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Reaction of Polymethylnaphthalenes with Dichlorocarbene. Formation of 1,2:3,4-Bis(dichloromethano)-1,2,3,4-tetrahydronaphthalenes and 1,2-Benzoheptafulvenes

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Addition of CCl_2 to eight polymethylnaphthalenes which have more than two methyl substituents has been examined. Major products were 1,2:3,4-bis(dichloromethano)-1,2,3,4-tetrahydronaphthalenes (2) and 1,2-benzoheptafulvenes (3). Benzospirononatrienes (4 and 5) were formed only from dimethyl- and 1,4,6,7-tetramethylnaphthalenes. Formation of 2 and 3 was facilitated by increasing the number of methyl substituents and was observed only in the case of naphthalenes which bear at least one 1,4-dimethyl substituent, whereas 3,4-benzoheptafulvenes were detectable only in the form of 3,4-benzospirononatrienes derived from 2,3-dimethyl-substituted rings. The structural determination of 3 is also described.

The preparation of benzoheptafulvene derivatives has been of interest in relation to the chemistry of nonbenzenoid aromatics. A common approach to the synthesis of heptafulvene series seems to start from tropones or benzoheptatrienes.[1] The reaction of methoxynaphthalenes with dichlorocarbene was reported to produce benzotropones.[2] Similarly, the intermediacy of methyl-substituted benzoheptafulvenes was postulated in the reaction of methylnaphthalenes with dichlorocarbene[3] where the isolated products were benzospirononatriene derivatives. However, benzoheptafulvenes were not isolated since they are unstable and undergo further reactions.

In the present paper, we would like to report the preparation of relatively stable polymethyl-substituted benzoheptafulvenes as well as the synthesis of bis(dichloromethano)tetrahydronaphthalenes by the reaction of highly methyl-substituted naphthalenes with dichlorocarbene. In the already reported reaction of octamethylnaphthalene,[4] a 3,4-benzoheptafulvene structure was assigned to one of the dibromocarbene addition products. Our present result, however, indicates that the correct structure must be the 1,2-benzo isomer.

Results and Discussion

An effective synthetic route to polymethylnaphthalenes has been reported[5] and it seems as useful as the long-known procedures involving alkylation and dehydrogenation.[6] Polymethylnaphthalenes which were prepared by the above methods and used in the present study have a C_2 axis of symmetry as to methyl substitution through both nuclei. Dichlorocarbene was generated from chloroform and potassium *tert*-butoxide in a benzene solution of a polymethylnaphthalene at 25°. Reaction products were separated by glpc and column chromatography and their structures were determined mainly by means of spectroscopic analyses. Results are shown in Table I.

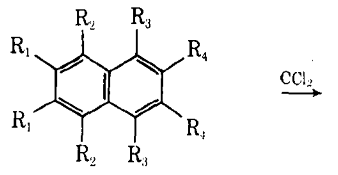
Table I
Reaction of Polymethylnaphthalenes with Dichlorocarbene[a]

Naphthalene (1)	CCl_2/1 mol ratio	Products, % 2	3	4	5	Total yield[e]
OMN (**1a**)	2	30	40			70
OMN (**1a**)	10	83	12			95[b]
1,2,3,4,5,8-HMN (**1b**)	2	16	16			32
1,2,3,4,6,7-HMN (**1c**)	2	17[c]	8			25
1,2,3,4-TMN (**1d**)	2	14	4			18
1,4,5,8-TMN (**1e**)	2	11	4			15
1,4,6,7-TMN (**1f**)	2	3[c]		0.2[c]	6[d]	9.2
1,4-DMN (**1g**)	4	1.5		0.5		2
2,3-DMN (**1h**)	4				5	5

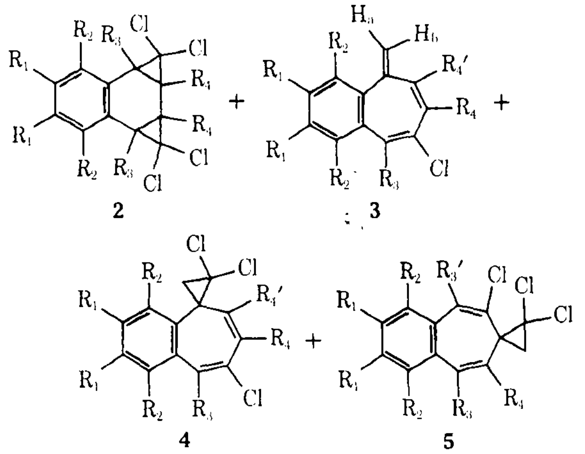
[a] At 25° in benzene. [b] At 0°. [c] CCl_2 added on the 1,4-dimethyl substituted ring. [d] CCl_2 added on the 6,7-dimethyl substituted ring. [e] Recovery of the unreacted naphthalenes was almost quantitative in each case.

In contrast to the study by Weyerstahl and Blume[3] on mono- and dimethylnaphthalenes where no products such as 2 or 3 were formed but only spirononatriene derivatives 4 or 5 (the same result was obtained in our study only for **1h**), the main products isolated in the reaction of highly methyl-substituted naphthalenes (**1a–g**) were the bis-addition products of CCl_2, *i.e.*, 1,2:3,4-bis(dichloromethano)-1,2,3,4-tetrahydronaphthalenes (**2**), and 4-chloro-1,2-benzoheptafulvenes (**3**). For example, octamethylnaphthalene (**1a**), the highest methyl-substituted homolog of this series, reacted most efficiently with CCl_2 to give **2a** and **3a** in good yields. It is also obvious that the minimum number of methyl substituents required for the formation as well as for the isolation of **2** is two, as indicated by **1g**, and it is four for the formation and isolation of **3**. The yields of both **2** and **3** increased when the number of methyl substituents increased (the total yield almost doubled with two additional methyls).

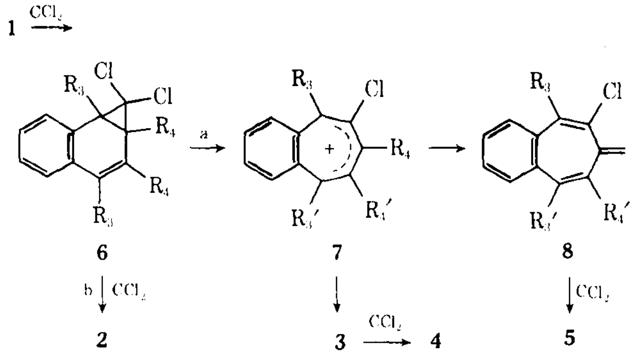
An increase in the amount of CCl_2 source enhanced the formation of **2** whereas higher temperature favored the formation of **3**; for example, when **1a** was treated with 10 equiv of CCl_2 source at 0°, the yield of **2a** increased to 83%. Since the intermediacy of a 2,3-benzonorcaradiene (**6**) can



1a, $R_1 = R_2 = R_3 = R_4 = Me$
b, $R_1 = H; R_2 = R_3 = R_4 = Me$
c, $R_2 = H; R_1 = R_3 = R_4 = Me$
d, $R_1 = R_2 = H; R_3 = R_4 = Me$
e, $R_1 = R_4 = H; R_2 = R_3 = Me$
f, $R_2 = R_4 = H; R_1 = R_3 = Me$
g, $R_1 = R_2 = R_4 = H; R_3 = Me$
h, $R_1 = R_2 = R_3 = H; R_4 = Me$



be postulated as the most rational reaction sequence, the two competing reactions (paths a and b in the following scheme) seem easily affected by the temperature, concentration, and substituents. In the reaction of unsubstituted naphthalene with dicyanocarbene generated thermally from the corresponding diazo precursor, the formation of three isomeric benzonorcaradienes was reported.[7] In the present study, however, although the attempt failed to isolate octamethylbenzonorcaradiene intermediates in the reaction of **1a**, a 2,3-benzonorcaradiene must be the only intermediate involved and the other benzo isomers (1,2 and 3,4) are not likely to be formed from CCl_2 generated from chloroform and potassium *tert*-butoxide.



Comparison in the reactivity of the 1,2 bond between 1,4- and 2,3-dimethyl-substituted rings indicates that 2,3-dimethyl substitution enhances the reactivity more than 1,4-dimethyl does[8] as shown in Table I. The total product yield from **1h** (5%) was higher than that from **1g** (2%), for example, and more illustrative was the behavior of **1h**, in which the 5,6 bond was twice as reactive as the 1,2 bond.

That highly methyl-substituted naphthalenes, **1a–e**, formed 1,2-benzoheptafulvenes but not their corresponding spirononatrienes implies that the reactivity of these naphthalenes with CCl_2 is much higher than that of the corresponding 1,2-benzoheptafulvenes. On the other hand, when the number of methyl substituents decreases, the reactivity of naphthalenes decreases and that of benzoheptafulvenes relatively increases to give spirononatrienes as illustrated in cases of **1f–h.**

Another substituent effect is that 1,4-dimethyl substitution seems either to stabilize the first-formed benzonorcaradiene skeleton or to enhance its 4,5-bond reactivity with CCl_2 more noticeably than 2,3-dimethyl substitution does. Thus, in all cases where 1,2-benzoheptafulvenes were isolated, the starting naphthalene necessarily had 1,4-dimethyl substitution and **2** was the main product. In contrast, none of the expected 1:2 adducts was formed from a naphthalene ring having only 2,3-dimethyl substitution (*cf.* **1f** and **1h**). This implies that the first-formed benzonorcaradiene intermediate undergoes ring opening much faster than CCl_2 addition. Most of the reported factors controlling the norcaradiene–cycloheptatriene equilibrium[9] may not be applicable to interpreting the stability of these benzo derivatives, because Cope-type rearrangement, if any, evidently perturbs the aromaticity of the system and therefore an ionic route becomes favorable for the formation of benzotropilium cation, which will be mentioned separately.

The preference of the 1,2-benzoheptafulvene structure to the 3,4-benzo structure was supported by the following nmr analyses. The first evidence was presented by classifying the chemical shift differences between two exo methylene hydrogens in benzoheptafulvene products (see Table II), where two values $\Delta\delta$ = 0.25 and 0.05 ppm were obtained, each corresponding to the structure with and without α-methyl groups on the unaffected benzene ring, respectively. In a 1,2-benzoheptafulvene structure, the expected peri interaction[10] between one of the exo methylene protons and α-methyl on the benzene ring increases the difference in chemical shifts between two methylene protons, whereas such an effect will not be significant in any 3,4-benzo structure (a similar effect is also shown in benzospirononatrienes, see Table III). The second nmr evidence is presented by the comparison of the chemical shifts of two α substituents (CH_3 or H) on the unaffected benzene ring with those of benzospirononatriene products (**4** and **5**) whose structures have been unequivocally established[3] (compare Tables II and III). Since the chemical shifts of two α hydrogens on the benzene ring of **4** appeared unequivalent whereas those of **5** appeared equivalent, we can presume to say that a closer location of the spiro moiety to the benzene ring will increase the chemical shift differences between two α substituents and also between two cyclopropane methylene hydrogens. With the same logic, the observed unequivalency in the chemical shifts of two R_2 groups in any of the isolated heptafulvenes leads us to support the 1,2-benzo structure.

A mechanistic consideration also gives a preference not only to the 1,2-benzo structure but also to the structure **10** over the alternative structure **12**. Among the three possible canonical structures **9a–c** of benzotropilium cation **7** which is formed by the solvolytic rearrangement of **6**, **9a** seems to have the lowest energy due to its benzylic character and the location of the electronegative chlorine atom substituted far from the cationic center, whereas both **9b** and **9c** have their chlorine on a vinyl position vicinal to the positive charge and the former may have a more or less nonplanar conjugation. Since any nucleophilic displacement by *tert*-butoxide or chloride anion is unlikely in this equilibrium, then, when $R_3 = R_3'$ = methyl, proton elimination from R_3' takes place to form 1,2-benzoheptafulvene (**10**). On the

Table II
Nmr Spectra of Methyl-Substituted 4-Chloro-1,2-benzoheptafulvenes (3)

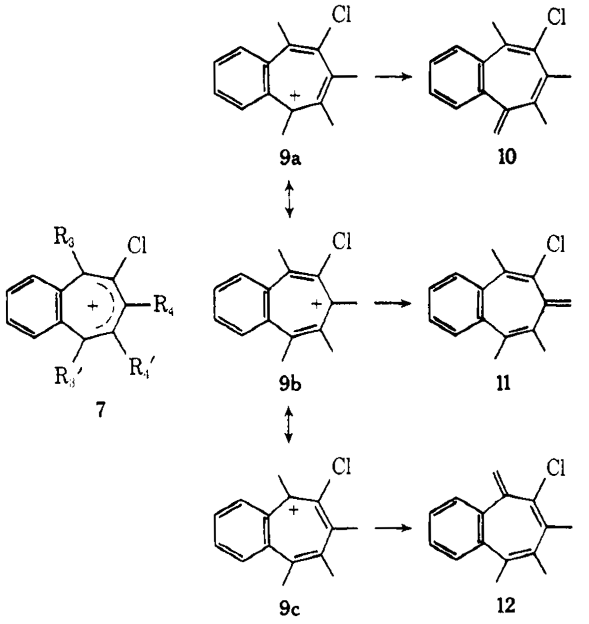
Compd no.	Starting naphthalene	Chemical Shifts, τ R_1	R_2	R_3	R_4	R_4'	exo-CH_2	$\Delta\delta(CH_2)$ ppm
3a	**1a**	Me 7.83	Me 7.83 7.90	Me 7.73	Me 8.22	Me 8.08	4.86 5.15 $J = 2.0$	0.29
3b	**1b**	H 3.00[a] 3.08	Me 7.69 7.71	Me 7.83	Me 8.18	Me 8.02	4.80 5.03 $J = 2.0$	0.23
3c	**1c**	Me 7.76	H 2.92 3.22	Me 7.68	Me 8.17	Me 8.02	4.97 5.02 $J = 2$	0.05
3d	**1d**	H 2.75–H 3.05[b]		Me 7.67	Me 8.14	Me 8.02	4.96 5.01 $J = 2$	0.05
3e	**1e**	H 2.99 3.08	Me 7.69 7.71	Me 7.77	H 4.10	H 3.64	4.76 4.97 $J = 1.7$	0.21
13	**1a**	Me 7.83	Me 7.83 7.90	Me 7.73	Me 8.20	Me 8.10	4.85 5.14 $J = 2.0$	0.29
16[c]	**1a**	Me 7.71,7.79, 7.80,7.82		Me 7.95	Me 8.34	Me 8.08	4.97 5.25 $J = 2.2$	0.28

[a] AB type, $J = 8$ Hz. [b] Multiplet. [c] Vinylic H which replaced Cl in **3a** appeared at 4.01.

Table III
Nmr Spectra of Benzospirononatrienes (4 and 5)

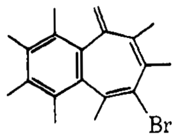
Compd no.	Chemical Shifts, τ R_1	R_2	R_3	R_3'	R_4	R_4'	exo-CH_2[a]	$\Delta\delta(CH_2)$, ppm
4f	Me 7.71 Me 7.73	H 2.73 H 3.14	Me 7.53[c]		H 3.80[c] ($J = 9$)	H 4.45 ($J = 9$)	7.75 8.13	0.38
4g	H 2.35–H 2.90[b]		Me 7.51		H 3.72 ($J = 10$)	H 4.40 ($J = 10$)	7.75 8.07	0.32
5f	H 3.06	Me 7.63	H 3.32 ($J = 1.5$)	H 3.03		Me 7.79 ($J = 1.5$)	8.00 8.14	0.14
5h	H 2.74	H 2.74	H 3.20 ($J = 1.5$)	H 2.93		Me 8.04 ($J = 1.5$)	7.90 8.10	0.20

[a] AB type, $J = 7.5$–8.0 Hz. [b] Multiplet. [c] $J = 0.5$ Hz.



other hand, when $R_3 = R_3'$ = hydrogen but R_4 = methyl, proton elimination from R_4 in the less favorable cation **9b** takes place to terminate the life of the cation. Therefore, from naphthalenes **1a–d** bearing four methyls on one ring, the formation of 1,2-benzoheptafulvenes is more favored, at least kinetically, than those of **12** and 3,4-benzo alternatives **11**.

Different from the above consideration, a 3,4-benzo structure **15** was postulated tentatively for a bromobenzo-



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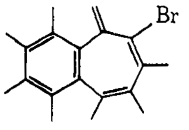

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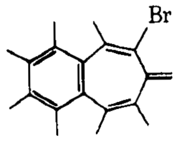

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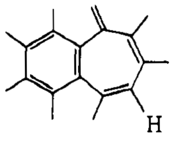
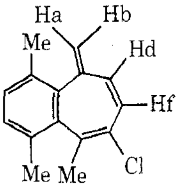


16

heptafulvene product obtained in the reaction of **1a** with CBr_2.[4,11] Though on reexamination we obtained the same reaction product as reported, its nmr spectrum was almost identical with the corresponding chloro derivative (*cf.* **13** and **3a** in Table II) and, moreover, the reduction of both **13** and **3a** with 2 equiv sodium naphthalene in THF at −50° gave the identical products[12] which were assigned the structure **16** on the basis of spectral evidence; therefore, the reported structure **15** should be replaced by **13**. The reduction product showed four aromatic methyls as singlets at τ 7.71, 7.79, 7.80, and 7.82, a doublet at 7.95 (3 H, $J = 1.4$ Hz coupling with a vinylic H, m, at 4.01), two broad singlets at 8.08 and 8.34 (allylic methyls coupling with each other by $J = 0.5$ Hz, and the latter also coupling slightly with H at 4.01), and a pair of doublets at 4.97 and 5.25 (exo methylene, J = 2.15 Hz). In this spectrum, three observations were made to assign the structure to 3,5,6-trimethyl-1,2(tetramethylbenzo)heptafulvene (**16**) rather than the 3,4,5-trimethyl isomer: (a) no coupling was observed between either of the exo methylene hydrogens and the vinylic hydrogen at 4.01, while in **3e** a coupling between each of the methylene hydrogens and the vinylic hydrogen (probably at the 6 position) was observed (J = 1.8 Hz, see the following paragraph); (b) the vinylic H at 4.01 couples with a methyl at 7.95 (J = 1.4 Hz) which appears at the lowest field among three allylic methyls; (c) the displacement of Cl by H does not influence the chemical shift difference between two exo methylene hydrogens in **3a** (see $\Delta\delta$ in Table II).

Additional support of the structure **10** may be presented by inspecting the spin–spin coupling mode in the product **3e**. The observed spectrum of this compound showed a triplet for one of the methylene hydrogens, and the J value between two endo vinylic hydrogens was as large as 10.2 Hz. Referring to the spectrum calculated for *trans*-1,3-butadiene,[13] the compound was assigned the structure **3e** having the chlorine atom at the 4 position.



3e

$J_{ab} = 1.8$

$J_{ad} = 1.8$

$J_{af} = 0.8$

$J_{bd} = 1.8$

$J_{df} = 10.2$

1,2-Benzoheptafulvenes, thus obtained in the present study, are not so stable except **3a** and darken on standing at room temperatures; on the other hand, 1,2:3,4-bis(dichloromethano)-1,2,3,4-tetrahydronaphthalenes (**2**), whose nmr spectra are tabulated in Table IV, are quite stable. And some novel reactions[14] of this geometrically strained system are now under way.

Table IV
Nmr Spectra of 1,2:3,4-Bis(dichloromethano)-1,2,3,4-tetrahydronaphthalenes (2)

	Chemical Shifts,[a] τ			
Compd no.	R_1	R_2	R_3	R_4
2a	Me 7.79	Me 7.72	Me 8.41	Me 8.69
2b	H 3.07	Me 7.68	Me 8.45	Me 8.68[b]
2c	Me 7.78	H 2.88	Me 8.43	Me 8.52
2d	H 2.80	H 2.60	Me 8.39	Me 8.46[c]
2e	H 3.06	Me 7.62	Me 8.50	H 8.13
2f	Me 7.76	H 2.87	Me 8.35	H 7.97
2g	H 2.75	H 2.65	Me 8.32	H 7.90[b, c]

[a] In CCl_4, singlet unless otherwise stated. [b] In $CDCl_3$, 60 MHz. [c] R_1 and R_2 showed an A_2B_2 pattern.

Experimental Section

Nmr spectra were recorded on Jeol 4H-100 and Varian HA-100 spectrometers (100 MHz) and chemical shifts are given in τ units. These data are tabulated in Tables II, III, and IV. Ultraviolet spectra were taken on a Hitachi 124 model. Melting points are uncorrected. Combustion analysis was performed by the Microanalytical Laboratory of Kyoto Univeristy.

Synthesis of Polymethylnaphthalenes. Four polymethylnaphthalenes, **1a–d**, were prepared according to the procedure reported.[4] Three naphthalenes, **1e–g**, were prepared by Mosby's method.[6] 2,3-Dimethylnaphthalene (**1h**) was commercially available.

Reaction of Polymethylnaphthalenes with Dichlorocarbene. To a stirred mixture of a polymethylnaphthalene (0.01 mol) and potassium *tert*-butoxide (0.02 mol) in 60 ml of dry benzene was added chloroform (0.02 mol) over a period of 30 min at 25°. After additional stirring at 25° for 4 hr, the reaction mixture was quenched by adding 20 ml of water. The organic layer was separated, the aqueous layer was extracted two times with 20 ml of benzene, and organic phases were combined, washed with water, and dried over anhydrous magnesium sulfate. A small portion of the benzene solution was analyzed by glpc (SE-30, 3%, 1 m) in which the eluting order of the reaction products was **3**, **1**, **4** or **5**, and **2**. The remainder of the solution was evaporated *in vacuo* to dryness and the product mixture was submitted to the separation procedures mentioned below for each reaction. In the following descriptions, column-chromatographic separations were carried out with silica gel using cyclohexane as eluent, and preparative glpc separations were carried out with a SE-30 column (3%, 1 m).

Octamethylnaphthalene (1a). The product mixture was chromatographed first to remove the unreacted **1a** and the obtained mixture of **2a** and **3a** was recrystallized from cyclohexane to give needle-like crystals of **2a:** mp 250–251°; P$^+$(*m/e*) 404; uv (cyclohexane) 223 nm (ϵ 35,300), 288 (302), and 297 (223).

Anal. Calcd for $C_{20}H_{24}Cl_4$: C, 59.13; H, 5.97. Found: C, 58.89; H, 5.98.

After removing **2a** as much as possible, the remainder was recrystallized from ethanol to give pure **3a** as block crystals: mp 125–126°; P$^+$(*m/e*) 286.

Anal. Calcd for $C_{19}H_{23}Cl$: C, 79.56; H, 8.08. Found: C, 79.30; H, 8.11.

1,2,3,4,5,8-Hexamethylnaphthalene (1b). The product mixture was separated into a mixture of **2b** and **3b** and unreacted **1b** by a column chromatography, in which the former eluted first. From the mixture of **2b** and **3b**, **2b** was isolated as colorless crystals by recrystallization from cyclohexane: mp 169.5–170.5°; P$^+$(*m/e*) 376.

Anal. Calcd for $C_{18}H_{20}Cl_4$: C, 57.16; H, 5.34. Found: C, 56.86; H, 5.28.

A preparative glpc of the cyclohexane filtrate gave **3b:** liquid; P$^+$ (*m/e*) 258; uv (cyclohexane) 225 nm (20,400), 260 (9080).

Anal. Calcd for $C_{17}H_{19}Cl$: C, 78.91; H, 7.41. Found: C, 78.62; H, 7.70.

1,2,3,4,6,7-Hexamethylnaphthalene (1c). Recrystallization of the product mixture from cyclohexane recovered a part of unreacted **1c**, and the filtrate was column chromatographed into two fractions. The first fraction consisted of **2c** and **3c**, and the second fraction of unreacted **1c**. Recrystallization of the first fraction from benzene afforded colorless solids of **2c:** mp 177.5–178°.

Anal. Calcd for $C_{18}H_{20}Cl_4$: C, 57.16; H, 5.34. Found: C, 56.99; H, 5.28.

A preparative glpc of the benzene filtrate gave **3c:** liquid; P$^+$(*m/e*) 258; uv (cyclohexane) 232 nm (23,200), 271 (9160).

Anal. Calcd for $C_{17}H_{19}Cl$: C, 78.91; H, 7.41. Found: C, 78.08; H, 7.75.

1,2,3,4-Tetramethylnaphthalene (1d). The procedure of the product separation was similar to that mentioned above for **1c**, except petroleum ether was used as a recrystallization solvent. **2d:** mp 113–114°.

Anal. Calcd for $C_{16}H_{16}Cl_4$: C, 54.88; H, 4.61. Found: C, 54.68; H, 4.87.

3d: liquid; P$^+$(*m/e*) 230; uv (cyclohexane) 225 nm (21,000), 263 (7000).

Anal. Calcd for $C_{15}H_{15}Cl$: C, 78.08; H, 6.55. Found: C, 77.81; H, 6.76.

1,4,5,8-Tetramethylnaphthalene (1e). Recrystallization of the product mixture from petroleum ether afforded a solid which consisted of **2e** and **1e**. This mixture was chromatographed to give pure **2e:** mp 171–171.5°.

Anal. Calcd for $C_{16}H_{16}Cl_4$: C, 54.88; H, 4.61. Found: C, 55.07; H, 4.64.

The petroleum ether filtrate was also chromatographed to give **3e** containing a small amount of **2e** which could be removed by a preparative glpc. **3e:** liquid; P$^+$(*m/e*) 230; uv (cyclohexane) 260 nm (9000).

Anal. Calcd for $C_{15}H_{15}Cl$: C, 78.08; H, 6.55. Found: C, 77.84; H, 6.79.

1,4,6,7-Tetramethylnaphthalene (1f). The product mixture was distilled using a saber-shaped flask to remove unreacted **1f**. The residual material was separated into three fractions by a column chromatography. The first fraction consisted of **2f** and **5f**, the second fraction consisted of **1f**, and the last consisted of **4f**. **4f:** mp 187–188.5°; P$^+$(*m/e*) 312; uv (cyclohexane) 219 nm (26,200), 274 (7920).

Anal. Calcd for $C_{16}H_{15}Cl_3$: C, 61.27; H, 4.82. Found: C, 61.15; H, 4.82.

Recrystallization of the first fraction from benzene afforded colorless crystals of **2f:** mp 217.5–218.5°.

Anal. Calcd for $C_{16}H_{16}Cl_4$: C, 54.88; H, 4.61. Found: C, 55.15; H, 4.43.

Pure **5f** was obtained from the filtrate by changing the recrystallization solvent to methanol: mp 92–93.5°; P$^+$(*m/e*) 312; uv (cyclohexane) 239 nm (32,100), 310 (1020).

Anal. Calcd for $C_{16}H_{15}Cl_3$: C, 61.27; H, 4.82. Found: C, 61.00; H, 5.07.

1,4-Dimethylnaphthalene (1g). The product mixture was distilled *in vacuo* to remove unreacted **1g**. The residual material was chromatographed into three fractions. The first fraction consisted of **2g** and **1g**, the second fraction consisted of **1g**, and the last consisted of **4g**. **4g:** liquid; P$^+$(*m/e*) 284; uv (cyclohexane) 228 nm (16,000), 272 (6310).

Anal. Calcd for $C_{14}H_{11}Cl_3$: C, 58.88; H, 3.88. Found: C, 59.28; H, 4.26.

Pure **2g** was obtained by a preparative glpc separation of the first fraction: mp 155–156°.

Anal. Calcd for $C_{14}H_{12}Cl_4$: C, 52.21; H, 3.76. Found: C, 52.50; H, 3.97.

2,3-Dimethylnaphthalene (1h). The product mixture was recrystallized from cyclohexane to remove the unreacted **1h**. The filtrate was chromatographed by preparative glpc to give **5h:** mp 93.5–95.5°; P$^+$(*m/e*) 284; uv (cyclohexane) 240 nm (40,680), 263 (5770).

Anal. Calcd for $C_{14}H_{11}Cl_3$: C, 58.88; H, 3.88. Found: C, 58.98; H, 3.81.

Reduction of 3a (as well as of 13) with Sodium Naphthalene. 4-Chloro-3,5,6-trimethyl-1,2-(tetramethylbenzo)heptafulvene (**3a**, 1.0 g, 3.5 mmol) was dissolved in dry THF (50 ml), and the solution was flushed with purified nitrogen stream for 20 min. To this solution at −50° was added dropwise 8 ml (*ca.* 7 mmol) of a THF solution of sodium naphthalene prepared from 2.3 g of sodium metal and 12.8 g of naphthalene in 100 ml of THF. After an additional 1 hr of stirring at −50°, 10 ml of a mixture of THF and water (3:1) was added to the reaction flask and the temperature was raised to 25°. Water (50 ml) was added, the reaction mixture was extracted with ether, and the ethereal solution was dried over anhydrous magnesium sulfate. After evaporating solvent, naphthalene was removed by sublimation at 40° (2 mm). The glpc analysis of the residue proved that **16** was the only product detectable and the remainder was chromatographed by silica gel and petroleum ether to give 3,5,6-trimethyl-1,2-(tetramethylbenzo)heptafulvene (**16**): 0.20 g (23%); mp 104.5–105°; P$^+$(*m/e*) 252. For the nmr spectrum, see the text.

Reduction of **13** with sodium naphthalene by the same procedure gave the identical product with **16** in a 48% yield.

Registry No.—1a, 18623-61-5; **1b**, 36230-30-5; **1c**, 17384-76-8; **1d**, 3031-15-0; **1e**, 2717-39-7; **1f**, 13764-18-6; **1g**, 571-58-4; **1h**, 581-40-8; **2a**, 52033-53-1; **2b**, 53849-11-9; **2c**, 53849-12-0; **2d**, 53849-13-1; **2e**, 53849-14-2; **2f**, 53849-15-3; **2g**, 53849-16-4; **3a**, 53849-17-5; **3b**, 53849-18-6; **3c**, 53849-19-7; **3d**, 53849-20-0; **3e**, 53849-21-1; **4f**, 53849-22-2; **4g**, 53849-23-3; **5f**, 53849-24-4; **5h**, 29042-89-5; **13**, 53849-25-5; **16**, 53849-26-6; dichlorocarbene, 1605-72-7.

References and Notes

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(11) When the reaction of **1a** with CBr_2 was carried out at higher temperatures than 30°, another product to which we tentatively assign the structure **14** was obtained in a low yield. The nmr spectrum of this product showed its exo methylene protons at 4.64 and 5.05 as a pair of doublets.
(12) When some excess amount of sodium naphthalene was used in this reduction, the exo double bond of **13** was reduced to give a mixture of two isomeric benzocycloheptatrienes.
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