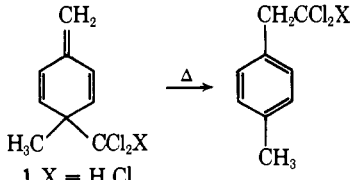
Concerted vs. Free Radical Migration Mechanisms in the Rearrangements of Seminaphthalenes

Bernard Miller* and Mohammed Reza Saidi

Contribution from the Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01002. *Received July 28, 1975*

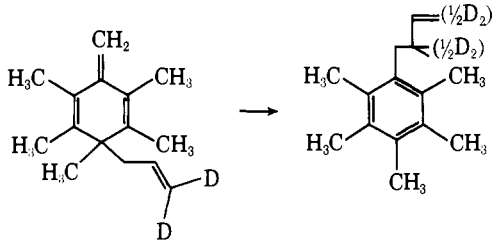
Abstract: Dehydration of 1-allyl-1,2-dimethyl-2-hydroxydihydronaphthalene with phosphorus oxychloride or thionyl chloride in pyridine gives a quantitative yield of 1-methyl-2-(3-butenyl)naphthalene, while dehydration of the 1-(*trans*-2-butenyl) analogue gives 1-methyl-2-(2-methyl-3-butenyl)naphthalene. These products are considered to arise via formation of seminaphthalenes (2-methylene-1,2-dihydronaphthalenes), which then undergo very rapid Cope rearrangements. Dehydration of 2-allyl- and 2-(*trans*-2-butenyl)-1,2-dimethyl-1-hydroxydihydronaphthalenes gives, in addition to the products which would be expected to arise by formation of the seminaphthalenes, the products which were obtained from rearrangement of the 1-allyl and 1-(2-butenyl)seminaphthalenes. These products were considered to arise from Wagner–Meerwein rearrangements in naphthalenyl carbonium ions. Dehydration of 1-benzyl-1,2-dimethyl-2-hydroxydihydronaphthalene gives the desired seminaphthalene, 1-benzyl-1-methyl-2-methylenedihydronaphthalene, which is thermally stable at 100 °C, or at 80 °C in the presence of strong base. On thermolysis at 165 °C, the seminaphthalene isomerizes via a formal [1,3] shift of a benzyl group, which is considered to proceed by a free radical chain reaction. No evidence for a Cope migration of a benzyl group is found in this reaction.

The von Auwers rearrangement of a substituent from C-4 to the exocyclic methylene group of a "semibenzene" (e.g., **1** → **2**) was first observed some 70 years ago.[1] Interest



1, X = H, Cl — **2**

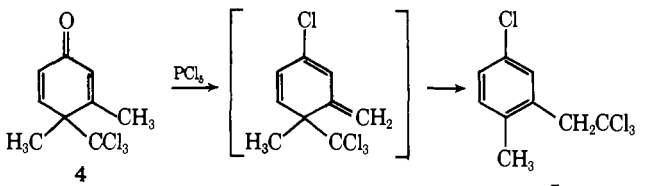
in the mechanism of these rearrangements has increased in the past decade. Recent work has demonstrated that migrations of methyl,[2] benzyl,[3] and trichloromethyl[4] groups in *p*-semibenzenes proceed via intermolecular paths, most probably by free radical chain processes. Miller and Lai[3] showed that migration of the allyl group in semibenzene **3**



3

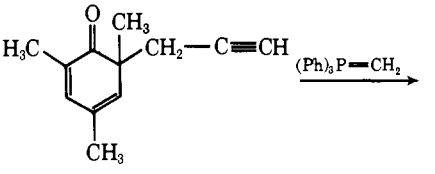
proceeds entirely by a path involving free allyl radical intermediates, rather than by sequences of [3,3] shifts or a single [1,5] shift.

In contrast to the rearrangements of *p*-semibenzenes, which occur fairly frequently, examples of rearrangements of "*o*-semibenzenes" (1-methylene-2,4-cyclohexadienes) are rare. Newman and Wood[5] reported that reaction of cyclohexadienone **4** with phosphorus pentachloride gives the aromatic product **5**, presumably by way of an intermediate

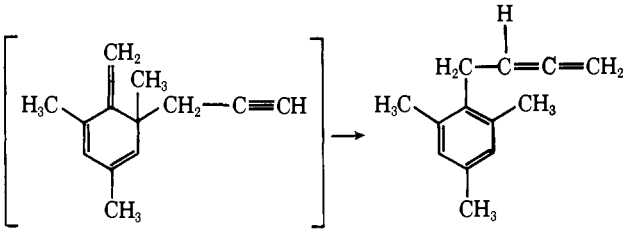


4 — **5**

o-semibenzene. Gilgen, Zsindely, and Schmid[6] found that reaction of cyclohexadienone **6** with triphenylmethylenephosphorane gave the allene **7**, presumably via a [3,3] sig-

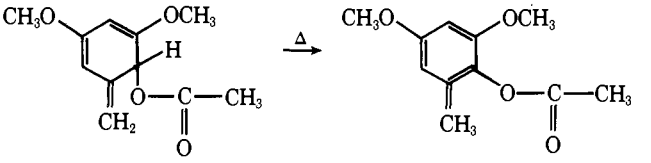


6



7

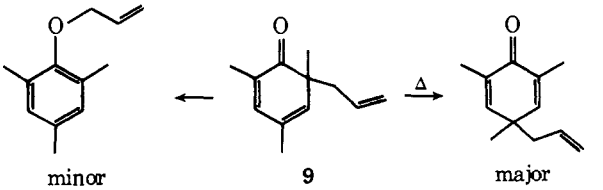
matropic shift. However, Jaeger[7] reported that semibenzene **8** rearranged in benzene at 55 °C via an apparent thermal



8

[1,3] hydrogen shift, rather than a [3,3] migration of the acetoxy group.

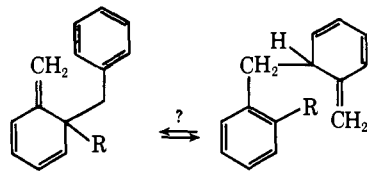
Several questions in regard to possible migrations of allyl and benzyl groups in *o*-semibenzenes aroused our interest. (1) In the possible competition between free radical and [3,3] migrations of allyl groups, which would win out? (2) Allyl groups in *o*-cyclohexadienones (such as **9**) migrate



minor — **9** — major

predominantly to C-4 rather than to oxygen,[8] even though

migration to oxygen gives by far the more stable product. The reason for this behavior is not known. Which type of reaction would be expected to occur in the corresponding rearrangement of an *o*-semibenzene? (3) Cope rearrangements requiring participation of an aromatic ring, rather than a double bond, do not normally occur. At exceptionally high temperatures in the presence of strong basic catalysts, products corresponding to those of Cope rearrangements have been obtained,[9] but the mechanisms of these reactions

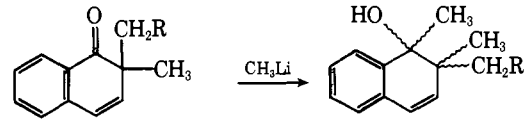


are still open to question. Could such Cope rearrangements of aromatic structures be observed in the rearrangement of an *o*-semibenzene, in which a new aromatic ring is being produced as the old one is being disrupted?

These results of earlier studies[3,6] suggested that *o*-semibenzenes with allyl or benzyl groups at C-6 would be extremely difficult to isolate. We therefore directed our efforts toward the preparation of *o*-seminaphthalenes, in the expectation (partially realized) that these would be more stable entities.

Allyl Migrations in *o*-Seminaphthalenes

Methyllithium added normally to the carbonyl groups of naphthalenones **10a–c**, giving a mixture of stereoisomeric

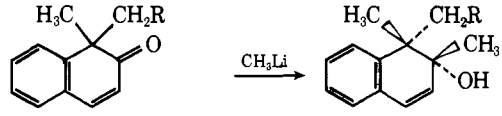


10a, R = CH=CH$_2$
b, R = CH=CHCH$_3$
c, R = 

11a–c

alcohols in each case. The major isomer from each reaction was assigned the *Z* configuration and the minor isomer the *E* configuration (*syn*-hydroxy and C-2 methyl groups) on the basis of the relative shifts of the resonances for the C-2 methyl groups in each isomer on addition of the paramagnetic shift reagent Eu(fod)$_3$[10] (see Experimental Section).

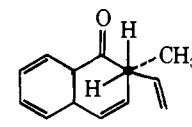
Addition of methyllithium to naphthalenones **12a–c** simi-



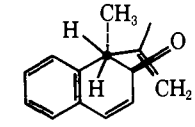
12a, R = CH=CH$_2$
b, R = CH=CH—CH$_3$
c, R = 

13a–c

larly proceeded smoothly to give the desired alcohols. However, the spectra of the products indicated that a single isomer was obtained from each reaction. In the absence of both isomers for comparison, a definitive assignment of configuration cannot be made.[10b] On chemical grounds, however, it seems highly probable that the *Z* isomer is obtained from each reaction. Inspection of molecular models shows a strong preference for **12a–c** to exist in conformations in which the double bonds or phenyl groups are as far as possible from the aromatic ring of the dihydronaphthalene system (e.g., conformation **12a'**). In these conformations, addition of the entering methyl group to the carbonyl is only feasible when attack is syn to the methyl at C-1. In naphthalenones **10a–c**, on the other hand, the preferred conformations (e.g., **10a'**) are those in which the R substituents



10a'

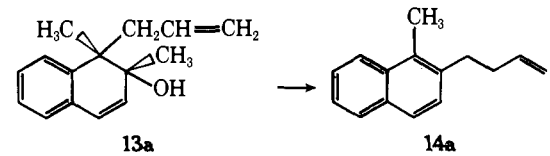


12a'

are distant from the carbonyl group, and attack at the carbonyl is relatively unhindered. Since the larger substituents on the cyclohexadienone ring will tend to be axial, however, normal addition by the entering methyl group anti to the axial group at C-2 will give the *Z* isomers as the major (though not the only) products.

Dehydration of **13a** with phosphorus oxychloride in pyridine at room temperature proceeded slowly, but the reaction was complete after 20 h. At 0 °C, using thionyl chloride in pyridine as the dehydrating agent, reaction was complete after 2 days. Attempts to follow the reaction at still lower temperatures in an NMR probe were unsuccessful, due to the rapid formation of precipitates in the NMR tube.

A single product was obtained from reaction of **13a** with



13a **14a**

either phosphorus oxychloride or thionyl chloride. It was clear from the NMR spectrum of the product, which showed a single aromatic methyl singlet at τ 7.44, a doublet of triplets for a methylene group attached to an aromatic ring at τ 7.20, and signals for a monosubstituted allyl group, that the desired seminaphthalene had not been obtained. The NMR spectrum of the product was consistent with two reasonable structures, **14a** and **15a**. Comparison of the NMR spectrum with that of **15a** (see below) indicated that the structure of the product was **14a**.

Examination of the NMR spectra of the reaction mixtures during dehydration of **13a** showed only signals for starting material and increasing amounts of **14a**. No signals which could be attributed to a seminaphthalene could be detected.

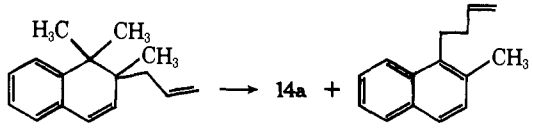
Table I. Chemical Shifts Induced by Addition of Eu(fod)$_3$

Alcohol	Methyl at C-1		Methyl at C-2		Methylene (CH_2—C=C or CH_2—Ph)	
	τ	Δ^a	τ	Δ^a	τ	Δ^a
11a	8.64	11.0	8.92	5.6		
	8.71	11.0	9.06	4.7		
11b	8.68	12.0	8.92	5.6		
	8.74	12.0	9.06	4.7		
11c	8.52	10.3	8.98	5.1		
	8.71	9.9	9.19	4.1		
13a	8.69	4.6	8.89	7.2	m, 7.48[b,c]	5.7[d]
13b	8.74	5.7	8.90	7.2	m, 7.45[b]	6.2
13c	8.77	4.6	8.83	7.2	d, 6.81	5.3
					d, 7.23	6.8

[a] $\Delta = -[\tau_{CCl_4} - \tau_{Eu(fod)_3}\ (N = 1)]$. [b] Reported value is apparent center of multiplet. [c] Collapses to doublet, J = 8 Hz, on addition of 0.2 equiv of Eu(fod)$_3$. [d] Value obtained from shift of doublet signal.

Dehydration of alcohol **11a** was much more difficult than dehydration of **13a**. No reaction could be detected between **11a** and phosphorus oxychloride in pyridine at room temperature. At 55 °C, signals due to the minor (*E*) isomer of **11a** had disappeared after 18 h, and signals due to aromatic products appeared. Unfortunately, it proved impossible to analyze the resulting mixture without causing further decomposition of the remaining starting material. At 70 °C, dehydration of **11a** was complete in 24 h. The slow reaction of **11a** compared with **13a** was presumably due to steric interference with phosphorylation of **11a**. The relatively rapid reaction of the *E* isomer can be attributed to the relative accessibility of the axial hydroxyl group.

Two products were obtained from dehydration of **11a** in approximately a 9 to 1 ratio. The minor product was identified as **14a**. The major product was an isomer of **14a**, with signals in its NMR spectrum for an aromatic methyl group at τ 7.61, a methylene on the aromatic ring at τ 7.00, and a terminal vinyl group. This product was assigned structure

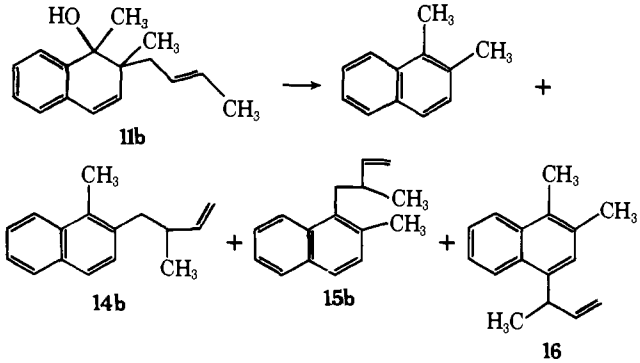


11a **15a**

15a. The facts that the methyl resonance in **15a** is ca. 0.2 ppm upfield from that in **14a** and the methylene signal ca. 0.2 ppm downfield demonstrate that the substituents in the two isomers are in the assigned positions.[11]

Dehydration of **13b** with phosphorus oxychloride in pyridine gave two products in an 8 to 1 ratio. The minor product was identified as 1,2-dimethylnaphthalene. The major product was tentatively identified by its analysis and spectra as **14b**. Again, possible ambiguity in the location of the substituents was resolved by comparison of its NMR spectrum with that of its isomer, **15b**.

Dehydration of the *E* isomer of **11b** was again feasible at 55 °C, but the *Z* isomer did not react at an appreciable rate below 70 °C. Reaction of **11b** with phosphorus oxychloride in pyridine at 70 °C gave four products, which were isolated by preparative VPC. The major product (34%) was 1,2-dimethylnaphthalene. The second largest component (32%) was **14b**. A third product (22% yield) was an isomer of **14b**, whose NMR spectrum showed the proper signals for structure **15b**. The aromatic methyl signal in the spectrum of **15b** was upfield from those of **14b** and the methylene signal downfield, in accordance with the assigned orientation of the substituents.



11b **14b** **15b** **16**

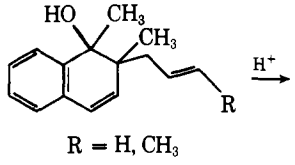
The final rearrangement product (8% yield) had NMR singlets for methyl groups in both the α and β positions, as well as signals for a 1-methylallyl group and a one-proton singlet upfield from the other aromatic signals. The presence of this singlet, which, from its high field location, appears to be in a β position, suggests that the structure of this product is **16**.

Table II. NMR Spectra of Seminaphthalenes

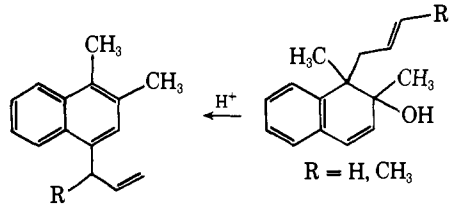
Compd	Chemical shifts (τ)			
	CH_3	CH_2Ph	$=CH_2$	-HC=CH-
17	s 8.57	s 7.19	s 5.01 (1 H) s 5.08 (1 H)	s 3.86 (2 H)
19	s 8.73	s 7.35[a]	s 4.61 (1 H)[b]	d, 3.63 (J = 9 Hz, 1 H, C-4)
		s 7.40[a]	s 4.86 (1 H)[c]	d, 4.26 (J = 9 Hz, 1 H, C-3)

[a] Presumably parts of doublets, with outer peaks hidden by other signals. [b] Syn to phenylene ring. [c] Trans to phenylene ring.

It seems probable that **16** arises from **11b** via a carbonium ion shift rather than by migration in an intermediate seminaphthalene. Indeed, rearrangement of either **11a** or **11b** in acid gives **16** and dimethylnaphthalene in a 2 to 1 ratio. Similarly, rearrangement of either **13a** or **13b** in acid



R = H, CH_3

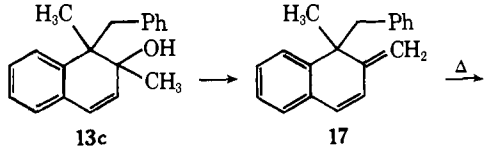


R = H, CH_3

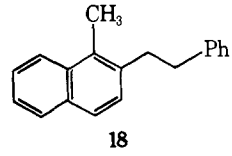
gave 4-allyl-1,2-dimethylnaphthalene in quantitative yield. Similar [3,3] and [3,4] shifts in cyclohexadienyl carbonium ions have been reported previously.[12]

Benzyl Group Migrations

Dehydration of alcohol **13c** in pyridine containing phosphorus oxychloride gave a product which showed olefinic absorptions in its NMR spectrum (see Table II). On the basis of its NMR and mass spectra and its behaviour on heating (see below), this product was assigned the seminaphthalene structure **17**.



13c **17**

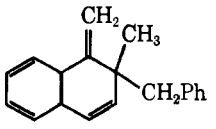


18

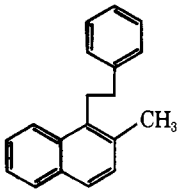
Seminaphthalene **17** was stable indefinitely on standing at room temperature and could be purified by column chromatography on alumina. No reaction could be observed on attempted thermal rearrangement at 100 °C—a dramatic contrast with the reactivity of *p*-semibenzenes.[3,13] Similarly, refluxing in 0.2 M potassium *tert*-butoxide in *tert*-butyl alcohol for 18 h resulted in no change. However, disappearance of **17** was complete after heating at 165 °C for 18 h in diglyme solution or after 6 h in the presence of benzoyl peroxide. The products obtained from each reaction were 1,2-dimethylnaphthalene (ca. 5–9%) and an isomer of **17**, which was assigned structure **18** on the basis of its NMR and mass spectra.

In contrast to the clean dehydration of **13c,** dehydration of **11c** gave a mixture of hydrocarbons which could not be separated. The NMR spectrum of the mixture showed the presence of aromatic methyl peaks corresponding to those in 1,2-dimethylnaphthalene, as well as all the signals for seminaphthalene **17.** When peaks for these two compounds were subtracted from the spectrum, there remained (in addition to the aromatic proton signals) a set of signals which are attributed to seminaphthalene **19.** These signals are listed in Table II. On the basis of the spectrum, the mixture was considered to contain approximately equal amounts of **17** and **19,** as well as ca. 10% of 1,2-dimethylnaphthalene.

Thermal rearrangements of this mixture in diglyme at 165 °C gave, in addition to 1,2-dimethylnaphthalene, a mixture of two hydrocarbons in the ratio 45:51. These products were isolated by preparative VPC and identified as **18** and an isomer of **18,** which was assigned the structure **20** on the basis of its NMR and mass spectra. Comparison of the



19

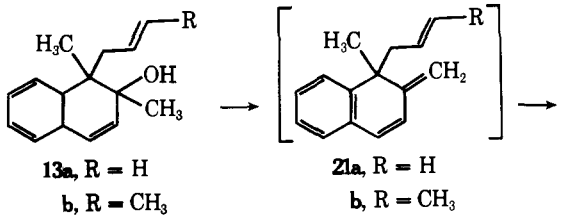


20

NMR spectra of **18** and **20** showed the methyl signal in **20** to be at higher field than that in **18,** in agreement with the assigned structures.

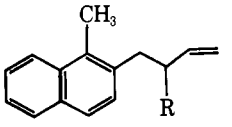
Discussion

There seems little doubt that seminaphthalenes are intermediates in the rearrangements of alcohols **11a, 11b, 13a,** and **13b** (eq 1 and 2). Any alternative mechanisms would



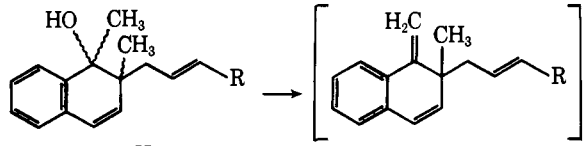
13a, R = H
b, R = CH_3

21a, R = H
b, R = CH_3

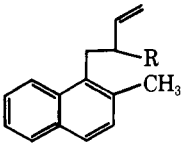


(1)

14a,b



11a, R = H
b, R = CH_3

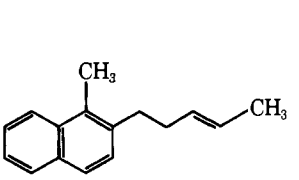


(2)

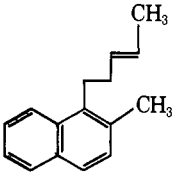
12a,b

have to involve quite improbable steps, such as the rearrangement of an allylic carbonium ion to an unstabilized primary carbonium ion.

The rearrangements of **13b** to **14b** and **11b** to **15b** unquestionably proceed by [3,3] sigmatropic shifts, since the isomers **22** or **23,** which would be formed by [1,3] shifts or



22

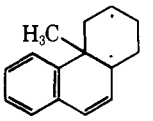


23

free radical paths, are not obtained. The corresponding rearrangements of the allyl derivatives **11a** and **13a** presumably proceed by similar paths.

The rearrangements of **13a** and **13b** proceed at exceptionally low temperatures for Cope rearrangements. The only Cope rearrangements which proceed at comparable or lower temperatures are those of *cis*-divinylcyclopropanes.[14] In the divinylcyclopropane reaction, formation of the product is exothermic by some 28 kcal per mol due to relief of angle strain. The seminaphthalene rearrangements are exothermic by some 30 kcal per mol, due to the appearance of a new aromatic ring in the product. A good deal of the stability of the product appears to be evident in the transition states for these reactions.

The question of concertedness of the Cope rearrangement is still a subject of discussion. Dewar and Wade[15] have recently suggested that some Cope rearrangements proceed by a two-step process in which the initial step is formation of a cyclic diradical. For the rearrangement of seminaphthalene **21,** an intermediate radical of this type would have structure **24.** It is clear that such a mechanism, regardless

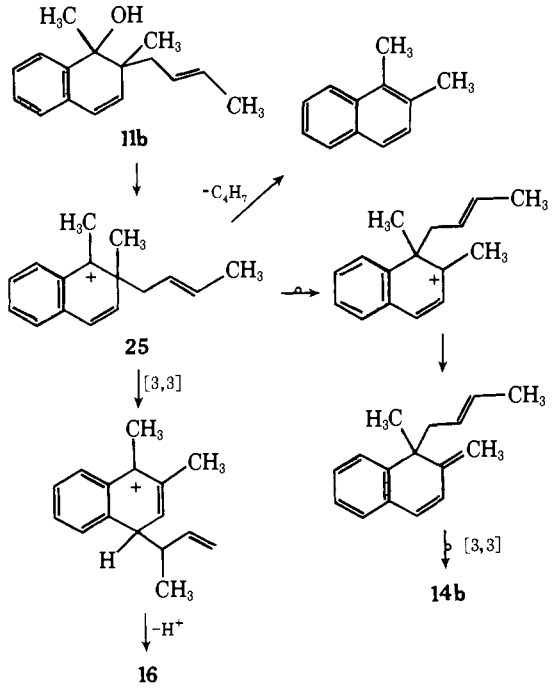


24

of whether the diradical is considered a discrete intermediate or a significant representation of the transition state, does not in any way explain the exceptional ease of rearrangements of seminaphthalenes. In view of the thermal stability of seminaphthalenes **17** and **19,** representations of the transition state for the Cope rearrangement resembling an allyl-naphthalenyl radical pair can similarly be rejected. Instead, the Cope rearrangements of *o*-seminaphthalenes must proceed by concerted mechanisms in which the transition states closely resemble the aromatic products.

The formation of the "abnormal" rearrangement products **14a** and **14b** from **11a** and **11b,** respectively, can most readily be explained by Wagner Meerwein shifts in carbonium ions such as **25.** That carbonium ions are formed during the dehydration of **11b** is evidenced by formation of **16,** as well as the large amount of 1,2-dimethylnaphthalene, which can be explained most readily by fragmentation of carbonium ion **25.** That much higher amounts of dimethylnaphthalene and of "abnormal" rearrangement products are obtained from reaction of **11b** than from **11a** is consistent with this mechanism, since the crotyl group is known to be a better migrator than the allyl group, as well as being more easily cleaved from the ring, in reactions of cyclohexadienyl carbonium ions.[16] Carbonium ion rearrangements only occur during dehydration of alcohols **11a–11c,** in which the resulting α-naphthyl carbonium ions can rearrange to the more stable β-naphthyl carbonium ions.

In contrast to the very rapid Cope migrations of allyl groups in seminaphthalenes, we have found no evidence for Cope migrations of benzyl groups. Instead, only the products of [1,3] migration are observed. Analogy with benzyl shifts in the migrations of *p*-semibenzenes, as well as the ev-



idence of catalysis by benzoyl peroxide, suggests that these reactions proceed by free radical chain processes.

The possibility was considered that benzyl groups in **17** and **19** do indeed undergo relatively rapid [3,3] shifts, but that in the absence of a facile method for aromatization of the resulting semibenzene they simply revert to the starting seminaphthalenes, which eventually undergo free radical reactions. However, if significant amounts of any semibenzene were formed on heating **17**, we would expect it to be aromatized readily in the presence of potassium *tert*-butoxide at 80 °C.[17] Since no products resulting from such a process are observed, we must conclude that even an "isothermic" Cope migration of a benzyl group requires an appreciable activation energy and is not competitive with a free radical chain process for aromatization of seminaphthalenes.

Experimental Section

General. NMR spectra were taken on Varian A-60 or Perkin-Elmer R12A spectrometers in carbon tetrachloride solution (unless otherwise indicated) using Me_4Si as an internal standard. Ir spectra were taken on Beckman IR-10 or Perkin-Elmer 273B spectrometers. Mass spectra were taken on a Hitachi Perkin-Elmer RMU-6L instrument. Relative areas of major peaks are reported in parentheses after peak weights.

Elemental analyses were carried out by the University of Massachusetts Microanalytical Laboratory, Amherst, Mass.

GLC analyses and separations were carried out on a Varian Aerograph Model 202c instrument using one of the following columns: column A, 6 ft × ¼ in., 5% SE-30 on Chromosorb W; column **B**, 5 ft × ⅜ in., 5% SE-30 on Chromosorb W; column C, 6 ft × ⅜ in., 5% SE-52 on Chromosorb W. Column temperature and carrier gas flow rates are described in parentheses for each separation.

Melting points were taken on a Mel-Temp apparatus and are uncorrected.

For preparation of benzcyclohexadienols, the phrase "worked up as usual" means that the solvent was evaporated under reduced pressure, and the residue was stirred with 100 ml of 3:1 methanol–water solution and then extracted with methylene chloride. The methylene chloride solution was washed with water and dried over magnesium sulfate, and the solvent was evaporated.

For dehydration of benzcyclohexadienols in pyridine, the phrase "worked up as usual" means that the reaction mixture was poured slowly into ice–water and extracted with petroleum ether. The organic layer was washed with water and dried over magnesium sulfate, and the solvent was evaporated.

Synthesis of Benzcyclohexadienols. (*Z*)-1-Allyl-1,2-dimethyl-2-hydroxy-1,2-dihydronaphthalene (13a). To a stirred solution of naphthalenone **12a**[18] (4.4 g, 0.022 mol) in 50 ml of dry benzene under a nitrogen atmosphere was added 16 ml of 2.2 M methyllithium in hexane (0.035 mol). After 15 min the reaction was worked up as usual to give 4.5 g of a yellow fluid. VPC of the product on column A (200 °C, 55 ml/min) showed the presence of one major peak at 1.7 min. The crude product was chromatographed on Florisil (80 g). Elution with 95:5 hexane–methylene chloride gave a white solid which was recrystallized from hexane to give white needles, mp 92–93 °C (3.1 g, 14.4 mmol, 63%).

The ir spectrum of the product had a hydroxy peak at 3400 cm^{-1}. Its NMR spectrum had peaks at τ 2.80–2.14 (m, 4 H), a pair of doublets at 3.20 and 4.24 (totaling 2 H, J = 9 Hz), 4.20–5.35 (m, 3 H), 7.20–7.74 (m, 2 H), 8.40 (s, 1 H), (the singlet at τ 8.40 shifted markedly when a few drops of pyridine was added and was therefore considered to be the hydroxy hydrogen), 8.69 (s, 3 H), 8.89 (s, 3 H). Anal. ($C_{15}H_{18}O$) C, H.

2-Allyl-1,2-dimethyl-1-hydroxy-1,2-dihydronaphthalene (11a). A solution of 2.2 M methyllithium in hexane (8 ml, 0.018 mol) was added to a stirred solution of 2-allyl-2-methyl-1-naphthalenone[18] (1.98 g, 0.01 mol) in 50 ml of dry benzene. The mixture was stirred under nitrogen for 15 min at room temperature and worked up as usual to give 2.2 g of yellow oil. VPC on column A (175 °C, 55 ml/min) showed one major peak at 2.1 min. The crude product was chromatographed on Florisil (40 g) eluting with 90:10 hexane–methylene chloride. A yellow oil (1.4 g, 0.006 mol, 60% yield) was obtained. Its ir spectrum showed a hydroxy peak at 3500 cm^{-1}. Its NMR spectrum had peaks at τ 2.40–2.58 (m, 1 H), 2.82–3.18 (m, 3 H), a pair of doublets at 3.78 and 4.40 (2 H, J = 9 Hz), 3.92–5.35 (m, 4 H), 7.60–8.08 (m, 2 H), 8.64 and 8.71 (two singlets in the area ratio of about 1 to 2, together 3 H), 8.92 and 9.04 (two singlets in the area ratio 2 to 1, together 3 H). Anal. ($C_{15}H_{18}O$) C, H.

2-(*trans*-2-Butenyl)-1,2-dimethyl-1-hydroxy-1,2-dihydronaphthalene (11b). Methyllithium in hexane (22 ml, 0.05 mol) was added with stirring under a nitrogen atmosphere to a solution of 2-(2-butenyl)-2-methyl-1-naphthalenone[18] (6.0 g, 0.03 mol) in 60 ml of dry benzene. After 20 min of stirring at room temperature, the reaction mixture was worked up as usual to give 5.3 g of yellow oil, which was chromatographed on Florisil (100 g) eluting with 90:10 hexane–methylene chloride. A yellow oil (3.7 g, 0.016 mol, 54% yield) was obtained. Its ir spectrum had a hydroxy peak at 3500 cm^{-1}. Its NMR spectrum had peaks at τ 2.39–2.58 (m, 1 H), 2.76–3.23 (m, 3 H), a pair of doublets at 3.78 and 4.40 (2 H, J = 9 Hz), 4.19–4.82 (m, 3 H), 7.62–8.07 (m, 2 H), 8.47 (d, 3 H, J = 4 Hz), 8.68 and 8.74 (2 singlets in the ratio 1 to 2, together 3 H), 8.92 and 9.06 (2 singlets in the ratio 2 to 1, together 3 H). Its mass spectrum had peaks at *m/e* 228 (M^+, 1) and 171 (30), 167 (13), 158 (14), 157 (22), 156 (18), 155 (14), and 129 (14). Anal. ($C_{16}H_{20}O$) C, H.

(*Z*)-1-(*trans*-2-Butenyl)-1,2-dimethyl-2-hydroxy-1,2-dihydronaphthalene (13b). A solution of 2.2 M methyllithium in hexane (0.030 mol) was added to a stirred solution of 1-(*trans*-2-butenyl)-1-methyl-2-naphthalenone[18] (2.4 g, 0.011 mol) in 30 ml of dry benzene. After stirring at room temperature for 15 min under nitrogen, the reaction mixture was worked up as usual to give 2.6 g of a yellow oil. VPC showed one major peak. The ir spectrum of the reaction product showed that no naphthalenone was present and showed an OH band at 3450 (s) cm^{-1}. Its NMR spectrum had peaks at τ 2.85–3.15 (m, 4 H), a pair of doublets at 3.80 and 4.25 (2 H, J = 9 Hz), 4.48–5.45 (m, 3 H), 7.33–7.58 (m, 2 H), 8.51 (d, 3 H, J = 4 Hz), 8.74 (s, 3 H), 8.90 (s, 3 H). Its mass spectrum had peaks at *m/e* 248 (M^+, 21) and 155 (100).

(*Z*)-1-Benzyl-1,2-dimethyl-2-hydroxy-1,2-dihydronaphthalene (13c). Methyllithium in hexane (0.026 mol) was added to a stirred solution of 1-benzyl-1-methyl-2-naphthalenone[18] (2.8 g, 0.012 mol) in 50 ml of dry benzene under a nitrogen atmosphere. After 15 min the reaction mixture was worked up as usual to give 2.9 g of a yellow fluid. The ir spectrum of the crude product showed that no naphthalenone was present. It showed a hydroxy peak at 3570 cm^{-1}. Its NMR spectrum had peaks at τ 2.71–3.76 (m, 10 H), 4.17 (1 H, J = 9 Hz), a pair of doublets at 6.81 and 7.23 (totalling 2 H, J = 12 Hz), 7.83 (broad singlet, 1 H), 8.77 (s, 3 H), and 8.83 (s, 3 H).

2-Benzyl-1,2-dimethyl-1-hydroxy-1,2-dihydronaphthalene (11c). Methyllithium in hexane (0.008 mol) was added to a stirred solution of 2-benzyl-2-methyl-1-naphthalenone[18] (1.0 g, 0.0040 mol) in 30 ml of dry benzene under a nitrogen atmosphere. After 15 min the reaction mixture was worked up as usual to give 1.1 g of yellow oil. The ir spectrum of the product showed a hydroxy peak at 3590 cm^{-1}. Its NMR spectrum had peaks at τ 2.35–3.02 (m, 9 H), a pair of doublets at 3.67 and 4.71 and a pair of doublets at 3.72 and 4.36 (together 2 H, J = 9 Hz in the area ratio 2 to 1), 7.31–7.67 (m, 2 H), 8.52 and 8.71 (2 singlets, together 3 H, in the area ratio 1 to 2), 8.98 and 9.19 (2 singlets, together 3 H, in the area ratio 2 to 1).

Dehydration of Benzcyclohexadienols. Reaction of 1-Allyl-1,2-dimethyl-2-hydroxy-1,2-dihydronaphthalene with Phosphorus Oxychloride in Pyridine. To a solution of **13a** (2.1 g, 0.01 mol) in 15 ml of pyridine was added 3.0 g (0.02 mol) of phosphorus oxychloride. The reaction mixture was stirred at room temperature for 48 h and worked up as usual to give 1.9 g of a yellow oil. VPC on column A (175 °C, 55 ml/min) showed the presence of one major peak at 3.4 min. A pure sample was isolated by VPC on column **B** (200 °C, 60 ml/min). Its NMR spectrum had peaks at τ 2.07–3.02 (m, 6 H), 3.87–5.23 (m, 3 H), 7.20 (dt, J = 8 Hz, 1 Hz, 2 H), 7.49–7.81 (m, 2 H), 7.44 (s, 3 H). Its mass spectrum had peaks at *m/e* 196 (M^+, 17) and 155 (100). Anal. ($C_{15}H_{16}$) C, H.

This compound was assigned the structure **2-(3-butenyl)-1-methylnaphthalene (14a).**

Reaction of 1-Allyl-1,2-dimethyl-2-hydroxy-1,2-dihydronaphthalene with Thionyl Chloride in Pyridine. To a solution of **13a** (1.0 g, 0.005 mol) in 30 ml of dry pyridine was added 6 ml of thionyl chloride. The reaction mixture was stirred at 0 °C for 2 days and then poured slowly into ice–water. It was worked up as described for the reaction with phosphorus oxychloride. The product had the same ir and NMR spectra and VPC retention times as **14a.**

Reaction of 2-Allyl-1,2-dimethyl-1-hydroxy-1,2-dihydronaphthalene (11a) with Phosphorus Oxychloride in Pyridine. Phosphorus oxychloride (2.0 g, 0.016 mol) was added to a solution of **11a** (1.4 g, 0.006 mol) in 15 ml of dry pyridine. The mixture was stirred at 70 °C for 24 h and was then worked up as usual to give 1.5 g of yellow oil. VPC on column A (180 °C, 55 ml/min) showed the presence of one major peak at 2.3 min and two small peaks at 2.7 and 5.3 min in the area ratio 39:5:5. The products were separated by VPC on column **B** (200 °C, 60 ml/min). The major component had peaks in its NMR spectrum at τ 1.98–2.94 (m, 6 H), 3.74–5.19 (m, 3 H), 7.00 (t, J = 8 Hz, 2 H), 7.48–7.93 (m, 2 H), 7.61 (s, 3 H). Its mass spectrum had peaks at *m/e* 196 (M^+, 67), 155 (87), and 154 (100). Anal. ($C_{15}H_{16}$) C, H.

This compound was assigned the structure **1-(3-butenyl)-2-methylnaphthalene (15a).**

The second component (with a retention time of 2.7 min) had the same ir and NMR spectrum as compound **14a.** The final component was the starting alcohol **11a.**

Reaction of 2-(*trans*-2-Butenyl)-1,2-dimethyl-1-hydroxy-1,2-dihydronaphthalene (11b) with Phosphorus Oxychloride in Pyridine. Phosphorus oxychloride (3.8 g, 0.025 mol) was added to a solution of **11b** (3.2 g, 0.014 mol) in 20 ml of dry pyridine, and the mixture was stirred at 60 °C for 15 h. It was then worked up as usual to give 2.3 g of yellow oil. VPC on column A (175 °C, 55 ml/min) showed the presence of three peaks at 1.5, 3.4, and 4.2 min, in the area ratio 34:22:31.5. The products were isolated by VPC on column **B** (200 °C, 60 ml/min). The first component (rt = 1.5 min) was identified as 1,2-dimethylnaphthalene by comparison of its spectra and retention time with those of an authentic sample.

The second component (rt = 3.4 min) had NMR peaks at τ 1.94–2.92 (m, 6 H), 3.84–5.30 (m, 3 H), 6.89–7.10 (m, 2 H), 7.13–7.61 (m, 1 H), 7.59 (s, 3 H), 8.98 (d, 3 H, J = 6 Hz). Its mass spectrum had peaks at 210 (M^+, 82) 156 (80), and 155 (100). Anal. ($C_{16}H_{18}$) C, H.

It was assigned the structure **1-(2-methyl-3-butenyl)-2-methylnaphthalene (15b).**

The third component (rt = 4.2 min) had NMR peaks at τ 1.92–2.93 (m, 6 H), 3.80–5.28 (m, 3 H), 7.05–7.65 (m, 3 H), 7.41 (s, 3 H), 8.95 (d, 3 H, J = 6 Hz). Its mass spectrum had peaks at 210 (M^+, 86), 156 (82), and 155 (100). Anal. ($C_{16}H_{18}$) C, H.

It was assigned the structure **2-(2-methyl-3-butenyl)-1-methylnaphthalene (14b).**

Reaction of 1-(*trans*-2-Butenyl)-1,2-dimethyl-2-hydroxy-1,2-dihydronaphthalene (13b) with Phosphorus Oxychloride in Pyridine. Phosphorus oxychloride (2.0 g, 0.0125 mol) was added to a solution of **13b** (1.15 g, 5.0 mmol) in 20 ml of dry pyridine, and the mixture was stirred overnight at 70 °C and worked up as usual to give 0.85 g of a yellow fluid. VPC on column A (175 °C, 55 ml/min) showed the presence of three peaks at retention times of 1.6, 4.8, and 5.1 min, in the area ratio 10:83:7. The products were isolated by VPC on column **B** (210 °C, 60 ml/min). The first and second components were identified as **1,2-dimethylnaphthalene** and **2-(2-methyl-3-butenyl)-1-methylnaphhalene (14b)** by comparison of their ir and NMR spectra and VPC retention times with those of samples previously obtained.

The third component (rt = 5.1 min) was identified as the starting alcohol **13b.**

Synthesis of 1-Benzyl-1-methyl-2-methylene-1,2-dihydronaphthalene (17). Phosphorus oxychloride (2.0 g, 8.0 mmol) was added to a solution of 1-benzyl-1,2-dimethyl-2-hydroxy-1,2-dihydronaphthalene (1.7 g, 0.06 mol) in 15 ml of pyridine. The reaction mixture was stirred overnight at 70 °C and then worked up as usual to give 1.6 g of yellow oil. VPC on column A (195 °C, 60 ml/min) showed the presence of a major peak with a retention time of 5.8 min and minor peaks at 1.2, 1.4, and 12.9 min. The crude product was chromatographed on Florosil, then on alumina, and again on Florosil, finally giving 0.60 g (2.6 mmol, 32%) of pale yellow oil which showed a single peak (rt = 5.8 min) on VPC. Its NMR spectrum ($CDCl_3$) showed peaks at 2.85–3.40 (m, 9 H), 3.86 (s, 2 H, protons at C-3 and C-4), 5.01 (s, 1 H), 5.08 (s, 1 H), 7.19 (s, 2 H), and 8.57 (s, 3 H).

Reaction of 2-Benzyl-1,2-dimethyl-1-hydroxy-1,2-dihydronaphthalene (11c) with Phosphorus Oxychloride in Pyridine. Phosphorus oxychloride (1.5 g, 0.012 mol) was added to a solution of **11c** (1.1 g, 4.0 mmol) in 10 ml of pyridine. The reaction mixture was stirred at 70 °C for 18 h and then worked up as usual to give 0.80 g of yellow oil. VPC on column A (200 °C, 60 ml/min) showed the presence of a minor peak at 1.6 min and major peaks at 10.8 and 12.4 min. The mass spectra of these compounds were identical with those of 1,2-dimethylnaphthalene, **18,** and **20,** respectively. The NMR spectrum of the reaction product showed, in addition to peaks attributable to seminaphthalene **17** and aromatic protons, the following peaks (with the area of the doublet at τ 3.63 arbitrarily set equal to 1 H): τ 3.63 (d, 1 H, J = 9 Hz), 4.26 (d, 1 H, J = 9 Hz), 4.61 (s, 1 H), 4.86 (s, 1 H), 7.35 and 7.40 (apparent singlets, totalling 2 H), 8.73 (s, 3 H), 7.46 (s, 1.5 H), 7.56 (s, 1.8 H). On this scale, the signal at τ 3.83 attributed to **17** totalled 1.9 H. Attempts to isolate individual components of this mixture by chromatography on Florisil or alumina were unsuccessful.

Thermal Rearrangements. Rearrangement of 1-Benzyl-1-methyl-2-methylene-1,2-dihydronaphthalene (17). A solution of **17** (0.1 g) in 0.5 ml of dry diglyme was heated for 18 h in a sealed tube kept in an oil bath at 165 °C. The tube was cooled and opened. The contents were poured into water and extracted with pentane. The organic layer was washed with water and dried, and the solvent was evaporated to give 0.1 g of a yellow fluid. VPC on column A (200 °C, 55 ml/min) showed peaks with retention times of 1.4 (1,2-dimethylnaphthalene) and 10.9 min in the area ratio 8:86. The major component was isolated by VPC on column C (200 °C, 65 ml/min). Its NMR spectrum had peaks at τ 1.97–2.94 (m, 11 H), 6.94–7.21 (m, 4 H), and 7.49 (s, 3 H). Its mass spectrum had peaks at 246 (M^+, 42) and 155 (100). This compound was assigned the structure **1-methyl-2-(2-phenylethyl)naphthalene (18).**

Attempted Rearrangement in Presence of Potassium *tert*-Butoxide. A solution of seminaphthalene **17** (62 mg) and potassium *tert*-butoxide (200 mg, 1.8 mmol) in 10 ml of *tert*-butyl alcohol was refluxed for 18 h. It was then diluted with water and extracted with methylene chloride, and the organic layer was washed three times with water. The solution was dried and evaporated under vacuum to give 54 mg of yellow oil whose ir and NMR spectrum were identical with those of **17.**

Rearrangement of Products of Dehydration of 11c. A solution of the mixture of products obtained by dehydration of **11c** (0.20 g) in 0.5 ml of dry diglyme was heated overnight in an oil bath at 165 °C. The tube was cooled and opened. The contents were dissolved in water and then extracted with *n*-pentene. The organic layer was washed with water and dried, and the solvent was evaporated to give 0.15 g of yellow oil. VPC on column A (200 °C, 55 ml/min) showed three peaks at 1.2 min (1,2-dimethylnaphthalene), 10.1

min, and 12.4 min in area ratios of 4:51:45. The components were isolated by VPC on column F (220 °C, 65 ml/min). The component with retention time of 12.4 min had NMR peaks at τ 2.24–2.98 (m, 11 H), 6.51–6.83 (m, 2 H), 6.96–7.18 (m, 2 H), 7.64 (s, 3 H). Its mass spectrum had peaks at *m/e* 246 (M^+, 60), 156 (60), 155 (100), and 140 (53). This compound was assigned the structure **2-methyl-1-(2-phenylethyl)naphthalene (20)**.

The other major product (rt = 10.1 min) was found to be **18**.

Acid-Catalyzed Rearrangements. Rearrangement of 1-Allyl-1,2-dimethyl-2-hydroxy-1,2-dihydronaphthalene (13a). 1-Allyl-1,2-dimethyl-2-hydroxy-1,2-dihydronaphthalene (0.1 g) was dissolved in 7 ml of 0.1 M sulfuric acid in acetic acid. After the solution was stirred at room temperature for 24 h, water was added (20 ml), and the mixture was extracted with methylene chloride. The organic fraction was washed with water, with aqueous sodium bicarbonate solution, again with water, dried, and evaporated. VPC on column A (185 °C, 55 ml/min) showed a single peak at 3.6 min. Its NMR spectrum had peaks at τ 1.98–2.21 (m, 2 H), 2.56–2.77 (m, 2 H), 2.96 (s, 1 H), 3.61–5.18 (m, 3 H), 6.32 (d, 2 H, J = 6 Hz), 7.54 (s, 3 H), 7.64 (s, 3 H). Its mass spectrum had peaks at 196 (M^+, 78) and 181 (100). This compound was assigned the structure **4-allyl-1,2-dimethylnaphthalene**.

Rearrangement of 11a. A solution of alcohol **11a** (0.10 g) in 5 ml of 0.1 M sulfuric acid in acetic acid was stirred at room temperature for 18 h and worked up as described for the rearrangement of **13a** to give 0.090 g of **4-allyl-1,2-dimethylnaphthalene**.

Rearrangement of 1-(*trans*-2-Butenyl)-1,2-dimethyl-2-hydroxy-1,2-dihydronaphthalene (13b). 1-(*trans*-2-Butenyl)-1,2-dimethyl-2-hydroxy-1,2-dihydronaphthalene (0.8 g) was dissolved in 15 ml of a 1 M solution of sulfuric acid in acetic acid. After 18 h of stirring at room temperature, water was added (20 ml), and the organic material was extracted with methylene chloride. The organic fraction was washed with water, aqueous sodium bicarbonate solution, and water and dried, and the solvent was evaporated. VPC on column A (190 °C, 55 ml/min) showed two major peaks at 1.4 and 4.1 min, in the area ratio 76:24. The two compounds were isolated by VPC on column F (210 °C, 65 ml/min). The component with retention time of 1.4 min was identified as 1,2-dimethylnaphthalene.

The component with a retention time of 4.2 min had NMR peaks at τ 1.80–2.10 (m, 2 H), 2.54–2.72 (m, 2 H), 2.89 (s, 1 H), 3.57–5.10 (m, 3 H), 5.63–5.93 (m, 1 H), 7.45 (s, 3 H), 7.55 (s, 3 H), 8.50 (d, 3 H, J = 6.5 Hz). Its mass spectrum had peaks at *m/e* 210 (M^+, 60), 195 (100), 181 (52), and 163 (56).

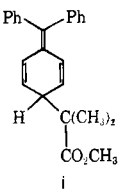
This compound was assigned the structure **1,2-dimethyl-4-(1-methylallyl)naphthalene (16)**.

Rearrangement of 11b. A solution of alcohol **11b** (0.10 g) in 5 ml of 0.1 M sulfuric acid in acetic acid was stirred at room temperature for 18 h and worked up as described for the rearrangement of **13b**. The products were identified as 1,2-dimethylnaphthalene and **16**.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for a grant in support of this work.

References and Notes

(1) K. von Auwers and G. Keil, *Chem. Ber.*, **36**, 1861 (1903); see also, K. von Auwers, *Justus Leibigs Ann. Chem.*, **352**, 219 (1907); K. von Auwers and W. Jühlicher, *Chem. Ber.*, **55**, 2167 (1922).
(2) H. Hart and J. D. DeVrieze, *Tetrahedron Lett.*, 4259 (1968).
(3) B. Miller and K.-H. Lai, *J. Am. Chem. Soc.*, **94**, 3472 (1972).
(4) M. S. Newman and R. M. Layton, *J. Org. Chem.*, **33**, 2338 (1968).
(5) M. S. Newman and L. L. Wood, Jr., *J. Org. Chem.*, **23**, 1236 (1958); *J. Am. Chem. Soc.*, **81**, 6450 (1959).
(6) P. Gilgen, J. Zsindely, and H. Schmid, *Helv. Chim. Acta*, **56**, 681 (1973).
(7) D. A. Jaeger, *J. Am. Chem. Soc.*, **96**, 6216 (1974).
(8) D. Y. Curtin and R. J. Crawford, *J. Am. Chem. Soc.*, **79**, 3156 (1957); B. Miller, *ibid.*, **87**, 5115, 5515 (1965).
(9) W. von E. Doering and R. A. Bragole, *Tetrahedron*, **22**, 385 (1966). See also, E. N. Marvell and C. Lin, *Tetrahedron Lett.*, 2679 (1973).
(10) (a) See B. C. Mayo, *Chem. Soc. Rev.*, **2**, 49 (1973), for references to applications of paramagnetic shift reagents. (b) Comparison of the Δ values for the C-1 methyls with those for each of the benzylic methylene protons in **13c**, or for the allylic methylene groups in **13a** and **13b**, shows larger downfield shifts for the methylene than for the methyl signals (see Table I). Although it is not clear that Δ values for methylene groups can be directly compared with those for methyl groups, the simplest explanation for these results is that the hydroxy groups in **13a–c** are syn to the allyl or benzyl groups, in agreement with the configuration assigned from chemical arguments.
(11) F. F. Yew, R. J. Kurland, and B. J. Mair, *Anal. Chem.*, **36**, 843 (1964).
(12) H.-J. Hansen, B. Sutter, and H. Schmid, *Helv. Chim. Acta*, **51**, 828 (1968); B. Miller and K.-H. Lai, *Tetrahedron*, **28**, 2221 (1972); *J. Org. Chem.*, **37**, 2505 (1972).
(13) K. J. Skinner, H. S. Hochster, and J. M. McBride, *J. Am. Chem. Soc.*, **96**, 4301 (1974).
(14) E. Vogel, K.-H. Ott, and K. Gajek, *Justus Liebigs Ann. Chem.*, **644**, 172 (1961); W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).
(15) M. J. S. Dewar and L. E. Wade, *J. Am. Chem. Soc.*, **95**, 290 (1973).
(16) B. Miller and K.-H. Lai, *J. Org. Chem.*, **37**, 2505 (1972).
(17) Semibenzene i, for instance, is aromatized by potassium *tert*-butoxide



i

in *tert*-butyl alcohol at 25 °C and by as weak a base as tripropylamine at 75 °C; [D. J. Cram, F. Willey, H. P Fisher, H. M. Relles, and D. A. Scott, *J. Am. Chem. Soc.*, **88**, 2759 (1966)].
(18) B. Miller and M. R. Saidi, *J. Am. Chem. Soc.*, **98**, 2227 (1976).