ference in the special interaction (*viz.* phenyl–phenyl, *n*-hexyl-phenyl) and the difference in the flexibility between phenyl and *n*-hexyl groups.

Solvent effects in the ratio of ethers obtained are shown in Tables I and II. In the epimerization reactions carried out in less polar solvent, *i.e.*, *n*-hexane or carbon tetrachloride, remarkable difference in the ratio of two isomers formed is observed. Presumably, steric interaction is mitigated because of solvation.

Experimental Section

(−)-α-Phenylethyl Alcohol. Material prepared according to the method of Pickard and Kenyon[17] had specific rotation ($[\alpha]^{25}$ D) of −45.7° (in CCl_4).

Authentic Bis(α-phenylethyl) Ether.[18] A mixture of 30 ml of concentrated sulfuric acid, 20 ml of water, and 150 ml of (±)-α-phenylethyl alcohol was stirred for 2 hr at room temperature. The organic layer was washed with water and distilled under reduced pressure. Ether obtained consisted of 45.4% *dl* and 54.6% meso isomer. Since epimerization of bis(α-phenylethyl) ether under the experimental condition was observed to occur very slowly, the composition of authentic ether is kinetically controlled.

2-Octyl α-Phenylethyl Ether. A mixture of 0.1 g-atom of sodium, 20 ml of toluene, and 20 g of 2-octanol was heated under reflux for 5 hr. To this solution 0.1 mol of α-phenylethyl chloride was added and the mixture was heated under reflux for 0.5 hr. The reaction mixture was washed with water and distilled under reduced pressure. 2-Octyl α-phenylethyl ether was separated from this distillate by glc using a 2.0-m poly(ethylene glycol isophthalate), 20% on chromosorb W, column. *Anal.* Calcd for $C_{16}H_{26}O$: C, 81.99; H, 11.18. Found: C, 81.11; H, 11.52. Two isomers of this ether were separated from the ether mixture using this column.

Isolation of Bis(α-phenylethyl) Ether. A solution of (−)-α-phenylethyl alcohol (1.6 g) in liquid sulfur dioxide (21 ml) was allowed to stand for 3 days and liquid sulfur dioxide was evaporated. From the residual liquid optically inactive bis(α-phenylethyl) ether was obtained using a 0.6-m silicone gum SE-30, 15% on Chromosorb W, column at 140°. *Anal.* Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 84.67; H, 8.52.

In Scheme I, a 0.6-m silicone gum SE-30, 15% on Chromosorb W, column was used at 140° in procedure a and a 2.0-m poly(ethylene glycol isophthalate), 20% on Chromosorb W, column was used at 160° in procedure b.

General Procedure of Epimerization. Ether and boron trifluoride etherate were sealed in separate glass phials. These phials were set in a reaction vessel, into which solvent was introduced. The reaction was started by breaking the phials. At an appropriate time the reaction was quenched by putting into a dilute alkaline aqueous solution. The product was extracted with ethyl ether and analyzed by glc using a 4.5-m ethylene glycol adipate polyester, 20% on Chromosorb W, column at 180° (for 2-octyl α-phenylethyl ether) or at 200° [for bis(α-phenylethyl) ether].

Registry No.—(−)-α-Phenylethyl alcohol, 1445-91-6; *meso*-bis(α-phenylethyl) ether, 53776-68-4; *dl*-bis(α-phenylethyl) ether, 53776-69-5; 2-octanol, 123-96-6; α-phenylethyl chloride, 672-65-1; *erythro*-2-octyl α-phenylethyl ether, 53716-30-6; *threo*-2-octyl α-phenylethyl ether, 53716-31-7.

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Thermal Decomposition of Some Bis(cyclododecylidene) Cycloalkylidene Triperoxides in Chlorobenzene

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The effect of substituent and ring size on the rate of decomposition of some bis(cyclododecylidene) cycloalkylidene triperoxides has been studied. Although the effect is not large, there are indications that both the substituent and the ring size may influence the rate of decomposition.

In 1967 Story and coworkers found that the thermal and photochemical decomposition of cyclic di-and triperoxides such as I and II produced macrocyclic hydrocarbons and lactones in fair to good yields.[2] The reaction is represented by eq 1 and 2.

As an extension of this earlier work, we have undertaken a detailed study on the thermal decomposition of peroxides such as I and II. These peroxides have been shown to be important both synthetically and economically.[3] In this paper, as a continuation of our studies on cyclic ketone peroxides, we wish to report our results on the thermal decomposition of the peroxides III and IV.

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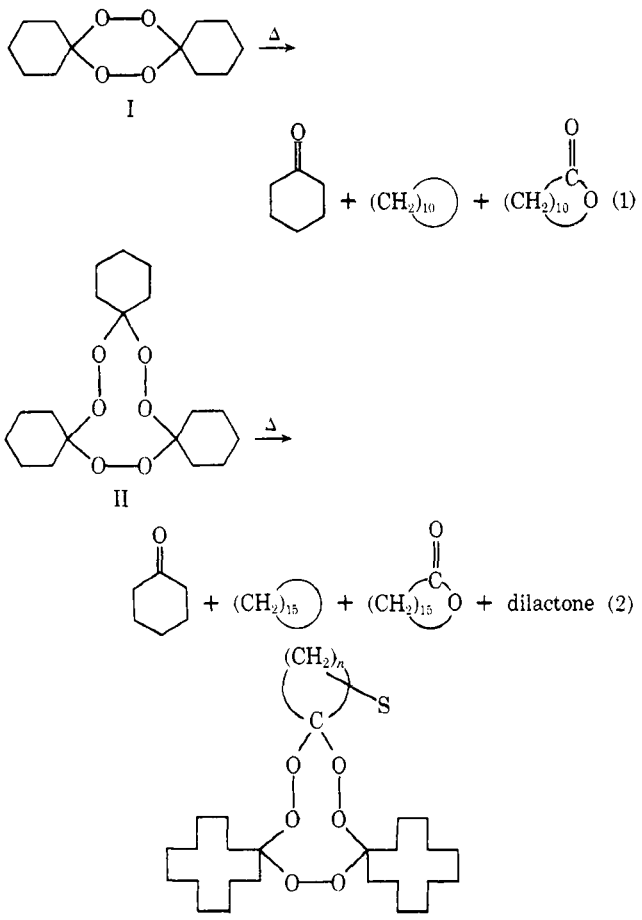
Results

Rate measurements were made on some bis(cyclododecylidene) substituted-cycloalkylidene triperoxides by the spectrophotometric singlet oxygen method previously reported.[4] We have found this method to be useful for following the rate of decomposition of a number of cyclic ketone peroxides. The data are shown in Table I.

For most cyclic ketone peroxides, the rate of decomposition could be monitored at such a low concentration of peroxide that induced decomposition was negligible,[5-7] The solvent chlorobenzene was chosen because it gave the most reproducible results. (Two runs at 155° on IIIa show the reproducibility.)

In order to confirm that this method was actually mea-



III, n = 5: a, S = H; b, S = 4-OMe; c, S = 4-t-Bu; d, S = 4-Et; e, S = 4-Me; f, S = 3-Me; g, S = 2-Me
IV, S = H: a, n = 4; b, n = 6; c, n = 7; d, n = 11

suring the rate of decomposition of the peroxide, several rate measurements were made on IIIa by infrared methods. The run determined at 155° is in excellent agreement with those determined spectrophotometrically. The measurement at 150° falls on the line determined by plotting log k *vs.* $1/T$(°K).

It is interesting to compare the rate of decomposition of this series of peroxides with dicyclohexylidene diperoxide (I) and tricyclohexylidene triperoxide (II). Compound I has a half-life of ~25 min at 160° in chlorobenzene. IIIa has a half-life of ~29 min at 160° in the same solvent. In benzene and toluene, II has a half-life of ~10 min. Thus, it appears that IIIa decomposes at about the same rate as I but at a slightly lower rate than II.

If one examines the other entries in Table I, it is obvious that there is not a large difference in the rate of decomposition although there is a definite trend. The exception is IIIg which decomposes significantly faster than the other entries in Table I.

A semilog plot of rate constant *vs.* σ_m, σ^*, or σ_I[8,9] gives a poor correlation with $\rho \lesssim 0.1$. Thus, the near-zero value of ρ (along with the poor correlation) suggests that inductive effects are not an important factor in the decomposition of this series of peroxides.

Rate measurements were also made on some bis(cyclododecylidene) cycloalkylidene triperoxides IV in chlorobenzene. The data are shown in Table II. Again, it is obvious that the effect of ring size on the rate of decomposition is not large but there is a trend.

This trend is very evident if one examines Figures 1 and 2. Figure 1 is a semilog plot of rate constant *vs.* ring size for some bis(cyclododecylidene) cycloalkylidene triperoxides

Table I
Rate Measurements for Some Bis(cyclododecylidene) Substituted-Cyclohexylidene Triperoxides in Chlorobenzene

Peroxide	T, °C	$10^3 P_0$,[a] M	$10^5 k$, sec^{-1} (±sd)	$t_{1/2}$,[b] min
IIIa	160.1	4.04	40.1 (±2.4)	28.8
	155.1[c]	60.4	30.3	38.0
	155.1	3.82	30.1 (±2.3)	38.3
	155.1	4.04	31.5 (±6.5)	36.7
	150.1[c]	60.0	15.8	73.0
	145.1	4.04	11.4 (±0.6)	101
IIIb	160.1	3.93	35.8 (±3.4)	32.3
	155.1		20.5 (±1.1)	56.5
	150.1		10.5 (±0.9)	110
IIIc	160.1	3.05	41.9 (±2.6)	27.6
	155.1		28.8 (±0.5)	40.1
	150.1		15.3 (±0.6)	75.7
	145.1		6.48 (±0.62)	178
IIId	160.1	2.36	53.5 (±4.3)	21.6
	155.1		27.4 (±1.4)	42.1
	145.1		12.0 (±1.7)	96.6
IIIe	160.1	3.38	47.7 (±2.7)	24.2
	155.1	4.07	27.0 (±0.9)	42.8
	145.1		9.44(±0.69)	122
IIIf	165.1	3.82	63.6 (±3.8)	18.2
	160.1		44.7 (±4.4)	25.8
	150.1		11.0 (±1.1)	105
IIIg	155.1	4.20	91.8 (±3.2)	12.6
	150.1		64.3 (±8.1)	18.0
	145.1		41.0 (±1.5)	28.2
	140.1		34.7 (±2.4)	33.3

[a] Initial peroxide concentration. [b] Half-life. [c] Rate constant obtained by ir methods.

Table II
Rate Measurements for Some Bis(cyclododecylidene) Cycloalkylidene Triperoxides in Chlorobenzene

Peroxide	T, °C	$10^3 P_0$,[a] M	$10^5 k$ sec^{-1} (±sd)	$t_{1/2}$,[b] min
IVa	160.1	3.83	80.6 (±2.5)	14.3
	150.1		32.9 (±1.4)	35.1
	145.1		21.5 (±0.5)	53.8
	140.1	2.78	11.5 (±1.1)	100
IVb	165.1	2.64	56.7 (±7.1)	20.4
	155.1		21.1 (±2.5)	54.7
	150.1		14.8	78.0
IVc	165.1	3.54	77.8 (±8.7)	14.6
	155.1		37.7 (±5.7)	30.6
IVd	165.1	3.54	88.0 (±9.4)	13.1
	160.1		65.2 (±7.8)	17.7
	150.1		30.2 (±4.2)	38.3

[a] Initial peroxide concentration. [b] Half-life.

at 150° in chlorobenzene. The minimum in the curve is around 6 or 7. (The rate constants which determine these two points are the same within experimental error.)

Figure 2 is a semilog plot of rate constant *vs.* ring strain.[10] The plot is typical for a reaction where rate is dependent on ring strain.[11]

Table III contains the activation parameters calculated for nine peroxides. The second, third, and sixth entries of the table contain values which seem to us to be 4–5 kcal high. (This may be due to the fact that values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were calculated from rate constants determined over only 10–15°.)

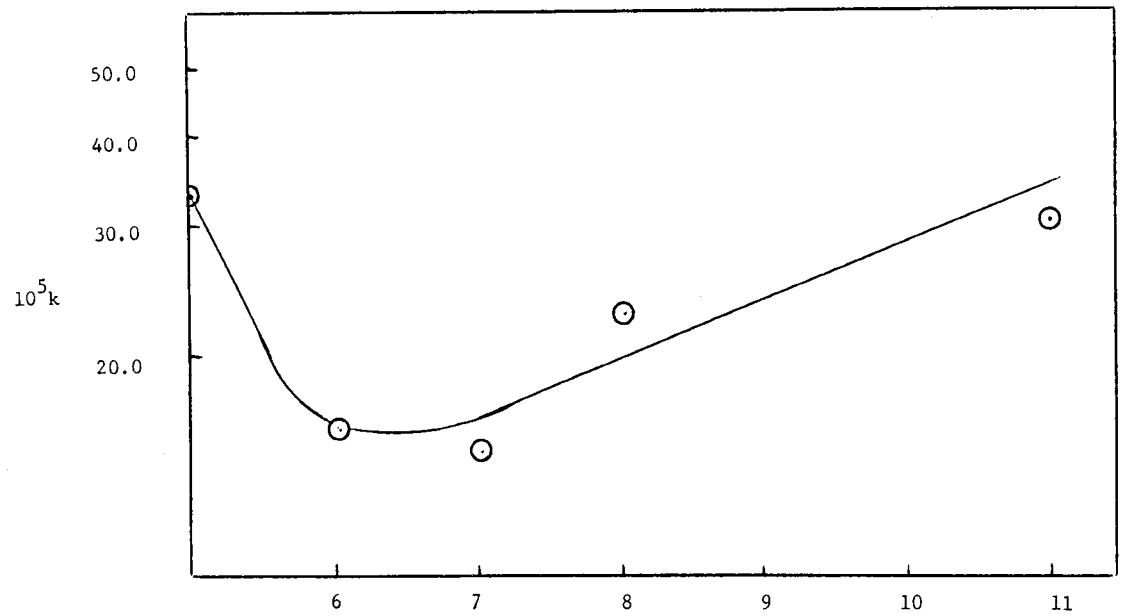


Figure 1. Semilog plot of rate constant *vs.* *n* (ring size) for some bis(cyclododecylidene) cycloalkylidene triperoxides in chlorobenzene at 150°.

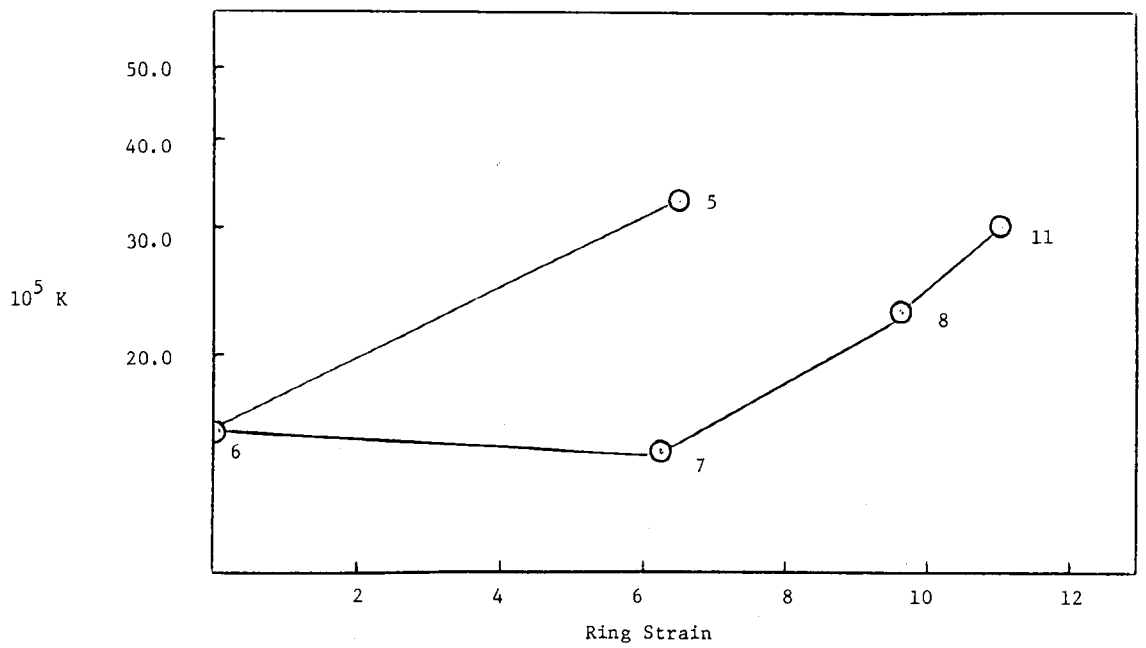


Figure 2. Semilog plot of rate constant *vs.* ring strain for some bis(cyclododecylidene) cycloalkylidene diperoxides in chlorobenzene at 150°.

Table III
Activation Parameters for Some Bis(cyclododecylidene) Cyclohexylidene Triperoxides in Chlorobenzene

Peroxide	$\Delta H^{\ddagger}$, kcal/mol (±sd)	$\Delta S^{\ddagger}$, eu (±sd)	Peroxide	$\Delta H^{\ddagger}$, kcal/mol (±sd)	$\Delta S^{\ddagger}$, eu (±sd)
IIIa	31.1 (±1.1)	1.5 (±2.4)	IIIf	44.1 (±1.7)	30.9 (±3.9)
IIIb	44.4 (±1.1)	31.3 (±2.4)	IIIg	23.8 (±1.7)	−13.8 (±3.8)
IIIc	45.3 (±2.5)	34.1 (±6.0)	IVa	34.0 (±1.0)	9.1 (±2.4)
IIId	34.8 (±1.2)	9.8 (±2.8)	IVb	33.5 (±1.5)	6.3 (±3.5)
IIIe	38.7 (±0.2)	18.7 (±0.5)			

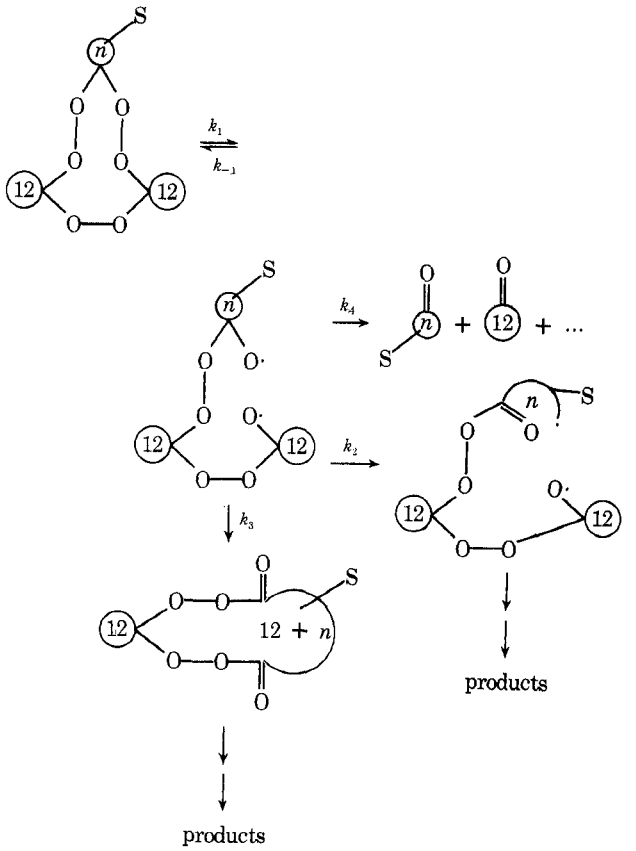
Discussion

The first step in the decomposition of cyclic ketone peroxides is undoubtedly the homolysis of the O–O bond (Scheme I).[12] The above data indicate that this bond is influenced only very slightly (if at all) by inductive effects. Because the diradical formed upon homolysis of one of the O–O bonds cannot diffuse from the solvent cage[13-17] (without rupture of another bond), it probably combines easily to re-form the peroxide.[18]

Once the diradical is formed, it may undergo the other reactions indicated in Scheme I as well as combination to re-form the peroxide. It is in these second steps (k_2, k_3, k_4) where ring size (and therefore ring strain) may influence the rate of decomposition. This may be more apparent if one examines eq 3 which was derived from the data in Scheme I.

$$-d(P)/dt = \frac{k_1 (k_2 + k_3 + k_4)[P]}{k_{-1} + k_2 + k_3 + k_4} = k_{obsd}[P] \quad (3)$$

Scheme I[18]

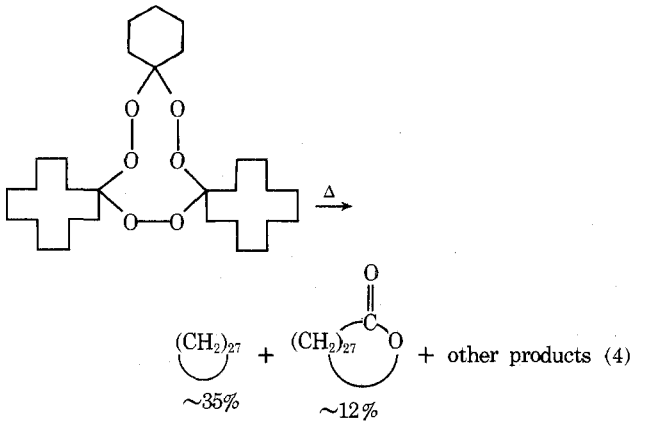


It is also possible for the substituent in III to exert its influence in the second steps (k_2, k_3, k_4) of the decomposition. This may be rationalized in terms of conformational effects.

The effect of alkyl groups on the stability of ring systems has been interpreted by Allinger in terms of the difference in the number of gauche interactions of cyclic and noncyclic analogs.[19] Indeed, it is well-known that alkyl substitution tends to promote cyclization (the so called *gem*-dimethyl effect).[20-23]

Therefore, if alkyl groups may influence the stability of a ring, the rates of the second steps (k_2, k_3, k_4) could well be influenced by the substituent. This would, of course, be reflected in the observed rate of decomposition of the peroxide.

The yields of macrocycles from the thermal decomposition of III and IV have been determined and are entirely typical for a trimeric cyclic peroxide (eq 4). The synthesis



(4)

and thermal decomposition of these peroxides for the purpose of macrocyclic synthesis is reported elsewhere.[24]

Experimental Section

Instrumentation. Quantitative ir analysis was done with a Perkin-Elmer IR-621.

A Beckman Model DU uv–visible spectrophotometer was used for the kinetic experiments with tetracyclone.

Two temperature baths were used: (a) a Sargent Model NSI-12 heater and circulator; (b) a Sargent Model NCI-33 heater with a built-in thermostat.

An IBM-360 computer was used for the least-squares treatment of the kinetic data.

Solvents and Reagents. Chlorobenzene (Aldrich) was distilled from a small quantity of tetracyclone and stored in a dark bottle over 4A molecular sieves.

Tetracyclone (Aldrich, mp 218–222°) was used without further purification.

Peroxides. The preparation of peroxides III and IV are given in detail elsewhere.[25]

Preparation of Cuvettes and Vials. Cuvettes were prepared from 10- and 8-mm (inside diameter) Pyrex tubing and were available commercially. A Pyrex glass tube of 5-mm diameter and 80-mm length was fused to the cuvette. A constriction was formed 20 mm from the open end to aid in sealing the cuvette after degassing.

Vials used in the infrared kinetic studies were made in the following manner. An 18 × 150 mm Pyrex test tube was constricted about 20–30 mm from the open end. The test tube was broken at the constriction and a Pyrex glass tube of 5-mm diameter and 80-mm length was fused on. A constriction was formed 20 mm from the open end of the glass tube to be used in sealing off the vial.

Beer's Law for Tetracyclone in Chlorobenzene Solution. Tetracyclone obeyed Beer's law throughout the concentration area of interest.

Infrared Rate Measurements. The procedure has been given in detail.[26]

Spectrophotometric Rate Measurements. Tetracyclone (enough to give 8.00×10^{-4} M solution) was weighed out and transferred quantitatively to a volumetric flask. The flask was filled to the mark with solvent and stored in the dark.

Peroxide was then weighed out in a 10- or 50-ml volumetric flask to give the desired concentration. (Ideally enough peroxide was weighed out to cause fading of the tetracyclone to about 0.1 of an absorbance unit.) The volumetric flask containing the peroxide was then filled to the mark with solvent (containing the tetracyclone which had been previously prepared).

The peroxide solution containing tetracyclone was transferred to the prepared cuvette with the aid of a long-stem disposable pipet. The cuvettes were degassed and stored in the icebox until the rate measurements were made.

The vials were placed in the bath at the desired temperature, removed at certain time intervals, quenched in tap water, and rinsed with acetone. The absorbance of tetracyclone monitored at 510 mμ for at least 10 half-lives of the peroxide.

The rate constants reported in the Results and Discussion were obtained by a least-squares treatment of the data thus obtained.

Registry No.—IIIa, 53783-69-0; IIIb, 53783-70-3; IIIc, 53783-71-4; IIId, 53783-72-5; IIIe, 53783-73-6; IIIf, 53783-74-7; IIIg, 53783-75-8; IVa, 53783-76-9; IVb, 53783-77-0; IVc, 53783-78-1; IVd, 53783-79-2.

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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.

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

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.