tetrahydrofuryl β-H), 3.6–4.5 (m, 4, tetrahydrofuryl α-H and benzyl H), 6.4–7.5 (m, 10, aromatic H's); *m/e* (rel intensity) 253 (8, M^+), 183 (31), 182 (100, $M^+ - C_4H_7O$), 104 (21), 77 (33).

Anal. Calcd for $C_{17}H_{19}NO$: C, 80.61; H, 7.56; N, 5.53. Found: C, 80.60; H, 7.36; N, 5.50.

The spectral properties of these two diastereomers were very similar. The most obvious difference was in the chemical shift of the benzylic proton doublet. In the solid isomer this was δ 4.41 (J = 5 Hz) while in the "liquid isomer" this was δ 4.20 (J = 5 Hz). This latter material was a mixture of the two isomers as indicated by the nmr spectra (30% solid isomer).

N-(*o*-Chlorophenylfurylmethyl)aniline (5b) was prepared by the addition of 2-furyllithium[26] (0.15 mol) to *N*-(*o*-chlorobenzylideneaniline (21.6 g, 0.1 mol) in *n*-hexane (30 ml). The crude product was distilled to give 26.1 g of viscous oil, bp 155–156° (0.2 mm). The nmr spectrum of this product showed the presence of 10% of the starting material. While the bulk of this product was used in the next step, an analytical sample was isolated by preparative vpc using a 5 ft × 1/4 in. column containing 10% Carbowax 20M on Chromosorb W and operated at 195° with a He flow rate of 50 ml/min: ir (max) 3420, 3060, 1600, 1500, 1320, 1250, 1010, 745, 690 cm^{-1}; nmr ($CDCl_3$) δ 6.04 (s, benzylic H), 6.1–7.6 (m, aromatic and furyl H's).

Anal. Calcd for $C_{17}H_{14}NOCl$: C, 71.95; H, 4.97; N, 4.94; Cl, 12.49. Found: C, 71.97; H, 4.91; N, 4.97; Cl, 12.71.

N-(*o*-Chlorophenyltetrahydrofurylmethyl)aniline (4b) was obtained by hydrogenation of 9.5 g (0.034 mol) of **5b** with 1.0 g of 5% rhodium on carbon in 150 ml of ethanol at 50 psi of hydrogen and 50° for 24 hr. The crude product was chromatographed on 80 g of silica gel with benzene as eluent. The first fraction (5.8 g) was **5b** while the second fraction was distilled to give 2.8 g, bp 175–176° (0.5 mm) of the diastereomeric mixture of **4b**: ir (max) 3400, 1600, 1500, 1310, 1055, 1025, 740, 680 cm^{-1}; nmr ($CDCl_3$) δ 1.5–2.1 (m, 4, β-tetrahydrofuryl H), 3.6–4.5 (m, α-tetrahydrofuryl H), 4.92 (d, 0.2, J = 5 Hz) and 5.07 (d, 0.8, J = 4 Hz) (benzylic H of the two isomers), 6.4–7.6 (m, 9, aromatic H); *m/e* (rel intensity) 289 (2, M^+), 287 (6, M^+), 218 (41, $M^+ - C_4H_7O$), 217 (19), 216 (100, $M^+ - C_4H_7O$), 180 (15), 104 (16), 77 (32), 71 (16).

Anal. Calcd for $C_{17}H_{18}NOCl$: C, 71.11; H, 6.32; N, 4.88; Cl, 12.35. Found: C, 71.15; H, 6.43; N, 4.80; Cl, 12.54.

Registry No.—**1**, 5877-49-6; *erythro*-**2a**, 36736-41-1; *threo*-**2a**, 36736-42-2; *erythro*-**2b**, 36736-43-3; *threo*-**2b**, 36736-44-4; (±)-**3**, 5297-98-3; *meso*-**3**, 6135-06-4, *erythro*-**4a**, 36736-45-5; *threo*-**4a**, 36736-46-6; *erythro*-**4b**, 36736-47-7; *threo*-**4b**, 36736-48-8; **5a**, 36749-19-6; **5b**, 36749-20-9; sodium, 7440-23-5; lithium, 7439-93-2; sodium naphthalenide, 3481-12-7.

Acknowledgment.—The research was financially supported by the National Research Council of Canada.

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[26] W. E. Truce and E. Wellisch, *J. Amer. Chem. Soc.*, **74**, 5177 (1952). We were unable to effect a successful reaction between *o*-chlorophenylmagnesium bromide and *N*-furfurylideneaniline.

The Diels–Alder Reaction of Polymethylnaphthalenes with Maleic Anhydride

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The effect of polymethyl substitution has been studied in the Diels–Alder reaction with maleic anhydride and eight polymethylnaphthalenes: 1,4-dimethyl- (**1**), 2,3-dimethyl- (**2**), 1,2,3,4-tetramethyl- (**3**), 1,4,5,8-tetramethyl- (**4**), 1,4,6,7-tetramethyl- (**5**), 1,2,3,4,5,8-hexamethyl- (**6**), 1,2,3,4,6,7-hexamethyl- (**7**), and octamethylnaphthalene (**8**). The reaction rates (in chloroform) were in the order of **6** (rel rate 40) > **8** (10) > **7** (3) > **3** (1) > **4** (0.4) > **5** > **2** > **1**. Nmr analysis of the products showed that **1** and **7** gave two structural isomers (1,4 and 5,8 adducts), **2**, **3**, **4**, and **6** gave only 1,4 adducts, and **5** gave the 5,8 adduct exclusively. The endo/exo isomer ratio of the adducts indicated a preferred configuration of the endo isomer (anhydride ring, anti to the benzene nucleus) for the naphthalenes bearing methyl groups on the reacting position while the exo isomer was preferred for the naphthalenes bearing no methyl group on that position. Examination of the reversibility of the reaction showed that the endo isomer is kinetically preferred while the exo isomer is thermodynamically more stable. A structural preference rule is discussed.

The Diels–Alder reaction of naphthalene with benzynes, acetylene dicarboxylates, and maleic anhydride exhibits only limited yields.[1] However, naphthalenes with alkyl substituents show enhanced reactivity towards dienophiles.[2] When methyl groups are in peri positions or even vicinal to each other, they may be shifted from their normal positions to out-of-plane positions and may complicate the diene system. This assumption is supported by X-ray analysis of octamethylnaphthalene by Donaldson and Robertson,[3] who mention that the methyl groups in this molecule are significantly displaced from the plane of the ring, but they gave little comment concerning the distortion of the naphthalene nucleus. Similarly, Gafner and Herbstein[4] have suggested a double-bladed propeller structure for octachloronaphthalenes. The possibility exists that the naphthalene nucleus itself loses its coplanarity, and the diminution of a planar geometry, if any, will change the electronic structure of the nucleus and may be reflected in the dienoid character of the ring halves.

In relation to the chemistry of octamethylnaphthalene,[1,5] we examined the Diels–Alder reaction of maleic anhydride with symmetrically substituted polymethylnaphthalenes with the purpose of obtaining further information on the effect of multialkyl substitution, especially in peri positions. In the present study it has been found that the reacting position in the naphthalene nucleus is influenced by varying positions of methyl substitution regardless of the number of methyl groups on the reacting ring, and that the endo/exo isomer distribution in the products depends on the position of methyl substituents as well. The peri interaction was also evidenced not only by the rate enhancement but in the high yields of thermally stable adducts for highly substituted polymethylnaphthalenes.

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[1] E. H. Rodd, "Chemistry of Carbon Compounds," Vol. III, Part B, Elsevier, Amsterdam, 1956, p 1361.

[2] M. C. Kloetzel, R. P. Dayton, and H. L. Herzog, *J. Amer. Chem. Soc.*, **72**, 273 (1950); M. C. Kloetzel and H. L. Herzog, *ibid.*, **72**, 1991 (1950).

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

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

[5] H. Hart and A. Oku, *J. Chem. Soc. D*, 254 (1972).

TABLE I
NMR CHEMICAL SHIFTS OF POLYMETHYLNAPHTHALENES[c]

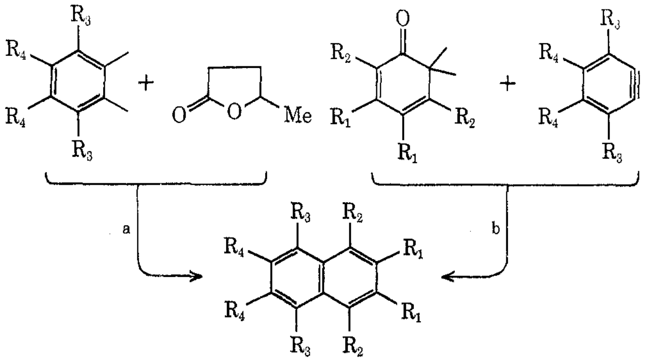
Polymethyl-naphthalene	Ring proton[a] 2,3	1,4	5,8	6,7	Methyl proton[a] 2,3	1,4	5,8	6,7
1	2.80		2.02[b]	2.50[b]		7.33		
2		2.44	2.31[b]	2.66[b]	7.60			
3			2.00[b]	2.60[b]	7.58	7.38		
4	2.82			2.82		7.19	7.19	
5	2.82		2.20			7.42		7.59
6				2.85	7.66	7.42	7.32	
7			2.16		7.63	7.43		7.58
8					7.68	7.51	7.51	7.68

[a] Singlet, unless otherwise mentioned. [b] Quartet: $J_1 = 7, J_2 = 3$ Hz. [c] In τ units, in $CDCl_3$, 100 MHz.

Results and Discussion

Preparation of Polymethylnaphthalenes and Their Spectra.—The introduction of methyl groups on a given position of the ring by a direct methylation of naphthalene is usually difficult. Mosby's method,[6] however, enabled us to prepare some naphthalenes bearing at least 1,4-dimethyl substituents (Scheme I, a). Also some highly substituted naphthalenes were prepared by treating benzyne adducts of hexamethyl-2,4-cyclohexadienone with methylsulfinylcarbinyl anion in dimethyl sulfoxide solution (Scheme I, b).[7]

SCHEME I



1, $R_1 = R_3 = R_4 = H$; $R_2 = Me$
2, $R_2 = R_3 = R_4 = H$; $R_1 = Me$
3, $R_3 = R_4 = H$; $R_1 = R_2 = Me$
4, $R_1 = R_4 = H$; $R_2 = R_3 = Me$
5, $R_1 = R_3 = H$; $R_2 = R_4 = Me$
6, $R_4 = H$; $R_1 = R_2 = R_3 = Me$
7, $R_3 = H$; $R_1 = R_2 = R_4 = Me$
8, $R_1 = R_2 = R_3 = R_4 = Me$

In spite of the extensive collection of nmr spectra catalogs, no systematic comparison of nmr spectra of polymethylnaphthalenes has been available. Comparative data obtained in the present study are listed in Table I.

Ultraviolet spectra of the polymethylnaphthalene system have been studied by a number of workers.[8,9] Dannenbergs[10] suggested that an additive value of +3 nm per one methyl group can be given to the bathochromic shift of the E_1 absorption band of this system. This value, however, does not fit the higher homologs than tetramethylnaphthalenes. A list of uv spectra (E_2 band) of the eight naphthalenes obtained in the present study is shown in Table II. Comparing the first three naphthalenes substituted on one half of the nucleus without steric hindrance, one can obtain the additive values of +14 and +4 nm bathochromic shift per one 1,4-dimethyl and 2,3-dimethyl substitution, respectively. The calculated wavelength according to eq 1 showed a comparatively good agreement with

$$\text{uv max (nm)} = 275 + 14a + 4b \qquad (1)$$

those observed except for **4**. So far as the minor difference between the calculated and the observed values for the E_2 band is concerned, one can hardly expect any appreciable perturbation of the electronic structure of the ring, which might be caused by losing the planarity of the ring.

TABLE II
ULTRAVIOLET SPECTRA OF POLYMETHYLNAPHTHALENES
(E_2 BAND, IN ETHANOL)

Polymethyl-naphthalene	λ_{max}, nm (log ϵ) Obsd	Calcd[a]	Obsd − Calcd
Naphthalene	275 (3.72)		(0)[b]
1	289 (3.79)		(0)[b]
2	279 (3.67)		(0)[b]
3	293 (3.76)	293	0
4	297 (3.87)	303	−6
5	291 (3.78)	293	−2
6	307 (3.82)	307	0
7	295 (3.71)	297	−2
8	311 (3.77)	311	0

[a] Calculated λ max (nm) = 275 + 14a + 4b (a, number of 1,4-Me_2 substitution; b, number of 2,3-Me_2 substitution). [b] Used as the standard of bathochromic shifts.

Diels–Alder Reaction of Polymethylnaphthalenes with Maleic Anhydride.—In spite of the earlier study[11] in which naphthalene itself had reacted with much difficulty, our previous study suggested that maleic anhydride could be a reactive dienophile toward polymethylnaphthalenes. The reaction was carried out at 110° in the molten state without solvent. When a powdered mixture of naphthalene and maleic anhydride melted in a sealed tube, the immediate appearance of a red color was observed, probably due to the formation of charge-transfer complex. The most typical example was exhibited by **6**, which melted and formed a red solution which solidified as a colorless solid in 5 min. The other mixtures remained as a red or orange solution through the heating period. The reaction was followed up by measuring the uv spectra of naph-

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(6) W. L. Mosby, *J. Amer. Chem. Soc.*, **74**, 2564 (1952).

(7) A. Oku, T. Kakihana, and H. Hart, *ibid.*, **89**, 4554 (1967).

(8) E. Heilbronner, U. Frolicher, and P. A. Plattner, *Helv. Chim. Acta*, **32**, 2479 (1949).

(9) W. L. Mosby, *J. Amer. Chem. Soc.*, **75**, 3348 (1953).

(10) H. Dannenberg and D. Dannenberg, *Chem. Ber.*, **89**, 1316, 1326 (1956).

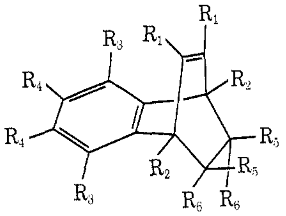
(11) K. Takeda, K. Kitahonoki, M. Sugiura, and Y. Takao, *Chem. Ber.*, **95**, 2344 (1962).

TABLE III

STRUCTURES OF THE DIELS–ALDER ADDUCTS AND THEIR NMR SPECTRA[g]

endo $\{R_5 = (\text{-COOCO-})/2, R_6 = H\}$

exo $\{R_5 = H, R_6 = (\text{-COOCO-})/2\}$

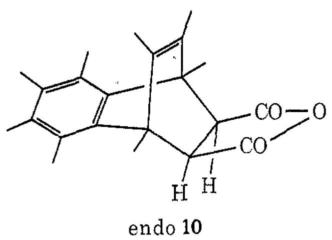


Poly-methyl-naphtha-lene	Adduct structure	¹H Chemical shifts[a] R₅	R₆	R₂	R₁	R₃	R₄
1	1,4 endo	[b]	H 7.03	Me 7.98	H 3.69	H 2.7	H 2.7
	exo	H 6.75		Me 8.00	H 3.65	H 2.7	H 2.7
	5,8 endo		H 6.80	H 5.25	H 3.33	Me 7.62	H 3.1
	exo	H 6.63		H 5.25	H 3.33	Me 7.69	H 3.1
2	1,4 endo		H 6.77[c]	H 5.84[c]	Me 8.22	H 2.8	H 2.8
	exo	H 6.61[c]		H 5.98[c]	Me 8.19	H 2.8	H 2.8
3	1,4 endo		H 7.13	Me 7.97	Me 8.27	H 2.7	H 2.7
	exo	H 6.95		Me 8.05	Me 8.25	H 2.7	H 2.7
4	1,4 endo		H 6.99	Me 7.84	H 3.82	Me 7.45	H 3.23
	exo	H 6.97		Me 7.80	H 3.80	Me 7.54	H 3.23
5	5,8 endo		H 6.82[d]	H 5.60[e]	Me 8.22	Me 7.62	H 3.14
	exo	H 6.61[d]		H 5.60[e]	Me 8.19	Me 7.69	H 3.14
6	1,4 endo		H 7.02	Me 7.79	Me 8.22	Me 7.50	H 3.22
7	1,4 endo		H 7.17	Me 8.01	Me 8.30	H 2.94	Me 7.73
	exo	H 6.93		Me 8.10	Me 8.20	H 2.74	Me 7.85
	5,8 endo		H 6.83[f]	H 5.52[f]	Me 8.23	Me 7.66	Me 7.80
	exo	H 6.65[f]		H 5.52[f]	Me 8.20	Me 7.72	Me 7.80
8	1,4 endo		H 7.05	Me 7.84	Me 8.23	Me 7.59	Me 7.75
	exo	H 6.89		Me 7.78	Me 8.26	Me 7.48	Me 7.76

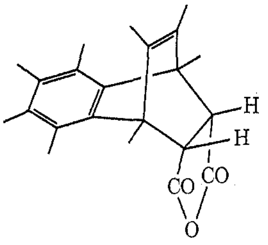
[a] Singlet, except ring protons. [b] (–COOCO–)/2. [c] Triplet: $J_1 = J_2 = 1.3\text{–}1.5$ Hz for both isomers. [d] Unclear triplet: $J_1 = J_2 = 1$ Hz. [e] Multiplet. [f] Unclear triplet: $J_1 = J_2 = 1\text{–}1.5$ Hz. [g] In τ units, in $CDCl_3$, 100 MHz.

thalenes and nmr spectra of the corresponding products. After heating for 6 hr at 110° all reactions seemed to have reached an equilibrium since no further decrease in naphthalene concentration nor the increase of products (by nmr) were detected. In some cases, prolonged heating caused the decomposition of products.

The structural determination of the Diels–Alder adducts was carried out on the basis of the nmr analysis of the products. Results are summarized in Table III. The endo and exo structures were assigned on the assumption that the methine proton which is on the α carbon to the carbonyl and anti to the benzene ring (exo isomer, **9**) should be relatively more deshielded than the syn methine proton of the corresponding endo isomer, **10**, in which the proton lies closer to the shielding region of the ring current.[12,13]



endo **10**



exo **9**

As illustrated in Tables III and IV, it is of interest that the position of methyl substituents affects not only the reaction rates (see Table VI) but also the positions to which maleic anhydride adds. Generally, the dienophile attacks a ring with a larger number of methyl substituents, as was first observed by Kloetzel and coworkers.[2] In the present study, however, some irregular addition occurred on the ring bearing a smaller number of methyl group (5,8 addition) as well as on the methyl-rich ring (1,4 addition) as illustrated by **1** and **7**. Moreover, an exclusive 5,8 addition was observed for **5**. Taking into account the significant

TABLE IV

ADDITION OF MALEIC ANHYDRIDE TO POLYMETHYLNAPHTHALENES[a]

Poly-methyl-naphtha-lene	Adduct structure[b]		Yield, % 1,4 Adduct	5,8 Adduct	exo/endo Ratio[c] 1,4 Adduct	5,8 Adduct
1	1,4	5,8	0.4	0.7	0.9	0.7
2	1,4		10		0.6	
3	1,4		82		0.05	
4	1,4		34		0.05	
5		5,8		20		0.55
6	1,4		100		0	
7	1,4	5,8	60	30	0.05	0.55
8	1,4		91		0.14	

[a] At 110°, [MA]/[naphthalene] = 1.0. Heated for 24 hr in sealed tubes without solvent. [b] 1,4 and 5,8 mean the adding position of maleic anhydride onto the ring based on the original numbering of the polymethylnaphthalenes. [c] Determined by nmr.

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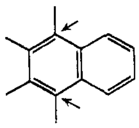
(12) *Cf.* C. D. verNooy and C. S. Rondestvedt, Jr., *J. Amer. Chem. Soc.*, **77**, 3583 (1955).

(13) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution NMR Spectroscopy," Vol. 1, Pergamon Press, Elmsford, N. Y., 1965, p 140. According to the equation by Johnson and Bovey, the chemical shift difference between exo and endo methine protons of a naphthalene–MA adduct was *ca.* 0.2 ppm, being consistent with the observed values. See Table III.



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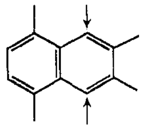
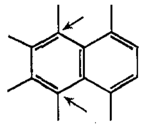


5



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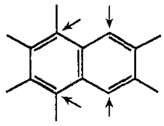


7

difference in reactivity between **1** and **2** as seen in Table IV, a general rule can be proposed as follows: (i) 1,4-dimethyl substitution somewhat disfavors 1,4 addition but favors 5,8 addition to some extent; (ii) 2,3-dimethyl substitution strongly favors 1,4 addition but disfavors 5,8 addition. A qualitative application of this empirical rule, which is also compatible with the results found by German workers,[14] to the other highly substituted homologs results in a comparatively good agreement with the reaction behaviors observed.[15] This rule presents a clear contrast to the reactive position of methyl-substituted nonaromatic 1,3-butadiene systems where, it has been known, trans 1- and/or 4-methyl substituents facilitate the 1,4 addition of a dienophile more effectively than 2- and/or 3-methyls.[16]

The preliminary uv and nmr analysis of the reaction mixtures showed that the substrate concentration reached a constant at 160° after 1 hr. Analogously to the earlier study,[2] it indicates a possible formation of an equilibrium and, therefore, the thermal dissociation of the isolated adducts was examined. Thermal reversibility of the reaction was demonstrated by the results shown in Table V. Thus, essentially the same equilibrium mixture was established in the following two cases: (a) a 1:1 mixture of an adduct and maleic anhydride; (b) a 1:2 mixture of a naphthalene and maleic anhydride. It is also shown that in the equilibrium dissociation is more facilitated at 155° than at 110° (see Table IV).

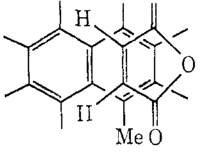
TABLE V

EQUILIBRATED THERMAL DISSOCIATION OF THE DIELS–ALDER ADDUCTS[a]

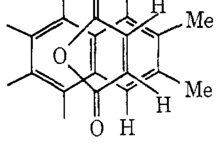
Starting adduct[b]	Equilibrated composition (%) Naphthalene	Equilibrated composition (%) Adduct[e]	Adduct structure	exo/endo Ratio[d] 1,4 Adduct	exo/endo Ratio[d] 5,8 Adduct
2-MA (**2′**)	90	10 (7)	1,4	0.6	
3-MA (**3′**)	60	40 (36)	1,4	0.5	
4-MA (**4′**)	77	23 (14)	1,4	0.13	
5-MA (**5′**)[c]	86	14 (14)	5,8		1.0
6-MA (**6′**)	0	100 (100)	1,4	0.0	
7-MA (**7′**)	30	70 (50)	1,4 and 5,8 (4:3)	0.3	0.7
8-MA (**8′**)	20	80 (60)	1,4	0.23	

[a] At 155°, [MA]/[adduct] = 1.0. Heated for 6 hr in sealed tubes. Maleic anhydride (MA) was mixed with the adduct to obtain an instant solution at the temperature. [b] Endo 1,4 adduct, unless otherwise stated. [c] Isomeric mixture (exo/endo = 0.55). [d] Determined by nmr with the data in Table III for comparison. [e] Values in parentheses are the yields of adducts obtained in the reaction at 160° with reactant ratio [MA]/[naphthalene] = 2.0.

The influence of the reaction temperature as well as of methyl substitution on the endo–exo orientation of the adduct is noticeable (compare Tables IV and V). The exo/endo ratios show that the exo isomer tends to increase as the temperature rises. This indicates that the exo form is thermodynamically more stable than the endo. The only exception was that the endo isomer obtained from **6** did not isomerize in the temperature range examined. On the other hand, the preferred formation of endo adduct at the lower temperature (110°) qualitatively indicates the kinetic preference of the endo form to the exo, and suggests that Alder's rule is applicable so that the maximum π accumulation is attained[17] between maleic anhydride and the one half of the naphthalene, as illustrated by the transition state A.[18] The ease of this thermodynamically controlled endo–exo isomerization also depends on the mode of methyl substitution. Thus, in case of **4**, **6**, **7**, and **8** where addition occurs to the 1,4-dimethyl-substituted position, the endo isomer predominates even at 155° (refer to the transition state A), whereas such systems as **2**, **5**, and **7** where no methyl group exists on the reacting position increase the amount of exo isomer (refer to the transition state B).



A



B

A kinetic study[19] on five naphthalenes (**3**, **4**, **6**, **7**, **8**) showed that their reaction rates with maleic anhydride are in the order of **6** (rel rate 40) > **8** (10) > **7** (3) > **3** (1) > **4** (0.4). (See Table VI.) The rates of the other three naphthalenes were incapable of being measured in this experiment. Interesting results are that **6** reacted four times faster than **8**, which is also four times faster than **7**, and that **4** showed a lower reactivity than **3**. Although the result shows some rate enhancement in the peri-substituted naphthalenes, the observed values are somewhat against our original expectation; that is, peri-substituted naphthalenes would react much faster than the other homologs where nonbonded methyl interaction does not exist, since the peri interaction would be released in the transition state where the atomic arrangement is rather close to that of the product in which no more appreciable interaction is likely to exist.[20] The peri dialkyl interaction in the naphthalene system has been known well,[21] and the acid-catalyzed isomerization of **6** into **7** as well as the

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[14] H. Plieninger, D. Wild, and J. Westphal, *Tetrahedron*, **25**, 5561 (1969).

[15] Mr. T. Hino of our group performed some extended LCAO-MO calculations on the polymethylnaphthalene systems. The result shows that the bond-order density and the atomic orbital population are higher at the 5,8 position for **1**, 1,4 for **2**, 1,4 for **3**, 5,8 for **5**, and 5,8 for **7**, than the other position. This result seems to account well for the reacting positions in these systems. We are indebted to Professor T. Yonezawa for allowing us to use his programming for the calculation.

[16] T. Inukai, *J. Syn. Org. Chem. Jap.*, **29**, 353 (1971).

[17] E. W. Butz and J. W. Butz, *J. Org. Chem.*, **7**, 199 (1942).

[18] This bimolecular orientation may be close to that of the corresponding CT complex. The CT bands of the complexes appear around 400 nm (maximum at 425 for **8**). A study of the CT equilibrium in connection with the naphthalene structure is under way.

[19] The rates were measured by two methods: (a) disappearance of the naphthalene by uv, (b) appearance of the adduct by nmr. Both methods agreed within the experimental error. Since Beer's Law is applicable (10^{-4}–10^{-6} mol/l. in $CHCl_3$) and the equilibrium constant for the formation of CT complex was very small in the above concentration range, only the result by a is presented here. In addition, no exo isomer was detected in this reaction by b.

[20] According to this assumption, the reactivity should have been in the order of **8** > **6** > **7** > **4** . . .

[21] For a review, see V. Balasubramaniyan, *Chem. Rev.*, **66**, 567 (1966).

TABLE VI

REACTION RATES OF POLYMETHYLNAPHTHALENES WITH MALEIC ANHYDRIDE IN CHLOROFORM[a]

Polymethylnaphthalene	Temp, °C	$k_2 \times 10^{-4}$, l./mol sec[b]
6	60 ± 0.5	4.45
	40 ± 0.5	1.14
8	60 ± 0.5	1.11
7	60 ± 0.1	0.31
3	60 ± 0.1	0.12
4	60 ± 0.1	0.04

[a] Concentration, 0.05 mol/l. for each reactant. Rates were determined by measuring the decrease in the strength of the E_2 band (uv) of naphthalenes. See also footnote 21. [b] Second-order rate constant for the equimolar reaction.

electrophilic oxidation of **8**[22,23] are also accounted for by this interaction. This discrepancy, however, could partly be rationalized by applying the general rule mentioned above. Thus, the methyl substitution on the 6,7 position of **6** should lower the reactivity of its 1,4 position down to a level somewhat higher than that of **7**. Similarly, the lower reactivity of **7** at its 1,4 position than that of **8** can be interpreted as the result of losing the 5,8-dimethyl group (which would activate the 1,4 position) from **8**.

To get a clearer view of this reaction, more experimental data and some theoretical treatment of polymethylnaphthalene systems[15] will be required.

Experimental Section

Nmr spectra were recorded on a LEOL 4H-100 spectrometer (100 MHz) and chemical shifts are given in τ units. These data are tabulated in Table III. Ultraviolet and ir spectra were taken on a Hitachi spectrophotometer Model 124 and JASCO IRA-1, respectively. Melting points are uncorrected.[24] Combustion analysis was performed by the Microanalytical Laboratory of Kyoto University. Product yields and isomer ratios are listed in Table IV.

Polymethylnaphthalenes.—The preparation of 1,4-dimethyl- and 1,4,5,8- and 1,4,6,7-tetramethylnaphthalenes has been reported by Mosby.[6] The purification of 1,4-dimethylnaphthalene (liquid) was achieved by forming the corresponding picrate. 2,3-Dimethylnaphthalene was commercially available. The other naphthalenes, 1,2,3,4-tetramethyl-, 1,2,3,4,5,8- and 1,2,3,4,6,7-hexamethyl-, and octamethylnaphthalene, were synthesized[1] from the Diels–Alder reaction of hexamethyl-2,4-cyclohexadienone with methyl-substituted benzynes.

Octamethylnaphthalene–Maleic Anhydride (MA) Adduct (8′).—In a sealed tube of 8 mm diameter × 80 mm length was charged a mixture of octamethylnaphthalene (0.242 g, 1 mmol) and MA (0.098 g, 1 mmol) under nitrogen. The tube was immersed in a bath controlled at 110 ± 2°. After 24 hr, the mixture was chromatographed (silica gel) with alcohol-free chloroform eluent. The first fraction contained the unreacted naphthalene (20 mg, 93% conversion) and the second fraction consisted of the isomeric mixture of the adduct (297 mg, 91%). Unreacted MA remained in the column. The adduct **8′**, *i.e.*, 1,4,5,6-tetramethyl-7,8-(tetramethylbenzo)bicyclo[2.2.2]octa-5,7-diene-2,3-dicarboxylic anhydride, consisted mainly of the endo isomer (7 parts) with a small amount of the exo isomer (1 part). The isomeric mixture had mp 153–160°; ir 1855, 1765 cm^{-1} (C=O, acid anhydride); uv max (chloroform) 280 nm (log ϵ 3.26).

Anal. Calcd for $C_{22}H_{26}O_3$: C, 78.07; H, 7.75. Found: C, 77.98; H, 7.68.

The pure endo isomer was separated by recrystallization from chloroform, mp 162°.

Similar experimental procedures were used for the reactions of MA with the other polymethylnaphthalenes.

1,2,3,4,6,7-Hexamethylnaphthalene–MA Adduct (7′).—Two structural isomers (1,4 and 5,8 adducts) were separated by recrystallizing the total isomeric mixture in chloroform. The major fraction (60%), mp 172–174°, was the endo 1,4 adduct and the minor fraction (30%), mp 175–185°, was a mixture of endo (2 parts) and exo (1 part) 5,8 adducts. The structural isomeric mixture had ir 1860, 1825, 1775 cm^{-1} (C=O); uv max (chloroform) 280 nm (log ϵ 3.16), 271 (3.14).

Anal. Calcd for $C_{20}H_{22}O_3$: C, 77.39; H, 7.14. Found: C, 77.29; H, 7.15.

1,2,3,4,5,8-Hexamethylnaphthalene–MA Adduct (6′).—The adduct, with quantitative yield, was composed exclusively of the *endo* 1,4 adduct (**6′**): mp 212–214°; ir 1860, 1825, 1772 cm^{-1} (C=O); uv max (chloroform) 283 nm (log ϵ 3.23), 275 (3.25).

Anal. Calcd for $C_{20}H_{22}O_3$: C, 77.39; H, 7.14. Found: C, 77.65; H, 7.08.

1,4,6,7-Tetramethylnaphthalene–MA Adduct (5′).—The isolated solid adduct was a mixture of endo and exo 5,8 adducts: mp 163–165°; ir 1855, 1825, 1775 cm^{-1} (C=O); uv max (chloroform) 279 nm (log ϵ 2.76), 270 (2.77).

Anal. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.08; H, 6.45.

1,4,5,8-Tetramethylnaphthalene–MA Adduct (4′).—The isolated product was a mixture of endo (more than 95 parts) and exo (less than 5 parts) adducts. The pure endo isomer was obtained by recrystallization from chloroform: mp 168–169°; ir 1855, 1825, 1765 cm^{-1} (C=O); uv max (chloroform) 283 nm (log ϵ 2.99), 275 (2.97).

Anal. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.53; H, 6.36.

1,2,3,4-Tetramethylnaphthalene–MA Adduct (3′).—The adduct was an isomeric mixture of endo (95 parts) and exo (5 parts) 1,4 adducts (not separated): mp 166–167°; ir 1850, 1820, 1765 cm^{-1} (C=O); uv max (chloroform) 272 nm (log ϵ 2.59), 265 (2.70).

Anal. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.27; H, 6.46.

2,3-Dimethylnaphthalene–MA Adduct (2′).—The isolated product was a mixture of endo (1 part) and exo (0.6 part) 1,4 adducts: mp 173–182°; ir 1858, 1835, 1770 cm^{-1} (C=O); uv max (chloroform) 273 nm (log ϵ 2.68), 266 (2.73), 259 (2.65).

Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 75.60; H, 5.64.

Recrystallization from carbon tetrachloride gave the endo isomer, mp 196°.

1,4-Dimethylnaphthalene–MA Adduct (1′).—Because of the lower reactivity of this liquid naphthalene, the reaction was carried out in 50-mmol scale. Only a small amount of the isomeric mixture (1,4 and 5,8 adducts) was obtained: mp 115–122°; ir 1855, 1775 cm^{-1} (C=O); uv max (chloroform) 281 nm (log ϵ 2.78), 272 (2.78).

Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 74.98; H, 5.97.

Kinetic Study.—A chloroform solution of a polymethylnaphthalene (100 mmol $l.^{-1}$) was mixed with an equal volume of a chloroform solution of MA (100 mmol $l.^{-1}$) under cooling. Immediately after the mixing, every 1.0 ml of the mixed solution (50 mmol $l.^{-1}$ for each reagent) was charged in a sealed tube, and the tubes were immersed in a bath (60 or 40 ± 0.2°). After every 75 min a tube was taken out and cooled to 0°, and the solution was diluted with chloroform for uv measurement. Simultaneously, every 5 ml of the kinetic solution was cooled down to 0° and quickly evaporated *in vacuo* to dryness, and the residue was diluted with deuteriochloroform for nmr measurement.

Retro Diels–Alder Reaction of the Isolated Adducts.—An equimolar mixture of an adduct (*ca.* 0.1–0.2 mmol) and MA was placed in a sealed tube, which was immersed in a bath (155 ± 2°) and shaken vigorously for 5 min until a clear solution was obtained. At this moment the immediate appearance of a color (yellow-red) was observed. After heating for 6 hr, the tube was quickly cooled down to 0° and the mixture was dissolved in deuteriochloroform for nmr analysis (see Table V).

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(22) Unpublished data. A quantitative isomerization of **6** to **7** was observed in a warm mixture of zinc cyanide and hydrogen chloride.

(23) H. Hart and A. Oku, *J. Org. Chem.*, **37**, 4274 (1972).

(24) By the capillary technique. The glass-plate technique, on the other hand, gave the higher melting point: **1′**, 115–125°; **2′**-endo, 220°; **3′**, 175–177°; **4′**-endo, 180–182°; **5′**, 176–179°; **6′**-endo, 234–235°; **7′**-1,4-endo, 178–180°; **7′**-5,8-, 210–220°; **8′**-endo, 163°. It seems difficult to get the precise melting point of these dissociable adducts.

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.

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Synthesis and Chemistry of Octamethylnaphthalene

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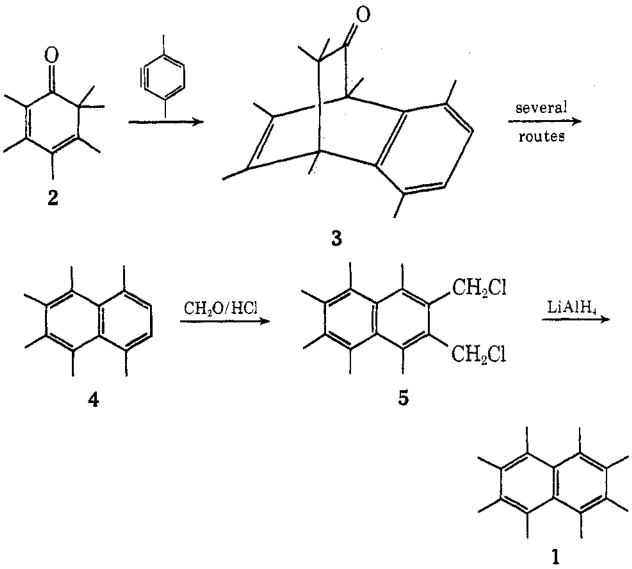
A five-step synthesis of octamethylnaphthalene (**1**) from hexamethylbenzene, overall yield 51%, is described. Addition of 3,6-dimethylbenzyne to hexamethyl-2,4-cyclohexadienone (**2**) gave adduct **3** which with dimsyl sodium eliminated butyric acid to give 1,2,3,4,5,8-hexamethylnaphthalene (**4**). 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 trifluoracetic 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.

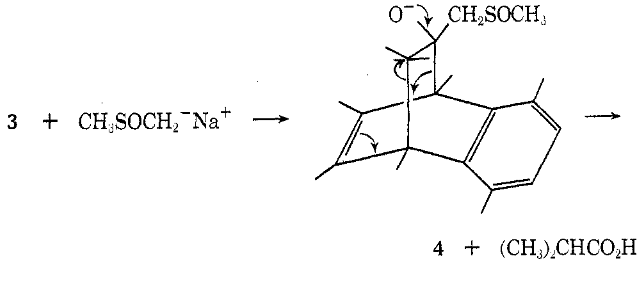
The original synthesis of **1**[6] unfortunately required many steps and was unattractive if **1** was to serve as the starting point for other investigations. Consequently, we developed and describe here a simple, high-yield synthesis of **1**.[7] We also describe here and in the following paper several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