Anal. Calcd for $C_{21}H_{18}N_2$: C, 84.53; H, 6.08; N, 9.39; MW 298. Found: C, 84.76; H, 5.73; N, 9.56; *m/e* 298.

β-(1-Hydroxymethylcyclopentyl)-α-cyano-*trans*-cinnamic Acid Lactone (29). A solution of 1.00 g (3.8 mmol) of **27b** in 7 mL of concentrated sulfuric acid was maintained at 50 °C for 15 min and then poured over ice. The combined organic layers from benzene and THF extractions were washed with 5% $NaHCO_3$, dried, and evaporated. Recrystallization of the residue from methanol gave 0.11 g (12%) of **29** as white crystals, mp 166.0–167.5 °C; IR (KBr) 3.41, 4.51, 5.81, 6.30, 6.85, 13.29, 14.15 μm; NMR ($CDCl_3$) δ 1.78 (s, 8 H, cyclopentyl), 4.31 (s, 2 H, CH_2), 7.2–7.7 (m, 5 H, aryl).

Anal. Calcd for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53; MW 253. Found: C, 75.73; H, 5.79; N, 5.80; *m/e* 253.

Registry No.—**3,** 64871-55-2; **4,** 64871-56-3; **7,** 64871-57-4; **8,** 64871-58-5; **9,** 64871-59-6; **11,** 4889-95-6; **12,** 64871-60-9; **13,** 64871-61-0; **15,** 1193-18-6; **16,** 21889-89-4; **21,** 64871-62-1; **22,** 64871-63-2; **22**-DNP, 64871-64-3; **23,** 64871-65-4; **24,** 64871-72-3; **25,** 64871-73-4; **26a,** 64871-66-5; **26b,** 64871-74-5; **26c,** 64871-75-6; **26d,** 77-57-6; **27a,** 64871-76-7; **27b,** 64871-77-8; **27d,** 64871-78-9; **27e,** 64871-67-6; **29,** 64871-68-7; phenylacetonitrile, 140-29-4; 1,4-dichlorobutane, 110-56-5; cyclopentanecarbonitrile, 4254-02-8; ethyl 1-cyanocyclopentanecarboxylate, 28247-14-5; 1,4-dibromobutane, 110-52-1; 2-methyl-2-phenylcyclohexylidenemalononitrile, 64871-69-8; 1-methylcyclopentanecarbonitrile, 64871-70-1; propionitrile, 107-12-0; α-cyano-β-(1-methylcyclopentyl)cinnamonitrile, 64871-71-2; phenyllithium, 591-51-5; malononitrile, 109-77-3; sodium cyanide, 143-33-9; methyl iodide, 74-88-4; benzyl chloride, 100-44-7; methyl chloromethyl ether, 107-30-2; methyl 2-chloroethyl ether, 627-42-9; bromobenzene, 108-86-1; *p*-bromoanisole, 104-92-7.

References and Notes

(1) (a) Cyclization of Ylidenemalononitriles, 9. Supported in part by Grant GM-10366 from the National Institutes of Health. Part 8: E. Campaigne and Dale E. Mais, *J. Heterocycl. Chem.*, **12,** 267 (1975). (b) Submitted in partial fulfillment of the requirements for the degree Doctor of Philosophy, Indiana University, July 1977.
(2) M. Menard et al., *Can. J. Chem.*, **54,** 429 (1976).
(3) I. Monkovic and H. Wong, *Can. J. Chem.*, **54,** 883 (1976).
(4) I. Monkovic et al., *Can. J. Chem.*, **53,** 2515 (1975).
(5) I. Monkovic et al., *Can. J. Chem.*, **53,** 3094 (1975).
(6) B. Belleau et al., *Can. J. Chem.*, **53,** 237 (1975).
(7) E. Campaigne and D. Maulding, *J. Org. Chem.*, **28,** 1391 (1963).
(8) (a) E. Campaigne and S. Schneller, *Synthesis,* 705 (1976); (b) E. Campaigne, D. Mais, and E. M. Yokley, *Synth. Commun.*, **4,** 379 (1974).
(9) T. Zalesskaya and O. Netsetskaya, *J. Org. Chem. USSR (Engl. Transl.)*, **5,** 1563 (1969).
(10) M. Larcheveque, P. Mulot, and T. Cuvigny, *J. Organomet. Chem.*, **57,** C33 (1973).
(11) C. Tilford, M. Van Campen, Jr., and R. Shelton, *J. Am. Chem. Soc.*, **69,** 2902 (1947).
(12) N. Sperber, D. Papa, and E. Schwenk, *J. Am. Chem. Soc.*, **70,** 3091 (1948).
(13) E. Campaigne et al., *J. Heterocycl. Chem.*, **8,** 65 (1971).
(14) S. Kulp et al., *J. Org. Chem.*, **40,** 453 (1975).
(15) T. Sasaki, K. Kanematsu, and K. Minamoto, *Yakugaku Zasshi,* **84,** 381 (1964); *Chem. Abstr.*, **61,** 4285b (1964).
(16) M. Makosza and B. Serafin, *Rocz. Chem.*, **40,** 1647 (1966); *Chem. Abstr.*, **66,** 94792x (1967).
(17) R. Arnold, J. Buckley, Jr., and R. Dodson, *J. Am. Chem. Soc.*, **72,** 3153 (1950).
(18) T. Payne and P. Jefferies, *Tetrahedron,* **29,** 2575 (1973).
(19) A. Platé et al., *J. Gen. Chem. USSR (Engl. Transl.)*, **30,** 1273 (1960).
(20) S. Natelson and S. Gottfried, *J. Am. Chem. Soc.*, **61,** 1001 (1939).
(21) W. Treibs, *Ber. Dtsch. Chem. Ges. B,* **66,** 1483 (1933).
(22) J. Huffman and T. Bethea, *J. Org. Chem.*, **30,** 2956 (1965).
(23) E. Campaigne and W. Roelofs, *J. Org. Chem.*, **30,** 2610 (1965).
(24) (a) V. Grignard and K. Ono, *Bull. Soc. Chim. Fr.*, **39,** 1593 (1926); (b) M. Newman and R. Closson, *J. Am. Chem. Soc.*, **66,** 1553 (1944).
(25) R. Wasson and H. House, "Organic Syntheses", Collect. Vol. IV, Wiley, New York, N.Y., 1963, p 552.
(26) E. Piers, W. de Waal, and R. Britton, *J. Am. Chem. Soc.*, **93,** 5113 (1971).
(27) L. Friedman and H. Shechter, *J. Org. Chem.*, **25,** 878 (1960).
(28) R. Paul and S. Tchelitcheff, *Bull. Soc. Chim. Fr.*, **16,** 470 (1949).
(29) P. Mueller and B. Siegfried, *Tetrahedron Lett.*, 3565 (1973).
(30) A. Krapcho and A. Lovey, *Tetrahedron Lett.*, 957 (1973).
(31) C. Tilford, M. Van Campen, Jr., and R. Shelton, *J. Am. Chem. Soc.*, **69,** 2902 (1947).
(32) E. Campaigne and D. Mais, *J. Heterocycl. Chem.*, **12,** 267 (1975).
(33) W. Bailey and J. Daly, Jr., *J. Am. Chem. Soc.*, **81,** 5397 (1959).
(34) M. Palomaa and A. Kenetti, *Ber. Dtsch. Chem. Ges. B,* **64,** 798 (1931).

Ring Expansions of Medium-Sized Ring Potassium Alkoxides. Unusually Fast [1,3]Sigmatropic Shifts

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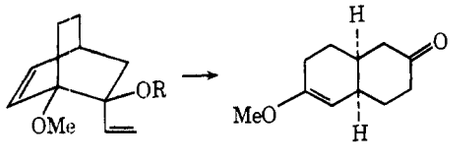
A series of cyclic 1-vinyl alcohols having either a double bond or a benzo group at the 3 position were rearranged under the influence of potassium hydride to the ring-expanded ketones, e.g., 1-vinylcyclonon-3-en-1-ol to 5-cycloundecenone. In hexamethylphosphoric triamide (HMPT) or dimethoxyethane (DME)/18-crown-6 media, the [1,3]sigmatropic shifts take place at room temperature. 1-Cyclopropyl analogues undergo ring cleavage rather than rearrangement.

Evans and Golob recently reported[1] that the bicyclic oxy-Cope system (1) underwent a [3,3]sigmatropic rearrangement



1a, R = H
b, R = K

at an enormously enhanced rate when treated with potassium hydride in tetrahydrofuran (THF) or HMPT. The epimer of **1**, where the geometry precludes a concerted 3,3-shift process, was reported to not rearrange when treated with potassium hydride in refluxing THF. Although [1,3]sigmatropic shifts are possible for 1 and its epimer, none were reported. It was not clear whether 1,3 shifts should be enhanced since they generally show activation parameters that are more suggestive of a nonconcerted process than is the case for 3,3-shift processes.[2,3] We have subsequently found that 1,3 shifts in oxy-Cope[4] systems are enhanced under appropriate conditions.[4,5]

Our previous studies[2,6,7] have shown that 1-trimethylsiloxy-1-vinyl-3-cycloalkenes, **2** (R = $SiMe_3$), undergo thermal rearrangements at 240–300 °C which lead mainly to two-carbon ring expansion products, **3** and **4**, except for **2d**, where the 3,3-shift product **5** predominates.

We now report the reactions of the potassium alkoxides of these and the related systems **6** and **8** in highly dissociating media.

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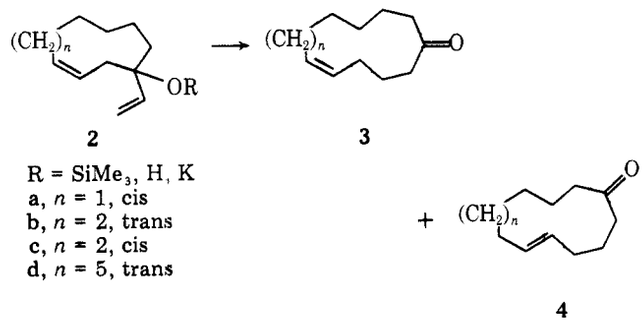
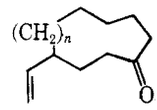
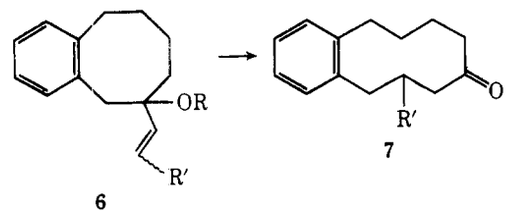
Table I. Products Resulting from Treatment of 1-Vinylcycloalk-3-en-1-ols with Potassium Hydride[a]

Compd	Registry no.	Time, h	Temp, °C	Solvent	Product, % 2	3	4	5	Acidic product, %	$\sim t_{1/2}$,[d] h
2a	31925-18-5	1.5	25	HMPT	5	30	19	6	5	0.67
		2.75	25	HMPT	1	34	20	7	7	
		2.75	25	HMPT[b]	2	36	23	7	3	
		5.5	25	HMPT	0	28	14	7	9	
		17	25	DME[c]	0	30	1	2	16	5
		2	66	THF	67	–	–	–	?	
2b	51284-48-1	3	25	HMPT	2	0	57	8	8	0.77
		14	25	DME[c]	3	0	39	7	?	
		183	66	THF	0	0	29	2	?	139
2c	51284-49-2	27.5	25	HMPT	11	31	0	0	10	15.7
2d	57969-16-1	4.5	60	HMPT	0	0	9	61	8	

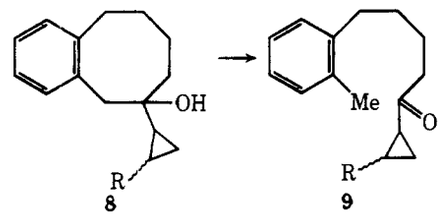
[a] The percentages of **2, 3, 4,** and **5** represent yields determined in triplicate by GLC by adding a known weight of internal standard. The percent of acidic product was determined by actual weight recovered by basic extraction, correcting for solvent by NMR. [b] HMPT was degassed by the freeze–thaw method. [c] A 1.1-equiv amount of 18-crown-6 was also present. Similar results were obtained with THF and added crown ether. [d] The approximate half-life was obtained by measuring the time when the volatile products peak areas equaled the peak area for the starting alcohol. This does not take into account the loss of starting material or products by other pathways. Reasonably good first-order plots were obtained in HMPT.



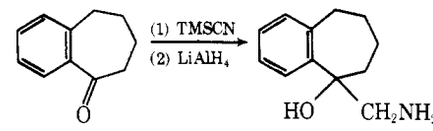


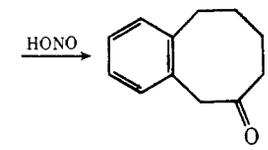


a, R = $SiMe_3$; R′ = H
b, R = H; R′ = H
c, R = H; R′ = CH=CH_2
d, R = H; R′ = CH=$CHCH_3$



a, R = H
b, R = CH=CH_2





Results

The syntheses of **2a–d** have been reported previously.[2,6,7] The syntheses of **6** and **8** are somewhat more challenging because relatively few effective routes to benzo-substituted medium-sized rings are available.[8] In this work, benzosuberone (**10**) was converted to the amino alcohol **11** using trimethylsilyl cyanide (TMSCN) followed by lithium aluminum hydride reduction.[9] Although yields of ca. 80% were realized with either potassium cyanide/18-crown-6 complex or zinc iodide catalysts, the yields with zinc iodide were less reproducible. Treatment of **11** with nitrous acid gave highly preferential aryl migration, leading to ketone **12** with less than 7% of the α-keto isomer[10] that would result from alkyl migration. The expansion of **10** to **12** was also carried out by adding dibromomethyllithium to the carbonyl of **10** followed by treatment with butyllithium.[11] Formation of **12** was highly selective, but the overall yields were erratic and at best 50% for that method. Conversion of **12** to **6** or **8** followed normal Grignard procedures, except as indicated below. For the diene cases (**6**, where R′ = CH=CH_2 and CH=$CHCH_3$) the acetylenic lithium reagent, generated from butenyne or pent-3-en-1-yne, was added, and the triple bond was reduced to a mixture of cis–trans double-bond isomers using lithium aluminum hydride. Formation of cis and trans isomers parallels one earlier result;[12] however, several earlier systems have been reported to give only the trans isomer.[13] Attempts to generate pure cis isomer by reduction with Lindlar catalyst failed even though the catalyst was demonstrated to give clean monoreduction with phenylacetylene. For the case of **8** where R = CH=CH_2, vinylcyclopropyllithium[14] was used rather than the Grignard reagent.

Alcohols **2a–d** (R = H) were rearranged by treatment with potassium hydride in highly dissociating media, viz., HMPT or 18-crown-6 with either dimethoxyethane (DME) or tetrahydrofuran (THF), with the results shown in Table I. The structures of **3a–d, 4a–d,** and **5a–d** were assigned by GLC and spectral comparisons with samples assigned in earlier work.[2,6,7] For the medium-sized rings **2a–c,** the predominant process is a 1,3-shift ring expansion leading to **3** and/or **4.** In contrast, the large ring system **2d** rearranges principally by the 3,3 process, leading to **5.** A substantial loss of double-bond stereochemistry is observed for the nine-membered ring case

Table II. Rearrangements of 6-Vinyl-7,8,9,10-tetrahydro-6(5*H*)-benzocyclooctenol (6) and Related Compounds[a]

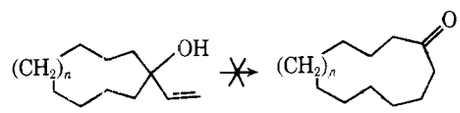
Compd	Conditions	Product, % 6	7	14	15	Acidic product, %
6a	350 °C, 9.75 h	13	31	–	–	–
	350 °C, 11 h	16	47	–	–	–
	350 °C, 24 h	4	9	14	–	–
6b	KH, HMPT, 25 °C, 5.5 h	3	56	–	–	5
	KH, DME,[b] 25 °C, 174 h	15	27	–	–	43
	KH, THF, 66 °C, 26.3 h	1	–	–	55[c]	*d*
6c	KH, HMPT, 25 °C, 3.92 h		20	–	–	*d*
6d	KH, HMPT, 25 °C, 4.5 h		33	–	–	3

[a] The percentages of **6, 7, 14,** and **15** are determined as in footnote *a*, Table I. [b] See footnote *c*, Table I. [c] Only one yield determination was made. A variety of other minor products were also formed (each <10%). [d] No analysis was made for acidic products.

2a, but no such loss is seen for the ten-membered ring cases **2b** and **2c** (see later discussion).

The yield of products **3–5** generally did not exceed 60%, partly because some sodium bicarbonate soluble material is usually formed. In one experiment where the solvent was degassed, the yield of this material decreased, suggesting a known process[15] in which adventitious oxygen in the presence of strong base in highly dissociating media oxidatively cleaves ketones to diacids. The spectral properties are consistent with such diacids, but the mixtures were too complex to assign further. The benzo analogue **6b** gave a clear example of this process (see below). Most of the remaining byproducts were nonvolatile, although a dimeric molecular weight (*m/e* 332) was observed in the mass spectrum for a long retention-time GLC peak from **2a,** suggesting "aldol" side reactions of the ketone products.

Unsaturation homoallylic to the hydroxyl appears to be critical to the rearrangement process. The saturated analogues of the above systems, i.e., **13a** and **13b,** were treated with po-



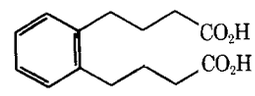
13a, $n = 1$
b, $n = 2$

tassium hydride in HMPT at room temperature for 4 h and 24 h, respectively, but gave no cyclododecanone or cycloundecanone.

The rearrangements of the previously unstudied benzo eight-membered ring cases **6a–d** are shown in Table II. The thermal rearrangement of **6a** to ketone **7** is clean since no 3,3 shift or geometric isomerism is possible, but the yield for the thermal isomerization was low, presumably because of the stringent conditions necessary to induce reaction. If the reaction was pushed to completion, unidentified shorter retention-time material (**14**) was also formed. The structural assignment for **7** is based largely on the NMR spectrum; viz., the relatively narrow four-proton aromatic band indicates that the substituents remain ortho and that the carbonyl is not α to the aromatic ring, the overlapping multiplets at ca. δ 2.7 indicate two benzylic methylenes and rule out a β-carbonyl, and the lack of terminal methyl peaks supports the ten-membered ring structure. The 1700-cm^{-1} IR band also supports the lack of a conjugated system. Shift reagent studies were undertaken to rule out the possibility that the carbonyl could be γ to the aromatic ring, which would leave the δ position as the only possible structure. Unfortunately, the shift reagents caused excessive peak broadening with either **7** or the corresponding alcohol such that no useful data could be obtained. Structure **7** has thus been assigned as the δ-carbonyl structure shown rather than the γ-carbonyl isomer from two chemical reactions: (1) the thermal 1,3-shift reaction has precedent in very similar systems, whereas a mechanism leading to a γ-carbonyl isomer is not obvious, and (2) oxidative cleavage (see below) leads mainly to *o*-benzenedibutanoic acid, which is only possible from the δ-carbonyl structure **7.**

Treatment of **6b** with potassium hydride in HMPT gave **7** in somewhat better yield than the thermal process. As in the earlier cases some acidic material was formed along with some nonvolatile product. When DME was used along with 18-crown-6 and potassium hydride the reaction was much slower and the cleavage to acidic products was much more pronounced. Fortunately, crystallization of the acidic material led to isolation of a pure diacid **15,** which could be assigned the *o*-benzenedibutanoic acid structure from the high degree of symmetry evident in the clean four-proton methylene patterns in the NMR spectrum. This presumably results from the known[15] oxidative cleavage α to ketone groups by adventitious oxygen under these conditions. In principle, cleavage could take place on either side of the carbonyl group, which would lead to **15** and an unsymmetrical diacid; however, since the crude diacid NMR spectrum looks nearly the same as recrystallized **15,** the cleavage must be highly selective.

The anionic rearrangements of all the above systems normally require either HMPT or 18-crown-6; however, Table I shows one case, system **2b** (R = K), that rearranges in THF alone at reflux temperature. Under the same conditions, **6b** gave an unusual result; viz., it eliminated water, forming **16.**



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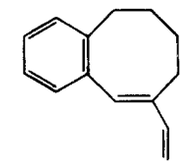

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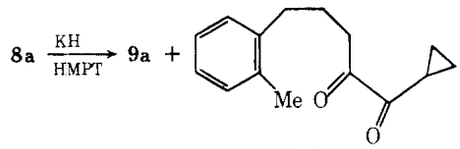
The structure of **16** follows from the UV and NMR spectra, in particular the coupling patterns of the vinyl protons.

The successful two-carbon ring expansion of **6b** prompted investigation of possible four-carbon ring expansions of **6c** and **6d.** A mixture of cis and trans isomers was used, recognizing that a concerted 1,5 shift is only possible for the cis isomer. In the event, only 1,3-shift products (**7c** and **7d**) were observed from **6c** and **6d** upon treatment with potassium hydride in HMPT. The NMR spectrum of **7c** clearly shows the characteristic terminal vinyl group coupling. For **7d** the NMR spectrum plus decoupling experiments clearly showed the two vinyl protons with couplings to a methyl and a single proton. Shift reagent studies were attempted to further substantiate the structural assignments, but no decisive evidence could be obtained. The structures shown are fully consistent with the spectral data and are mechanistically reasonable; however, the data do not completely rule out the vinyl or propenyl groups being attached at another carbon on the ring.

Since **7c** and **7d** showed no propensity toward further rearrangement under anionic conditions, the gas phase thermal rearrangements of **7d** were examined. Stringent conditions (350 °C, 5 h) were required to effect rearrangement, and the

yields were extremely low (<1%). Two rearranged ketones were formed in a 2:1 ratio; the major ketone showed spectral data that is consistent with a 1,3-shift product, but no definite assignment could be made. Thermal rearrangements of the trimethylsilyl derivatives of **6c** and **6d** were also examined in the 260–350 °C range, but only low yields of complex mixtures were obtained.

Possible three- or five-carbon ring expansions were also examined for **8a** and **8b**, respectively. Unfortunately, treatment of either **8a** or **8b** with HMPT/KH gave no ring expanded ketone products, but rather gave only cleavage (ca. 30% yield) to the open-chain ketones **9a** and **9b.** In the case of **8a**, formation of dione **17** was also observed in variable



17

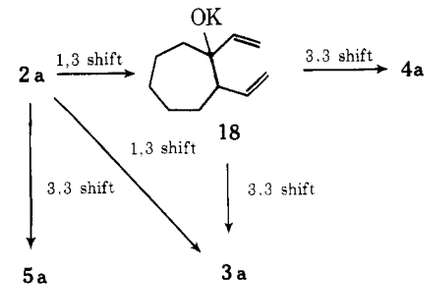
amounts, presumably depending on the amount of adventitious oxygen present.

Discussion

It is most striking that these [1,3]sigmatropic rearrangements normally requiring temperatures near 300 °C, with activation parameters consistent with a diradical process,[2,3] proceed at room temperature for the potassium alkoxides in highly dissociating media. Comparing the half-life estimates for the alkoxides **2a–c** (R = K) in HMPT (Table I) with the earlier thermal rates for the trimethylsiloxy derivatives[2,6,7] gives approximate rate enhancements for the alkoxide process of 10^{15}–10^{17}, which are comparable to those observed by Evans and Golob[1] for the 3,3 shift of **1b** in HMPT relative to the thermal rearrangement of **1a.** As was the case for **1b,** 18-crown-6 promotes the rearrangements of the **2** and **6** systems; however, it is markedly less effective for these rearrangements than HMPT. For example, rearrangement of **2a** is 5–7 times faster and is higher in yield in HMPT than with DME/18-crown-6. In contrast, the 3,3 rearrangement of **1b** is about twofold faster in THF/18-crown-6 than in HMPT. The rearrangement of **1b** in THF is 180 times slower if no 18-crown-6 is added, whereas the rearrangements of the **2** and **6** systems generally will not take place at all in THF without added crown ether. The one exception is the trans-ten-membered ring case **2b** (R = K) that rearranges in poor yield in refluxing THF with an approximate half-life which indicates that at the same temperature the rate would be >2000 times slower without crown ether. Of the systems studied, **2a** and **2b** have the greatest ring strain, but **2b** releases more ring strain upon two-carbon ring expansion,[2] which may explain why **2b** is the only one to rearrange in THF with no crown ether. It is the most reactive system thermally and is about the same reactivity as **2a** in HMPT.

It is clear that dissociation of the potassium alkoxide is critical for both the 1,3 and 3,3 shifts. Evans[1] has ruled out a homolytic cleavage mechanism for the 3,3-shift cases on the basis that the decrease in the bond dissociation energy on going from hydroxyl to alkoxide for such a process is too small to account for the observed rate enhancement. Complete retention of stereochemistry supports a concerted process for the 3,3-shift cases.[1] In like manner, the rate enhancement for the 1,3 shifts is too large to indicate a homolytic process. We postulate that if these rearrangements are concerted, the enormous rate enhancements seen for the anionic shifts are partly due to the naked anion becoming delocalized in the transition state leading to the resonance-stabilized enolate and partly due to the better donor properties of the anion moiety relative to the neutral compounds. The latter postulate

Scheme I



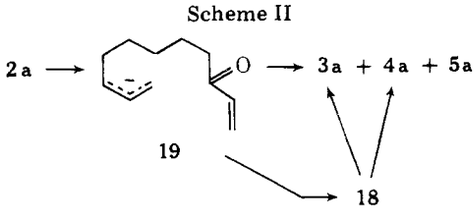
derives from the suggestion by Epiotis[16] that concerted processes become more favorable as the donor–acceptor qualities of the system increase. This implies that electron-accepting groups on the π bond (or benzo group) in the ring should accelerate the rate, providing that they don't simply give fragmentation of the type illustrated by system **8.**

The rearrangements of **2** and **6** may be easily visualized in terms of concerted rearrangements; however, the geometrically isomerized ring-expansion product from **2a** (i.e., **4a**) would require more than one step. As in the thermal cases,[6,2] a 1,3-shift ring contraction to **18** would allow formation of both **3a** and **4a** via 3,3 shifts (Scheme I). Ring strain changes for **2a** going to **18** are somewhat more favorable[2] than for the ten-membered ring systems **2b** and **2c** going to the eight-membered ring analogue of **18;** however, it is surprising that **2a** shows more geometric isomerization than the thermal reaction, whereas **2b** and **2c** show no such isomerization.

Usually, concerted [3,3]sigmatropic shifts are much more favorable than 1,3 shifts; however, for the medium-sized ring systems **2a–c** the transition states for such 3,3 shifts are highly unfavorable because of the crowded center of the ring.[7] Thus, it is consistent with the concerted scheme that both thermal and KH treatments of **2a–c** produce only a small amount of 3,3-shift product **5,** whereas **5d** becomes the major product for the large ring system **2d,** where the concerted 3,3-shift transition state is much less hindered.[7]

To our knowledge, systems **2a–d** are the only reported cases of anionic 1,3 rearrangements of 1,5-hexadien-3-ol systems, but a few other anionic 1,3 shifts are known; e.g., treatment of certain β,γ-unsaturated carboxylic acids with methyllithium leads to products in which the carbonyl group has undergone a 1,3 shift,[17] certain bicyclic semidiones (radical anions) interconvert by 1,3 shifts,[18] and 7-norbornadienol rearranges in the presence of sodium hydroxide to tropyl oxide, apparently by way of a 1,3 anionic shift.[19] The alkoxide of 3-methyl-3-vinyldec-1-en-4-ol has recently been shown to undergo 1,3 shifts with dramatic cation and solvent effects.[20] Perhaps the most interesting example is that of rearrangements of the alcohols that result from addition of allyl Grignard reagents to hindered ketones.[21] For these cases, anionic 1,3 shifts are observed; crossover experiments indicate a fragmentation–recombination mechanism. Such a mechanism provides an alternative rationale for the present results.[5] For example, **2a** could cleave to an allylic anion and an α,β-unsaturated ketone connected by the methylene chain (**19,** Scheme II). Michael addition from the two ends of the allylic anion would give **3a** and **5a.** The geometrically isomerized

Scheme II



product **4a** could arise by geometric isomerization of the allylic anion prior to the Michael addition or by formation of **18** followed by 3,3 shifts. It is not clear at the present time whether **19** is an intermediate along the pathway to **3–5,** but if not it clearly can become a competing process. The cyclopropyl systems **3a,b** cleave and presumably transfer an α hydrogen rather than undergo a homo Michael addition. No such cleavage was seen for the **6** systems, where the "toluene" methyl should be readily seen in the NMR, but such cleavage has been seen in the reaction of 3-methyl-4-phenylbut-1-en-3-ol, an open-chain analogue.[22] The lack of reactivity of the saturated ring compounds **13a,b** would be consistent with the Scheme II mechanism since a nonallyl anion would be much higher in energy than the allylic anions from **2a–d.** It should be noted, however, that the unsaturation in the ring appears to be highly important to the concerted process as well,[2,3] so that Scheme I is also viable.

From the synthetic standpoint, the anionic 1,3-shift ring expansion offers a useful alternative to the thermal counterpart. Although the media is highly basic, it avoids the high temperatures and gas phase conditions, it can give appreciably better yields (e.g., **6b** vs. **6a**), and it can give a cleaner product (e.g., **2b** and **2c**). The major side reactions give acidic or nonvolatile byproducts which are readily removed.

Experimental Section

General. Spectral measurements utilized Beckman IR-8, Perkin-Elmer 727B, Perkin-Elmer 621, Varian Associates HA-100, Cary 15, Atlas CH-7, and CEC 110B instruments. Gas–liquid chromatography (GLC) analyses were carried out on Varian 920 (thermal conductivity detector, 0.25 in columns) and Varian 1200 instruments (flame ionization detector, 0.125 in or less columns) using the columns designated below: (A) 9 ft × 0.25 in, 3% AN600 on Chromosorb B, (B) 50 ft × 0.03 in, OV-101 P.L.O.T.,[23] (C) 16 ft × 0.25 in, 2.5% OV-101 on Chromosorb G, (D) 20 ft × 0.125 in, 4.9% OV-101 on Chromosorb G, (E) 5 ft × 0.25 in, 1.6% stabilized DEGS on Chromosorb G, (F) 75 ft × 0.01 in, DEGS capillary, (G) 4.8 ft × 0.25 in, 6.5% OV-101 on Chromosorb G, (H) 5 ft × 0.25 in, 1.5% OV-101 on Chromosorb G, (I) 5 ft × 0.25 in, 5% OV-101 on Chromosorb G, (J) 8.5 ft × 0.25 in, 3% AN600 on Chromosorb G, (K) 6 ft × 0.125 in, 7.5% OV-101 on Chromosorb W, (L) 50 ft × 0.03 in, DEGS P.L.O.T.,[23] (M) 5.25 ft × 0.25 in, 7.4% stabilized DEGS on Chromosorb G, and (N) 6 ft × 0.375 in, 4.9% OV-101 on Chromosorb B.

Tetrahydrofuran (THF), 1,2-dimethoxyethane (DME), and bis(2-methoxyethyl) ether (diglyme) were distilled from the sodium benzophenone dianion under nitrogen. Hexamethylphosphoric triamide (HMPT) was dried by heating the solvent under nitrogen at 200 °C over 13× molecular sieves (predried under nitrogen at 350 °C for 4 h) overnight.[24] Other solvents were dried by standard published procedures.[25,26] All reactions involving air- or moisture-sensitive materials were conducted under a nitrogen atmosphere.

Benzosuberone (10). Cyclization of 25.0 g of δ-phenylvaleric acid by the method of Gilmore and Horton[27] followed by distillation (97 °C at 3 mm) gave 8.9 g (40%) of a clear liquid. The IR spectrum of the liquid (neat) matched that of an authentic sample (Aldrich).

5-Aminomethyl-6,7,8,9-tetrahydro-5-benzocycloheptenol (11) was prepared by a procedure similar to that of Evans, Carroll, and Truesdale.[9] A 100-mL, one-neck flask (equipped with a magnetic stirrer and nitrogen atmosphere) was charged with 2.0 g (0.05 mol) of lithium aluminum hydride and 50 mL of dry ether. This mixture was stirred for 30 min and then allowed to settle. Another 100-mL flask (similarly equipped) was charged with 5.02 g (0.031 mol) of benzosuberone (Aldrich, freshly vacuum transferred), and the flask was cooled in an ice bath. Meanwhile, a 4-in test tube was loaded with ca. 1 g (3 mmol) of zinc iodide (City Chemical Co.) and quickly evacuated to 0.2 mm. The zinc iodide was then sublimed twice with gentle flame heating, cooled, and placed under a nitrogen atmosphere. The test tube was then equipped with a stirring bar, 5 mL (ca. 0.043 mol) of trimethylsilyl cyanide was added via syringe, and the mixture was stirred for 5 min. The trimethylsilyl cyanide/zinc iodide slurry was added to the ice-cold benzosuberone over ca. 1 min, and this mixture was stirred for 15 min. The reaction vessel was then equipped with a dropping funnel which was loaded with the clear part of the lithium aluminum hydride/ether mixture (prepared in the first part of the procedure). This solution was added (over 15 min) to the ice-cold trimethylsilyl cyanohydrin just formed. The rest of the gray lithium aluminum hydride/ether suspension was added dropwise with a large bore pipette. The mixture was then stirred vigorously for 15 min at ice temperature and 30 min at room temperature and recooled in the ice bath. The reaction mixture was then quenched by cautious addition of 2 mL of water, 2 mL of 15% sodium hydroxide, and 6 mL of water. The mixture was stirred until the solids became white and granular (ca. 1 h) and then filtered. The solids were washed thoroughly with twelve 25-mL portions of ether, and the combined ether layer was extracted with six 50-mL portions of 8.6% sulfuric acid. The acidic extract was made basic (pH ca. 10) with ca. 125 mL of 15% sodium hydroxide with frequent cooling in a cold water bath. The basic layer was then extracted with six 50-mL portions of chloroform, and the chloroform extract was dried over magnesium sulfate, filtered, and most of the solvent removed by rotary evaporation. The material was placed under a 0.2-mm vacuum overnight, and 5.07 g (84%) of a white solid (mp 74.0–76.3 °C) was obtained. This material was recrystallized from redistilled petroleum ether to yield crystals of mp 73.0–73.8 °C. The material was recrystallized again from petroleum ether to give a white solid, mp 94.3–94.5 °C. Samples of the material from different preparations gave the higher melting range when recrystallized from petroleum ether. The spectral data and analysis are for the material with the higher melting range: NMR ($CDCl_3$) δ 7.6–7.8 (m, 1 H), 7.0–7.35 (m, 3 H), 2.7–3.36 (m, 4 H), 1.5–2.5 (broad m, 9 H; reduces to 6 H when treated with D_2O); IR (KBr) 3350, 3300, 3100, 2910, 2850, 1600, 1480, 1450, 1360, 1330, 1280, 1230, 1200, 1170, 1120, 1090, 1040, 1000, 990, 950, 860, 760, 740 cm^{-1}; mass spectrum, *m/e* 191 (1.7), 161 (100). Anal. Calcd for $C_{12}H_{17}NO$: C, 75.35; H, 8.96; N, 7.32. Found: C, 75.49; H, 8.95; N, 7.41.

Essentially the same procedure was used with a 1:1 complex of NaCN and 18-crown-6 as the catalyst instead of ZnI_2, which gave similar yields and was more reproducible.

7,8,9,10-Tetrahydro-6(5*H*)-benzocyclooctenone (12). A 4.77-g (0.025 mol) portion of unrecrystallized **11** was taken up in 50 mL of 10% acetic acid, and the mixture was cooled in an ice bath. Then 32 mL (0.04 mol) of 1.25 M sodium nitrite was added, and the mixture was stirred for 30 min at ice temperature and overnight at room temperature. The reaction mixture was then rechilled in an ice bath and made basic (pH ca. 10) with 15% NaOH. The basic mixture was extracted with five 20-mL portions of ether. The ether extract was washed with two 10-mL portions of saturated ammonium chloride, dried over magnesium sulfate, concentrated, and vacuum transferred (120 °C at 1 mm), producing 3.49 g (80%) of a clear liquid that was 82% pure by GLC (column L, 155 °C). The semicarbazone was prepared and precipitated twice from benzene to give a white solid, mp 163–166.5 °C (lit.[28] 177.5–178 °C). The material was purified by GLC (column I, 215 °C) to provide the analytical samples: NMR (CCl_4) δ 7.05–7.2 (m, 4 H), 3.68 (s, 2 H), 2.73–2.9 (m, 2 H), 2.17–2.33 (m, 2 H), 1.55–2.0 (broad m, 4 H); IR (neat) 3060, 2030, 2940, 2860, 1700, 1600, 1580, 1500, 1450, 1350, 1330, 1280, 1260, 1240, 1190, 1170, 1120, 1040, 1000, 960, 880, 760, 720, 710 cm^{-1}; mass spectrum, *m/e* 174 (68.3), 118 (100). Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.45; H, 8.13.

7,8,9,10-Tetrahydro-6-vinyl-6(5*H*)-benzocyclooctenol (6b). A vinylmagnesium bromide in THF solution was prepared as described earlier[6] from 7 mL (ca. 0.1 mol) of vinyl bromide, 1.4 g (0.06 g-atom) of magnesium, and 20 mL of THF. To this was added dropwise a solution of 3.00 g (0.014 mol) of 82% ketone **12** and 10 mL of THF. The mixture was heated at ca. 40 °C for 1.5 h and then quenched by the cautious addition of 15 mL of water. The organic layer was washed with 10% H_2SO_4 and saturated $NaHCO_3$ and then dried ($MgSO_4$), concentrated, and vacuum transferred (130–140 °C at ca. 0.1 mm), which produced 3.22 g (91% yield) of a clear, viscous oil (81% pure by GLC, column I, 225 °C). Analytical samples were purified by GLC (column I, 235 °C): NMR (CCl_4) δ 7.06 (s, 4 H), 6.03 (dd, J = 11, 18 Hz, 1 H), 5.26 (dd, J = 2, 18 Hz, 1 H), 5.05 (dd, J = 2, 11 Hz, 1 H), 2.6–3.0 (broad m, 4 H), 1.2–1.9 (broad m, 7 H); IR (neat) 3400 broad, 3070, 3030, 2940, 2860, 1645, 1500, 1475, 1455, 1420, 1170, 1140, 1120, 1050, 1000, 930, 760, 715 cm^{-1}; mass spectrum, *m/e* 202 (8.3), 184 (100), 55 (100). Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.93; H, 8.75.

7,8,9,10-Tetrahydro-6-trimethylsiloxy-6-vinyl-5*H*-benzocyclooctene (6a) was prepared by the published method[29] and vacuum transferred (120 °C at 0.2 mm; 70% yield). The 91% pure clear oil was purified by GLC (column I, 210 °C): NMR (CCl_4, *p*-dioxane reference) δ 7.05 (s, 4 H), 6.04 (dd, J = 11, 17 Hz, 1 H), 5.12 (dd, J = 2, 17 Hz, 1 H), 5.10 (dd, J = 2, 11 Hz, 1 H), 2.56–2.88 (broad m, 4 H), 1.26–1.86 (broad m, 6 H), 0.04 (s, 9 H); IR (neat) 3070, 3030, 2950, 2870, 1640, 1500, 1480, 1460, 1420, 1360, 1310, 1260, 1230, 1190, 1170, 1140, 1120, 1090, 1070, 1050, 1000, 960, 920, 910, 840, 760, 730 cm^{-1}; mass spectrum, *m/e* 274 (2.7), 140 (100); exact mass, *m/e* 274.174 (calcd for

$C_{17}H_{26}OSi$, 274.175).

6-(3-Buten-1-ynyl)-7,8,9,10-tetrahydro-6(5*H*)-benzocyclooctenol (21). The procedure for making the lithium salt of 1-buten-3-yne was similar to that used earlier[30] for the production of propynyllithium. A mixture of 25 mL of ether and 8 mL (21 mmol) of 2.6 M methyllithium in ether was cooled under N_2 in an ice bath as 3.5 mL (ca. 24 mmol) of 1-buten-3-yne (Chemical Samples Co., 50% in xylene) was added with a cold syringe. The ice bath was removed after a few minutes, and the reaction mixture was stirred overnight at room temperature. The ether was evaporated under a nitrogen stream, and then 25 mL of THF was added. The mixture was warmed in a 50-°C bath, and a solution of 2.03 g (9.6 mmol) of **12** (82% pure) in 8 mL of THF was added over 5 min. The mixture was stirred for 8 h and then cooled in an ice bath and quenched by the cautious addition of 10 mL of water. The organic layer was washed with saturated NaCl, dried ($MgSO_4$), concentrated, and vacuum transferred (130–150 °C at 0.2 mm) to give 2.33 g of a viscous oil that contained 77% of **21** by GLC analysis (column C, 254 °C). Purification by GLC (column G, 235 °C) gave the analytical samples: NMR (CCl_4) δ 7.0–7.3 (m, 4 H), 5.81 (dd, J = 10, 17 Hz, 1 H), 5.53 (dd, J = 4, 17 Hz, 1 H), 5.41 (dd, J = 4, 10 Hz, 1 H), 3.03 (s, 2 H), 2.65–2.9 (broad m, 2 H), 1.2–2.0 (broad m, 7 H); IR (neat) 3600–3150, 3100, 3060, 3010, 2930, 2850, 1610, 1490, 1470, 1450, 1410, 1360, 1340, 1300, 1260, 1230, 1160, 1150, 1110, 1070, 1020, 975, 950, 920, 750, 725 cm^{-1}; UV (95% EtOH) λ_{max} 214 nm (ϵ 15 000), 223 (13 000), 234 (10 000); mass spectrum, *m/e* 226 (17.7), 79 (100); exact mass, *m/e* 226.135 (calcd for $C_{16}H_{18}O$, 226.136).

***cis*- and *trans*-6-(1,3-Butadienyl)-7,8,9,10-tetrahydro-6(5*H*)-benzocyclooctenol (6c)** were formed by the method of Chanley and Sobotka.[31] A solution of 0.404 g (1.4 mmol) of 77% pure **21** and 3.2 mL of ether was added at 25 °C to a suspension of 0.12 g (3 mmol) of $LiAlH_4$ and 4 mL of ether, and the mixture was refluxed for 4 h. The excess $LiAlH_4$ was quenched by the cautious addition of 0.12 mL of water, 0.12 mL of 15% sodium hydroxide, and 0.36 mL of water, and the white precipitate which formed was filtered off and washed thoroughly with ether. The filtrate and washings were dried over $MgSO_4$ and concentrated, giving 0.382 g of **6c**, which showed a strong band at 3600–3100 cm^{-1} (OH) in the IR spectrum. The NMR spectrum indicated that no starting butenynol **21** remained.

The above **6c** alcohols were silylated,[6] affording 0.63 g of crude silyl derivative. A 187-mg portion was vacuum transferred (115 °C at 0.45 mm) to give 0.170 g of a clear oil, which was purified and analyzed by GLC (column F, 255 °C). The analysis indicated that the material contained 70% of the trimethylsiloxy derivative of the **6c** alcohols in a 1:3 ratio of the shorter and longer retention-time isomers. The shorter retention-time isomer: NMR (CCl_4) δ 7.06 (s, 4 H), 4.95–6.4 (m), 2.65–2.85 (m, 4 H), 1.15–1.85 (broad m); UV (95% EtOH) λ_{max} 218 nm (ϵ 27 000), 227 (25 000); mass spectrum, *m/e* 300 (5), 285 (1), 210 (25), 105 (100); exact mass, *m/e* 300.191 (calcd for $C_{19}H_{28}OSi$, 300.191).

The longer retention-time isomer: NMR (CCl_4) δ 7.01 (s, 4 H), 5.31–6.51 (m, 3 H), 5.15 (dd, J = 2, 15 Hz, 1 H), 5.01 (dd, J = 2, 8 Hz, 1 H), 2.55–3.05 (broad m, 4 H), 1.3–1.87 (broad m, 6 H); IR (CCl_4) 3055, 3015, 2920, 2845, 1255, 1245, 1175, 1000, 970, 900, 840, 735 cm^{-1}; UV (95% EtOH) λ_{max} 218 nm (ϵ 25 000), 227 (25 000); mass spectrum, *m/e* 300 (20.8), 285 (5.8), 247 (18.6), 73 (100); exact mass, *m/e* 300.190 (calcd for $C_{19}H_{28}OSi$, 300.191).

(*cis*-3-Penten-1-ynyl)-7,8,9,10-tetrahydro-6(5*H*)-benzocyclooctenol (20). The lithium salt of *cis*-3-penten-1-yne was formed as above (see **21**) from 4.6 g (0.070 mol) of *cis*-3-penten-1-yne[32] in ether, which was replaced by 50 mL of THF. A 20-mL solution in THF of 10.0 g (0.047 mol) of 82% pure **12** was added over 2 h to the refluxing solution, which was then cooled and quenched with 10 mL of saturated NH_4Cl. The organic layer was washed successively with H_2O, saturated NH_4Cl, 10% H_2SO_4, and saturated $NaHCO_3$ and then dried ($MgSO_4$) and concentrated. Vacuum transfer (100 °C at 0.1 mm) gave 10.6 g of clear oil. Remaining starting ketone was removed using 7.0 g of Girard's Reagent T as described earlier.[33] This gave 7.43 g (43% yield) of pentenynol **20**, which was 79% pure by GLC (column H, 205 °C).

The pentenynol was silylated[29] and purified by GLC (column O, 260 °C): NMR (CCl_4, Me_4Si reference) δ 6.95–7.3 (m, 4 H), 5.9 (dq, J = 7, 10 Hz, 1 H), 5.47 (dq, J = 2, 10 Hz, 1 H), 3.05 (s, 2 H), 2.65–2.9 (broad m, 2 H), 1.3–2.0 (broad m, 9 H, 1.82 (dd, J = 2, 7 Hz); NMR (CCl_4, CH_2Cl_2 reference) δ 0.19 (s, 9 H); IR (neat) 3060, 3030, 2940, 2850, 1495, 1470, 1450, 1400, 1360, 1320, 1300, 1250, 1230, 1190, 1160, 1150, 1110, 1070, 1030, 990, 950, 920, 900, 890, 840, 755, 720, 680 cm^{-1}; mass spectrum *m/e* 312 (15.7), 297 (34.7), 73 (100); exact mass, *m/e* 312.190 (calcd for $C_{20}H_{28}OSi$, 312.191).

***cis* and *trans*-6-(1,3-(*Z*)-Pentadienyl)-7,8,9,10-tetrahydro-6(5*H*)-benzocyclooctenol (6d)** were prepared by $LiAlH_4$ reduction of **20** in the same way as above (see **6c**). A 0.286-g portion was silylated[29] and vacuum transferred (115 °C at 0.35 mm), yielding 0.320 g (64% yield) of clear oil, which GLC (column, C, 235 °C) indicated was 76% trimethylsiloxy dienes. The two isomers (2:1 ratio) were separated by GLC (column O, 260 °C) to give long and short retention-time components. The shorter retention-time component: NMR (CCl_4) δ 7.0–7.1 (s, 4 H), 5.3–6.6 (m, 4 H), 2.65–3.0 (broad m, 4 H), 1.3–1.9 (broad m, 9 H), 1.75 (dd, J = 2, 7 Hz); IR (CCl_4) 3060, 3020, 2940, 2860, 1495, 1470, 1455, 1410, 1375, 1360, 1255, 1080, 980, 975, 845, 750 cm^{-1}; UV (95% EtOH) λ_{max} 235 nm (ϵ 19 000); mass spectrum, *m/e* 314 (47), 299 (30), 73 (100); exact mass, *m/e* 314.207 (calcd for $C_{20}H_{30}OSi$, 314.207).

The longer retention-time component: NMR (CCl_4) δ 6.91–7.15 (s, 4 H), 5.3–6.91 (m, 4 H), 2.99 (s, 2 H), 2.6–2.9 (broad m, 2 H), 1.1–1.9 (broad m, 9 H), 1.78 (dd, J = 2, 7 Hz); IR (CCl_4) 3060, 3020, 2930, 2850, 1265, 1255, 1070, 1000, 915, 846, 740 cm^{-1}; UV (95% EtOH) λ_{max} 239 nm (ϵ 22 000); mass spectrum, *m/e* 314 (100), 299 (48), 196 (100).

6-Cyclopropyl-7,8,9,10-tetrahydro-6(5*H*)-benzocyclooctenol (8a). A mixture of 0.60 g (5 mmol) of cyclopropyl bromide (Aldrich), 5 mL of THF, and 0.11 g (4.5 g-atom) of magnesium was treated with a few crystals of iodine.[34] A vigorous reaction ensued, and the mixture was stirred for 30 min. A solution of 0.533 g (2.5 mmol) of 82% pure **12** in 3.5 mL of THF was then added over 10 min, and the mixture was stirred for another 1.33 h, at which time 5 mL of saturated NH_4Cl and 30 mL of ether were added. The organic layer was washed with saturated $NaHCO_3$, dried over $MgSO_4$, and concentrated to afford 0.613 g of a light amber oil. A 241-mg portion was vacuum transferred (90–100 °C at 0.4 mm) to give 0.180 g (50% yield) of a clear oil, which was analyzed by GLC (column G, 215 °C) and found to contain 33% of starting ketone **12** and 58% of **8a**. Pure **8a** was obtained by preparative GLC (column G, 225 °C): NMR (CCl_4, CH_2Cl_2 reference) δ 7.15 (s, 4 H), 2.7–3.0 (m, 4 H), 1.3–1.95 (m, 6 H), 0.85–1.2 (m and broad s, 2 H; s shifts on warming to 60 °C), 0.25–0.7 (m, 4 H); IR (neat) 3700–3200, 3080, 3070, 3000, 2910, 2850, 1600, 1490, 1470, 1450, 1390, 1360, 1330, 1310, 1300, 1250, 1220, 1200, 1170, 1140, 1100, 1040, 1020, 1000, 990, 940, 920, 890, 880, 860, 820, 750, 730, 700 cm^{-1}; mass spectrum, *m/e* 216 (50.9), 198 (11.3), 84 (100); exact mass, *m/e* 216.151 (calcd for $C_{15}H_{20}O$, 216.151).

1-Bromo-2-vinylcyclopropanes. The method of Seyferth, Yamazaki, and Alleston[35] produced 3.88 g (82%) of 1-bromo-2-vinylcyclopropanes from 7.29 g (32 mmol) of 1,1-dibromo-2-vinylcyclopropane[36,37] and 9.42 g (32 mmol) of tri-*n*-butyltin hydride. The material was isolated by distillation of the crude product at room temperature (0.2 mm) into a 78-°C trap. An earlier attempt to distill the material at 62–74 °C (90 mm)[35] resulted in extensive decomposition of the product. The NMR and IR spectra agreed with the spectra described by Landgrebe and Becker,[38] and the NMR spectrum indicated that the trans/cis ratio is ca. 40:60.

7,8,9,10-Tetrahydro-6-(2-vinylcyclopropanyl)-6(5*H*)-benzocyclooctenols (8b). Use of the general procedure of Wender and Filosa[39] produced 0.60 g of the vinylcyclopropanols **8b** from 2.5 mL (5.8 mmol) of 2.3 M *tert*-butyllithium in pentane (Ventron), 0.80 g (5.4 mmol) of a mixture of 1-bromo-2-vinylcyclopropanes, and 0.48 g (2.3 mmol) of 82% pure **12**. The oil was vacuum transferred (135 °C at 0.4 mm) to give 0.55 g (63% yield) of product. GLC analysis (column J, 225 °C) showed that the product contained 14% of **13** and 77% of **8b** (28:72 ratio). Purification by GLC (column O, 250 °C) gave the analytical samples of **8b**. The shorter retention-time sample: NMR (CCl_4) δ 7.05 (s, 4 H), 4.66–5.56 (m, 3 H), 2.66–2.94 (m, 4 H), 1.2–1.85 (broad m, 7 H), 0.7–1.1 (m, 4 H); IR (CCl_4) 3620, 3400, 3070, 3050, 3010, 2990, 2920, 2840, 1630, 1490, 1465, 1450, 980, 890 cm^{-1}; mass spectrum, *m/e* 242 (2), 188 (100); exact mass, *m/e* 242.165 (calcd for $C_{17}H_{22}O$, 242.167).

The longer retention-time sample: NMR (CCl_4) δ 7.06 (s, 4 H), 5.76–6.32 (m, resembles septet, 1 H), 5.0–5.3 (m, 1 H), 4.76–4.98 (m, 1 H), 2.84–2.96 (m, 2 H), 2.64–2.84 (m, 2 H), 1.24–1.86 (broad m, 7 H), 0.7–1.24 (m, 4 H); IR (CCl_4) 3620–3400, 3070, 3050, 3010, 2990, 2920, 2840, 1625, 1490, 1465, 1450, 995, 890 cm^{-1}; mass spectrum, *m/e* 242 (5), 188 (100); exact mass, *m/e* 242.166 (calcd for $C_{17}H_{22}O$, 242.167).

1-Vinylcyclononanol (13a). Cyclooctanone was ring expanded using the same sequence[9] as for ketone **12** and gave cyclononanone (matches published spectra[40]) in 68% yield. Treatment with vinylmagnesium bromide as before[6] gave a 45% yield of **13a**: NMR (CCl_4) δ 5.92 (dd, J = 11, 18 Hz, 1 H), 5.14 (dd, J = 2, 18 Hz, 1 H), 4.92 (dd, J = 2, 11 Hz, 1 H), 1.2–1.9 (m, 17 H); IR (neat) 3600–3200, 3090, 2920, 1640, 995, 910 cm^{-1}; exact mass, *m/e* 168.151 (calcd for $C_{11}H_{20}O$, 168.151).

General Procedure for Rearrangements in Hexamethylphosphoric Triamide (HMPT). A 50-mL conical flask was charged

with 0.75 g (4.7 mol) of 25% potassium hydride in oil (Ventron) and placed in a nitrogen atmosphere. The oil was rinsed from the potassium hydride with five 7.5-mL portions of hexane by adding hexane, stirring briefly (magnetic stirrer), and allowing the hydride to settle. The hexane–oil layer was carefully removed with a pipette. A 23-mL amount of HMPT was added, followed by a solution of 1.5 mmol of alcohol in 2 mL of HMPT. The mixture was stirred for 10 min and then allowed to stand for the required amount of time at room temperature, unless otherwise noted in the tables. The reaction was then quenched by addition of a few milliliters of water, acidified with 10% sulfuric acid, and diluted with 125 mL of water. The aqueous layer was either continuously extracted with 200 mL of ether or manually extracted with five 25-mL portions of ether. The ether layer was extracted with five 30-mL portions of 5% sodium hydroxide and washed with two 30-mL portions of saturated ammonium chloride and 30 mL of brine. Finally, the ether layer was dried over magnesium sulfate and filtered, and the ether was removed by rotary evaporation. The basic extract from above was acidified with 6 N hydrochloric acid, cooled, and extracted with five 30-mL portions of ether. The ether extract was then washed with three 30-mL portions of water and 30 mL of brine, dried over magnesium sulfate, and filtered, and the ether was removed at reduced pressure.

General Procedure for Rearrangements in 1,2-Dimethoxyethane (DME) with 18-Crown-6. A factory bottle containing 18-crown-6 (Aldrich) was warmed to just above the melting point (ca. 40–50 °C), and about 1 g of the crown ether was transferred to a dry, tared 5-mL volumetric flask. The flask was evacuated to 1 mm and warmed at 80 °C for 2 h. The flask was then weighed, and enough DME was added to make 5 mL of solution. A 25-mL conical flask was charged with 0.5 g (3.1 mmol) of 22.1% potassium hydride in oil (Ventron) and placed under a nitrogen atmosphere. The oil was rinsed from the potassium hydride with five 5-mL portions of hexane in the same manner as in the experiments with HMPT. A 13-mL amount of DME was then added, followed by a solution of 0.75 mmol of alcohol in 2 mL of DME and enough crown ether solution to contain 0.80 mmol of 18-crown-6. The mixture was stirred for 10 min and allowed to stand for the required amount of time. The reaction was then quenched by addition of 1 mL of water and transferred to a separatory funnel with 25 mL of ether. The organic layer was extracted with five 5-ml portions of saturated sodium bicarbonate, dried over magnesium sulfate, and filtered, and the ether was removed by rotary evaporation. The basic extract was cautiously acidified with 6 N hydrochloric acid and extracted with five 5-mL portions of ether. The ether layer was then dried and concentrated as above.

Rearrangements of the 1-vinyl-3-cycloalkenols 2a–d were carried out by the standard procedures and analyzed by GLC on columns A–E at temperatures ranging from 110 to 180 °C. Yields were determined by adding starting alcohol (**2a–d**) as an internal standard. The yields and product ratios are presented in Table I. All products were identified by GLC and spectral comparison with known compounds.[2,6,7]

Attempted Rearrangements of the Potassium Salt of 1-Vinylcyclodecanol (13b) and 1-Vinylcyclononanol (13a). 1-Vinylcyclodecanol[2] was subjected to the usual conditions for rearrangements in HMPT for 4.17 h at 25 °C. The progress of the reaction was followed by GLC (column F, 105 °C), and the formation of a new product at ca. 60% of the retention time of the starting material was observed. The standard workup (manual extraction) produced an oil containing 31% of the starting alcohol **13b** and 23% of the new product. The yields were determined by GLC (column B, 140 °C) using cycloundecanone (Aldrich) as an internal standard and assuming the response factors to be equal. The retention time of the new product was shorter than that of cycloundecanone. If cyclododecanone had been formed, it would be expected to have a longer retention time than cycloundecanone.

A similar experiment with **13a** reacting for 24 h gave back only starting material (54% recovery; identical GLC, IR, and NMR).

Rearrangements of the potassium salt of 6-vinyl-7,8,9,10-tetrahydro-6(5*H*)-benzocyclooctenol (6b) in HMPT were conducted by the standard procedure, and the yields of the reaction are presented in Table II. The yield studies were done by GLC (column G, 210 °C, and column H, 175 °C) using benzosuberone as an internal standard correcting for response factor. The product, ketone **7b**, was purified by GLC (column A, 225 °C, or column I, 210 °C) to provide the analytical samples: NMR (CCl_4) δ 7.0–7.25 (m, 4 H), 2.5–2.8 (m, 4 H), 1.5–2.4 (broad m, 10 H); IR (neat) 3055, 3010, 2995, 2930, 2860, 1700, 1600, 1490, 1470, 1445, 1420, 1410, 1370, 1330, 1260, 1240, 1215, 1200, 1160, 1150, 1120, 1105, 1045, 1000, 960, 950, 840, 800, 785, 760, 730, 700 cm^{-1}; mass spectrum, *m/e* 202 (89.8), 129 (100); exact mass, *m/e* 202.138 (calcd for $C_{14}H_{18}O$, 202.136).

Rearrangements of the potassium salt of 6b in DME with 18-crown-6 were carried out in the standard way with the results shown in Table II. The yield studies were carried out by the same procedure used for the analogous HMPT rearrangement. This particular set of conditions gave a considerable amount of acidic product which was isolated by $NaHCO_3$ extraction, followed by acidification, and purified by recrystallization twice from benzene, giving a white solid (**15**), mp 118.0–118.5°C; NMR ($CDCl_3$) δ 10.7–10.9 (broad s, 2 H; shifts on warming to 60 °C), 7.15 (s, 4 H), 2.72 (m, 4 H), 2.45 (t, J = 7 Hz, 4 H), 1.90 (p, J = 7 Hz, 4 H); IR ($CHCl_3$) 3500–2400, 3010, 1710 cm^{-1}; mass spectrum, *m/e* 250 (4.5), 131 (100); exact mass, *m/e* 250.121 (calcd for $C_{14}H_{18}O_4$, 250.121).

Attempted Rearrangement of the Potassium Salt of 6b in THF. A solution of the potassium salt of 0.10 g (ca. 0.4 mmol) of 81% pure **12** in 15 mL of THF was refluxed for 26.33 h. The reaction mixture was then taken up in 25 mL of ether, which was washed with 10 mL of water, dried ($MgSO_4$), and concentrated. A 148-mg sample of this material was then vacuum transferred to give 0.077 g of a clear oil. The oil was analyzed and purified by GLC (column M, 210 °C), which indicated that the oil consisted of ca. 50% of **16**, 1% of starting alcohol **6b**, and a variety of other compounds none of which made up greater than 10% of the total area. This analysis indicates a crude yield of ca. 55% for the conversion of alcohol **6b** to compound **16**: NMR (CCl_4) δ 7.0–7.2 (m, 4 H), 6.54 (s, 1 H), 6.45 (dd, J = 11, 18 Hz, 1 H), 5.23 (d, J = 18 Hz, 1 H), 5.04 (d, J = 11 Hz, 1 H), 2.55–2.72 (m, 2 H), 2.05–2.22 (m, 2 H), 1.35–1.90 (m, 4 H); IR (neat) 2950, 2920, 2850, 1470, 1380 cm^{-1}; UV (95% EtOH) λ_{max} 216 nm (ϵ 17 000), 261 (19 000); mass spectrum, *m/e* 184 (39.1), 128 (100); exact mass, *m/e* 184.126 (calcd for $C_{14}H_{16}$, 184.125).

In another experiment the potassium salt of **6b** was refluxed in THF, and the reaction was followed by GLC (column I, 225 °C). Samples were taken at 45 min, 1.75 h, 2.72 h, and 18.25 h, and no appearance of ketone **7b** was observed.

Pyrolyses of 7,8,9,10-tetrahydro-6-trimethylsiloxy-6-vinyl-5*H*-benzocyclooctenes (6a) and subsequent hydrolyses of the trimethylsilyl products were carried out in the same manner as described previously.[6] The product and yield studies used the same conditions as reported above for the HMPT work and are shown in Table II.

Rearrangement of the Potassium Salts of *cis*- and *trans*-6-(1,3-Butadienyl)-7,8,9,10-tetrahydro-6(5*H*)-benzocyclooctenol (6c). A solution of 0.326 g of the crude butadienols (**6c**) in 5 mL of HMPT was added to 20 mL of HMPT containing excess potassium hydride and allowed to stand for 3.9 h. The usual workup (continuous extraction) afforded 0.265 g of neutral material. The material was analyzed by GLC (column K, 175 °C) using butenynol **21** as an internal standard with the results presented in Table II. The product was purified on a 2 ft × 0.375 in stainless steel column containing 33 g of Woelm neutral alumina (activity II), eluting with hexane and then a linear gradient[41] of ether/hexane. Fractions containing material with R_f 0.38 (TLC on silica gel; solvent, chloroform) were collected and repurified by GLC (column G, 240 °C) to provide the analytical samples of 5,6,9,10,11,12-hexahydro-6-vinyl-8(7*H*)-benzocyclodecenone (**7c**): NMR (CCl_4) δ 6.95–7.25 (m, 4 H), 5.9–6.4 (broad m, 1 H), 5.01 (dd, J = 2, 11 Hz, 1 H), 4.99 (dd, J = 2, 16 Hz, 1 H), 2.85–3.2 (broad m, 2 H), 2.45–2.85 (broad m, 3 H), 1.9–2.45 (broad m, 6 H), 1.55–1.9 (m, 2 H); IR (neat) 3060, 3010, 3000, 2930, 2680, 1700, 1640, 1490, 1470, 1450, 1425, 1410, 1370, 1120, 1000, 990, 920, 800, 780, 760, 740, 710 cm^{-1}; mass spectrum, *m/e* 228 (47.9), 174 (33.4), 118 (100); exact mass, *m/e* 228.151 (calcd for $C_{16}H_{20}O$, 228.151).

Rearrangement of the Potassium Salts of *cis*- and *trans*-6-(1,3-*cis*-Pentadienyl)-7,8,9,10-tetrahydro-6(5*H*)-benzocyclooctenol (6d) in HMPT. A solution of 0.77 g of 81% pure dienols **6d** in 5 mL of HMPT was added to 45 mL of HMPT containing excess potassium hydride, and the whole solution was allowed to stand for 4.5 h at room temperature. The usual workup (continuous extraction) afforded 0.66 g of neutral material and 0.022 g (adjusted for HMPT content by NMR) of acidic material. A 278-mg portion of the neutral material was purified on a 2 ft × 0.375 in stainless steel column containing 33 g of Woelm neutral alumina (activity II). The column was eluted with hexane and then a linear gradient[41] of hexane and 50:50 ether/hexane. Fractions containing material with R_f 0.5 (TLC on silica gel; solvent, chloroform) were collected to give 0.086 g of material. A 50-mg amount of this material was vacuum transferred (130 °C at 0.35 mm) to give 0.047 g of 6-(*cis*-1-propenyl)-5,6,9,10,11,12-hexahydro-8(7*H*)-benzocyclodecenone (**7d**): NMR ($CDCl_3$) δ 7.03–7.3 (m, 4 H), 5.3–5.8 (m, 2 H), 3.12–3.5 (broad s, 1 H), 2.8–3.12 (m, 1 H), 2.45–2.8 (m, 3 H), 2.2–2.45 (m, 3 H), 1.87–2.2 (m, 3 H), 1.5–1.87 (m, 5 H), 1.72 (d, J = 5 Hz); IR (neat) 3050, 3010, 2930, 2860, 1700, 1490, 1470, 1450, 1420, 1400, 1360, 1330, 1270, 1230, 1190, 1110, 990, 920, 790, 770, 750, 730, 710 cm^{-1}; mass spectrum, *m/e* 242 (23.2), 174 (32.3), 118 (100);

exact mass, *m/e* 242.167 (calcd for $C_{17}H_{22}O$, 242.167).

Pyrolysis of 6-(1-*cis*-Propenyl)-5,6,9,10,11,12-hexahydro-8(7*H*)-benzocyclodecenone (7d) was carried out as described previously.[2] A 3 cm × 28 cm glass ampoule containing 0.36 g of crude **7d** was heated for 6.25 h at 350 °C. Separation of the products by GLC (column I, 265 °C) gave a very low yield (<1%) of two ketones in a 2:1 ratio, for which spectra are listed although the samples were too weak for reliable integration. Major ketone: NMR (CCl_4) δ 6.9–7.3 (m), 5.2–5.65 (m), 3.7–4.1 (m), 2.5–3.1 (broad m), 1.9–2.4 (m), 2.15 and 2.08 (s), 1.5–1.9 (broad m), 0.85–1.15 (m, possible overlapping triplets, J = 7 Hz); IR (neat) 3070, 3020, 2960, 2940, 2860, 1710, 1500, 1460, 1360, 1170, 980, 760 cm^{-1}; mass spectrum, *m/e* 242 (25.4) 224 (10.7), 213 (11.7), 199 (100); exact mass, *m/e* 242.165 (calcd for $C_{17}H_{22}$, 242.167).

Minor ketone: NMR (CCl_4) δ 6.9–7.3 (m), 5.2–5.7 (m), 0.8–3.1 (broad m); IR (neat) 3070, 3020, 2960, 2940, 2880, 1710, 1500, 1460, 980, 750 cm^{-1}; mass spectrum, *m/e* 244 (21.8), 243 (14.9), 242 (86.0), 299 (12), 129 (100); exact mass, *m/e* 242.166 (calcd for $C_{17}H_{22}O$,[42] 242.167).

Rearrangement of the Potassium Salt of 6-Cyclopropyl-7,8,9,10-tetrahydro-6(5*H*)-benzocyclooctenol (8a) in HMPT. A solution of the potassium salt of 0.029 g (0.1 mmol) of **8a** in 1.2 mL of HMPT was allowed to stand at room temperature for 45.6 h. Quenching the reaction mixture with water followed by the normal workup (manual extraction) afforded 0.010 g of neutral material. The material was analyzed by GLC (column J, 205 °C) and found to contain 18% starting material, 5% unknown substances, and 77% (<34% overall yield) of 1-cyclopropyl-5-(*o*-tolyl)-2,3-pentanedione (**17**). The mixture was purified by GLC (column J): NMR (CCl_4) δ 7.01 (s, 4 H), 2.5–2.9 (m, 4 H), 2.28 (s, 3 H), 1.6–2.2 (m, 2 H), 1.2–1.4 (m, 1 H), 0.8–1.2 (m, 4 H); IR (CCl_4) 3080, 3020, 2940, 2860, 1700, 1500, 1460, 1390, 1040, 950 cm^{-1}; mass spectrum, *m/e* 230 (23.5), 161 (100), 105 (69.9), 69 (64.1); exact mass, *m/e* 230.130 (calcd for $C_{15}H_{18}O_2$, 230.131).

In another experiment a solution of the potassium salt of 0.114 g of a mixture containing 58% of **8a** and 33% of **12** in 5 mL of freshly dried HMPT was allowed to stand at 25 °C for 46 h. The reaction mixture was quenched with water and worked up by the normal procedure (manual extraction), giving 0.089 g of neutral material and 0.019 g of acidic material. A 70-mg amount of the neutral material was then vacuum transferred (120 °C at 0.35 mm), producing 0.064 g of a light yellow oil, which was separated by GLC (column J, 210 °C) and shown to contain 32% of **12**, 6% of **8a**, and 59% of 1-cyclopropyl-5-(*o*-tolyl)-1-pentanone (**9a**): NMR (CCl_4, CH_2Cl_2 reference) δ 7.15 (s, 4 H), 2.55–3.01 (m, 4 H), 2.38 (s, 3 H), 1.45–2.09 (m, 5 H), 0.75–1.21 (m, 4 H); IR (neat) 3050, 3000, 2920, 2850, 1695, 1600, 1490, 1460, 1450, 1390, 1190, 1080, 1050, 1020, 900, 820, 740 cm^{-1}; mass spectrum, *m/e* 230 (3.4), 216 (33.3), 105 (63.5), 84 (63.5), 69 (100); exact mass, *m/e* 216.151 (calcd for $C_{15}H_{20}$, 216.151).

Rearrangements of the potassium salts of 7,8,9,10-tetrahydro-6(2-vinylcyclopropanyl)-6(5*H*)-benzocyclooctenols 8b in HMPT were carried out by the standard procedure and analyzed by GLC (column K, 165 °C) using **20** as an internal standard. Separation by GLC (column A, 190 °C) gave 5-(*o*-tolyl)-1-(2-vinylcyclopropyl)-1-pentanone (**9b**): NMR (CCl_4) δ 7.01 (s, 4 H), 5.11–5.56 (m, 2 H), 4.85–5.01 (m, 1 H), 2.43–2.67 (m, 4 H), 2.25 (s, 3 H), 1.25–1.91 (m, 7 H), 0.75–0.91 (m, 1 H); IR (CCl_4) 3080, 3020, 2940, 2870, 1700, 1640, 1500, 1460, 1390, 1100, 990, 910 cm^{-1}; mass spectrum, *m/e* 242 (1.6), 105 (100); exact mass, *m/e* 242.166 (calcd for $C_{17}H_{22}O$, 242.167).

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Registry No.—**6a**, 62297-12-5; **6b**, 64871-09-6; **6b** (K salt), 62297-13-6; *cis*-**6c**, 64871-11-0; *trans*-**6c**, 64871-12-1; *cis*-**6c** (Me_4Si deriv), 64871-13-2; *trans*-**6c** (Me_4Si deriv), 64871-14-3; *cis*-**6c** (K salt), 64871-15-4; *trans*-**6c** (K salt), 64871-16-5; *cis,cis*-**6d**, 64871-17-6; *trans,cis*-**6d**, 64871-03-0; *cis,cis*-**6d** (Me_4Si deriv), 64871-04-1; *trans,cis*-**6d** (Me_4Si deriv), 64871-05-2; *cis,cis*-**6d** (K salt), 64871-06-3; *trans,cis*-**6d** (K salt), 64871-07-4; **7b**, 62297-14-7; **7c**, 64870-85-5; **7d**, 64870-86-6; **8a**, 64870-87-7; **8a** (K salt), 64870-89-9; **8b**, 64870-88-8; **8b** (K salt), 64870-90-2; **9a**, 64870-91-3; **9b**, 64870-92-4; **10**, 826-73-3; **11**, 64870-93-5; **12**, 62297-15-8; **13a**, 64870-94-6; **13b** (K salt), 64870-95-7; **15**, 64870-96-8; **16**, 64870-97-9; **17**, 64870-98-0; **20**, 64871-00-7; **20** (Me_4Si deriv), 64871-01-8; **21**, 64870-99-1; δ-phenylvaleric acid, 2270-20-4; trimethylsilyl cyanide, 7677-24-9; vinyl bromide, 593-60-2; 1-buten-3-yne (Li salt), 51042-24-1; methyllithium, 917-54-4; 1-buten-3-yne, 689-97-4; *cis*-3-penten-1-yne (Li salt), 64871-02-9; *cis*-3-penten-1-yne, 1574-40-9; cyclopropyl bromide, 4333-56-6; *trans*-1-bromo-2-vinylcyclopropane, 15136-02-4; *cis*-1-bromo-2-vinylcyclopropane, 15136-01-3.

References and Notes

(1) D. A. Evans and A. M. Golob, *J. Am. Chem. Soc.*, **97**, 4765 (1975); D. A. Evans, 25th National Organic Symposium of the American Chemical Society, Morgantown, West Virginia, June 1977, Abstracts, pp 109–119.
(2) R. W. Thies and J. E. Billigmeier, *J. Am. Chem. Soc.*, **96**, 200 (1974).
(3) J. A. Berson, *Acc. Chem. Res.*, **5**, 406 (1972).
(4) See J. A. Berson and M. Jones, *J. Am. Chem. Soc.*, **86**, 5017, 5019 (1964), for the oxy-Cope definition.
(5) R. W. Thies and E. P. Seitz, *J. Chem. Soc., Chem. Commun.*, 846 (1976).
(6) R. W. Thies, *J. Am. Chem. Soc.*, **94**, 7074 (1972).
(7) R. W. Thies and R. E. Bolesta, *J. Org. Chem.*, **41**, 1233 (1976).
(8) For some alternative routes, see (a) H. O. House, "Modern Synthetic Reactions", 2nd ed, W. A. Benjamin, Menlo Park, Calif., 1972, p 810, (b) P. Caubere, *Acc. Chem. Res.*, **7**, 301 (1974), (c) S. Durani, R. S. Kapil, and N. Amand, *Indian J. Chem.*, **13**, 946 (1975), (d) H. Heaney and S. V. Ley, *J. Chem. Soc., Perkin Trans. 1*, 2693 (1974), (e) E. M. Fry and L. F. Fieser, *J. Am. Chem. Soc.*, **62**, 3489 (1940), (f) G. Wittig, H. Eggers, and P. Duffner, *Justus Liebigs Ann. Chem.*, **619**, 10 (1959), (g) J. A. Elix and M. V. Sargent, *J. Am. Chem. Soc.*, **91**, 4734 (1969), (h) R. Huisgen and G. Seidl, *Tetrahedron*, **20**, 231 (1964).
(9) D. A. Evans, G. L. Carrol, and L. K. Truesdale, *J. Org. Chem.*, **39**, 914 (1974); D. A. Evans and L. K. Truesdale, *Tetrahedron Lett.*, 4929 (1973).
(10) R. W. Thies and H. J. Shih, *J. Org. Chem.*, **42**, 280 (1977).
(11) H. Taguchi, H. Yamamoto, and H. Nozaki, *J. Am. Chem. Soc.*, **96**, 3010, 6510 (1974).
(12) W. T. Borden, *J. Am. Chem. Soc.*, **92**, 4898 (1970).
(13) (a) E. N. Marvell and T. Li, *Synthesis*, 457 (1973); (b) L. Crombie, S. H. Harper, and R. J. D. Smith, *J. Chem. Soc.*, 2754 (1957); (c) J. D. Chanley and H. Sobotka, *J. Am. Chem. Soc.*, **71**, 4140 (1949); (d) E. B. Bates, E. R. H. Jones, and M. C. Whiting, *J. Chem. Soc.*, 1854 (1954), and references cited therein; (e) R. G. Powell, C. R. Smith, Jr., C. A. Glass, and I. A. Wolff, *J. Org. Chem.*, **31**, 528 (1966).
(14) J. P. Marino and L. J. Brown, *Tetrahedron Lett.*, 3241 (1976).
(15) T. J. Wallace, H. Pobiner, and A. Schriesheim, *J. Org. Chem.*, **30**, 3768 (1965).
(16) N. D. Epiotis, *Angew. Chem., Int. Ed. Engl.*, **13**, 751 (1974).
(17) J. C. Dalton and H.-F. Chan, *Tetrahedron Lett.*, 3145 (1973); J. C. Dalton and B. G. Stokes, *ibid.*, 3179 (1975).
(18) G. A. Russell and K. Schmitt, *J. Am. Chem. Soc.*, **94**, 8918 (1972).
(19) B. Franzus, M. L. Scheinbaum, D. L. Waters, and H. B. Bowlin, *J. Am. Chem. Soc.*, **98**, 1241 (1976).
(20) S. R. Wilson, D. T. Mao, K. M. Jemberg, and S. T. Ezmirly, *Tetrahedron Lett.*, 2559 (1977).
(21) R. A. Benkeser and W. E. Broxterman, *J. Am. Chem. Soc.*, **91**, 5162 (1969); R. A. Benkeser and M. P. Siklosi, *J. Org. Chem.*, **41**, 313212 (1976).
(22) R. W. Thies, E. P. Seitz, M. Meshgini, and R. Chiarello, 32nd Northwest Regional American Chemical Society Meeting, Portland, Oregon, June 1977, Abstract 180.
(23) J. G. Nikelly and M. Blumer, *Am. Lab.*, **12**, (1974).
(24) T. J. Wallace and A. Schriesheim, *Tetrahedron*, **21**, 2271 (1965).
(25) K. B. Wiberg, "Laboratory Technique in Organic Chemistry", McGraw-Hill, New York, N.Y., 1960.
(26) L. F. Fieser and M. Fieser, "Reagents for Organic Chemistry", Vol. 1, Wiley, New York, N.Y., 1967.
(27) R. C. Gilmore, Jr., and W. J. Horton, *J. Am. Chem. Soc.*, **73**, 1411 (1951).
(28) R. Huisgen, E. Rauenbusch, and G. Seidl, *Chem. Ber.*, **90**, 1958 (1957).
(29) C. C. Sweeley, R. Bentley, M. Makita, and W. W. Wells, *J. Am. Chem. Soc.*, **85**, 2495 (1963).
(30) D. Tarrant, J. Savoy, and E. S. Iglehart, *J. Org. Chem.*, **29**, 2009 (1964).
(31) J. D. Chanley and H. Sobotka, *J. Am. Chem. Soc.*, **71**, 4140 (1949).
(32) We thank Dr. E. N. Marvell for a gift of this material.
(33) R. W. Thies and H. J. Shih, *J. Org. Chem.*, **42**, 280 (1977).
(34) G. Fontaine, C. André, C. Joliet, and P. Maitte, *Bull. Soc. Chim. Fr.*, 1444 (1963).
(35) D. Seyferth, H. Yamazaki, and D. L. Alleston, *J. Org. Chem.*, **28**, 703 (1963).
(36) L. Skattebol, *J. Org. Chem.*, **29**, 2951 (1964).
(37) P. S. Skell and A. Y. Garner, *J. Am. Chem. Soc.*, **78**, 5340 (1956).
(38) J. A. Landgrebe and L. W. Becker, *J. Org. Chem.*, **33**, 1173 (1968).
(39) P. A. Wender and M. P. Filosa, *J. Org. Chem.*, **41**, 3490 (1976).
(40) C. J. Pouchert, "Aldrich Library of Infrared Spectra", 3rd ed, Aldrich Chemical Co., Inc., Milwukee, Wis., 1975, p 231.
(41) J. M. Bobbitt, A. E. Schwarting, and R. J. Gritter, "Introduction to Chromatography", Van Nostrand-Reinhold Co., New York, N.Y., 1968, p 96.
(42) It was originally thought that *m/e* 242 was the molecular ion, but logical mass loss and peak intensity analysis indicated later that *m/e* 244 is the probable molecular ion. It is highly probable that the remaining 2 mass units are 2 H and that the true formula is $C_{17}H_{24}O$.