Registry No.—**1**, 571-58-4; **2**, 581-40-8; **3**, 3031-15-0; **4**, 2717-39-7; **5**, 13764-18-6; **6**, 36230-30-5; **7**, 17384-76-8; **8**, 18623-61-5; maleic anhydride, 108-31-6.

Acknowledgment.—The authors wish to thank Professor H. Hart of Michigan State University for his valuable comments.

Synthesis and Chemistry of Octamethylnaphthalene

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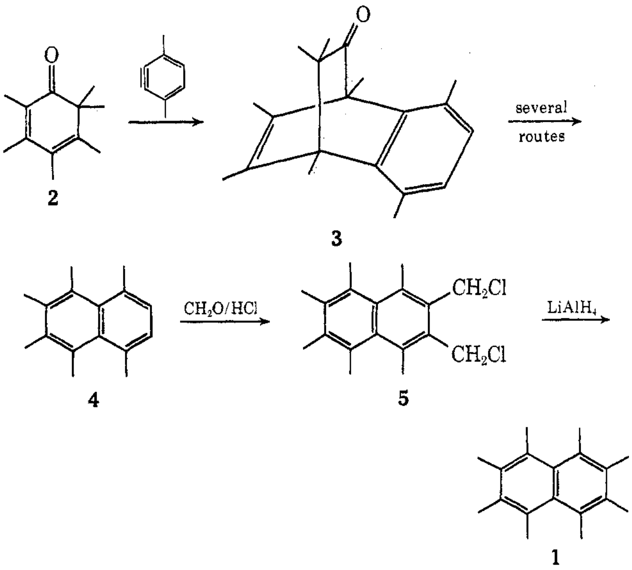
A five-step synthesis of octamethylnaphthalene (**1**) from hexamethylbenzene, overall yield 51%, is described. Addition of 3,6-dimethylbenzyne to hexamethyl-2,4-cyclohexadienone (**2**) gave adduct **3** which with dimsyl sodium eliminated butyric acid to give 1,2,3,4,5,8-hexamethylnaphthalene (**4**). Bischloromethylation of **4**, followed by lithium aluminum hydride reduction, gave **1**. Octamethylnaphthalene gave 1,4 adducts with maleic anhydride, dimethyl acetylenedicarboxylate, benzyne, and 4,5-dimethylbenzyne. Tetracyanoethylene gave a deep blue color with **1** in nonpolar solvents, and singlet oxygen reacted with **1** to give a stable 1,4-endoperoxide (**13**). With dibromocarbene, **1** gave a homoannular bis adduct **14** and a benzomethylenecycloheptatriene **15**, the latter from rearrangement and HBr elimination from the monoadduct. Octamethylnaphthalene is protonated at an α position by trifluoroacetic acid at room temperature to give a long-lived arenonium ion.

Octamethylnaphthalene (1) is not planar, owing mainly to strong interactions between the peri methyl groups.[1] An early structure determination[2] showed that the α-methyl carbon atoms are displaced about 0.73 Å from the mean molecular plane; the β-methyls are also displaced, but only by one-third that distance. Adjacent α and β methyl groups are displaced in the same sense, whereas adjacent α,β pairs are alternatively displaced above and below the mean molecular plane.[3,4] It seems likely that the aromatic ring carbon atoms themselves are also distorted from the mean molecular plane. This twisting should alter the π overlap from that in naphthalene itself, and might be reflected in the reactivity of **1** toward electrophiles.

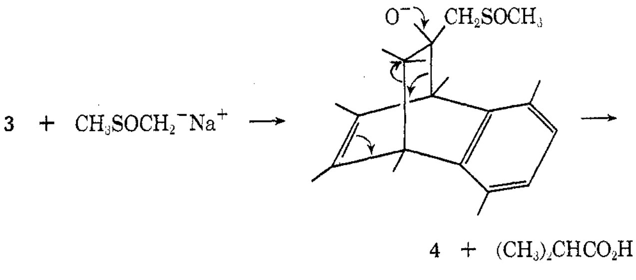
The original synthesis of 1[6] unfortunately required many steps and was unattractive if **1** was to serve as the starting point for other investigations. Consequently, we developed and describe here a simple, high-yield synthesis of 1.[7] We also describe here and in the following paper several reactions of octamethylnaphthalene.

Synthesis of Octamethylnaphthalene (1).—In the synthesis which we devised (Scheme I), the step which produces both peri interactions also introduces aromaticity into the second ring, thus providing a strong driving force for the reaction. The last two methyl groups are added in the final steps, *via* chloromethylation and reduction, at the less hindered β positions.

SCHEME I



Reaction of hexamethyl-2,4-cyclohexadienone (2)[8] with 3,6-dimethylbenzyne[9] afforded the adduct **3** in 76% yield. The adduct was converted to 1,2,3,4,5,8-hexamethylnaphthalene by three routes. The best of these, which was essentially quantitative, involved the reaction of **3** with dimsyl sodium.[10] Pyrolysis of **3** also gave **4** (and dimethylketene) but conversions at



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[1] For a review on peri interactions in naphthalenes, see V. Balasubramaniyan, *Chem. Rev.*, **66**, 567 (1966).

[2] D. M. Donaldson and J. M. Robertson, *J. Chem. Soc.*, 17 (1953).

[3] G. Gafner and F. H. Herbstein, *Nature* (*London*), **200**, 130 (1963).

[4] In the abstract of the paper on the X-ray structure of octamethylnaphthalene,[2] the methyls are said to alternate in their up-and-down displacement around the ring. However, the original structure was based only on a two-dimensional X-ray analysis. A three-dimensional X-ray analysis of octa*chloro*naphthalene[3] showed that the chlorines at C-1, -2, -5, and -6 are displaced in one sense from the mean molecular plane and those at C-3, -4, -7, and -8 are displaced in the opposite sense. A recent reexamination of the octamethylnaphthalene structure[5] shows that its structure is analogous to that of the octachloro derivative.

[5] Private communication from Professor Iain C. Paul.

[6] B. J. Abadir, J. W. Cook, and D. T. Gibson, *J. Chem. Soc.*, 8 (1953).

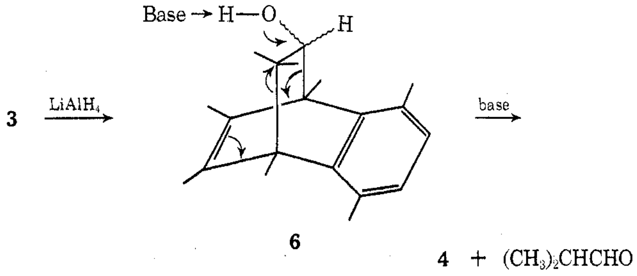
[7] For a preliminary report, see A. Oku, T. Kakihana, and H. Hart, *J. Amer. Chem. Soc.*, **89**, 4554 (1967). We are indebted to Dr. Tsuyoshi Kakihana for his contributions to the early phases of this work.

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

[9] Produced from the corresponding diazonium carboxylate hydrochloride, using the procedure of Professor L. Friedman (private communication).

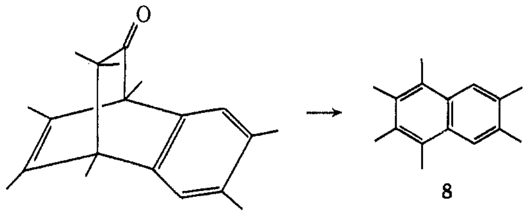
[10] E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1345 (1965).

moderate residence times were only modest (~20%), even at 450°. Reduction of **3** with lithium aluminum hydride gave a mixture of epimeric alcohols **6** which, when refluxed with sodium hydride in DMSO, gave **4** (overall yield from **3**, 95%).



The hexamethylnaphthalene **4** was readily bischloromethylated to give **5**, which was reduced without purification to give **1**. The overall yield from hexamethylbenzene to octamethylnaphthalene (five steps) was 51%, and further work on the final reduction could probably improve this to 70%.

The importance of introducing the peri methyl groups in a step (**3** → **4**) which also involves the formation of an aromatic ring is seen from the following results. Addition of 4,5-dimethylbenzyne to **2** gave the adduct **7** (76%), which could be converted to **8** in good yield.

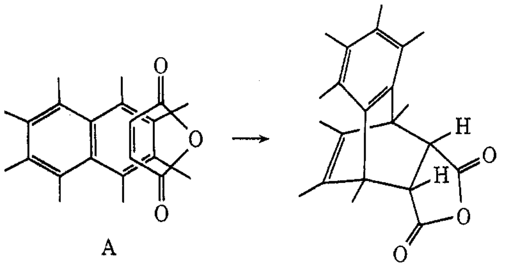


7 **8**

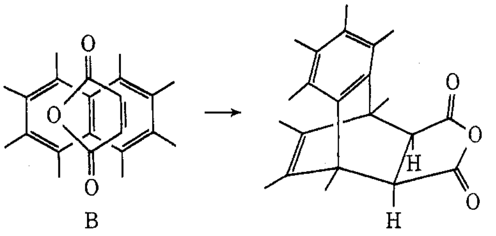
However, chloromethylation and reduction of **8** gave only very low yields of heptamethylnaphthalene (~6%) and octamethylnaphthalene (~3%), even under rather forcing conditions.

Diels–Alder Additions of Octamethylnaphthalene.—Octamethylnaphthalene is more reactive than naphthalene itself toward dienophiles. This may be because the ring framework is distorted from planarity, thus making the compound somewhat less aromatic and more diene-like.

Maleic anhydride, when heated at 132° for several hours with **1**, gave an 83% yield of the endo and exo adducts *endo*-**9** and *exo*-**9**, in a ratio of 2:1 in accord with the Alder rules.[11] The isomers were not separated, but were readily distinguished by their nmr spectra, and the mixture was analyzed in that way. The transition state A, with the anhydride ring oriented away from the second ring of the naphthalene, is preferred.

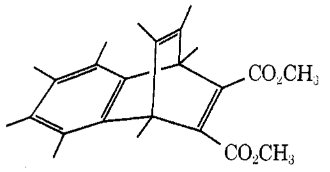


A *endo*-**9**



B *exo*-**9**

Reaction of **1** with dimethyl acetylenedicarboxylate and with the appropriate arynes gave adducts **10–12** in fair yield. 3,6-Dimethylbenzyne was apparently too hindered to react with **1**. The structures of the adducts were clear from nmr and other spectral data. Tetracyanoethylene produces a deep blue color with octamethylnaphthalene in nonpolar solvents such as benzene, chloroform, or hexane, but no color is produced in ethanol. The color can be discharged from the nonpolar solutions by adding a little alcohol. All attempts to isolate a simple adduct from the blue solutions were unsuccessful; some crystalline products which contained both moieties were isolated, but they contained considerable amounts of oxygen and did not correspond to the 1:1 adduct; their structures are as yet undetermined.



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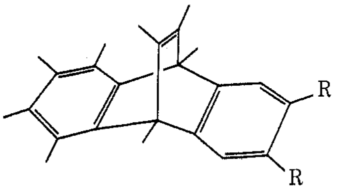
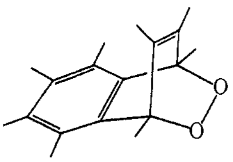


11, R = H
12, R = CH_3

Octamethylnaphthalene readily adds 1 mol of oxygen, either on direct or dye-sensitized irradiation, to form the stable crystalline 1,4-endoperoxide **13**. The reaction



13

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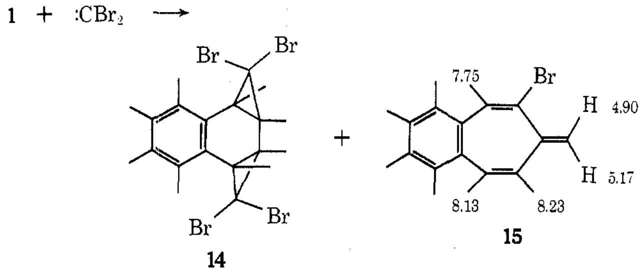
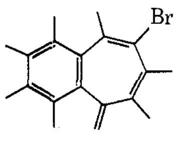
[11] Kinetic measurements [A. Oku, Y. Ohnishi, and F. Mashio, *J. Org. Chem.*, **37**, 4264 (1972)], show that **1** reacts with maleic anhydride in chloroform at 60° ten times faster than does 1,2,3,4-tetramethylnaphthalene; under these conditions naphthalene itself reacts at a rate too slow to measure.

involves singlet oxygen, and can be reversed by refluxing **13** in di-*n*-butyl ether.[12]

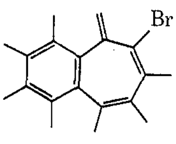
Addition of Dibromocarbene to Octamethylnaphthalene.—Dibromocarbene, generated from bromoform and potassium *tert*-butoxide in benzene at room temperature, gave two products with octamethylnaphthalene, assigned structures **14** and **15**. The yields of pure, crystalline material were 30 and 59%, respectively. Compound **14** gave the correct analysis for a bis adduct, and its nmr spectrum consisted of four equal singlets, two in the region of aromatic methyls (τ 7.74, 7.80) and two in the region of aliphatic methyls (τ 8.33, 8.65). These data are consistent with either a cis or a trans bis adduct. The trans geometry seems the more likely of the two possibilities, since nonbonded interactions between two bromine atoms would be very severe in the cis structure.



The second product, **15**, analyzed correctly for a monocarbene adduct minus the elements of HBr. The infrared spectrum showed a strong terminal methylene absorption at 918 cm^{-1}; the uv spectrum had an intense maximum at 245 nm (log ε 4.67) and shoulders at 267 (4.30) and 270 (3.95), indicative of the extensive conjugation present. The nmr spectrum had a broad singlet for the four aromatic methyl groups at τ 7.88 and other bands as shown in the formula. The peak at τ 7.75 was a sharp singlet, whereas those at τ 8.13 and 8.23 were mutually coupled (*J* = 0.8 Hz), as were the two vinyl protons (*J* = 1.8 Hz). The mechanistically accessible fully conjugated alternative structures **15a** and **15b** appear to be less likely from these data.

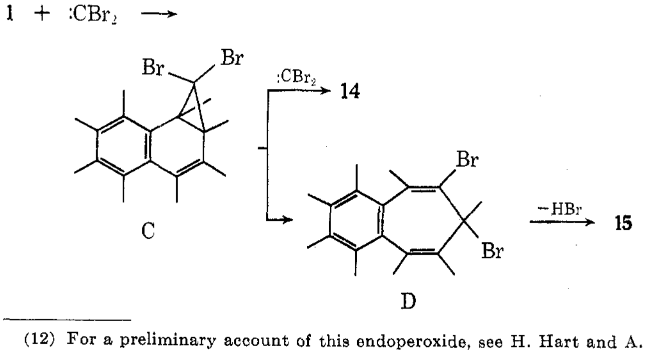


15a



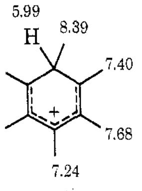
15b

The mechanism presumably involves the formation of a monoadduct C, which can either react with a second carbene to give **14** or ring open to D which eliminates HBr to give **15**. The monoadduct was not isolated.



The formation of **15** is analogous to the formation of chlorobenzotropones from methoxynaphthalenes and dihalocarbenes.[13]

Protonation of Octamethylnaphthalene.—It was of interest to compare the basicities of octamethylnaphthalene and hexamethylbenzene. The behavior of all the methylbenzenes in strong acids has been studied, and the nmr spectra of the benzenonium ions which result from their protonation are recorded.[14] In trifluoroacetic acid containing boron fluoride, or in 96% sulfuric acid at 20°, the protons of all six methyl groups of hexamethylbenzene appear as a single sharp peak at τ 7.65[15] (shifted only 0.15 ppm downfield from its position in carbon tetrachloride). Under these conditions, proton exchange is so rapid that the spectrum of the hexamethylbenzenonium ion **16** is not seen. However, in HF + BF$_3$ at −80° this ion is clearly seen, with a quartet at τ 5.99 and a doublet at 8.39 (*J* = 6.8 Hz), and the para methyl shifted 0.41 ppm downfield from its position in trifluoracetic acid. When this solution is warmed above −20° the detail of this spectrum is lost owing to rapid exchange.



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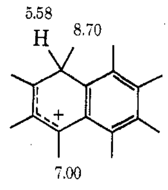

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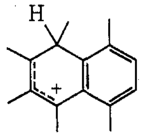

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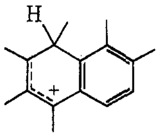

19

In sharp contrast with hexamethylbenzene, octamethylnaphthalene is fully protonated on an α carbon at room temperature in trifluoroacetic acid.[16] The spectrum is stable indefinitely. Although an absolute assignment of all the chemical shifts is not yet possible, there is good evidence that protonation occurs at an α-ring position (**17**). Both 1,2,3,4,5,8- and 1,2,3,4,5,6-hexamethylnaphthalene behaved similarly to give **18** and **19**, respectively. The nmr spectra of the three ions are compared in the Experimental Section. Under identical conditions 1,2,3,4-tetramethylnaphthalene gives an nmr spectrum virtually identical with that obtained in carbon tetrachloride. The relief of strain resulting from nonbonded peri interactions clearly must provide a strong driving force for protonation; consequently octamethylnaphthalene and other methylnaphthalenes with peri interactions are very much more basic than is hexamethylbenzene.

Conclusions

The facile addition of a variety of dienophiles, singlet oxygen, carbenes, and a proton by octamethylnaph-

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[12] For a preliminary account of this endoperoxide, see H. Hart and A. Oku, *J. Chem. Soc. D*, 254 (1972).

[13] W. E. Parham, D. A. Bolon, and E. E. Schweizer, *J. Amer. Chem. Soc.*, **83**, 603 (1961).

[14] For a review, see D. M. Brouwer, E. L. Mackor, and C. MacLean in "Carbonium Ions," Vol II, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1970, pp 837–897.

[15] Tetramethylammonium tetrafluoroborate is taken as reference, at τ 6.87.

[16] We are indebted to George M. Love for obtaining several spectra of the protonated naphthalenes.

thalene is contrasted with the difficulty or absence of these reactions under comparable conditions with either naphthalene itself or with hexamethylbenzene. The severe peri methyl interactions in octamethylnaphthalene apparently distort the π-electron system and enhance its reactivity toward dienophiles and electrophiles. This effect is likely to be general, and we are exploring this possibility with other strained aromatic systems.

Experimental Section[17]

3,6-Dimethylbenzenediazonium-2-carboxylate Hydrochloride (20).—To a suspension of 16.8 g (0.1 mol) of 3,6-dimethylanthranilic acid[18] in 270 ml of ethanol at 0° was added slowly 10 ml of concentrated hydrochloric acid. The resulting clear solution was kept below 8° as 25 ml of isoamyl nitrite was added dropwise (15 min). After the solution was stirred at 4° for 1 hr, 300 ml of ether was added, and the mixture was stirred for another hour at 0°, during which a slightly brown precipitate of **20** separated. The product was rinsed with ether and dried under vacuum at room temperature, yield 17.1 g (81%), mp 88° (with explosion[19]).

1,3,3,4,7,8-Hexamethyl-5,6-(3,6-dimethylbenzo)bicyclo[2.2.2]-octa-5,7-dien-2-one (3).—A stirred mixture of 8.5 g (0.04 mol) of **20**, 7.1 g (0.04 mol) of **2**,[8] and 12 ml (0.16 mol) of propylene oxide in 100 ml of ethylene dichloride was gradually warmed. As gas evolution commenced, the temperature was controlled to prevent vigorous foaming. After 10 min of gas evolution the solution became clear. It was heated under reflux for 1 hr, solvent was removed under vacuum, and the brown liquid residue was taken up in ether, washed with aqueous sodium hydroxide and water, and dried ($MgSO_4$). Evaporation of the solvent gave a reddish-brown liquid which solidified on standing. Recrystallization from methanol gave 8.6 g (76%) of **3** as colorless crystals: mp 103.5–104°; ir $\nu_{C=O}$ 1705, other major peaks at 1460–1480 (br), 1395, 1360, 1265, 1180, 1100, 1075, 1065, and 1030 cm^{-1}; nmr τ 9.28 (3, s, C-3 methyl syn to the aromatic ring), 9.01 (3, s, C-3 methyl anti to the aromatic ring), 8.17, 8.21, 8.24 (12, m, vinyl and bridgehead methyls), 7.52 (3, s, aromatic methyl), 7.47 (3, s, aromatic methyl), 3.33 (2, s, aromatic protons).

Anal. Calcd for $C_{20}H_{26}O$: C, 85.05; H, 9.28. Found: C, 85.10; H, 9.30.

Alternative Preparation of 3.—To a refluxing methylene chloride (60 ml) solution of **2** (4.09 g, 0.023 mol) and isoamyl nitrite (3.9 g, 0.033 mol) there was added over 80 min a solution of 4.95 g (0.03 mol) of 3,6-dimethylanthranilic acid in 110 ml of acetone. After an additional 2 hr reflux, solvent was removed under vacuum, and the oily residue was taken up in ether, washed with aqueous sodium hydroxide and water, dried (Na_2SO_4), and distilled (40–70°, 0.1 Torr) to give 2.5 g of unreacted **2** and an undistillable residue. Chromatography of the latter [activated alumina, petroleum ether (bp 30–60°) eluent] gave 1.7 g (28%) of colorless crystals of **3**, mp 103–104°. Although this procedure eliminates the need to convert the anthranilic acid to its diazoniumcarboxylate hydrochloride, the overall yield is lower and the work-up procedure is more tedious.

1,2,3,4,5,8-Hexamethylnaphthalene (4).—This is the preferred procedure. The sodium salt of dimethyl sulfoxide was prepared from 200 ml of DMSO and 10 g of sodium hydride (50% dispersion in mineral oil).[10] To this clear solution was added at 50° during 15 min 27.5 g (0.097 mol) of **3**. The mixture was stirred at 50–70° for 3 hr, then poured into ice water. The white solid which separated was collected, dissolved in ether, washed with water, and dried (Na_2SO_4). Evaporation of the solvent gave 22 g (about 100%) of **4** as white crystals, mp 42.5–43°. This material was sufficiently pure for further reactions, but further purification could be achieved by column chromatography (silica gel, petroleum ether eluent) to give product with mp 43.5–44.0° (lit.[20] mp 62–63.5°); ir 1820 (w), 1630 (w), 1590 (m), 1350 (s), 1060 (m), 1040 (m), 1010 cm^{-1} (m); nmr τ 7.72 (6, s, C-2 and C-3 methyls), 7.48 (6, s, C-1 and C-4 methyls), 7.37 (6, s, C-5 and C-8 methyls), 3.13 (2, s, aromatic protons).

The aqueous filtrate from the initial separation of the hexamethylnaphthalene was strongly acidified with concentrated hydrochloric acid and extracted with ether. Evaporation of the ether gave an oily residue (0.35 g) which was analyzed by vpc (Apiezon L column, 163°). Comparison with authentic material showed that the oil contained 0.12 g (43%) of isobutyric acid.

Analogous attempts to convert **3** to **4** with other bases such as sodium methoxide in methanol, or sodium hydride, were unsuccessful.

1,2,3,4,5,8-Hexamethylbenzene (4) from the Pyrolysis of 3.—**3** was recovered unchanged when heated in hexylcarbitol (bp 260°) for 25 hr, and when heated neat for 10 hr at 300°. Molten **3** (2.7 g) was dropped through a quartz pyrolysis tube at 450° over 30 min under mild vacuum in a nitrogen atmosphere; the pyrolysate was collected and the exit gases were passed through a trap which contained a carbon tetrachloride solution of aniline. Vpc analysis of the pyrolyzate (Apiezon L column, 250°) showed it to contain a 17.8% yield of **4**, and unchanged **3**. Work-up of the aniline trap contents gave 0.28 g of colorless crystals which on recrystallization from benzene gave isobutyroyl anilide, mp 101–101.5° (lit.[21] mp 105°), in 17.9% yield.

Alternate Preparation of 1,2,3,4,5,8-Hexamethylnaphthalene (4) from 3 *via* 6.—To a suspension of 2.0 g of lithium aluminum hydride in 100 ml of absolute ether was added at 0° over 30 min a solution of 7.4 g (0.0262 mol) of **3** in 50 ml of ether. After the mixture was stirred at room temperature for 16 hr, work-up gave a colorless oil which had a ν_{OH} at 3650 cm^{-1} and contained no carbonyl absorption. To a solution of this crude product **6** in 50 ml of dimethyl sulfoxide was added 3.5 g of sodium hydride (50% dispersion in oil), and the mixture was heated for 17 hr at 40–45°. Work-up gave 5.3 g (95.5% overall) of 1,2,3,4,5,8-hexamethylnaphthalene, mp 42.5–43.0°.

Octamethylnaphthalene (1).—Dry hydrogen chloride was bubbled through a suspension of 27 g (0.9 mol) of paraformaldehyde in 200 ml of glacial acetic acid for 2 hr, when the solution became clear. 1,2,3,4,5,8-Hexamethylnaphthalene (17.9 g, 0.084 mol) was added in one batch and the mixture was stirred for 2 hr at 35° and 1 hr at 40–45°. The mixture became green to dark blue. Hydrolysis in ice water gave a light brown solid which was collected, dissolved in ether, washed with aqueous sodium bicarbonate and water, and dried ($CaCl_2$). Evaporation of the solvent gave 25.2 g (97%) of crude 6,7-bischloromethyl-1,2,3,4,5,8-hexamethylnaphthalene (**5**). This compound decomposed on attempts at purification and was immediately reduced as follows.

To a suspension of lithium aluminum hydride (15 g, 0.4 mol) in 150 ml of anhydrous ether was added at 0–5° over 30 min a solution of crude **5** from above in 650 ml of anhydrous ether. After being stirred for 6 hr at room temperature the mixture was hydrolyzed, extracted with ether, and dried ($MgSO_4$). Evaporation of the ether left a yellow solid which was chromatographed through silica gel using petroleum ether as eluent. Fine, colorless crystals of octamethylnaphthalene (11.8 g, 64%) were obtained: mp 181–181.5° (lit.[6] mp 174°); ir 1585 (m), 1480 (s), 1450 (s), 1393 (s), 1345 (m), 1220 (w), 1140 (w), 1090 (m), 1070 (m), 1000 cm^{-1} (m); nmr τ 7.75, 7.59 (sharp singlets, equal in area); λ_{max}^{EtOH} 308 nm (log ϵ 3.76), 251 (4.70).

1,3,3,4,7,8-Hexamethyl-5,6-(4,5-dimethylbenzo)bicyclo[2.2.2]-octa-5,7-dien-2-one (7).—4,5-Dimethylbenzenediazonium-2-carboxylate hydrochloride, mp 132–133°, was prepared in 89% yield from the corresponding anthranilic acid[18] by a procedure analogous to that described above for the 3,6 isomer. A mixture of 7.5 g (0.035 mol) of the diazoniumcarboxylate hydrochloride, 6.2 g (0.035 mol) of 2,3,4,5,6,6-hexamethyl-2,4-cyclohexadienone (**2**), 10 ml of propylene oxide, and 100 ml of ethylene chloride was stirred and heated at reflux for 3 hr. After gas evolution

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[17] Analyses were by Spang Microanalytical Laboratories, Ann Arbor, Mich. 48106. Melting points are uncorrected. Infrared and nmr spectra were taken in carbon tetrachloride solution unless otherwise stated, and are calibrated against polystyrene film and tetramethylsilane, respectively. All nmr chemical shifts are in τ units.

[18] B. R. Baker, R. E. Schaub, J. P. Joseph, F. J. McEvoy, and J. H. Williams, *J. Org. Chem.*, **17**, 149 (1952).

[19] The compound is stable at room temperature and can be kept for considerable time periods, though the yields of dienone–aryne adducts are somewhat improved if freshly prepared diazoniumcarboxylate hydrochloride is used.

[20] This value, reported by W. L. Mosby, *J. Amer. Chem. Soc.*, **74**, 2564 (1952), is probably in error; we have checked our value in numerous preparations.

[21] "Handbook of Tables for Organic Compound Identification," 3rd ed, compiled by Z. Rappoport, Chemical Rubber Co., Cleveland, Ohio, 1967, p 190.

ceased the mixture became homogeneous. Work-up as in the preparation of **3** gave 11.6 g of an oil which on vacuum distillation gave 1.3 g of unreacted **2**. The distillation residue was chromatographed (alumina, petroleum ether eluent) to give 7.5 g (76%) of **7**: mp 131–132° from methanol; ir $\nu_{\mathrm{C=O}}$ 1708, other bands at 1500, 1460 (broad), 1390 (broad), 1294, 1240, 1175, 1130, 1100, 1078, 1025, 1015, 920, 890, 830 $\mathrm{cm^{-1}}$; nmr τ 9.52 and 8.98 (3 each, s, *gem*-dimethyl), 8.44 (6, s, bridgehead methyls), 8.32, 8.25 (3 each, s, allylic methyls), 7.78 (6, s, aromatic methyls) 3.15 (2, s, aromatic). The compound was not analyzed, since its structure is certain from the method of synthesis and from its conversion to the known **8**. The alternative preparation from 4,5-dimethylanthranilic acid (analogous to the alternate preparation of **3**) gave **7** in 27% yield.

1,2,3,4,6,7-Hexamethylnaphthalene (**8**).—To a suspension of lithium aluminum hydride (0.38 g, 0.01 mol) in 30 ml of anhydrous ether at 0° was added over 60 min a solution of **7** (2.0 g, 0.0071 mol) in 20 ml of ether. After 5 hr of stirring at 0°, work-up gave 2.14 g of a colorless, viscous oil with no carbonyl and a strong hydroxyl absorption in the infrared. The mixture of epimeric alcohols was used directly in the next step.

The mineral oil was removed from 2.0 g of sodium hydride (50% dispersion) with petroleum ether, 30 ml of dimethyl sulfoxide was added followed by the epimeric alcohols from the reduction of **7**, and the mixture waa stirred at room temperature for 22 hr. The mixture was poured into ice water and the white precipitate was collected and chromatographed (silica gel, petroleum ether eluent) to give 1.22 g (77%) of 1,2,3,4,6,7-hexamethylnaphthalene (**8**): mp 145–145.5° (lit.[6] mp 145°); nmr τ 7.70 (6, s, C-2 and C-3 methyls), 7.62 (6, s, C-6 and C-7 methyls), 7.49 (6, s, C-1 and C-4 methyls), 2.39 (2, s, aromatic).

Chloromethylation of 1,2,3,4,6,7-Hexamethylnaphthalene.—The same procedure used to bischloromethylate **4**, but with somewhat longer reaction times, gave, after lithium aluminum hydride reduction, predominantly recovered **8**, with some (∼30%) 1,2,3,4,5,6,7-heptamethylnaphthalene (aromatic proton at τ 2.55). The following more vigorous chloromethylation procedure was then tried.

A mixture of 0.90 g of **8**, 3 ml of chloromethyl methyl ether, 3 ml of carbon disulfide, and 0.1 ml of stannic chloride was heated at 40° for 15 hr. The resulting dark brown solid was reduced with 0.7 g of lithium aluminum hydride in 25 ml of ether for 48 hr to give, after work-up, 0.82 g of crude product. Chromatography on silica gel with petroleum ether eluent gave recovered **8**, but careful analysis of the nmr spectrum showed the presence of 27 mg (2.7%) of octamethylnaphthalene and 63 mg (6.2%) of 1,2,3,4,5,6,7-heptamethylnaphthalene.

Maleic Anhydride Adducts of Octamethylnaphthalene (*endo*-**9** **and** *exo*-**9**).—A mixture of 0.48 g (0.002 mol) of octamethylnaphthalene, 0.196 g (0.002 mol) of maleic anhydride, and 2 ml of chlorobenzene was heated at 132° for 13.5 hr. After removal of the solvent, the residue was chromatographic (silica gel, benzene eluent) to give some recovered **1** and 0.34 g (50.3%; 83% based on consumed **1**) of adducts *endo*-**9** and *exo*-**9**, mp 151–153° from benzene and 161–162° from carbon tetrachloride. The two isomers were not separated, but analysis of the nmr spectrum (in $CDCl_3$) showed that the ratio of *endo*-**9**, to *exo*-**9**, was 2 and permitted the following nmr assignments: *endo*-**9**, τ 8.22 (6, s), 7.83 (6, s), 7.75 (6, s), 7.58 (6, s), 7.03 (2, s); *exo*-**9**, τ 8.25 (6, s), 7.78 (6, s), 7.76 (6 s), 7.48 (6, s), 6.90 (2, s).[22]

Anal. Calcd for $C_{22}H_{26}O_3$: C, 78.07; H, 7.75. Found: C, 77.91; H, 7.60.

1,2,3,4-Tetramethyl-5,6-dicarbomethoxy-7,8-tetramethylbenzobicyclo[2.2.2]octa-2,5,7-triene (**10**).—A solution of 0.37 g (0.0016 mol) of octamethylnaphthalene and 0.33 g (0.0023 mol) of dimethyl acetylenedicarboxylate in 5 ml of chlorobenzene was heated at 130° for 20 hr. Removal of the solvent by vacuum distillation left a brown solid which was extracted with hot methanol (most of the unreacted **1** is not extracted by this solvent). Evaporation of the methanol and chromatography of the residue (silica gel, benzene eluent) gave some recovered **1** and 0.10 g (36% based on consumed **1**) of adduct **10**: mp 170–171° from cyclohexane; nmr τ 8.27 (6, s, allylic methyls), 7.93 (6, s, bridgehead methyls), 7.91 and 7.61 (6 each, s, aromatic methyls) and 6.42 (6, s, methoxyls).

Anal. Calcd for $C_{24}H_{30}O_4$: C, 75.36; H, 7.91. Found: C, 75.48; H, 8.04.

1,2,3,4-Tetramethyl-5,6-benzo-7,8-tetramethylbenzobicyclo[2.2.2]octa-2,5,7-triene (**11**).—A stirred suspension of 0.36 g (0.0015 mol) of octamethylnaphthalene, 0.64 g (0.0030 mol) of benzenediazoniumcarboxylate hydrochloride, 0.60 g (0.01 mol) of propylene oxide, and 5 ml of chlorobenzene was gradually heated until gas evolution occurred. After 1 hr, the volatile solvents were removed by vacuum distillation. The solid residue was dissolved in ether, washed with cold 2% sodium hydroxide and water, and dried ($CaCl_2$). The brown residue which remained after the solvent was evaporated was chromatographed (silica gel, carbon tetrachloride eluent). The first fraction was a solid, mp 115–130°, 0.35 g; a second, slowly eluting oily fraction was not examined further. Rechromatography (silica gel, cyclohexane eluent) gave recovered **1** and 0.14 g (30%) of the benzyne adduct **11**: mp 188.5–189° from cyclohexane; ir 1480 (s), 1460 (s), 1395 (s), 1090 (m), 1070 (m), 1045 (m), 880 $\mathrm{cm^{-1}}$ (s); $\lambda_{\max}^{\mathrm{EtOH}}$ 269.5 nm (log ε 3.49), 262 (3.48), 228 (4.29); nmr τ 8.27 (6, s, allylic methyls), 7.97 (6, s, bridgehead methyls), 7.71 and 7.59 (6 each, s, aromatic methyls), 2.7–3.2 (4, m, aromatic).

Anal. Calcd for $C_{24}H_{28}$: C, 91.09; H, 8.91. Found: C, 91.10; H, 8.86.

1,2,3,4-Tetramethyl-5,6-(4,5-dimethylbenzo)-7,8-tetramethylbenzobicyclo[2.2.2]octa-2,5,7-triene (**12**).—The procedure was analogous to that used to prepare **11**. From identical amounts of starting materials there was obtained, after chromatography, 0.14 g (27%) of adduct **12**: mp 220–225° from cyclohexane; ir 1085, 1070, 1005, 895 $\mathrm{cm^{-1}}$; nmr τ 8.27 (6, s, allylic methyls), 7.95 (6, s, bridgehead methyls), 7.83, 7.70, 7.57 (6 each, s, aromatic methyls), 3.08 (2, s, aromatic protons).

Anal. Calcd for $C_{26}H_{32}$: C, 90.64; H, 9.36. Found: C, 90.75; H, 9.27.

When the chlorobenzene was replaced with ethylene chloride and the mole ratio of diazoniumcarboxylate hydrochloride to octamethylnaphthalene was raised to 3, the yield of **12** was increased to 42%.

Attempted Synthesis of the 3,6-Dimethylbenzyne Adduct of Octamethylnaphthalene.—Replacement of 4,5-dimethylbenzenediazonium-2-carboxylate hydrochloride in the above procedure of the preparation of **12** by the 3,6-dimethyl isomer failed to give an aryne adduct. Solvent changes (ethylene chloride, diglyme), an increase in the mole ratio of aryne precursor to **1** of 4:1, and a change from propylene oxide to styrene oxide were to no avail.

Octamethylnaphthalene-1,4-endoperoxide (**13**).—A solution of 1.20 g (0.005 mol) of octamethylnaphthalene in 400 ml of purified hexane was irradiated (Hanovia Type L, 450-W lamp) at 20° in a Pyrex reactor with a stream of dry air continuously passing through the solution. After 2.5 hr the solution was filtered to remove a small amount of hexane-insoluble material. Evaporation of the solvent left a white residue (mp 115–120°) whose ir spectrum showed $\nu_{\mathrm{C=O}}$ at 1700 $\mathrm{cm^{-1}}$. Chromatography through silica gel (chloroform eluent) gave three fractions: 0.10 g of unreacted **1**, 0.94 g (70%) of **13**, mp 139–140° from cyclohexane, and a yellow oil which showed a strong carbonyl absorption and was not examined further. The endoperoxide had the following properties: ir 1440–1480 (broad), 1390, 1315, 1275, 1210, 1165, 1090, 1065, 1010, 690 $\mathrm{cm^{-1}}$; nmr τ 8.23 (6, s), 8.21 (6, s), 7.84 and 7.67 (6 each, s, aromatic methyls). Iodine formed instantly when hydriodic acid (57%) was added to an acetic acid solution of **13**.

Anal. Calcd for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88. Found: C, 79.51; H, 9.05.

A solution of **13** in di-*n*-butyl ether, refluxed briefly, gave a quantitative yield of **1**.

Reaction of Octamethylnaphthalene with Dibromocarbene.—Bromoform (3.1 g, 0.012 mol) was added at 0° over 10 min to a slurry of freshly prepared potassium *tert*-butoxide (1.4 g, 0.012 mol) in 60 ml of benzene containing 2.4 g (0.01 mol) of octamethylnaphthalene. The mixture was stirred at room temperature for 4 hr, during which the color changed to yellow. Cold water (50 ml) was added, the organic layer was washed twice with water, and the aqueous layer was extracted twice with benzene. The combined organic layers were dried ($MgSO_4$) and solvent was evaporated to leave a yellow solid which showed two spots on tlc (silica gel H, cyclohexane). Washing the solid with cyclohexane left a cyclohexane-insoluble product assigned structure **14**: 1.55 g (30%); mp 267–268°; ir 1465 (s), 1390 (vs), 1090 (m), 940 (m), 910 (w), 890 (w), 850 $\mathrm{cm^{-1}}$ (m); nmr τ 8.65 (6, s), 8.33 (6, s), 7.80 and 7.74 (6 each, s, aromatic methyls). There was no uv maximum in ethanol above 225 nm.

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[22] These assignments are clear from a study of the maleic anhydride adducts of eight different polymethylnaphthalenes: A. Oku, Y. Ohnishi, and F. Mashio, *J. Org. Chem.*, **37**, 4264 (1972).

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); λ_{max}^{hexane} 270 nm (sh, log ϵ 3.95), 267 (sh, 4.30), 245 (4.67), 218 (sh, 4.20); nmr τ 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 $C_{19}H_{23}Br$: C, 68.88; H, 6.99. Found: C, 68.91; H, 6.93.

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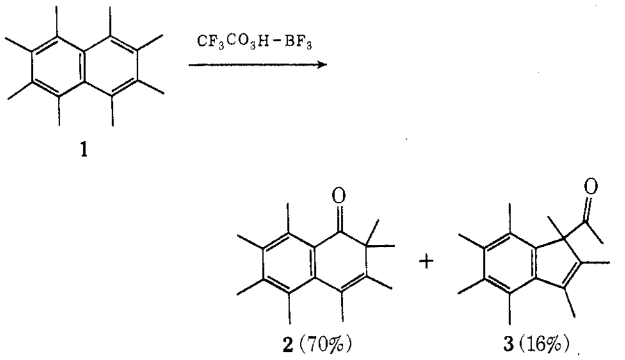
Oxidation of octamethylnaphthalene (**1**) with peroxytrifluoroacetic anhydride–boron fluoride occurred exclusively at the α position, to give 2,2,3,4,5,6,7,8-octamethyl-1(2*H*)naphthalenone (**2**, 70%) and 1-acetyl-1,2,3,4,5,6,7-heptamethylindene (**3**, 16%), formed as a result of methyl and aryl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

In the preceding paper[1] 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,[2] done for the purpose of comparing the reactivity of **1** with that of hexamethylbenzene[3] and 1,2,3,4-tetramethylnaphthalene.[4] 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 π 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 products, 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.[4] The nmr spectrum of **2** had a sharp singlet for the *gem*-dimethyl group at τ 8.88, two homoallylically coupled methyl signals at τ 8.21 and 8.02 (J = 1.1 Hz), three aromatic methyl protons in a broad singlet at τ 7.78, and one sharp aromatic methyl singlet at τ 7.70, consistent with the assigned structure. The alternative structure **5** (a possible product of β electrophilic attack, the analog of which was a minor oxidation product of 1,2,3,4-tetramethylnaphthalene[4]) and **6** (a possible

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[1] A. Oku, T. Kakihana, 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).