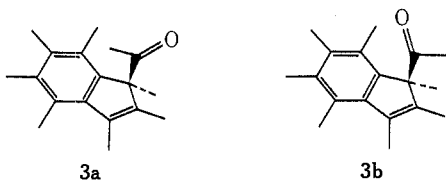


product of  $\alpha$  electrophilic attack followed by an overall 1,4-methyl shift) were excluded by the observation that **2** did not undergo any hydrogen-deuterium exchange on prolonged reflux with sodium methoxide in  $\text{CH}_3\text{OD}$ . If the structure were either **5** or **6**, the methyl protons at the terminus of the  $\alpha,\beta$ -unsaturated ketone moiety would have been exchanged. Finally, catalytic hydrogenation of **2** gave a dihydro compound whose nmr spectrum is consistent with the expected structure **7**.



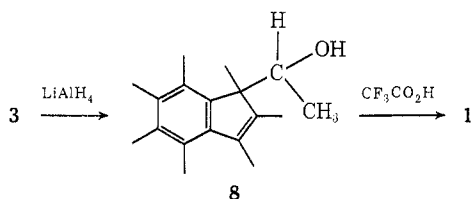
The ir spectrum of the minor oxidation product of octamethylnaphthalene had a  $\nu_{\text{C=O}}$  at  $1695\text{ cm}^{-1}$ , a little low for a simple ketone, possibly suggesting some homoconjugation. The uv spectrum showed that there was no direct conjugation of the carbonyl group. The nmr spectrum had bands at  $\tau$  8.30 and 7.73 for two homoallylically coupled methyl groups ( $J = 1.1\text{ Hz}$ ), four singlets corresponding to aromatic methyl groups at  $\tau$  7.93, 7.84, 7.82, and 7.53, and two sharp aliphatic methyl singlets at  $\tau$  8.73 and 8.57. The latter signal was completely eliminated when **3** was refluxed with sodium methoxide in  $\text{CH}_3\text{OD}$ ; no other change in the nmr spectrum of **3** resulted from this treatment. This result requires that the singlet at  $\tau$  8.57 be due to an acetyl group, despite its high chemical shift.

These data cannot be accommodated by any reasonable alternative structure to **3**. The high chemical shift of the acetyl methyl suggests that the favored conformation may be **3a**, not **3b**; the methyl is then placed



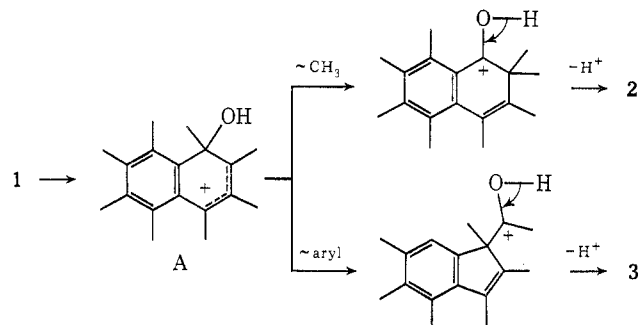
in the shielding region of the indene ring system. Consistent with this notion, catalytic hydrogenation of **3** gave a dihydro derivative in which the acetyl methyl group was shifted downfield to a more normal region ( $\tau$  8.10). Alternative rationalizations of the high acetyl methyl shift in **3** are possible.

Reduction of **3** with lithium aluminum hydride gave a secondary alcohol **8** which, when treated with tri-

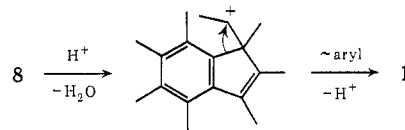


fluoroacetic acid, dehydrated with rearrangement to give octamethylnaphthalene, as well as some other products which were not investigated.

The formation of **2** and **3** as the major monooxidation products of octamethylnaphthalene can be rationalized



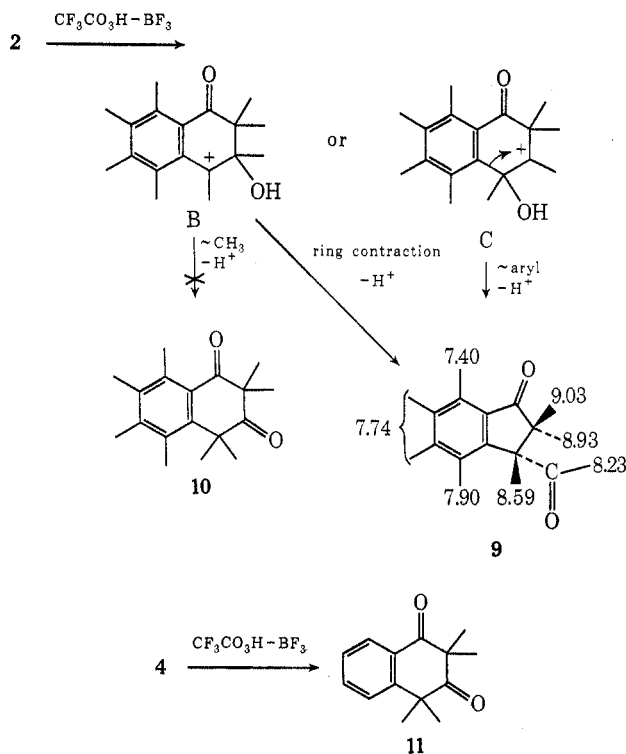
by an electrophilic attack at a peri position followed by methyl or aryl migration, respectively. We believe that this is the first example of conversion of a naphthalene to an indene on electrophilic attack. The analogous reaction was not observed during the oxidation of 1,2,3,4-tetramethylnaphthalene,<sup>4</sup> which suggests that one driving force may be the additional relief from the second peri interaction that is obtained when one of the rings is contracted. However the driving force for rearomatization can overcome the peri interactions, as shown by the conversion of **8** to **1** in acid. Finally,



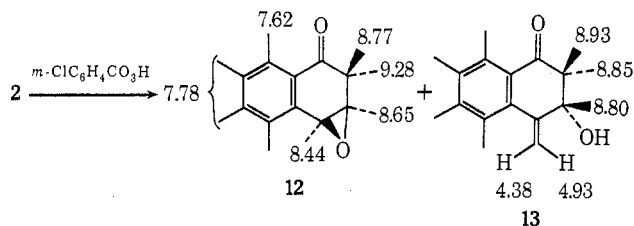
in contrast with 1,2,3,4-tetramethylnaphthalene, no oxidation product was obtained from **1** corresponding to  $\beta$  attack by the electrophile. Such attack would not give any relief from the peri interactions such as is experienced in the intermediate benzenonium ion A.

The overoxidation product of **1** contained one more oxygen atom than **2** or **3**. Its uv spectrum was similar to that of indanone, and the ir spectrum had a  $\nu_{\text{C=O}}$  at  $1700\text{ cm}^{-1}$  but no  $\text{C=C}$  absorption. The nmr spectrum showed four aromatic methyl groups [ $\tau$  7.90, 7.74 (6 H), and 7.40] and four additional sharp methyl singlets at  $\tau$  9.03, 8.93, 8.59, and 8.23. The only change brought about by treatment with sodium methoxide in  $\text{CH}_3\text{OD}$  was the complete removal of the  $\tau$  8.23 signal, suggesting the presence of one acetyl group, and this was confirmed by a positive iodoform test. Finally, oxidation of **2** with peroxytrifluoroacetic acid-boron fluoride gave the same overoxidation product in good yield. These data suggest that the structure of this product is **9**. This product could arise from intermediates such as B or C. In the tetramethylnaphthalene series, the sole overoxidation product of **4** (the analog of **2**) was the dione **11**.<sup>4</sup> The corresponding reaction of **2** to give **10** was not observed in the octamethyl series, possibly because of the severe repulsion which would exist between the *gem*-dimethyl group and the adjacent aromatic methyl group in **10**. If **9** is formed *via* the less likely nonbenzylic intermediate C, then aryl migration wins out over methyl migration, which would lead to a strained and unobserved 1,4-dione.

In an attempt to synthesize **9** more directly, the primary oxidation product **2** was treated at room tempera-



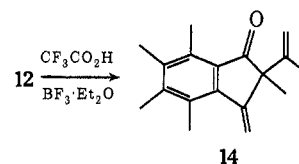
ture with *m*-chloroperbenzoic acid. Two products were obtained; the yield of each depended very sensitively on the reaction conditions. The structures tentatively assigned to these products are 12 and 13, which could



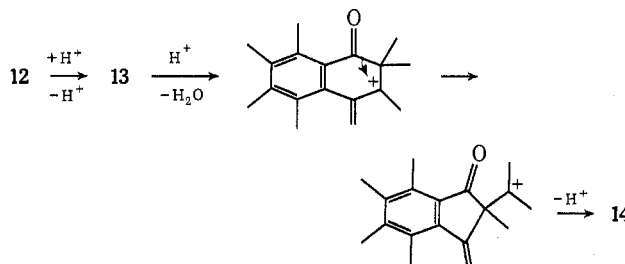
be obtained in yields as high as 83 and 70%, respectively. The structures are assigned from spectral data and mechanistic considerations. The epoxy ketone 12 had a  $\nu_{\text{C}=\text{O}}$  at 1692  $\text{cm}^{-1}$  and  $\lambda_{\text{max}}$  at 300 nm ( $\log \epsilon$  3.20), 261 (3.91), and 222 (4.26), showing considerably less conjugation than 2. The hydroxy ketone 13, on the other hand, had a  $\nu_{\text{C}=\text{O}}$  at 1678  $\text{cm}^{-1}$  and  $\lambda_{\text{max}}$  at 324 nm ( $\log \epsilon$  3.38), 272 (4.09), and 240 (4.42), as well as a  $\nu_{\text{OH}}$  at 3680  $\text{cm}^{-1}$  and a strong terminal methylene band at 925  $\text{cm}^{-1}$ . The nmr spectra, as shown in the formulas, are consistent with the assigned structures. The nmr spectrum of 13 had signals at  $\tau$  7.79 (3 H), 7.73 (3 H), and 7.58 (6 H) for the aromatic methyl groups.

It seems likely that 13 arises from 12 by proton loss from the intermediate ion B. Apparently under the less acidic conditions used for this oxidation, compared with those used to oxidize 1, proton loss occurs faster than the ring contraction which gave 9.

The epoxy ketone was treated briefly at room temperature with a little trifluoroacetic acid and boron fluoride etherate, with the hope of obtaining 9. Although the crude product had some nmr peaks corresponding to 9, the major product (85%) was yet another unsaturated ketone to which we tentatively assign structure 14.



The uv spectrum showed considerable conjugation, with  $\lambda_{\text{max}}$  at 335 nm ( $\log \epsilon$  3.41), 268 (4.11), 244 (4.56), and 206 (3.93), but the  $\nu_{\text{C}=\text{O}}$  at 1700  $\text{cm}^{-1}$  suggests that the carbonyl group is in a five-membered ring. Bands for the terminal methylene groups appeared at 930 and 905  $\text{cm}^{-1}$ . The nmr spectrum of 14 had signals for four vinyl protons at  $\tau$  4.96 (2 H), 4.70, and 4.21, two aliphatic methyls at  $\tau$  8.69 and 8.50, and four aromatic methyl singlets at  $\tau$  7.72, 7.65, 7.45, and 7.34. A possible route to 14 is shown. Acyl migration and the



relief of strain which comes from the ring contraction are apparently preferable to alternative rearrangements, which one can readily envision. It appears that the course taken during the rearrangements of these systems is delicately balanced among many alternatives, and depends very much on the reaction conditions, particularly the acidity or basicity of the reaction medium. Further work is needed to unequivocally establish the structures of 13 and 14.

In conclusion, electrophilic oxidation of octamethylnaphthalene occurs exclusively at an  $\alpha$  position, and involves both alkyl migration to give 2 and aryl migration with ring contraction to give 3. This is in contrast with the behavior of 1,2,3,4-tetramethylnaphthalene, which is oxidized at the  $\alpha$  and  $\beta$  positions of the substituted ring. This difference, as well as others which occur when the primary oxidation products of 1 are further oxidized, is ascribed to efforts to relieve the strain associated with peri methyl interactions.

### Experimental Section<sup>5</sup>

**Oxidation of Octamethylnaphthalene with Peroxytrifluoroacetic Acid-Boron Fluoride.**—To a solution of 2.40 g (0.01 mol) of octamethylnaphthalene in 40 ml of methylene chloride at  $-20^\circ$  was added during 15 min a methylene chloride (8 ml) solution of peroxytrifluoroacetic acid prepared from 2.31 g (0.011 mol) of trifluoroacetic anhydride and 0.35 g (0.0102 mol) of 98% hydrogen peroxide. Boron fluoride etherate (47%, 3.08 g, 0.0102 mol) was added concurrently. After addition, stirring was continued at  $-20^\circ$  for 25 min, 50 ml of water was added, and the organic layer was washed with water (50 ml), 3% sodium hydroxide ( $2 \times 50$  ml), and water ( $3 \times 50$  ml) and dried ( $\text{MgSO}_4$ ). Evaporation of the solvent gave 2.38 g of a yellow solid which showed four spots on tlc (silica gel G, chloroform eluent). The mixture was chromatographed through silica gel (21  $\times$  500 mm column) using carbon tetrachloride, which gave as the first fraction 0.81 g (34%) of recovered octamethylnaphthalene. A change in the eluent to chloroform gave three additional fractions.

(5) Melting points are uncorrected. Ir and nmr spectra were recorded in  $\text{CCl}_4$  solution, calibrated against polystyrene and tetramethylsilane, respectively. Chemical shifts are in  $\tau$  units. Analysis were by Spang Micro-analytical Laboratories, Ann Arbor, Mich.

The first was identified as 2,2,3,4,5,6,7,8-octamethyl-1(2*H*)-naphthalenone (2), 1.20 g (71%), mp 89–90° from petroleum ether (bp 30–60°). The second was 1-acetyl-1,2,3,4,5,6,7-heptamethylindene (3), 0.28 g (16%), mp 140–140.5° after recrystallization from petroleum ether, then methanol. The third, which was eluted from the column much more slowly, is thought to be 3-acetyl-2,2,4,5,6,7,8-heptamethyl-1-indanone (9), 0.27 g (14%), mp 123.5–124.5° from methanol. Only traces of tars were produced during the oxidation. When the mole ratio of oxidant to octamethylnaphthalene was doubled, the amount of unreacted octamethylnaphthalene dropped to 0.24 g, the yield of 2 decreased to 0.54 g, the yield of 3 was unchanged, and the yield of 9 increased to 1.57 g.

**Structural Evidence for Compound 2.**—Compound 2 had the following properties: ir 1685 (vs), 1624 (w), 1563 (m), 1465 and 1455 (s, br), 1385 (m), 1360 (w), 1320 (w), 1295 (m), 1270 (w), 1118 (m), 1090 (s), 1005 (m), 950 (m), 870 cm<sup>-1</sup> (m);  $\lambda_{\text{max}}^{\text{EtOH}}$  353 nm (log  $\epsilon$  3.02), 280 (3.27), 250 (4.54), 212 (4.14); nmr  $\tau$  8.88 (6, s, *gem*-dimethyl), 8.21 (3, d,  $J = 1.1$  Hz, C-3 methyl), 8.02 (3, d,  $J = 1.1$  Hz, C-4 methyl), 7.78 (9, br s, C-5, C-6, and C-7 methyls), 7.70 (3, s, C-8 methyl). This nmr spectrum was unchanged when 0.23 g of 2 was refluxed with a solution of 0.02 g of sodium in 4.4 g of CH<sub>3</sub>OD for 42 hr.

*Anal.* Calcd for C<sub>18</sub>H<sub>24</sub>O: C, 84.32; H, 9.44. Found: C, 84.17; H, 9.34.

Catalytic hydrogenation of 0.128 g of 2 in 25 ml of absolute ethanol using 0.128 g of 5% Pd/C catalyst resulted in the uptake of 91% of theory for 1 mol of hydrogen and gave a nearly quantitative yield of 7: mp 63–65° (not sharp); *m/e* 258; nmr  $\tau$  9.05 (3, d,  $J = 6.5$  Hz, C-3 methyl), 9.02 and 8.84 (3 each, s, *gem*-dimethyls at C-2), 8.92 (3, d,  $J = 6.0$  Hz, C-4 methyl), 7.83 (9, br s, C-5, C-6, and C-7 methyls), 7.77 (3, s, C-8 methyl), 8.12 (1, q,  $J = 6.5$  Hz, methine at C-3), 7.17 (1, q,  $J = 6.0$  Hz, methine at C-4).

**Structural Evidence for Compound 3.**—Compound 3 had the following properties: ir 1695 (vs), 1455 (br m), 1392 (w), 1370 (w), 1355 (m), 1090 (m), 1015 cm<sup>-1</sup> (m);  $\lambda_{\text{max}}^{\text{EtOH}}$  267 nm (log  $\epsilon$  3.96), 222 (4.39); nmr  $\tau$  8.73 (3, s, C-1 methyl), 8.57 (3, s, acetyl methyl), 8.30 (3, q,  $J = 1.1$  Hz, C-2 methyl), 7.93 (3, s, C-7 methyl), 7.84 and 7.82 (3 each, s, C-5 and C-6 methyl), 7.73 (3, q,  $J = 1.1$  Hz, C-3 methyl), 7.53 (3, s, C-4 methyl).

*Anal.* Calcd for C<sub>18</sub>H<sub>24</sub>O: C, 84.32; H, 9.44. Found: C, 84.32; H, 9.45.

A solution of 45 mg of 3 in 4 ml of CH<sub>3</sub>OD containing 0.01 g of dissolved sodium was refluxed for 22 hr. Work-up gave recovered 3, whose nmr spectrum was unchanged except that the singlet at  $\tau$  8.57 was absent. Compound 3 absorbed bromine (in CCl<sub>4</sub>) rapidly, but there was no change in  $\nu_{\text{C=O}}$ , showing that the double bond is not conjugated with the carbonyl group.

A solution of 3 (100 mg) in 23.5 ml of ethanol containing 50 mg of 5% palladium on charcoal was hydrogenated at 5-atm pressure for 3.5 hr, at which time no further hydrogen was absorbed. Work-up gave dihydro-3 with the following nmr spectrum:  $\tau$  9.04 (3, d,  $J = 7.5$  Hz, C-2 or C-3 methyl), 8.94 (3, d,  $J = 7.5$  Hz, C-2 or C-3 methyl), 8.60 (3, s, C-1 methyl), 8.10 (3, s, acetyl methyl), 7.99 (3, s, aromatic methyl), 7.85 (6, s, aromatic methyls), 7.78 (3, s, aromatic methyl). The methine protons appeared as a complex multiplet in the region of  $\tau$  8.0.

To a suspension of lithium aluminum hydride (30 mg) in 6 ml of anhydrous ether was added a solution of 3 (50 mg) in 6 ml of ether, and the mixture was stirred at room temperature for 3 hr. The usual work-up gave 1-(1-hydroxyethyl)heptamethylindene (8): mp 125–126.5° from benzene; ir 3680 (m), 1630 (w), 1455 (s, br), 1390 (m), 1375 (m), 1265 (m), 1100–1140 (s, br), 930 (m), 910 cm<sup>-1</sup> (m);  $\lambda_{\text{max}}^{\text{EtOH}}$  270 nm (log  $\epsilon$  4.04), 228 (4.20); nmr  $\tau$  9.20 (3, d,  $J = 6.5$  Hz, -CHCH<sub>3</sub>), 8.67 (3, s, C-1 methyl), 8.19 (3, br s, C-2 methyl), 7.82 (9, br s, C-3 C-5, and C-6 methyls), 7.58 (6, s, C-4 and C-7 methyls), 5.92 [1, m, -CH(OH)CH<sub>3</sub>]. A solution of 8 (17 mg) and 1 drop of trifluoroacetic acid in 2 ml of methylene chloride was allowed to stand at room temperature for 5 hr. Cyclohexane (10 ml) was added, and the organic layer was washed with 5% aqueous sodium hydroxide and water and dried (MgSO<sub>4</sub>). Tlc on silica gel afforded a few milligrams of octamethylnaphthalene.

**Structural Evidence for Compound 9.**—Compound 9 had the following properties: ir 1700 (vs), 1570, 1470–1450 (br m), 1385 (m), 1375 (m), 1355 (m), 1310 (m), 1280 (w), 1265 (w), 1220 (m), 1180 (w), 1145 (w), 1110 (s), 1080 (m), 995 (m), 895 cm<sup>-1</sup> (w);  $\lambda_{\text{max}}^{\text{EtOH}}$  310 nm (log  $\epsilon$  3.29), 265 (4.18), 218 (4.46); nmr  $\tau$  9.03, 8.93 (3 each, s, *gem*-dimethyl), 8.59 (3, s, C-3 methyl), 8.23 (3, s,

acetyl methyl), 7.90, 7.74, and 7.40 (3, 6 and 3, s, aromatic methyls). When a solution of 9 (50 mg) in 5 ml of CH<sub>3</sub>OD containing 10 mg of sodium metal was refluxed for 20 hr, 9 was recovered unchanged except that the singlet at  $\tau$  8.23 was missing from its nmr spectrum. Compound 9 also gave a positive iodoform test.<sup>6</sup> Compound 9 absorbed bromine only gradually and did not absorb any hydrogen when treated with 5% Pd/C in ethanol at room temperature and 5 atm of hydrogen. Compound 9 was recovered unchanged after 5.5 hr reflux with acetic acid in benzene and after 2 days at room temperature with boron fluoride etherate in methylene chloride (that is, an epoxide moiety is not present).

**Oxidation of 2 with Peroxytrifluoroacetic Acid–Boron Fluoride.**—To a solution of 2 (0.80 g, 0.0031 mol) in 15 ml of methylene chloride was added at -23 to -25° over 15 min 0.96 g (0.0032 mol) of 47% boron fluoride etherate and a solution of peroxytrifluoroacetic acid prepared from 0.72 g (0.0034 mol) of trifluoroacetic anhydride, 0.11 g (0.0032 mol) of 98% hydrogen peroxide, and 3 ml of methylene chloride. After 1.5 hr at -23 to -5°, the mixture was worked up as in the oxidation of 1. The crude product (0.78 g) was chromatographed (silica gel, chloroform eluent) to give only recovered 2 (a few milligrams) and 9 (0.88 g, 81%), identical (melting point, ir, nmr) with the same product isolated from the oxidation of octamethylnaphthalene.

**Oxidation of 2 with *m*-Chloroperbenzoic Acid.**—To a solution of 2 (0.195 g, 0.76 mmol) in 15 ml of benzene cooled in an ice bath was added a solution of 0.165 g of 87% *m*-chloroperbenzoic acid in 10 ml of benzene. After 1.5 hr, the solution was washed with 5% sodium carbonate and water and dried (MgSO<sub>4</sub>). Evaporation of the solvent gave a white solid (0.198 g) which, on recrystallization from methanol, gave 0.170 g (83%) of the epoxide 12: mp 145–149°; ir 1692 (vs), 1475 (m), 1385 (m), 1370 (w), 1320 (m), 1280 (w), 1225 (w), 1170 (w), 1130 (w), 1105 (m), 1095 (s), 945 (m), 890 cm<sup>-1</sup> (m);  $\lambda_{\text{max}}^{\text{EtOH}}$  300 nm (log  $\epsilon$  3.20), 261 (3.91), 222 (4.26); nmr  $\tau$  9.28, 8.77 (3 each, s, *gem*-dimethyls), 8.65, 8.44 (3 each, s, epoxide methyls), 7.78, 7.62 (9 and 3, s, aromatic methyls).

*Anal.* Calcd for C<sub>18</sub>H<sub>24</sub>O<sub>2</sub>: C, 79.37; H, 8.88. Found: C, 79.41; H, 8.93.

To a solution of 2 (0.10 g, 0.37 mmol) in 8 ml of methylene chloride was added 0.080 g of *m*-chloroperbenzoic acid in 7 ml of methylene chloride. After 6 min, work-up showed that only 50% of 2 was oxidized. The mixture of starting material and product was redissolved in methylene chloride and 0.07 g of *m*-chloroperbenzoic acid was added. After 20 min the reaction was worked up to give 0.075 g (70%) of alcohol 13: mp 125–127° from methanol; ir 3680 (w), 1678 (vs), 1470–1460 (s, br), 1420 (w), 1395 (s), 1380 (s), 1298 (s), 1120 (s, br), 1080 (m), 1040 (w), 1010 (w), 950 (m), 925 cm<sup>-1</sup> (vs);  $\lambda_{\text{max}}^{\text{EtOH}}$  324 nm (log  $\epsilon$  3.38), 272 (4.08), 240 (4.42); nmr  $\tau$  8.93, 8.85 (3 each, s, *gem*-dimethyl), 8.80 (3, s), 7.79, 7.73, 7.58 (3, 3, and 6, s, aromatic methyls), 4.93 (1, d,  $J = 1.5$  Hz), 4.38 (1, d,  $J = 1.5$  Hz).

*Anal.* Calcd for C<sub>18</sub>H<sub>24</sub>O<sub>2</sub>: C, 79.37; H, 8.88. Found: C, 79.28; H, 8.96.

Another oxidation of 2 in methylene chloride at room temperature for 1 hr gave a mixture of 12 and 13; the former crystallized from methanol; and the latter was obtained from the mother liquors of this crystallization by adding cyclohexane.

**Rearrangement and Dehydration of Epoxy Ketone 12 in Acid.**—Two drops each of trifluoroacetic acid and 47% boron fluoride etherate were added to a solution of 12 (0.060 g, 0.22 mmol) in methylene chloride (6 ml). After 10 min at room temperature the mixture was washed with 5% sodium carbonate and water, and dried (MgSO<sub>4</sub>). Evaporation of the solvent left a yellow solid, the nmr spectrum of which showed the presence of traces of 9. However, the major component (0.048 g, 85%), isolated by chromatography on alumina with cyclohexane and chloroform as eluents, was a yellow, crystalline, unsaturated ketone 14: mp 119–122° after recrystallization from 75% aqueous ethanol; ir 1700 (vs), 1638 (w), 1630 (m), 1575 (w), 1455 (m), 1380 (m), 1310 (m), 1275 (w), 1100 (w), 930 (m), 905 cm<sup>-1</sup> (s);  $\lambda_{\text{max}}^{\text{EtOH}}$  335 nm (log  $\epsilon$  3.41), 268 (4.11), 244 (4.56), 206 (3.93); nmr  $\tau$  8.69 (3, s, C-2 methyl), 8.50 (3, s, allylic methyl), 7.72, 7.65, 7.45, 7.34 (3 each, s, aromatic methyls), 4.96 (2, br s, methylene protons), 4.70 and 4.21 (1 each, slightly split, methylene protons).

*Anal.* Calcd for C<sub>18</sub>H<sub>22</sub>O: C, 84.99; H, 8.72. Found: C, 84.98; H, 8.70.

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## Fundamental Studies of Substituted Ferrocene Systems. VI. Electronic Effects in the Alkylferrocenes

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The 220-MHz proton magnetic resonance spectra of methyl-, ethyl-, isopropyl-, and *tert*-butylferrocene are reported. The improved resolution allows differentiation of resonances in all but isopropylferrocene, thus allowing investigation of chemical shift trends for the various protons involved. Spectra were also obtained for the specifically deuterated molecules necessary to establish the identity of the various resonances. Of interest is the predominant shielding effect experienced at the 3,4-position protons contrary to previous predictions and assignments.

Proton magnetic resonance spectroscopy has proven to be a valuable tool in the analysis of ferrocenes, both for the determination of structure and for the investigation of the modes of transmission of electronic effects. A complete spectral analysis of the alkylferrocenes has been absent from the literature because of the failure of the 60- and 100-MHz instruments to resolve the weakly perturbed ring proton resonances. We wish to report here the 220-MHz spectra of methyl-, ethyl-, isopropyl-, and *tert*-butylferrocene along with the appropriately deuterated molecules necessary to unambiguously assign the various resonances.

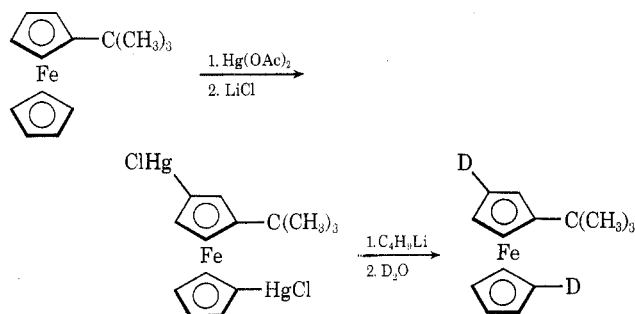
The 60- and 100-MHz spectra of this series of alkylferrocenes have been reported by a number of research groups. Benkeser and coworkers<sup>1,2</sup> observed ring proton resonances for methylferrocene at  $\delta$  3.99 and 3.94 and on the basis of integration alone assigned the downfield resonance to the 1'- and 3,4-position protons and the upfield resonance to the 2,5-position protons. Resolution was not sufficient to separate the homoannular ring resonances of the other alkylferrocenes. In contrast, Rausch and Siegel<sup>3</sup> reported that the pmr spectrum of 2,5-dideuteriomethylferrocene exhibited a partial decrease in absorption for the upfield resonance, concluding that this resonance in the undeuterated molecule was in fact due to both the 2,5- and 3,4-position protons. Similarly, Nesmeyanov and coworkers<sup>4</sup> have reported the spectra of this same series of compounds and claimed to have obtained sufficient resolution to partially resolve the upfield resonance in both methyl- and *tert*-butylferrocene. Citing Benkeser, *et al.*,<sup>1,2</sup> and a paper by Levenberg and Richards,<sup>5</sup> they assigned the upfield resonance to the 2,5-position protons. These inconsistencies are mainly the result of insufficient resolution afforded by the 60- and 100-MHz spectrometers, which prohibits reliable assignment of the homoannular ring resonances and hence meaningful assessment of electronic effects of the substituents.

Recent results from this laboratory have demonstrated that for strong electron-donating substituents an upfield shift is experienced predominately by the 3,4-position protons.<sup>6</sup> Since alkyl groups are weak electron donors, a distinct possibility of a parallel electronic effect was seen to exist between these two systems such that the homoannular ring assignments of Benkeser, *et al.*,<sup>1,2</sup> and Nesmeyanov, *et al.*,<sup>4</sup> would need to be reversed.

### Results and Discussion

The 220-MHz spectral data for these alkylferrocenes are summarized in Table I along with "corrected" chemical shift data of the previous authors. Assignments of the substituted ring resonances were made on the basis of comparison to the spectra of specifically deuterated molecules. 2-Deuteriomethylferrocene and 2,5-dideuterioethylferrocene were prepared *via* routes involving lithiation-deuteration procedures on *N,N*-dimethylaminomethylferrocene<sup>7</sup> and *N,N*-dimethylaminoethylferrocene,<sup>8</sup> respectively, in which the metalation has been demonstrated unequivocally to occur at the 2 position. 3,1'-Dideuterio-*tert*-butylferrocene was prepared by the sequence of reactions shown in Scheme I.

SCHEME I



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