Rearrangements of Dibenzobarrelene Epoxides. Ring Rigidity and Restricted Rotation of Substituents in Dibenzocycloheptatrienes

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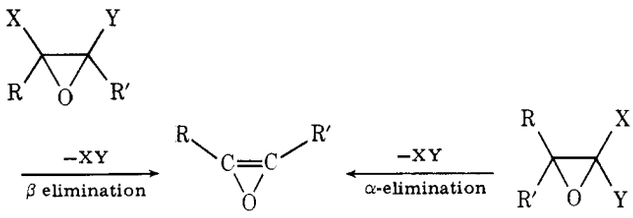
1,4,7,8-Tetramethyldibenzobarrelene epoxide (**10**) rearranges quantitatively in refluxing chloroform to 1-acetyl-1,4,5-trimethyldibenzocycloheptatriene (**14**) as a consequence of traces of acid which are present. The cycloheptatriene ring in **14** exists in a rigid boat conformation, with the acetyl group axial and the C(1) methyl group equatorial. Variable temperature NMR studies of **14** showed that rotation around the acetyl carbon–C(1) bond is restricted, with a barrier of 15.7 kcal/mol at 25 °C. Changes in the NMR spectrum which can be ascribed to restricted rotation of the C(1) methyl group were also observed. On treatment with acid, epoxide **10** and ketone **14** rearrange stereoselectively to the syn-bicyclic unsaturated alcohol **17s**. It is thought that **14** is the product of kinetic control and **17** the product of thermodynamic control of proton loss from a bridged ion intermediate. The octamethyldibenzobarrelene oxide **11** rearranges in a manner similar to **10** to give the ketone **20** and alcohol **21**. The rearrangements of **11** and **20** are more facile than those of **10** and **14**. Rotation of the acetyl group in **20** is restricted at room temperature. The strategy of using dibenzobarrelene oxides and related compounds as potential precursors of oxirenes via the retro-Diels–Alder route is discussed.

We were led to carry out the present research as a consequence of two interests. One of these was in oxirenes (**1**), a class



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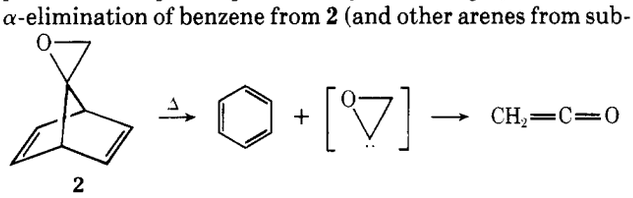
of compounds of considerable theoretical interest,[2] no member of which has yet been isolated. Oxirenes have been proposed as intermediates in the peroxidation of acetylenes[3] and in other acetylene oxidations,[4] in the reaction of methylene with carbon monoxide,[5] and in the Wolff rearrangement of α-diazo ketones.[6,7] Each of these approaches involves formation of the heterocyclic ring from an acyclic precursor, in our view a relatively unpromising route from a synthetic standpoint.

An alternative approach to oxirenes would start with the heterocyclic ring already intact, and introduce the double bond. This could in principle be done in two ways, using an α or a β elimination. Both approaches have been either proposed or attempted experimentally. For example, the thermal α-elimination of benzene from **2** (and other arenes from sub-



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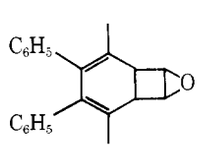
stituted analogues) was studied recently.[8] However, the presumed oxirane–carbene intermediate rearranged to a ketene without any evidence for the formation of an oxirene. Compounds **3**[7] and **4**[10] have been proposed as potential oxirene precursors through β elimination, but attempts to prepare **3** failed[9] and the dehalogenation of **4** has not yet been described. Phenyloxirene has been proposed as an intermediate in the Norrish Type II photoelimination of **5**.[11]



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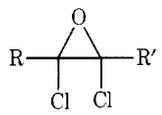

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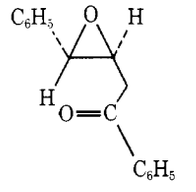

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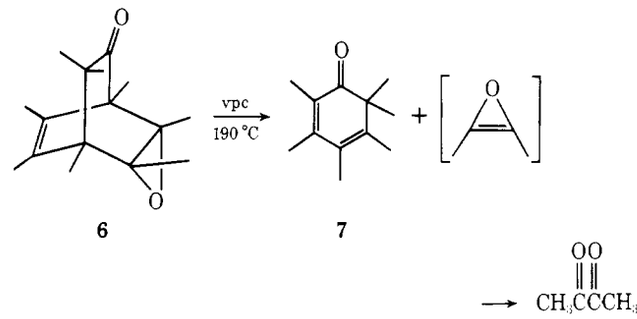
We recently observed[12] that subjection of the epoxide **6** to vapor phase chromatography gave the dienone **7** and biacetyl



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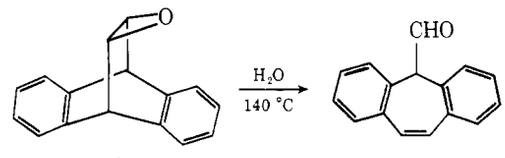
in fair yield. The source of the second oxygen atom in the biacetyl has not yet been established, but dimethyloxirene is a possible precursor of this product.[13] The formation of these retro-Diels–Alder products from **6** was somewhat surprising, since there is no special stability associated with the dienone **7** that would make it a good leaving group in this reaction (this is particularly true if the other component of the reaction is an oxirene, expected[2] to be a high-energy compound).

A better approach to oxirenes via the retro-Diels–Alder reaction would involve the formation of an aromatic compound as the second product, since this would provide a driving force for the reaction. This is a common technique for the introduction of a double bond in a strained ring.[14,15] We therefore decided to prepare and pyrolyze certain dibenzobarrelene oxides, in which case the retro-Diels–Alder reaction, if it proceeded, would produce an anthracene as one of the products. Although a greater driving force would be obtained by pyrolyzing a barrelene oxide, we chose to first examine the dibenzo derivatives because of a second interest of ours, the synthesis of highly substituted, strained anthracenes.[16,17]

What were the chances for success in generating an oxirene in this manner? Perhaps not very high, in view of the known propensity for dibenzobarrelene derivatives to rearrange. For example, many years ago Cristol and Bly showed[18] that dibenzobarrelene oxide rearranged to the dibenzocycloheptatriene carboxaldehyde **9** when heated at 140 °C in water.[19] To



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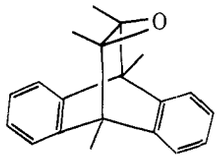
decrease the propensity for this type of rearrangement, we decided to have methyl substituents at the bridgehead positions (to facilitate bond cleavage) and methyl substituents on the epoxide ring (to diminish the need for phenyl participation). This led us to synthesize and study the effect of heat on compound **10**. We also prepared and heated **11** because if it



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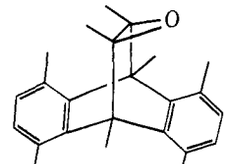

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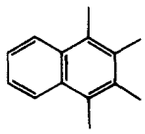
were to rearrange in a manner analogous to **8** → **9**, molecular models showed that the product would be extremely strained; indeed, the molecules could not be constructed with CPK space-filling models. Consequently, we thought that instead it might eliminate the epoxide bridge, perhaps as an oxirene.

We describe here the synthesis and rearrangement of **10** and **11**, and some of the properties of the highly hindered compounds that were obtained from them.

Results and Discussion

Addition of benzyne to 1,2,3,4-tetramethylnaphthalene gave the dibenzobarrelene **13** which was converted to the epoxide **10** with *m*-chloroperbenzoic acid. The NMR spectra of **10** and **13** had peaks consistent with the symmetry of their



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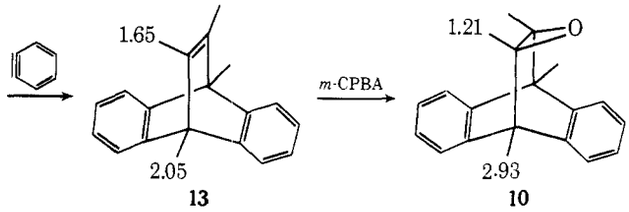


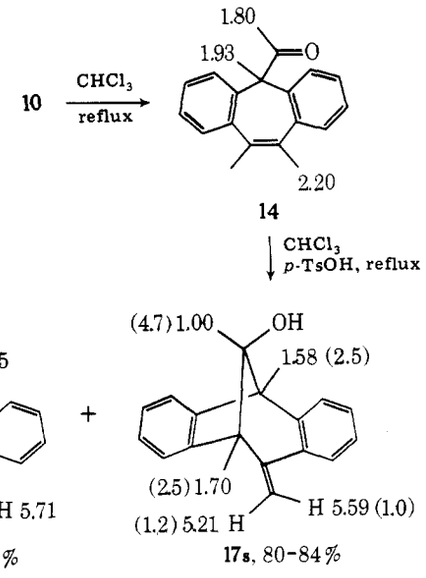
13 **10**

structures, with singlets for the equivalent methyls as shown on the formulas. The mass spectra of **10** and **13** each showed modest intensity peaks at *m/e* 206 (9,10-dimethylanthracene) presumably due to the loss of the nonbenzo bridge.

When **10** was heated at reflux in chloroform for several hours it was converted quantitatively to an isomer assigned structure **14**. The compound had a carbonyl absorption at 1703 cm^{-1} and an NMR spectrum at room temperature consistent with the structure (however, see below for the low-temperature spectra of **14**). Ketone **14** could be reduced with lithium aluminum hydride to the corresponding alcohol **15**, and epoxidized to an epoxy ketone **16** (see Experimental Section for details), thus confirming the presence of the carbonyl and double-bond functions.

The question of whether the rearrangement of **10** to **14** was thermal or acid catalyzed was answered when we found that **10** could be recovered quantitatively from being heated in pyridine rather than chloroform (otherwise, identical conditions). We conclude that the rearrangement of **10** to **14** in chloroform is acid catalyzed.

Although **14** was stable to prolonged reflux in chloroform, addition of *p*-toluenesulfonic acid caused its rearrangement to a mixture of two unsaturated alcohols believed to be the syn and anti isomers **17s** and **17a**. The syn isomer predominated

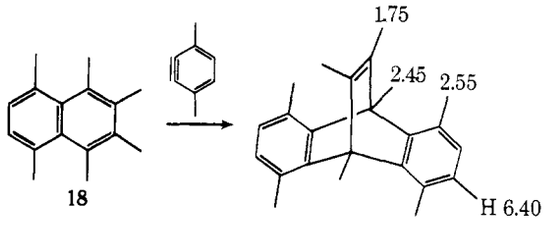


17a, 16–20% **17s**, 80–84%

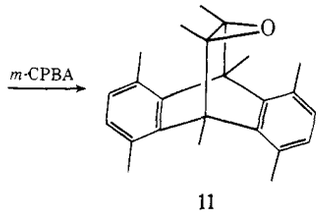
by a ratio of 4 or 5 to 1. A similar mixture was obtained when the epoxide **10** was treated directly with *p*-TsOH in $CHCl_3$. The stereochemical assignments of **17s** and **17a** are based on two features of their NMR spectra. The methyl group attached to the hydroxyl-bearing carbon was at appreciably higher field in the major isomer than in the minor isomer; since this methyl group would be shielded by the aromatic ring in the syn isomer, we assign that stereochemistry to the major isomer. Europium-shift data tend to support this assignment. Since we were not able to separate the isomers cleanly, shift data were obtained on the mixture. The vinyl protons in the major isomer moved downfield at a faster rate than did the vinyl protons of the minor isomer (the slopes for the vinyl protons of the minor isomer, if placed on the same scale as those of the major isomer, would be 0.75 and 0.68 for the high- and low-field vinyl protons, respectively). This result was consistent with the stereochemical assignment based on the methyl chemical shifts (provided that the complexation constants for the two alcohols with the shift reagent are essentially identical).

We postpone for later (vide infra) a discussion of the rearrangement mechanism, since it requires a prior discussion of the conformational structure of **14**.

Epoxide **11** was prepared from the octamethyldibenzobarrelene **19**, which in turn was obtained (in low yield) from



18 **19**



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the addition of 3,6-dimethylbenzyne to the hexamethylnaphthalene **18**. The NMR spectrum of **19** showed that the aryne had added to the tetrasubstituted ring of **18**, since it consisted of four sharp singlets assigned as shown on the structure. The conversion of **19** to **11** had to be done with extreme care, and

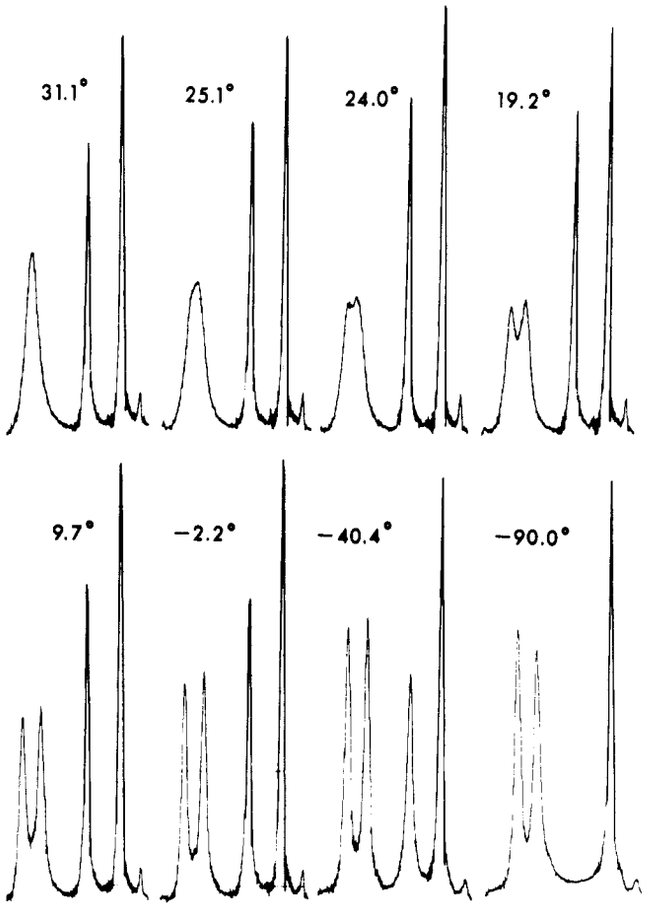
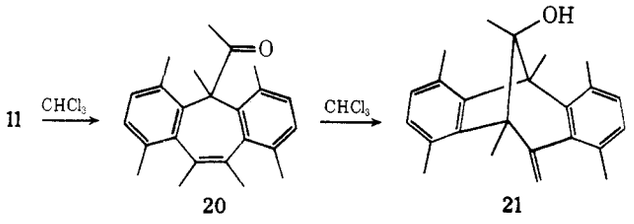


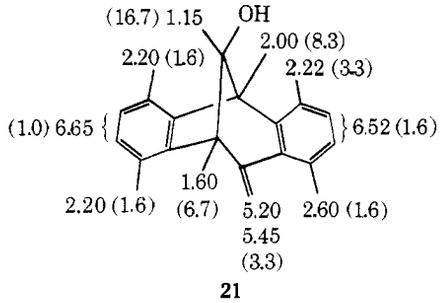
Figure 1. The proton NMR spectrum of **14** as a function of temperature.

was complete in 1 min at room temperature. Epoxide **11** could be isolated, but it was extremely sensitive to heat and acid. On standing overnight in chloroform it rearranged to the ketone **20** and, on further standing or on reflux, to the alcohol **21.** It was not necessary to add any acid other than what was already present in the chloroform or on the glass surfaces to bring about these rearrangements.



20 **21**

Although ketone **20** almost certainly has the structure shown (carbonyl at 1690 cm^{-1}, analogy with the formation of **14** from **10**), its NMR spectrum was not consistent with a symmetric structure, in that all eight methyl signals were unique. However, rearrangement of **20** gave **21** (analogous to the formation of **17** from **14**) which had an NMR spectrum consistent with its structure. Only one epimer was formed. The NMR spectrum, together with the relative shifts of each signal with europium-shift reagent, is shown on the structure. Note particularly that one of the aryl methyl signals appears at lower field than the other three. The rather large europium shift of the vinyl protons supports their location syn to the hydroxyl group, and this assignment is consistent with **17s** being the major isomer formed from **14.** However, the absence of the NMR spectrum of the epimer of **21** for comparison limits the certainty of the assignment.



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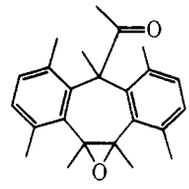
When the epoxidation of **19** was carried out with excess *m*-CPBA and without workup until 15 h of reaction time two products were obtained. One of these was the alcohol **21** (70%). However, the other product was the epoxy ketone **22** (30%); apparently, further epoxidation of **20** competes with the rearrangement to **21.** As with **20,** the NMR spectrum of **22** is not



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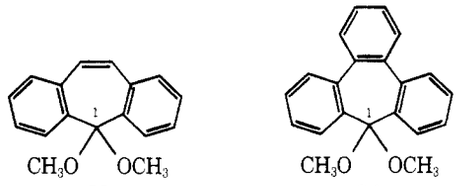
consistent with the symmetry of the structure as shown (for example, the two methyl groups on the epoxide ring have different chemical shifts). The reason for this will be apparent shortly. Only one stereoisomer of **22** was formed, but we cannot assign its geometry.

Restricted Rotation of the Acetyl Group in 14. The NMR spectrum of **14** showed an interesting temperature dependence (Figure 1). At 24 °C the six-proton singlet at δ 2.20 due to the vinyl methyl groups began to split, and by −12 °C the separation into two sharp three-proton singlets was complete. During this time there was no significant change in the singlets at δ 1.80 or 1.93 due to the acetyl and C(1) methyls, respectively.[20] However, as the temperature was lowered further, the signal at δ 1.93 began to broaden and to decrease in area (easily noticeable at −40 °C, Figure 1) and eventually (−75 °C) it became so broad as to be unobservable. Meanwhile, the remaining three peaks were essentially unchanged, except for viscosity broadening.

We believe these observations permit only one interpretation. The cycloheptatriene ring in dibenzocycloheptatrienes such as **14** has a boat conformation, with one of the substituents at C(1) pseudoaxial and the other pseudoequatorial.[21] The barrier to "flipping" from one boat conformation to the other, which interchanges the C(1) substituents, can often be quite high. For example, in **23** the barrier is 15 kcal/mol and in **24** it is >23 kcal/mol.[22] If the process being observed, as **14**



23 **24**

was cooled, was the slowing down of this ring flipping, then two sets of peaks for the C(1) and acetyl methyls would have appeared as the temperature was lowered. Since at all temperatures only one peak was seen for each of these groups, we conclude that the seven-membered ring in **14** exists as a single conformer. Furthermore, the acetyl group must be axial, an assignment which can be supported by the following arguments. Only when the acetyl group is axial can the C(4)–C(5) double bond interact with the carbonyl group to convert **14**

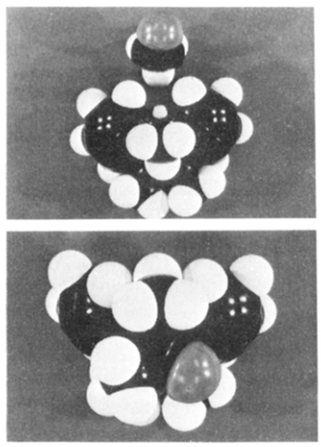
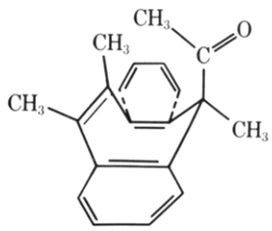


Figure 2. CPK models of **14.** (Top model) With the C(1) methyl in an axial position, it is not possible to attach the acetyl group to the equatorial position; (bottom model) with the acetyl group axial. The C(1) methyl group barely fits between the hydrogens of the flanking aromatic rings.



14

(preferred ring conformer)

to **17.**[23] Space-filling models of **14** can only be made with the acetyl group axial (Figure 2). The high-field position of the acetyl methyl signal in **14** (δ 1.80) can be rationalized by having the acetyl group axial (shielding by the aromatic rings and/or the C(4)–C(5) double bond). And finally, only if the acetyl group is axial can we rationalize the NMR behavior shown in Figure 1.

We believe that rotation about the C(1)–acetyl carbon bond in **14** is restricted. As the temperature is lowered, the favored conformation, with the carbonyl oxygen directed toward one of the two aromatic rings and the acetyl methyl directed toward the other aromatic ring, is assumed (Figure 3, top model). The C(4) and C(5) methyl substituents are quite close to the acetyl group, and the effect on their chemical shifts is large. Rotation of the acetyl group brings about severe interactions either with the C(1)-methyl group or the C(4) and C(5) methyl groups (Figure 3, middle and lower models). Consequently, the barrier is fairly high (15.7 kcal/mol).[24-26]

Finally, we regard the gradual decrease in area of the peak at δ 1.93 due to the C(1) methyl group (Figure 1) as being due to restricted rotation of the methyl group itself. Unfortunately, we could not run spectra of **14** at sufficiently low temperatures to see the reappearance of the (heavily split) methyl proton signals. Several examples of restricted rotation of methyl groups are now known.[27] The environment around the equatorial group in **14** is extremely crowded, since the two adjacent aromatic protons jut inwards (Figure 2, lower model). Indeed, it is impossible to make space-filling models of the analogous **20,** in which these two hydrogens are replaced by methyl groups. It is truly remarkable that **20** can be synthesized at all, and it is not surprising that even at room temperature in chloroform it rearranges to the less hindered **21.** It is also clear why the NMR spectrum of **20** was not consistent with its apparent symmetry (vide supra); rotation of the acetyl group must be restricted even at room temperature.

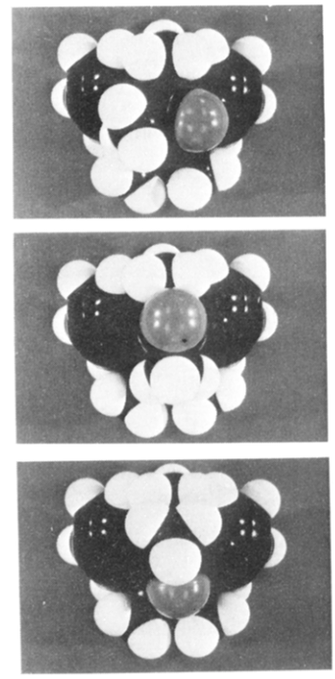
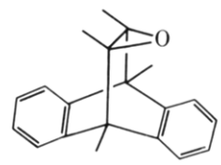


Figure 3. CPK models of **14,** acetyl axial. (Top model) Favored conformation, with the acetyl group lying "crosswise", accounting for the large difference in chemical shifts of the vinyl methyls at low temperature; (middle and bottom models) disfavored symmetric conformations of the acetyl group as it rotates in one direction or the other from the configuration in the top model.

Finally, there is the question of the stereoselectivity with which the ketones **14** and **20** and epoxides **10** and **11** rearrange to the bicyclic alcohols **17s** and **21,** respectively. A rationale



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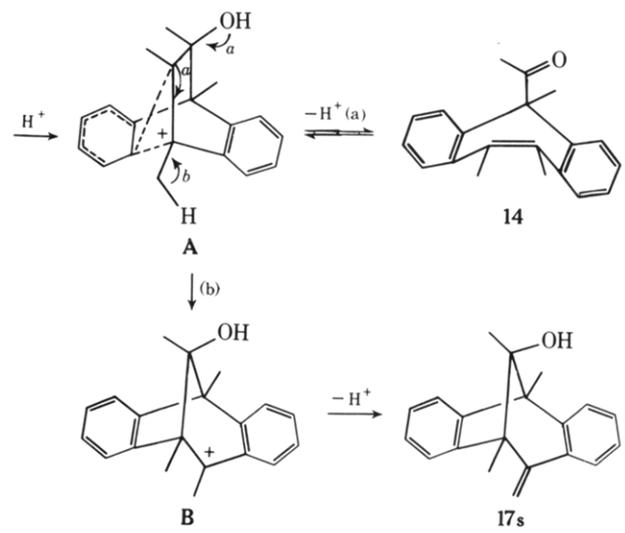

A **14**

B **17s**

is shown in the scheme for the tetramethyl system. Protonation of the epoxide **10** and ring opening with participation of the benzo group should lead to the bridged ion A. Proton loss from A can give either **14** (a arrows) or **17s** via the benzyl cation B (b arrow). We believe that **14** is the product of kinetic control, whereas **17s** is the product of thermodynamic control. This scheme rationalizes why the hydroxyl group in **17** (and

21) is predominantly or entirely syn to the exocyclic methylene. The small amount of **17a** which is formed could be explained by cyclization, on protonation of **14**, to give a bridged ion epimeric with A. The above scheme also shows that the acetyl group in **14** (and **20**) will be formed in an axial conformation.

Although we did not obtain evidence for oxirenes from the thermal treatment of dibenzobarrelenes, we believe that the retro-Diels–Alder approach to this class of compounds, as outlined in the introduction, still holds promise, and we are continuing to pursue this approach in other systems.

Experimental Section

1,4,7,8-Tetramethyl-2,3:5,6-dibenzobicyclo[2.2.2]octa-2,5,7-triene (13). A mixture of 1,2,3,4-tetramethylnaphthalene (**12**) (1 g, 5.4 mmol), benzenediazonium-2-carboxylate hydrochloride (1.2 g, 5.6 mmol), propylene oxide (15 mL), and 1,2-dichloroethane (50 mL) was heated gradually, until gas evolution commenced. When the solution became clear, the reaction was continued at reflux for 2 h. The volatile solvents were removed under vacuum. The oily residue was dissolved in ether and washed with cold 2% sodium hydroxide, water, and dried ($MgSO_4$). The brown residue which remained after the solvent evaporated was chromatographed on silica gel with cyclohexane as eluent. The first fraction was recovered as **12**; the second fraction gave 448 mg (32%) of the desired **13**: mp 178–180 °C (methanol); NMR ($CDCl_3$) δ 1.65 (s, 6 H, vinyl methyls), 2.05 (s, 6 H, bridgehead methyls), 6.74–7.15 (m, 8 H, arom); mass spectrum (70 eV) *m/e* (rel intensity) 260 (54), 245 (100), 230 (42), 215 (32), 206 (18).

Anal. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.29; H, 7.74.

7,8-Epoxy-1,4,7,8-tetramethyl-2,3:5,6-dibenzobicyclo[2.2.2]-octa-2,5,7-triene (10). A methylene chloride (10 mL) solution of 85% *m*-chloroperbenzoic acid (467 mg, 2.3 mmol) was added dropwise at 0 °C to a solution of **13** (500 mg, 1.92 mmol) in 5 mL of methylene chloride. The mixture was stirred at 0 °C for 7 h, during which time *m*-chlorobenzoic acid precipitated from solution. The solid was removed by suction filtration and the filtrate was washed with aqueous sodium bisulfite. The aqueous layer was separated and extracted with ether, and the combined organic layers were then washed with potassium bicarbonate, water, and dried ($MgSO_4$). The solvent was removed under vacuum at room temperature and the residue (474 mg, 90%) which was nearly pure was recrystallized from a mixture of methylene chloride and hexanes to give pure **10**: mp 154–155 °C (dec 120 °C if heated slowly); NMR ($CDCl_3$) δ 1.21 [s, 6 H, C(7) and C(8) methyls], 2.93 (s, 6 H, bridgehead methyls), 6.9–7.2 (m, 8 H, arom); UV (CH_3CN) λ_{max} 274 nm (ϵ 1460), 266 (1280), 233 (br, 1640); mass spectrum (70 eV) *m/e* (rel intensity) 276 (28), 234 (20), 233 (100), 218 (26), 215 (13), 206 (13), 203 (22), 202 (25), 191 (23).

Anal. Calcd for $C_{20}H_{20}O$: C, 86.92; H, 7.29. Found: C, 86.98; H, 7.34.

1-Acetyl-1,4,5-trimethyl-2,3:6,7-dibenzocyclohepta-2,4,6-triene (14). A solution of **10** (98 mg, 0.355 mmol) in 5 mL of chloroform was heated at reflux for 4.5 h and then cooled. Evaporation of the solvent gave 98 mg (100%) of **14**, mp 173–175 °C (methanol): IR (KBr) 3050 (m), 1703 (s), 1480 (br, m), 1390 (w), 1360 (m), 1190 (m), 780 (s), 760 (m) cm^{-1}; NMR ($CDCl_3$) δ 1.80 (s, 3 H, acetyl methyl), 1.93 (s, 3 H, C(1) methyl), 2.20 (s, 6 H, vinyl methyls), 7.0–7.4 (m, 8 H, arom); UV (CH_3CN) λ_{max} 266 nm (ϵ 9300), 228 (15 400) 215 (sh); mass spectrum (70 eV) m/e (rel intensity) 276 (33), 234 (22), 233 (100), 218 (25), 215 (18), 206 (16), 203 (25), 202 (29), 191 (25).

Anal. Calcd for $C_{20}H_{20}O$: C, 86.92; H, 7.29. Found C, 86.85; H, 7.34.

Thermal Stability of 10. In a flask previously rinsed with concentrated ammonium hydroxide and oven dried, a solution of **10** (20 mg) in pyridine (3 mL) was heated at 65–75 °C for 5 h and then evaporated to dryness. An NMR spectrum of the residue in $CDCl_3$ showed only recovered **10**.

4-Methylene-1,5,8-trimethyl-2,3:6,7-dibenzobicyclo[3.2.1]-octa-2,6-dien-8-ols 17s and 17a. To a solution of the epoxide **10** (68 mg, 0.25 mmol) in 5 mL of chloroform was added a few crystals of *p*-toluenesulfonic acid, and the mixture was heated at reflux for 12 h. The cooled solution was washed with sodium bicarbonate solution and dried ($MgSO_4$). The residue obtained after evaporation of the solvent which showed NMR peaks due to **14** (16%), **17s** (68%), and **17a** (16%) was chromatographed on silica gel with 20% ether in hexane as the eluent. The first fraction (7 mg, 10%) was methyl ketone **14**. The second fraction (60 mg, 88%) was a mixture of the alcohols **17s** and **17a**, mp 170–173 °C (methanol). For **17s**: NMR ($CDCl_3$) δ 1.00 [s, 3 H, C(8) methyl], 1.58, 1.70 (s, 3 H each, bridgehead methyls), 5.15, 5.55 (s, 1 H each, vinyl), 6.95–7.5 (m, 8 H, arom). For **17a**: NMR ($CDCl_3$) δ 1.12 (s, 3 H, C(8) methyl), 1.55, 1.67 (s, 3 H each, bridgehead methyls), 5.32, 5.71 (s, 1 H each, vinyl); mass spectrum (70 eV) *m/e* (rel intensity) 276 (95), 233 (100).

Anal. Calcd for $C_{20}H_{20}O$: C, 86.92 H, 7.29. Found: C, 86.93; H, 7.33.

A similar result was obtained when ketone **14** was used in place of epoxide **10** as the starting material.

1-(1-Hydroxyethyl)-1,4,5-trimethyl-2,3:6,7-dibenzocyclohepta-2,4,6-triene (15). A solution of **14** (99 mg, 0.36 mmol) in 5 mL of tetrahydrofuran (THF) was added slowly at room temperature to a suspension of lithium aluminum hydride (70 mg, 1.8 mmol) in 5 mL of THF. After the mixture was stirred at room temperature for 1 h, it was poured over ice and extracted with ether. The organic layer was washed with water, dried ($MgSO_4$), and chromatographed on alumina with 50% ether in hexane as the eluent to give 95 mg (98%) of **15** as a colorless oil: IR (neat) 3480 (s), 3010 (s), 1485 (s), 1400 (m), 1270 (m), 1050 (s) cm^{-1}; NMR ($CDCl_3$) δ 0.85 (d, 3 H, J = 6 Hz, $\mathbf{CH_3}CH$), 1.85 (s, 3 H, C(1) methyl), 2.24 (s, 6 H, vinyl methyls), 3.26 (s, 1 H, hydroxyl), 5.0 (q, 1 H, J = 6 Hz, $CH_3\mathbf{CH}(OH)$), 6.80–7.30 (m, 8 H, arom); mass spectrum (70 eV) *m/e* (rel intensity) 278 (4), 260 (34), 245 (17), 234 (36), 233 (100), 219 (27), 218 (28), 206 (34), 203 (28), 202 (28), 191 (28), 179 (21), 178 (21). The alcohol was not analyzed.

1-Acetyl-1,4,5-trimethyl-2,3:6,7-dibenzocyclohepta-2,4,6-triene 4,5-epoxide (16). A solution of the ketone **14** (276 mg, 1 mmol) in 5 mL of methylene chloride was treated overnight at room temperature with *m*-chloroperbenzoic acid (215 mg, 1.25 mmol) which had been previously washed with pH 7 buffer and dried in vacuo. The usual workup gave **16** (289 mg, 99%), mp 140–143 °C, from ether/petroleum ether (30–60 °C): IR (KBr) 3000 (m), 1710 (s), 1480 (w), 1390 (m), 1180 (m), 1100 (m), 770 (s) cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 292 (3), 277 (7), 259 (4), 249 (11), 207 (38), 206 (42), 192 (13), 191 (12), 178 (5), 165 (5), 146 (52), 43 (100); NMR ($CDCl_3$) δ 1.70 [s, 6 H, C(4) and C(5) methyls], 1.97 (s, 3 H, acetyl), 2.15 [s, 3 H, C(1) methyl], 7.0–7.5 (m, 8 H, arom).

1,4,7,8-Tetramethyl-2,3:5,6-di(3,6-dimethylbenzo)bicyclo[2.2.2]octa-2,5,7-triene (19). A mixture containing 1.06 g (5 mmol) of 3,6-dimethylbenzenediazonium-2-carboxylate hydrochloride, 0.53 g (2.5 mmol) of 1,2,3,4,5,8-hexamethylnaphthalene[28] and 2 mL of propylene oxide in 15 mL of 1,2-dichloroethane was refluxed (80–90 °C) for 1.5 h. Evaporation of the solvent left a dark-brown oil which was dissolved in ether and washed with dilute sodium hydroxide solution, water, and dried ($MgSO_4$). Evaporation of the solvent gave an oil which was diluted with a little ether and cooled in ice. The solid which formed was filtered, recrystallized from a chloroform/ether mixture, and proved to be 1,4,5,8-tetramethylbiphenylene (the aryne dimer). The filtrate was chromatographed on silica gel with cyclohexane as eluent. The first fraction was recovered as hexamethylnaphthalene (**18**) (400 mg, 75%). The second fraction gave a few mg of an unidentified product. The third fraction gave a white solid which, after recrystallization from a chloroform/petroleum ether mixture, gave 40 mg (20% based on consumed **18**) of **19**: mp 160 °C (sublimed); NMR ($CDCl_3$) δ 1.75 (s, 6 H, vinyl methyls), 2.45 (s, 6 H, bridgehead methyls), 2.55 (s, 12 H, aromatic methyls), 6.40 (s, 4 H, arom); UV (CH_3CN) λ_{max} 332 nm (ϵ 14 200), 288 (sh, 4200), 215 (sh, 11 500); mass spectrum (70 eV) *m/e* (rel intensity) 316 (54), 301 (100), 286 (82), 271 (61).

Anal. Calcd for $C_{24}H_{28}$: C, 91.08; H, 8.92. Found: C, 91.33; H, 8.93.

1,4,7,8-Tetramethyl-2,3:5,6-di(3,6-dimethylbenzo)bicyclo[2.2.2]octa-2,4,6-triene 7,8-epoxide (11). A methylene chloride solution of *m*-chloroperbenzoic acid (50 mg, 0.29 mmol, previously washed with pH 7 buffer and dried in vacuo) was added dropwise to a solution of **19** (64 mg, 0.20 mmol) in 5 mL of methylene chloride at room temperature. After 1 min, the mixture was poured into aqueous sodium sulfite. The aqueous layer was separated and extracted with ether, and the combined organic layers were washed with aqueous potassium bicarbonate, water, and dried ($MgSO_4$). The solvent was removed under vacuum at room temperature, leaving a white solid which was recrystallized from methylene chloride/hexane to give 42.5 mg (65%) of **11**. The compound was very sensitive to heat or traces of acid, and even rearranged at room temperature in chloroform (vide infra): mp 125 °C (dec); NMR ($CDCl_3$) δ 1.30 [s, 6 H, C(7) and C(8) methyls], 2.35 (s, 6 H, bridgehead methyls), 2.50 and 2.52 (s, 6 H each, aromatic methyls), 6.52 and 6.60 (s, 2 H each, arom); mass spectrum (70 eV) *m/e* (rel intensity) 332 (95), 317 (43), 289 (100).

Anal. Calcd for $C_{24}H_{28}O$: C, 86.70; H, 8.49. Found: C, 87.20; H, 8.81.

Rearrangement of 11 to 1-Acetyl-1,4,5-trimethyl-2,3:6,7-di(3,6-dimethylbenzo)cyclohepta-2,4,6-triene (20) and to 4-Methylene-1,5,8-trimethyl-2,3:6,7-di(3,6-dimethylbenzo)bicyclo[3,2,1]octa-2,6-dien-8-ol (21). A 20% solution of **11** in $CDCl_3$ in an NMR tube was allowed to stand at room temperature and the spectra were recorded at periodic intervals. After 24 h, rearrangement to the ketone **20** was complete: NMR ($CDCl_3$) δ 1.87 (s, 3 H, acetyl), 1.90 [s, 3 H, C(1) methyl], 1.99 and 2.15 (s, 3 H each, vinyl methyls), 2.09, 2.25, 2.55, 2.60 (s, 3 H each, aromatic methyls), 6.65, 6.70 (s, 2 H each, arom). The solution was evaporated to dryness under vacuum at room temperature and an infrared spectrum (KBr) was quickly taken: 3000 (s), 1690 (s), 1470 (s), 1390 (m), 1360 (m), 830 (s), 800 (m) cm^{-1}.

Further spectral changes occurred when **20** was redissolved in $CDCl_3$ and allowed to stand at room temperature. Rearrangement to the alcohol **21** was complete and quantitative in 6 days. The quantitative rearrangement of **11** to **21** was also accomplished by refluxing **11** in chloroform for 12 h, or by VPC of **11** (5 ft × 0.25 in., 15% SE-30 on 30/60 Chromosorb W, 230 °C). Recrystallization from chloroform/absolute methanol gave pure **21**: mp 205–207 °C; IR (KBr) 3500 (s), 3000 (s), 1620 (m), 1470 (s), 1390 (s), 1340 (s), 920 (m), 830 (s) cm^{-1}; UV (MeOH) λ_{max} 308 nm (sh, ϵ 1000), 283 (sh, 3400), 265 (sh, 7100), 235 (22 800); NMR ($CDCl_3$) δ 1.15 (s, 3 H, C(8) methyl), 1.60, 200 (s, 3 H each, bridgehead methyls), 2.10 (br s, 1 H, hydroxyl), 2.20 (s, 6 H, aromatic methyls), 2.22, 260 (s, 3 H each, aromatic methyls), 5.20 and 5.45 (s, 1 H each, vinyl), 6.52, 6.65 (s, 2 H each, arom); for Eu-shift data, see structure; mass spectrum (70 eV) *m/e* (rel intensity) 332 (97), 317 (43), 299 (15), 289 (100), 274 (49), 259 (63), 244 (30), 243 (30), 235 (30), 229 (25).

Anal. Calcd for $C_{24}H_{28}O$: C, 86.70; H, 8.49. Found: C, 86.59; H, 8.46.

1-Acetyl-1,4,5-trimethyl-2,3:6,7-di[3,6-dimethylbenzo]cyclohepta-2,4,6-triene 4,5-epoxide (22). A solution of the hydrocarbon **19** (64 mg, 0.20 mmol) in 5 mL of methylene chloride was stirred at room temperature for 15 h with 50 mg (0.29 mmol) of *m*-chloroperbenzoic acid. Following the usual workup, two products were obtained. They were separated by preparative VPC (5 ft × 0.25 in., 15% SE-30 on 30/60 Chromosorb W, 225 °C). The first fraction, obtained in 70% yield, was the alcohol **21** (vide supra). The second fraction, obtained in 30% yield, is assigned the structure of the epoxy ketone **22**: IR (KBr) 3000 (s), 1620 (m), 1460 (s), 1390 (s), 1340 (s), 1150 (m), 1120 (m), 920 (s), 830 (s) cm^{-1}; NMR ($CDCl_3$) δ 1.57, 1.70 [s, 3 H each, C(4) and C(5) methyls], 2.20 [s, 6 H, acetyl and C(1) methyls], 2.40, 2.45 (m, 6 H each, aromatic methyls), 6.74, 6.77 (s, 2 H each, arom); mass spectrum (70 eV) *m/e* (rel intensity) 348 (7), 330 (44), 315 (17), 288 (21), 287 (64), 272 (28), 257 (20), 175 (60), 174 (100), 173 (88), 159 (38).[28]

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Registry No.—**10,** 63548-67-4; **11,** 63548-68-5; **12,** 3031-15-0; **13,** 63548-69-6; **14,** 63548-70-9; **15,** 63548-71-0; **16,** 63548-72-1; **17a,** 63548-73-2; **17s,** 63548-06-1; **18,** 36230-30-5; **19,** 63548-74-3; **20,** 63548-75-4; **21,** 63548-76-5; **22,** 63548-77-6; benzenediazonium-2-carboxylate HCl, 4661-46-5; propylene oxide,75-56-9; 3,6-dimethylbenzenediazonium-2-carboxylate HCl, 36794-93-1; 1,4,5,8-tetramethylbiphenylene, 63548-78-7.

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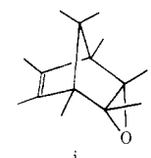

i

(13) We call attention to the different behavior of **2** and **6.** When both bonds broken in the pyrolysis are to the same carbon atom of the oxirane ring (as in **2**) the product is a ketene, whereas when the bonds broken during pyrolysis are to adjacent atoms the product is an α-diketone. α-Diketones have only been observed previously in "symmetrical" approaches to oxirenes, as in the oxidation of acetylenes,[3] whereas ketenes are observed in "asymmetric" approaches to oxirenes, as in the Wolff rearrangement.[6,7] Dimethylketene has been observed in the high-temperature (600 °C) flash pyrolysis of **6.** However, deuterium labeling experiments showed that the ketene came from cleavage of the ketone bridge rather than the epoxide bridge (unpublished results with S.-M. Chen).

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(25) The ^{13}C spectra of **14** also are consistent with this interpretation. For example, the allylic methyl carbons appeared at δ 18.50 and the other two methyl carbons at δ 23.54 and 56.95 in a 25 °C spectrum of **14.** However at −40 °C the peak formerly at δ 18.50 was split into two distinct peaks with about δ 0.5 difference in chemical shifts, whereas the other two methyl signals remained singlets. We are indebted to Judy Stegman for running these spectra.

(26) Calculated from the equations $k_c = \pi\Delta\nu/\sqrt{2}$ and $\Delta G^{\ddagger}_c = 2.3RT_c[10.32 + \log(T_c/k_c)]$, where T_c = 298 K and $\Delta\nu$ = 8.7 Hz; see G. Binsch, *Top. Stereochem.*, **3,** 97 (1968); J. B. Lambert and S. I. Featherman, *Chem. Rev.*, **75,** 611 (1975).

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(28) **Note added in proof.** In CS_2, the peak due to the C(1) methyl group in **14** had decreased in area and broadened considerably, but was still discernible at −90 °C.