MeOH was stirred at room temperature for 2 hr and the bulk of the MeOH removed under vacuum. A residual suspended solid was collected on a filter, washed with Et_2O, and recrystallized from MeOH–EtOAc to give 0.65 g (39.5%) of the butyrophenone: mp 194–197°; ir 2760, 2720, 1685, 1600, 835, and 770 cm^{-1}.

Anal. Calcd for $C_{25}H_{31}ClFNO$: C, 72.18; H, 7.51; N, 3.37. Found: C, 72.42; H, 7.66; H, 3.14.

4′-Fluoro-4-(3′,4′-dihydrospiro[cyclohexane-1,1′(2′*H*)-naphthalen]-4-yl-*N*-methylamino)butyrophenone Hydrochloride (43). A mixture of the amine free base [prepared from 0.81 g (3.06 mmol) of the amine salt], 0.63 g of KI, 0.96 g of K_2CO_3, and 0.87 g of 4-chloro-*p*-fluorobutyrophenone 2,2-dimethylpropylene acetal in 15 ml of DMF was heated together in an oil bath at 90° for 20 hr. The solvent was removed under vacuum and the residue dissolved in H_2O and C_6H_6. The organic layer was washed with H_2O and brine and taken to dryness.

A mixture of the residue, 6.0 ml of 2.5 *N* HCl, and 12 ml of MeOH was stirred at room temperature for 1.5 hr and the bulk of the MeOH was removed under vacuum. A residual suspended solid was collected on a filter, washed with Et_2O, and recrystallized from MeOH–EtOAc to yield 0.59 g (44.8%) of the butyrophenone: mp 204–205.5°; ir 2660, 1675, 1225, 1210, 1150, and 755 cm^{-1}.

Anal. Calcd for $C_{26}H_{33}ClFNO$: C, 72.62; H, 7.74; N, 3.26. Found: C, 72.69; H, 7.93; N, 3.03.

Registry No.—**5,** 56868-61-2; **6,** 56868-62-3; **7,** 56868-63-4; **9,** 56868-64-5; **10,** 56868-65-6; **11,** 56868-66-7; **12,** 56868-67-8; **13,** 56868-68-9; **19,** 56868-69-0; **20,** 56868-70-3; **22,** 56868-71-4; **23,** 56868-72-5; **24,** 56868-73-6; **25,** 56868-74-7; *cis*-**27** tosylate, 56868-76-9; *trans*-**27** tosylate, 56868-78-1; **28,** 56868-79-2; **29,** 51509-98-9; **30,** 56327-24-3; **32,** 2572-26-1; **33,** 56868-88-3; **34,** 56868-89-4; **35,** 56868-90-7; **36,** 56868-91-8; *cis*-**37,** 56868-80-5; *trans*-**37,** 56868-81-6; **38,** 56868-82-7; **39,** 56868-83-8; **40,** 56868-84-9; **41,** 56868-85-0; **42,** 56868-86-1; **43,** 56868-87-2; 4-chloro-*p*-fluorobutyrophenone neopentyl glycol acetal, 36714-65-5; 2,2-dimethylpropanediol, 126-30-7.

References and Notes

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(9) All melting points are uncorrected and recorded as observed on a Thomas-Hoover capillary melting point apparatus. NMR spectra were determined in deuteriochloroform on a Varian A-60D NMR spectrometer. Infrared spectra were obtained on either a Perkin-Elmer Model 421 or on a Digilab Model 14D spectrophotometer. Solids were prepared as mineral oil mulls while liquids were prepared neat between sodium chloride plates. Mass spectra were obtained with an Atlas MAT CH4 instrument. NMR spectra (100 MHz) were determined in deuteriochloroform on a Varian X6100 spectrometer. The authors are indebted to the Department of Physical and Analytical Chemistry of The Upjohn Co. for elemental analyses.

Acid-Catalyzed Rearrangements of Polymethylnaphthalenes

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Received May 12, 1975

α,β-Methyl migrations were found to occur smoothly in trifluoroacetic acid in seven polymethylnaphthalenes with methyl substituents in peri positions and with at least one adjacent β position unsubstituted. For example, 1,2,3,4,5,8-Me_6-naphthalene gave the 1,2,3,4,5,7 isomer, which, in turn, gave the 1,2,3,4,6,7 isomer; 1,4,5,8-Me_4-naphthalene gave the 1,3,5,8 isomer, which further gave a mixture (10:1) of 1,3,5,7 and 1,4,6,7 isomers. In naphthalenes without peri position methyl groups, little rearrangement occurred but, instead, intermolecular methyl and hydride transfer took place at slow rates; e.g., 1,2,3,4-Me_4-naphthalene in CF_3COOH gave 1,2,3-Me_3- and a Me_5-naphthalene as well as 1,2,3,4-tetrahydro-5,6,7,8-Me_4-naphthalene; Me_8-naphthalene, though with peri position methyl groups, gave 1,2,3,4,5,6,7-Me_7- and 1,2,3,5,6,7-Me_6-naphthalene. The basicity of polymethylnaphthalenes, structures of naphthalenium ions, and methyl migrating forces were discussed in terms of peri dimethyl interaction. A kinetic study of the rates of rearrangement for seven naphthalenes showed that the rates do not always follow a first-order rate equation.

It has been well known that introduction of two bulky groups in the peri position of a naphthalene causes steric crowding (so-called peri interaction)[1] as most evident in the crystal structure of octamethyl- and octachloronaphthalene.[2] Hart and one of the authors (A.O.)[3] observed the formation of stable naphthalenium ions of octamethylnaphthalene and 1,2,3,4,5,8- and 1,2,3,4,5,6-hexamethylnaphthalene by NMR in trifluoroacetic acid (CF_3COOH), and suggested that the observed increase in basicity is characteristic of naphthalenes with methyl substituents in peri positions and that the primary force to increase the stability of carbocations must be the relief of steric strain in peri interaction. In the present study, we have found that a smooth migration of peri methyl groups can be induced from naphthalenium ions where the β position adjacent to the protonated peri position is unsubstituted. On the assumption that the peri interaction not only increases the basicity of a naphthalene but also accelerates the migration of peri substituents, we have carried out the experiments reported here in order to clarify the characteristics of this effect.

Protonation and rearrangements in carbocyclic systems promoted by the accompanying relief of steric strain have often been encountered.[4] Additionally, methyl migration in methylbenzenes as well as in mono- and dimethylnaphthalenes has been known to occur at a slow rate measurable only in such strong acids as $HF–BF_3$ or superacids.[5] Our work, however, found a significant difference in the ease of methyl migration between polymethylnaphthalenes with and without methyl substituents in peri positions; for example, the former naphthalenes undergo methyl rearrangement readily in such relatively weak acids as CF_3COOH or HCl, but the latter do not. It was also found even among peri-substituted naphthalenes that the rate of rearrangement depends markedly upon the number and position of methyl substituents. Therefore, with the purpose of reveal-

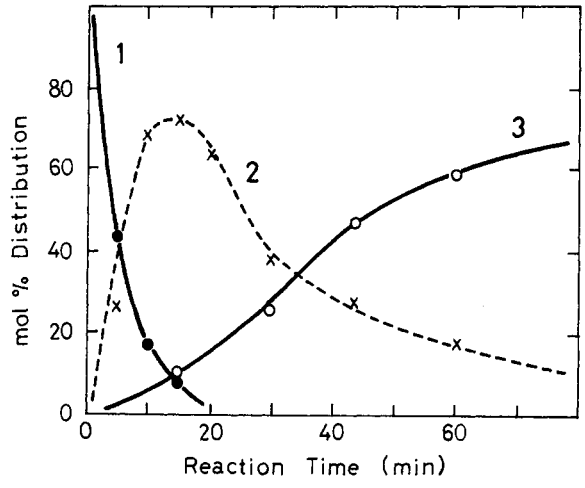


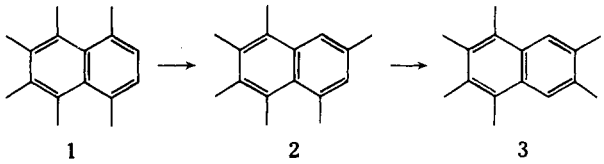
Figure 1. Rearrangement of 1,2,3,4,5,8-Me_6-naphthalene in CF_3COOH at 77°: **1**, 1,2,3,4,5,8-Me_6; **2**, 1,2,3,4,5,7-Me_6-; **3**, 1,2,3,4,6,7-Me_6-naphthalene.

ing the interrelationship between the existence of peri methyls and the substituent effect of other methyl groups, a kinetic study has been conducted.

The rearrangement reported here provides simple methods for the preparation of some polymethylnaphthalenes—1,2,3,4,5,7- and 1,2,3,4,6,7-Me_6-naphthalene, 1,2,3,4,6-Me_5-naphthalene, 1,3,5,8-, 1,3,5,7-, 1,4,6,7-, and 1,3,6,7-Me_4-naphthalene, and 1,7-Me_2-naphthalene—starting from those whose efficient preparative routes have been known.

Results

When 1,2,3,4,5,8-Me_6-naphthalene (**1**) was heated in boiling CF_3COOH (0.34 mol/l.) for 1 hr, 1,2,3,4,6,7-Me_6-naphthalene (**3**) was obtained (70%) as the final rearranged



1 **2** **3**

product besides some by-products.[6] Analogous treatment at 25° gave an intervening isomer, 1,2,3,4,5,7-Me_6-naphthalene (**2**), which, isolated, proved to be the precursor of **3**. Figure 1 shows the change in naphthalene distribution in this rearrangement. Thus, the optimum preparation of **2** was attained (72%) in 15 min at 77°.

The composition of by-products was complex. It was found by GLC–mass spectroscopy that they consisted of three Me_5- (*m/e* 198) and two Me_7-naphthalenes (*m/e* 226), dihydro- and tetrahydro-Me_6-naphthalenes (*m/e* 214 and 216, respectively), and a polymeric product. Their formation, however, was suppressed by dilution. There are only two possible structures for Me_7 isomers, i.e., 1,2,3,4,5,6,7- (**19**) and 1,2,3,4,5,6,8-Me_7-naphthalene (**38**). As for Me_5 isomers, two of them were identified with **12** and 1,2,3,5,7-Me_5-naphthalene (**40**) by comparison with the authentic compound and the reported data.[7]

Other acidic media than CF_3COOH were also examined for the rearrangement (see Table I). Hydrogen chloride was found to induce the rearrangement with relatively low yields of by-products in acetic acid and more effectively by the addition of Lewis acid [$AlCl_3$, BF_3, $Zn(CN)_2$[8]]. However, they are still not so effective as CF_3COOH with regard to yields, reaction time, and simplicity of products.

1,4,5,8-Me_4-Naphthalene (**4**) gave 1,3,5,7 (**6**, 87%) and 1,4,6,7 (**7**, 8%) isomers as the final rearrangement products

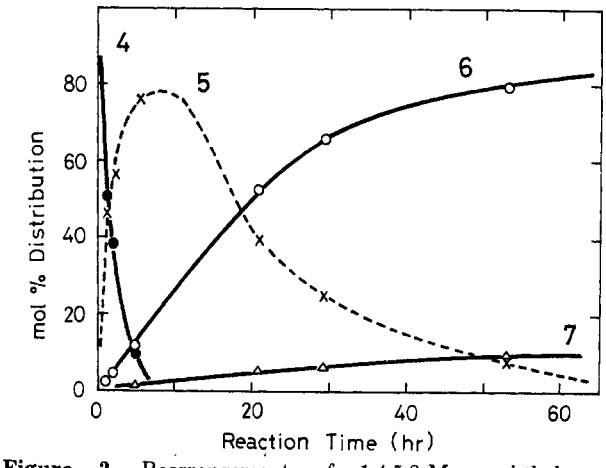


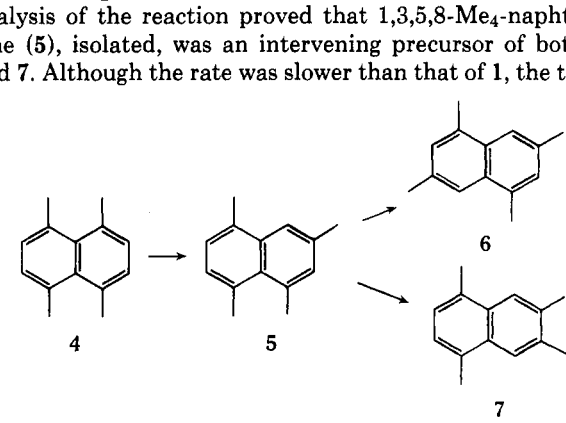
Figure 2. Rearrangement of 1,4,5,8-Me_4-naphthalene in CF_3COOH at 77°: **4**, 1,4,5,8-Me_4-; **5**, 1,3,5,8-Me_4-; **6**, 1,3,5,7-Me_4-; **7**, 1,4,6,7-Me_4-naphthalene.

Table I
Rearrangement of 1,2,3,4,5,8-Hexamethylnaphthalene in Various Acids (1.4 mmol/10 g acid)

Run	Acid	Temp, °C	Time, hr	Product ratio[c,d] 1	2	3
1	AcOH, HCl[a]	115	4	100	0	0
2	AcOH, HCl	115	4	75	25	0
3	AcOH, H_2SO_4 (10%)	115	1	15	82	3
4		115	2	0	75	25
5	AcOH, HCl, $AlCl_3$[b]	80	20	39	61	1
6	AcOH, HCl, BF_3·Et_2O[b]	80	20	56	44	0
7	Cl–AcOH	135	3	19	78	3
8	CF_3COOH	77	0.25	4	86	10
9		77	1	0	25	75

[a] HCl was passed through the solution at 115° in run 1, saturated at 0° and sealed in other runs. [b] Lewis acid; 0.86 mol/l. [c] Based on 1 + 2 + 3 = 100%, determined after removing polymeric products, which weighed 15–20% in runs 3 and 4, less than 5% in other runs. [d] 1, 1,2,3,4,5,8-Me_6-; 2, 1,2,3,4,5,7-Me_6-; 3, 1,2,3,4,6,7-Me_6-naphthalene.

after heating in CF_3COOH for 60 hr (0.42 mol/l.). A GLC analysis of the reaction proved that 1,3,5,8-Me_4-naphthalene (**5**), isolated, was an intervening precursor of both **6** and **7**. Although the rate was slower than that of **1**, the total



4 **5** **6** **7**

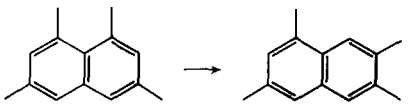
yield of **6** plus **7** was over 90% unless the reaction was carried out at high concentrations. Figure 2 shows the change in product distribution in this rearrangement and the optimum preparation of **5** (76%) was attained in 5 hr at 77°. The main by-products were two tetrahydro-Me_4-naphthalenes (*m/e* 188), three Me_3-naphthalenes (*m/e* 170), and a Me_5-naphthalene (*m/e* 198), as analyzed by GLC–mass spectroscopy.

Treatment of 1,3,6,8-Me_4-naphthalene (**8**) in boiling CF_3COOH (0.172 mol/l.) for 110 hr gave 1,3,6,7-Me_4-naphthalene (**9**) in 90% yield. Under the above conditions, fur-

Table II
Rates of Rearrangement of Polymethylnaphthalenes in CF_3COOH Calculated from the First-Order Rate Equation

Rearrangement[b]	$[A_0]$, mmol/l.	$k_1 \times 10^5$ sec^{-1}, 40°	50°	60°	70°	E_a[a]	ln A
1 → 2	15.1	6.20	18.6	52.3	114	20.9	23.9
2 → 3	15.1	1.60	3.94	9.46	19.5	17.9	17.7
4 → 5	16.8	3.50	10.4	27.5	74.6	21.7	24.7
5 → 6	14.8	0.245	0.786	2.40	6.20	23.2	24.3
5 → 7	14.8	0.0205	0.0687	0.222	0.501	24.1	23.4
8 → 9	16.9			0.217			
10 → 11	96	0.0028	0.0102	0.0275	0.0718	22.1	22.7
12 → 13	84				3.20		
21 → 1,3-Me_2					$<10^{-4}$		

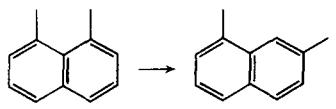
[a] ±0.2–0.5 kcal/mol. [b] 1, 1,2,3,4,5,8-Me_6-; 2, 1,2,3,4,5,7-Me_6-; 3, 1,2,3,4,6,7-Me_6-; 4, 1,4,5,8-Me_4-; 5, 1,3,5,8-Me_4-; 6, 1,3,5,7-Me_4-; 7, 1,4,6,7-Me_4-; 8, 1,3,6,8-Me_4-; 9, 1,3,6,7-Me_4-; 10, 1,8-Me_2-; 11, 1,7-Me_2-; 12, 1,2,3,4,5-Me_5-; 13, 1,2,3,4,6-Me_5-; 21, 1,4-Me_2-naphthalene.



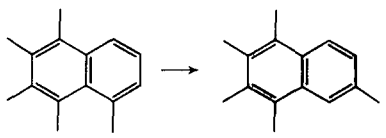
8 9

ther rearrangement of **9** did not occur but, instead, a trace amount of by-product (methyl disproportionation and reduction products) was formed (<2%).

Although at a very slow rate, 1,8-Me_2-naphthalene (**10**) rearranged into the 1,7 isomer (**11**) without forming by-products. Similarly, despite structural similarity to **1**, 1,2,3,4,5-Me_5-naphthalene (**12**) rearranged into the 1,2,3,4,6 isomer (**13**) more slowly than **1** or **4** (see Table II).



10 11

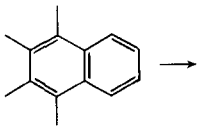


12 13

However, **13** was the only product not accompanied by an appreciable amount of by-products.

It was independently confirmed that the rearrangements mentioned above were irreversible processes.

In all the naphthalenes examined above, α,β-methyl migration was the main reaction. However, the formation of some anomalous products, though in low yields, necessitated the examination of such naphthalenes as 1,2,3,4-Me_4- (**14**) and Me_8-naphthalene (**18**). In **14**, essentially no rearrangement was observed as predicted from the lack of peri strain. However, treatment of **14** in boiling CF_3COOH over 1100 hr gave a mixture of 1,2,3-Me_3-naphthalene (**15**, 13%), 1,2,3,4-tetrahydro-5,6,7,8-Me_4-naphthalene (**16**, 4%), and a Me_5-naphthalene (**17**, 1%) besides unreacted **14** (80%).



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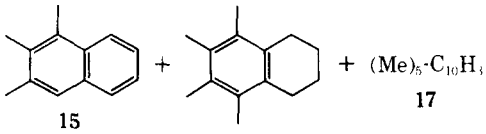
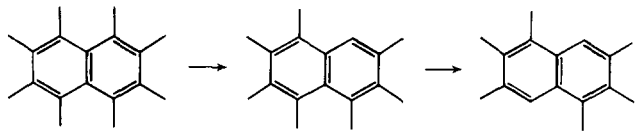


15 16 17

These products were isolated and their structures were determined by the comparison of their NMR and mass spectra and melting point of picrates with those reported.[9]

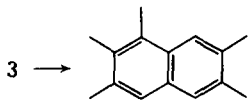
When a CF_3COOH solution of Me_8-naphthalene (**18**, 0.05 mol/l.) was heated for 72 hr, a Me_6-naphthalene (**20**, 20%) and a Me_7-naphthalene (**19**, 2%), whose precursory role to the formation of **20** was confirmed independently, were obtained besides unreacted **18** (38%) and polymeric



18 19 20

materials (40%). Both **19** and **20** were isolated and their structures determined as 1,2,3,4,5,6,7-Me_7- and 1,2,3,5,6,7-Me_6-naphthalene for **19** and **20**, respectively, by spectroscopy joined with a rational mechanistic account.[10]

Analogously, the main reaction of the following naphthalenes, none of which has any methyl substituents in peri positions, was the dealkylation. Thus, 1,4- (**21**, 0.254 mol/l.) and 2,3-Me_2-naphthalene (**22**, 0.190 mol/l.) in CF_3COOH produced a very small amount of Me_1-naphthalene (1- and 2-Me, respectively) in less than 0.1% yield after heating for 720 hr.[11] 1,4,6,7-Me_4- (**7**, 0.08 mol/l.) and 1,3,5,7-Me_4-naphthalene (**6**, 0.09 mol/l.), after heating for 720 hr, produced methyl disproportionation products (Me_3- and Me_5-naphthalenes, *m/e* 170 and 198, respectively) in relatively high yields (12.7% from **7**, 8% from **6**, and ratios Me_5/Me_3 slightly lower than unity in both cases). Similarly, **3** gave a Me_5-naphthalene (*m/e* 198, 4%). Its structure is assumed to be



1,2,3,6,7-Me_5, since it is not identical with **13** and the possibility of 1,2,4,6,7-Me_5 seems unlikely when compared with the result from **14**.

In order to estimate a quantitative character of peri dimethyl interaction as well as substituent effects of other methyl groups participating in the rearrangement, the rates of rearrangement of seven polymethylnaphthalenes, i.e., **1**, **2**, **4**, **5**, **8**, **10**, and **12**, were measured in CF_3COOH. All rearrangements were carried out in diluted solutions (<20 mmol/l.) to suppress the formation of by-products. In fact, **1**, which is most susceptible to side reactions, did not form an appreciable amount of by-products under this condition. Thus, neglecting side reactions, we assumed that

Table III
Rate Constants Recalculated from the Rate Equation $d[B]/dt = k_n[A]^n$ ($n < 1$)

Rearrangement[a]	Reaction order, n	$k_n \times 10^5$, (l./mol)$^{1-n}$ sec^{-1} 40°	50°	60°	70°	E_a, kcal/mol	ln A
2 → 3	0.82	0.866	1.85	4.08	8.17	15.8 ± 0.3	14.0
4 → 5	0.70	0.84	2.48	7.50	23.7	22.6 ± 0.5	24.5
5 → 6	0.86	0.132	0.437	1.31	3.04	21.3 ± 0.3	19.7
5 → 7	0.86	0.0111	0.0382	0.121	0.291	22.1 ± 1.5	20.8

[a] 2, 1,2,3,4,5,7-Me_6-; 3, 1,2,3,4,6,7-Me_6-; 4, 1,4,5,8-Me_4-; 5, 1,3,5,8-Me_4-; 6, 1,3,5,7-Me_4-; 7, 1,4,6,7-Me_4-naphthalene.

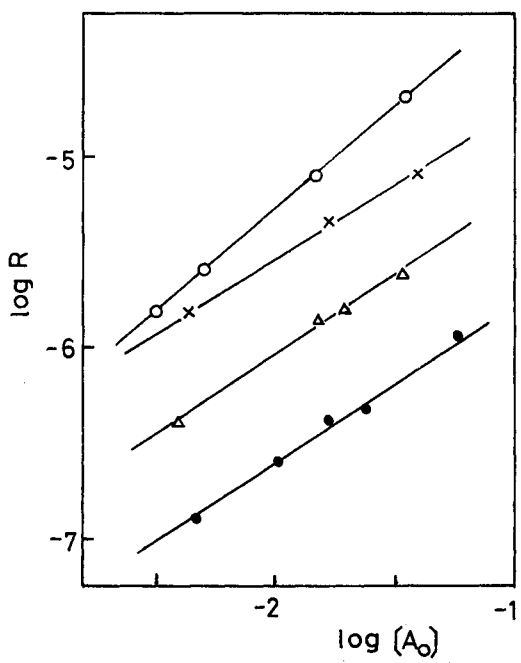


Figure 3. Plots of log R ($R = k_1[A_0]$) for the rearrangements of 1,2,3,4,5,8-Me_6- (○), 1,2,3,4,5,7-Me_6- (△), 1,4,5,8-Me_4- (×), and 1,3,5,8-Me_4-naphthalene (●) at 60° in CF_3COOH. $[A_0]$ is initial substrate concentration.

the total molar amount of substrates was unchanged throughout the treatment. Results are listed in Table II, where rate constants K_1 are calculated based on the first-order rate equation

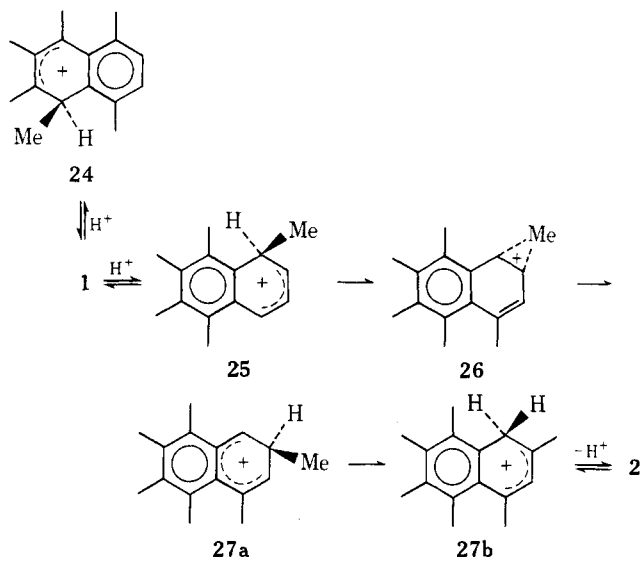
$$d[\text{product}]/dt = k_1[\text{starting naphthalene}] \quad (1)$$

However, careful examination of k_1 values at 60° resulting from changes in the initial substrate concentration showed that they were not constant in the cases of **2, 4, 5,** and **8,** as long as they were calculated from eq 1. For example, as to the rearrangement of **2** → **3,** k_1 values were 1.08×10^{-4}, 7.37×10^{-5}, and 6.83×10^{-5} sec^{-1}, for 3.97×10^{-3}, 2.03×10^{-2}, and 3.40×10^{-2} mol/l. concentrations, respectively. In contrast, k_1 for **1** → **2** remained unchanged over various concentrations. Therefore, kinetic orders, n, were calculated for five rearrangements (**1** → **2**, **2** → **3**, **4** → **5**, **5** → **6**, **5** → **7**) according to the rate equation $R = d[B]/dt = k_n[A]^n$, for the reaction A → B. By plotting log R against log $[A_0]$ (see Figure 3), the n values were found: 1.05 ± 0.02 (**1** → **2**), 0.82 ± 0.07 (**2** → **3**), 0.70 ± 0.06 (**4** → **5**), 0.86 ± 0.05 (**5** → **6, 7**). The rearrangements, except **1** → **2,** seem to follow the equation where $n = 0.8$ on the average. The calculated rate constants k_n, which remained almost constant over various concentrations, are listed in Table III.

Discussion

Rearrangement. It has been known that the general-acid-catalyzed α,β-alkyl shifts in naphthalene systems are caused by protonation on an α position though the kinetically controlled first σ protonation may not necessarily be on the same α position but may be on the other unsubstituted position as indicated by the NMR study of methylarenes.[12,5] On the other hand, the first kinetically controlled σ protonation seems to occur on the substituted α position in such naphthalenes as **18, 1,** and 1,2,3,4,5,6-Me_6-naphthalene (**50**) according to the NMR observation of their corresponding stable arenium ions, e.g., **24** from **1**.[3] However, the observed intramolecular rearrangement of **1** indicates that another naphthalenium ion, **25,** which alone can give rise to the formation of **2,** must be involved in the protonation equilibrium (Scheme I), although its stability must be relatively lower than that of **24.** The higher basicity of the peri carbons of **1** than that of other naphthalenes, such as **3,** which do not have any methyl substituents in peri positions, can reasonably be attributed to the strain release of peri interaction as the result of protonation.[13,14] Between the two peri positions in **1,** the basicity of C-1 (or C-4) is higher than that of C-5 (C-8), which is caused mainly by differences in hyperconjugative and inductive effects of methyl groups and, secondly, by differences in the extent of strain release between naphthalenium ions **24** and **25.**[15]

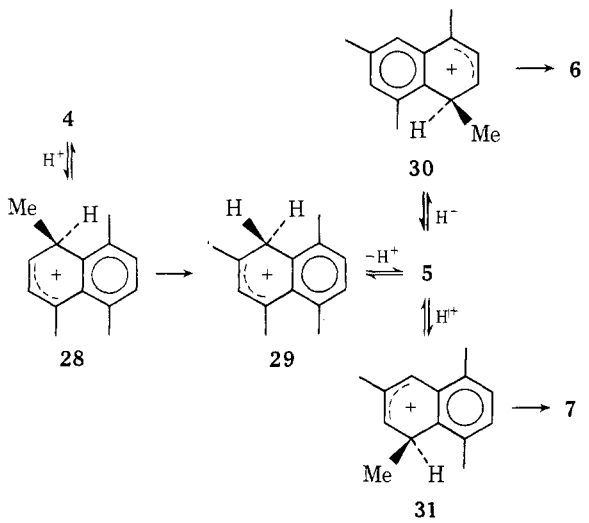
Scheme I



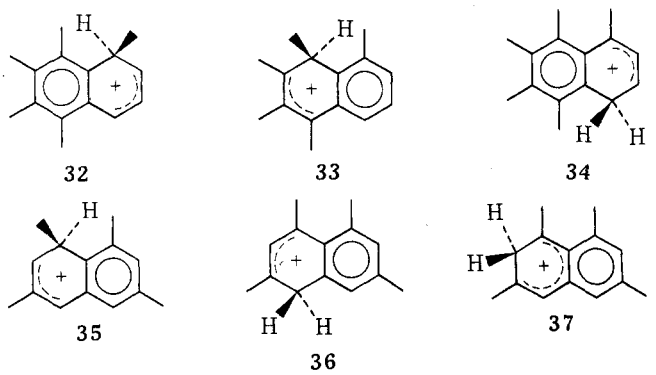
With this logic, protonation and rearrangement of **4** can be explained in terms of peri interaction. In the first step (Scheme II), naphthalenium ion **28** seems to be the sole protonated species but the basicity of **4** is not high enough to enable NMR observation of **28** in CF_3COOH. Protonation of **5** can take place on either C-1 or C-8. The predominant formation of **6** over **7** ($k_{5\to7}/k_{5\to6} = 0.105$) indicates that naphthalenium ion **30** predominates over the alternative **31.** This is because, though the peri interactions in both **30** and **31** are essentially the same, the basicity of C-8 is higher than that of C-1 because of the difference in the position of methyl substitution.

The unexpectedly slow rate of rearrangement of **12** indi-

Scheme II



cates another substituent effect. Naphthalenium ion **32**, which must be the rearrangement precursor but may not be as major a carbocation as **33** (or **34**), has no methyl group in



the C-8 position but four methyl groups on the A ring. If the A ring contributes significantly to delocalize the positive charge, then the rate would not be remarkably slower than that of **1**. However, the observed slow rate, even slower than that of **4**, implies that this is not the case and that the presence of methyl substituent in the para position to the reacting site, together with the peri interaction, is a requirement for increasing basicity. This is in accord with the reported effect for monomethylnaphthalenes.[12]

The rate of rearrangement of **8** was as slow as that of **5** → **7** owing to the structural similarity of **35** to **31**. Naphthalene **8** could also give rise to the formation of other ions **36** and **37** judging from the report of thermodynamically favored 2,4-dimethyl-1-hydronaphthalenium ion from **21**.[5] However, we have not yet obtained information enough to predict the priority among these three cations.

In relation to this argument, the apparent lack of migrating power in **6**, **7**, **9**, and **21** (their rates of rearrangement were more than 10^{-2} times slower than that of **10**) will partly enable us to differentiate carbocation stability and methyl migrating force: that is, the migrating force mainly derives from the strain release of peri interaction, and the carbocation stability from both the strain release and the electronic effects of methyl substitution.

On the above assumption as well as taking into account the positive charge being delocalized mainly in the protonated ring, the rate of **4** → **5** would be comparable to that of **1** → **2**. In fact, this speculation seems supported by the observation that the rate of **4** is slightly lower than that of **1** (see Table II). The slight difference in rate may be attributed to the difference in the way the unprotonated ring participates partially in sharing the positive charge. In addition, the difference can be explained by referring to the crystal structure of **18** where both α and β methyl (as well as ring carbons) are largely displaced from the mean plane.[2] Analogous to **18**, the strength of nonbonded peri interaction in **1** must be higher than in **4** where β positions are unsubstituted, and this difference in strain will be reflected in the basicity; and the secondary peri interaction which still remains around the protonated sp^3 carbon of naphthalenium ions[15] must be greater in **25** than in **28**, being reflected in the methyl migrating rate.

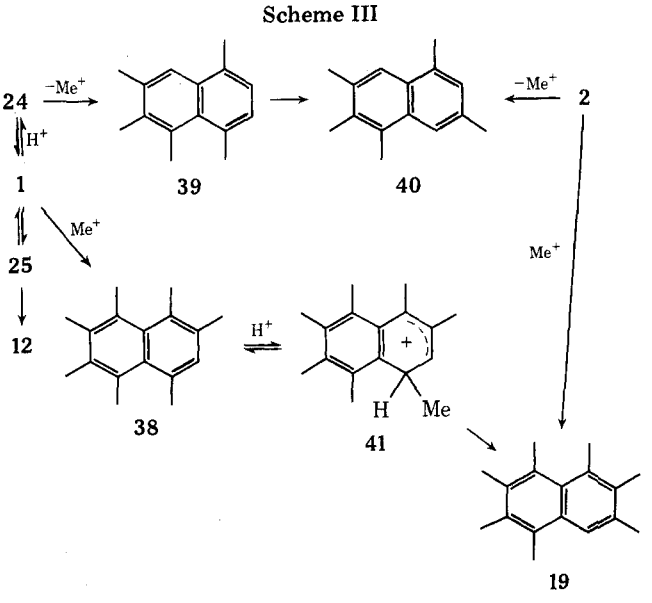
The formation of polymeric products was not negligible in **1**, **4**, and **18**, whose peri positions are all substituted by methyl groups, and was promoted by increasing the substrate concentration as well as by lowering the temperature. The sequence most rationally accounting for this intermolecular reaction with a low activation energy seems to involve the formation of ArH^+Ar complex[16] in which a pair of peri strains are relieved simultaneously without the molecule's undergoing the high energy rearrangement; and, consequently, a telomerization is induced.

Methyl Disproportionation and Reduction. As most typically illustrated by the behavior of 1,2,3,4-Me_4-naphthalene (**14**), polymethylnaphthalenes undergo methyl disproportionation (dealkylation and alkylation) and reduction. These side reactions became major for **21**, **6**, **7**, and **9** and the α,β-methyl migrations were negligible.

Intermolecular alkyl shifts for arenes have been widely reported[17,18] in the cases of *tert*-butyl, isopropyl, ethyl, and their homologues as the migrating groups, but the methyl group has been known to hardly migrate intermolecularly. Roberts proposed that the disproportionation of primary alkylarenes proceeds by the chain mechanism via benzyl-type carbocations.[19] This sequence, however, seems not applicable to the peri-substituted polymethylnaphthalenes and, instead, the methyl migration via ArH^+Ar complexes resulting in the strain relief seems most likely.[20] According to this sequence, α-methyl was eliminated much faster than β-methyl in **18** to give **19**, which in turn gave **20**.

The ratio of two heptamethylnaphthalenes formed from **1** was time dependent. In the light of the argument for the relief of peri strain, the increasing isomer must be **19**, which was identical with the product formed from **18**, and the decreasing isomer must be **38**. The formation of **12** indicates that naphthalenium ion **25** undergoes demethylation as well, and the formation of **40** suggests the existence

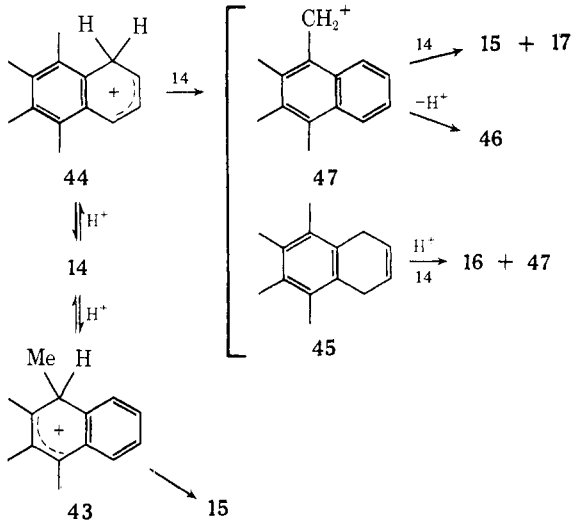
Scheme III



of its precursor **39** whose rate of rearrangement must be similar to that of **1** (see Scheme III).

The isolation of **16** from **14** as well as the detection of dihydro- and tetrahydronaphthalenes in the product mixture of **1**, **4**, and **18** demonstrates that the reduction of naphthalene nuclei took place almost with the same ease as the methyl disproportionation. Although some examples of the reduction of alkenes by the hydride transfer from alkylarenes have been known,[21] very few have been reported for the reduction of arene nuclei.[32] The reaction proceeds via the intermolecular hydride shift (Scheme IV) where methyl

Scheme IV

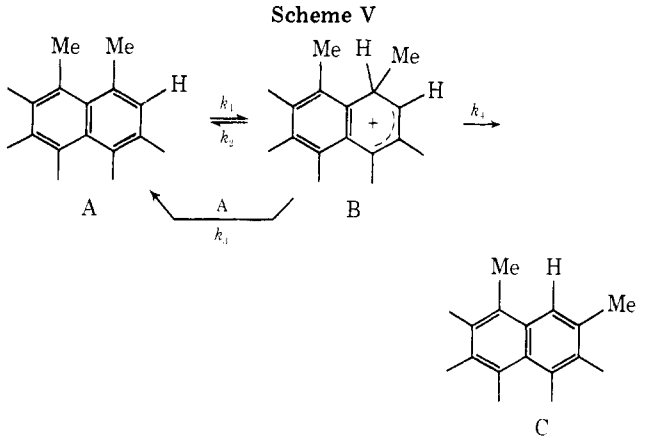


groups are the hydride donor, thus resulting in the formation of hydronaphthalenes and naphthylcarbinyl cation **47** (which can be the precursor of methyl disproportionation[19]). It is also interesting that **14** undergoes reduction preferentially on the ring that has no methyl substituent. Presumably, hydride transfer occurs through the ArH^+Ar complex where the sterically less crowded transition state may be favored.[16]

Kinetics. The rate of reaction for the present type of rearrangement, seemingly accountable in terms of an unimolecular protonation–deprotonation mechanism, is supposed to be proportional to the first order of substrate concentration. In order to interpret the smaller order of the reaction observed in the cases of **2**, **4**, and **5**, we postulate a sequence in which the basic naphthalene molecule participates in both the deprotonation (reversible) and irreversible side reactions (Scheme V); that is, the rate of deprotonation depends upon both first- and second-order terms of substrates as expressed in eq 2. Then, by the method of stationary state approximation, eq 3 is derived from eq 2 for the rate of formation of the product C. This equation obviously indicates that the observed rate constant depends on [A]; as [A] increases the apparent rate constant decreases and vice versa. Consequently, it can be re-formulated with approximation into eq 4. Thus, in the cases of **2**, **4**, and **5**, n appeared between 0.7 and 0.86 since [A] must be considerably higher than [B]. However, in **1**, $n = 1.0$, since [A] must be much lower than [B] or almost negligible owing to the extraordinarily higher basicity in C-1 positions, as evidenced by the NMR observation of **24** in CF_3COOH.[3]

Results in either Table II or III lead to the following sequence for decreasing rate of rearrangement: **1 > 4 > 2 > 5 → 6 > 12 > 5 → 7 > 10 > 21.** Since the rate depends not on the total basicity of a naphthalene molecule but mainly on the basicity of the peri carbon on which protonation can induce the rearrangement, we can estimate the factors necessary and/or facilitating the reaction: (a) existence of at least a pair of peri dimethyl substituents; (b) the position ortho to the protonated peri carbon being unsubstituted; (c) existence of a methyl group in the position para to the protonated site; (d) the unprotonated ring of a cation possessing many methyl groups. Usually, protonated species that satisfy the above conditions are not observed by NMR in CF_3COOH and a predominant species in a protonated equilibrium is not necessarily the one that causes rearrangements.

Scheme V



$$\frac{d[B]}{dt} = k_1[A] - (k_2 + k_4)[B] - k_3[A][B] \quad (2)$$

$$\frac{d[C]}{dt} = k_4[B] = \frac{k_1k_4}{k_2 + k_4 + k_3[A]}[A] \quad (3)$$

$$\frac{d[C]}{dt} = k_n[A]^n \ (n < 1) \quad (4)$$

Activation parameters, E_a and A, were obtained by fitting rate constants to the Arrhenius equation (Tables II and III). The average value of E_a (21–23 kcal/mol) is almost the same as that reported for methylbenzenium ions.[31] However, since the present calculation is based on the consumption and formation of naphthalenes but not on the concentration of arenium ions, the values for the methyl migration in ions would be lower than those in the tables.

Preparative Utilization. Although relatively easy preparations of C_2-symmetric polymethylnaphthalenes have been known,[22] the procedures hitherto known for unsymmetric homologues[23] seem troublesome. Instead, the present rearrangement can be used as a simple method to prepare such unsymmetrical polymethylnaphthalenes as **2**, **5**, **6**, **9**, and **13** from the corresponding isomers whose preparations are easy. The isolation and purification of products can be achieved by column chromatography and recrystallization.

Experimental Section

General. All melting points are uncorrected. Mass spectra were taken on a Hitachi Model RMU-6L spectrometer, which was connected to a Hitachi Model 063 gas chromatograph equipped with a single column of Apiezon Grease L, 5%, 3 mm × 4 m. NMR spectra (60 and 100 MHz) were recorded on either a Varian T-60A or a Jeol 4H-100 spectrometer in carbon tetrachloride solution, unless otherwise stated. All chemical shifts are given in τ units. Uv and ir spectra were taken on a Hitachi Model 124 and a Jasco Model IRA-I spectrometer, respectively.

Polymethylnaphthalenes. 1,2,3,4,5,8-Me_6- (**1**), 1,2,3,4,6,7-Me_6- (**3**), 1,2,3,4,5,6-Me_6- (**50**), 1,2,3,4,5-Me_5- (**12**), 1,2,3,4-Me_4- (**14**), and Me_8-naphthalene (**18**) were prepared from hexamethyl-2,4-cyclohexadienone (**53**)[24] and methylbenzynes according to the procedure reported.[22] 1,4,5,8-Me_4- (**4**), 1,4,6,7-Me_4- (**7**), and 1,4-Me_2-naphthalene (**21**) were prepared according to Mosby's procedure,[25] 1,3,6,8-Me_4-naphthalene (**8**) from 3,5-dimethylbenzyl bromide and diethyl allylmalonate,[26] and 1,8-Me_2-naphthalene (**10**) from

naphthalic anhydride.[27] Preparative procedures for **12** and **50** will be described in this section.

A General Procedure for the Rearrangement. Commercially available CF_3COOH of guaranteed grade with the same batch number was used in all treatments. A CF_3COOH solution of a polymethylnaphthalene was heated under solvent reflux (77°) for a certain period. After cooling, the reaction mixture was poured into an excess amount of cold 5% aqueous sodium carbonate and the precipitate separated was extracted with diethyl ether three times. The ethereal solution was again washed with aqueous sodium bicarbonate and then with water three times. After drying over anhydrous $MgSO_4$, ether was removed in vacuo and the residue was dissolved in cyclohexane and chromatographed through a silica gel column (Merck silica gel 60, 70–230 mesh) by using cyclohexane as eluent to remove polymeric by-products. The eluted substance was dissolved in benzene and then analyzed by GLC (using a 3 mm × 3 m column packed with Apiezon Grease L, 10%, on Chromosorb W).

Kinetics. Rates of rearrangement of seven polymethylnaphthalenes, **1, 2, 4, 5** (at 40, 50, 60, and 70°), and **8, 10, 12** (at 70°), in CF_3COOH were measured by GLC analysis of the reaction mixtures whose initial substrate concentrations were kept as low as indicated below to suppress the formation of by-products; **1** and **2** (15.1 mmol/l.), **4** (16.8–17.1), **5** (14.8–17.4), **8** (16.9), **10** (96), **12** (84). In all analyses, molar change of substrates vs. reaction time was measured by the method of calibration curves. The number of sample collections per reaction at a temperature was more than six in all cases. Work-up procedure for the collected samples was the same as the above-mentioned general procedure for the rearrangement. The 0.8-order rate constants $k_{0.8}$, for example, were calculated according to eq 5, which can be derived by integrating eq 4.

$$1 - ([A]/[A_0])^{0.2} = k_{0.8}t/5[A_0]^{0.2} \quad (5)$$

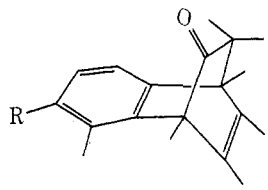
Rearrangement of 1,2,3,4,5,8-Me_6-naphthalene (1). A solution of **1** (0.51 g, 2.4 mmol) dissolved in 7 ml of CF_3COOH was heated under reflux for 10 min. After work-up, about 20% of the initial weight was lost by column chromatography. The substance which was trapped in the column was then extracted with benzene to give a resinous material,[28] whose NMR spectrum showed a complex pattern between 7.0 and 8.5 ppm. The eluted substance consisted of **1** (17%), **2** (69%), and **3** (5%) besides a small amount of by-products. Column chromatography followed by recrystallization from methanol afforded **2**,[29] mp 79.5–81.0°, NMR (all singlet) Me at 7.74, 7.71, 7.64, 7.53, 7.43, and 7.29, 1 H at 3.16 and 2.59. When the solution was heated for 1 hr, the obtained column eluate consisted of **2** (19%) and **3** (58%) and the latter was identified with the authentic sample. As to the composition of by-products, see the results in the text.

Rearrangement of 1,4,5,8-Me_4-naphthalene (4). A solution of **4** (1.56 g, 8.5 mmol) in 19 ml of CF_3COOH was heated at 77° for 5 hr. After work-up, the product mixture was chromatographed (ca. 10% was trapped in the column) and the eluate was analyzed by GLC to find that it consisted of unreacted **4** (9.5%), **5** (75.6%), **6** (12.4%), and **7** (1.2%). Column chromatography (or a preparative GLC) of the mixture afforded **5**, whose melting point (57°) and uv were identical with those reported. NMR of **5**: 7.59 (Me, s), 7.49 (Me, s), 7.20 (2 Me, br s), 3.06 (3 H, br s), and 2.51 ppm (H, s). When the same solution of **4** was heated for 100 hr, the obtained product mixture (93% of the initially charged weight of **4**) consisted of **6** (88.2%) with a small amount of **7** (9%) which was removed by recrystallization from methanol. The melting point and other spectral data of **6** were identical with those reported.[26]

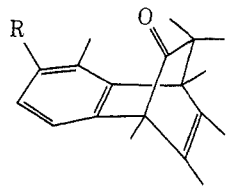
Rearrangement of 1,3,6,8-Me_4-naphthalene (8). A solution of **8** (0.41 g/15 ml CF_3COOH) was heated for 110 hr. The product mixture consisted of **9** (93%) and **8** (7%). **9**: mp 46–47°; λ_{max} (ethanol) 283 nm (ϵ 5200); NMR 7.59 (3 Me, s), 7.41 (Me, s), 3.03 (H, s), 2.73 (H, s), 2.63 (H, s), 2.44 ppm (H, s).

Rearrangement of 1,8-Me_2-naphthalene (10). A solution of **10** (0.50 g/20 ml CF_3COOH) was heated for 24 hr. The product mixture consisted of unreacted **10** (85%) and **11** (15%), whose melting point and NMR were identical with those reported.[7]

Preparation of 1,2,3,4,5-Me_5-naphthalene (12). A stirred mixture of **53** (62 mmol), propylene oxide (0.25 mol), 3-methylbenzenediazonium 2-carboxylate hydrochloride (62 mmol), and 1,2-dichloroethane (150 ml) was heated under reflux for 30 min. After work-up in the same manner as reported before,[3] a mixture of two isomers of 1,3,3,4,7,8-hexamethyl-5,6-(methylbenzo)bicyclo[2.2.2]octa-5,7-dien-2-one (**51** and **52**) was obtained, ν (C=O) 1705 cm^{-1}. NMR chemical shifts corresponding to each isomer are obtained by comparing spectrum intensity on the basis that is applied in distinguishing two isomers **54** and **55** in the following paragraph. **51**: *gem*-Me at 9.46 and 8.96, Ar-Me 7.53, other Me 8.2–8.45, ArH 3.0–3.25 ppm. **52**: *gem*-Me 9.39 and 9.02, ArMe 7.49, other Me 8.2–8.45, ArH 3.0–3.25 ppm. **51/52** = 1.75. The above mixture of **51** and **52** (not separated) was treated with a Me_2SO solution of dimsyl sodium[30] to give **12** (4.2 g, 35%) in white crystals, mp 75–76°. Further purification was done by column chromatography.



51, R = H **54**, R = Me



52, R = H **55**, R = Me

Rearrangement of 1,2,3,4,5-Me_5-naphthalene (12). A solution of **12** (0.5 g/20 ml CF_3COOH) was heated for 5 hr. The product mixture consisted of **13** (88%) and **12** (12%). **13**: mp 85°;[10] NMR 7.70 (2 Me, s), 7.54 (Me, s), 7.50 (2 Me, s), 2.85–3.0 (H), 2.2–2.4 ppm (2 H).

Preparation of 1,2,3,4,5,6-Me_6-naphthalene (50). A mixture of two structural isomers of 1,3,3,4,7,8-hexamethyl-5,6-(dimethylbenzo)bicyclo[2.2.2]octa-5,7-dien-2-one (**54** and **55**) was obtained according to the previous report.[3] Separation of the isomers was possible by recrystallization from methanol. With varying amount of Eu(fod)$_3$ in carbon tetrachloride, one of the isomers exhibited a more sensitive separation of two aromatic hydrogens (which appeared equivalent without the shift reagent) than the other isomer. Therefore, this was assigned to **55** where the aromatic hydrogens are placed closer to the carbonyl group than in **54**. **54**: mp 154–156.5; NMR *gem*-Me at 9.44 and 9.00, allylic Me 8.27, bridgehead Me 8.48 and 8.20, ArMe 7.79 and 7.63, ArH 3.17 ppm, with relative areas 3:3:6:3:3:3:3:2; ν (C=O) 1710 cm^{-1} (for both isomers). **55**: mp 127–130°, NMR *gem*-Me 9.38 and 9.03, allylic Me 8.33 and 8.23, bridgehead Me 8.48 and 8.16, ArMe 7.77 and 7.59, ArH 3.19 ppm, with relative areas 3:3:3:3:3:3:3:2. Isomer ratio **54/55** = 1.71. Treatment of the above mixture, or separated isomer, with dimsyl sodium gave **50** (98%): mp 55.5–56.5°; NMR 7.69 (Me, s), 7.68 (Me, s), 7.66 (Me, s), 7.49 (3 Me, brs), 2.98 and 2.44 (H for each, AB type, J = 9 Hz).

Rearrangement of 1 in Acetic Acid. In each of five tubes 10 g of acetic acid and 0.30 g (1.4 mmol) of **1** were placed. Three of them were saturated with dry HCl at 0°; the first of the three tubes was sealed without additives. To the second and third tubes were added $AlCl_3$ (1.0 g) and boron trifluoride etherate (1.1 g), respectively. Two remaining tubes were sealed after adding to each 1.0 g of H_2SO_4. Another tube containing chloroacetic acid and **1** was also prepared. Six tubes, thus prepared, were heated under the conditions cited in Table I.

Treatment of 1,2,3,4-Me_4-naphthalene (14) in CF_3COOH. A solution of **14** (0.584 g/11 ml CF_3COOH) was heated for 1100 hr. The originally colorless solution turned to dark blue during the above period. The reaction mixture, after work-up, was chromatographed through a silica gel column (cyclohexane). About 20% of the original weight was removed as a cyclohexane-insoluble material. The eluted mixture was then analyzed to find that it consisted of **15** (15%), **16** (4%), **17** (1%), and unreacted **14** (82%). A preparative GLC afforded **15** and **16**. **15**: mp 140.5–142° (picrate); NMR 7.65 (Me, s), 7.59 (Me, s), 7.42 (Me, s), 2.0–2.8 ppm (5 H, m); P^+ *m/e* 170. **16**: mp 77.5–78.5°;[9] NMR 8.27 (4 H, m), 7.92 (2 Me, s), 7.84 (2 Me, s), 7.41 ppm (4 H, m); P^+ *m/e* 188. **17**: P^+ *m/e* 198.

Treatment of Me_8-naphthalene (18) in CF_3COOH. A solution of **18** (0.52 g/30 ml CF_3COOH) was heated for 30 hr. By chromatographing the reaction mixture through a silica gel column (cyclohexane), about 40% of the original weight was removed as polymeric materials. The eluted mixture consisted of several components in which **20** and **19** (2 and 20%, respectively) were the main products. **20**: P^+ *m/e* 226; mp 133–136°; NMR 7.68 (3 Me, br s), 7.61 (Me, s), 7.48 (3 Me, s), 2.54 (H, s). **19**: P^+ *m/e* 212; mp 176–177°;[10] λ_{max} (ethanol) 274 nm (ϵ 6450), 284 (6080); NMR 7.67 (2 Me, s), 7.58 (2 Me, s), 7.46 (2 Me, s), 2.49 ppm (2 H, s). When the heating was stopped after 8 hr, a mixture of **20** (4%) and **19** (14%) was obtained.

Treatment of Other Polymethylnaphthalenes in CF_3COOH. Solutions of **3, 6, 7, 21,** and **22** (0.08–0.25 mol/l.) in CF_3COOH were heated for 720 hr. After work-up and column chromatography, the product mixtures were analyzed by GLC–mass spectroscopy as well as by GLC. Results are shown in the text.

Acknowledgment. The authors gratefully acknowledge the valuable comments of Professors Harold Hart and George A. Olah. We also thank Mr. Kenzo Iwai and Mr. Tetsuo Ishioka for their assistance in the laboratory.

Registry No.—**1**, 36230-30-5; **2**, 56908-77-1; **3**, 17384-76-8; **4**, 2717-39-7; **5**, 14558-12-4; **6**, 7383-94-0; **7**, 13764-18-6; **8**, 14558-14-6; **9**, 7435-50-9; **10**, 569-41-5; **11**, 575-37-1; **12**, 56908-78-2; **13**, 56908-79-3; **14**, 3031-15-0; **15**, 879-12-9; **15** picrate, 56908-80-6; **16**, 19063-11-7; **17**, 56908-81-7; **18**, 18623-61-5; **19**, 56908-82-8; **20**, 51958-57-7; **21**, 571-58-4; **22**, 581-40-8; **50**, 56908-83-9; **51**, 56908-84-0; **52**, 56908-85-1; **54**, 56908-86-2; **55**, 56908-87-3; 3,5-dimethylbenzyl bromide, 56908-88-4; diethyl allylmalonate, 2049-80-1; naphthalic anhydride, 81-84-5; dimsyl sodium, 15590-23-5; 1,3-dimethylnaphthalene, 575-41-7.

References and Notes

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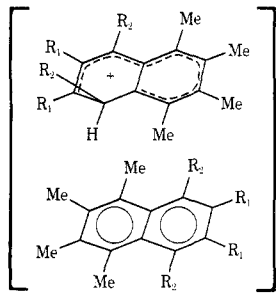
(16) One of the tentative models for the hypothetical complex ArH⁺Ar is illustrated below as an overlapping double-layered form. (1) Telomerization may take place via σ complex resulting in the strain relief at the position para to the protonated carbon; (2) hydrogen transfer may take place via π complex from the Me substituents of the basic Ar to the protonated ring most favorably when $R_1 = R_2 = H$.



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Ion Radicals. XXXV. Reactions of Thianthrene and Phenoxathiin Cation Radicals with Ketones. Formation and Reactions of β-Ketosulfonium Perchlorates and Ylides[1,2]

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Received May 27, 1975

Thianthrene cation radical perchlorate (**1**) and phenoxathiin cation radical perchlorate (**3**) react with ketones to give, in most cases, a β-ketoalkylsulfonium perchlorate and the parent heterocycle (thianthrene or phenoxathiin) in equimolar amounts. Reaction with diketones or β-keto esters leads, in some cases, directly to a sulfur ylide. Some of the β-ketosulfonium perchlorates were themselves easily converted into sulfur ylides by treatment with base. Reaction of selected β-ketosulfonium perchlorates with nucleophiles led easily, also, to displacement of the parent heterocycle and formation of an α-substituted ketone bearing the nucleophile at the α-carbon atom.

Several methods of preparing β-ketosulfonium salts are to be found in the literature. Most common among these is the reaction of a dialkyl or alkyl aryl sulfide with an α-halogeno ketone or ester. Phenacyl bromide[3-6] and α-bromo esters[5,7] are often used. This method is quite old, having been used years ago by Clarke in measuring the reactivities of some dialkyl and cyclic sulfides,[8] but in those cases the salts were not isolated. Alternatively, in another common method, a β-ketoalkyl sulfide is alkylated. Methylation is most common, dimethyl sulfate,[9] methyl tosylate,[9] and trimethyloxonium fluoroborate[10,11] having been used.

Carbonyl-stabilized sulfur ylides are not as long known. In fact, until 1965–1966 these ylides appear to have been unknown as isolable compounds,[12-14] having been prepared and used until then only in situ.[15,16] Isolable carbonyl-stabilized sulfur ylides are prepared usually by the deprotonation of β-ketosulfonium ions with bases such as triethylamine.[17] This method, and direct ones, such as the reactions of Me_2SO and dicyclohexylcarbodiimide (DCC) with activated methylene groups (such as in 1,3-diketones), have been reviewed by Ratts.[18] More recently, reaction of carbonyl-containing carbenes with a sulfide, e.g., in the pho-