Photochemistry of 2,3-Benzo-2,4-cyclooctadienones: Isolation and Chemistry of $\Delta^{4,5}$-Trans Isomers

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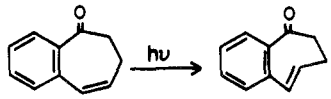
Abstract: Irradiation of the two 2,3-benzo-2,4-cyclooctadienones **8** and **20** gave the corresponding $\Delta^{4,5}$-trans isomers, whose physical properties (IR, NMR, UV) were determined. The IR spectrum of **8t** suggests transannular conjugation between the carbonyl and carbon–carbon double bonds, and chemical evidence (for example, stereoselective transannular methanol addition) supports the view that the trans double bond is polarized δ^+ at C(4), δ^- at C(5), opposite to that in the cis isomer. Thus methanol adds to **8t** at room temperature to give **10**, and **20t** similarly gives **21**. The trans ketones **8t** and **20t** were reduced stereospecifically with lithium aluminum hydride to give only one of the two possible diastereomeric alcohols, **12t** (crystalline) and **22t**, respectively. Chromatography of **8t** on silica gel caused stereoselective transannular addition of water to give the diol **9**. Irradiation of **8** absorbed on silica gel (cyclohexane) gave the unsaturated alcohol **13**. Irradiation of **14** in methanol also gave a stereoselective methanol adduct **18** (analogous to **10** and **21**). However, in this case the intermediate trans ketone **14t** could not be detected physically. Presumably the methyl groups are located in such a position as to sharply increase the strain and reactivity of **14t** as compared with **8t** or **20t**. Irradiation of **14** in ether caused both isomerization of the $\Delta^{4,5}$ double bond (to give **15**) and α-cleavage (to give **16** and **17**). The synthesis of **8**, which proceeded via the hemiketal **24** (Scheme V) required critical control of reaction conditions to avoid the undesired transannular products **25** and **26**.

In the preceding paper[1] we presented evidence that irradiation of 2,3-benzo-2,4-cycloheptadienone (**1**) produces a highly reactive $\Delta^{4,5}$-trans intermediate (**2**). Six examples of



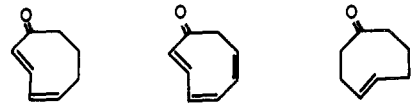
1 **2**

this reaction (with different aryl rings and with different substituents on the seven-membered ring) were described. In each case a trans intermediate analogous to **2** was efficiently trapped with furan. However other reactions of the trans intermediates (dimerization, for example) varied with the particular structure.

We extended this study to the eight-membered ring analogues of **1** with the expectation that the corresponding trans photoproducts might be isolable and more amenable to direct systematic study. It is known, for example, that *trans*-2-cyclooctenone (**3**)[2] is considerably less reactive than *trans*-2-cycloheptenone (**4**).[2d,3]

3 **4**

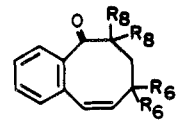
When more than one double bond is present in an unsaturated eight-membered ring ketone, only the α,β-double bond is known to photoisomerize. For example, irradiation of 2,4-cyclooctadienone and 2,4,6-cyclooctatrienone gives only the $\Delta^{2,3}$-trans isomers **5**[4] and **6**.[5] It is possible, however, to photo-



5 **6** **7**

isomerize the $\Delta^{4,5}$ double bond, as in the formation of **7**.[6] We expected, therefore, that if the 2,3-double bond were incorporated in a benzene ring it ought to be possible to isomerize the 4,5-double bond.

In this paper we describe the synthesis and irradiation of three 2,3-benzo-2,4-cyclooctadienones **8**, **14**, and **20**.[7] We find that in all cases a $\Delta^{4,5}$-trans isomer is formed, but that the re-



8 (R_6 = CH_3, R_8 = H)

14 (R_6 = H, R_8 = CH_3)

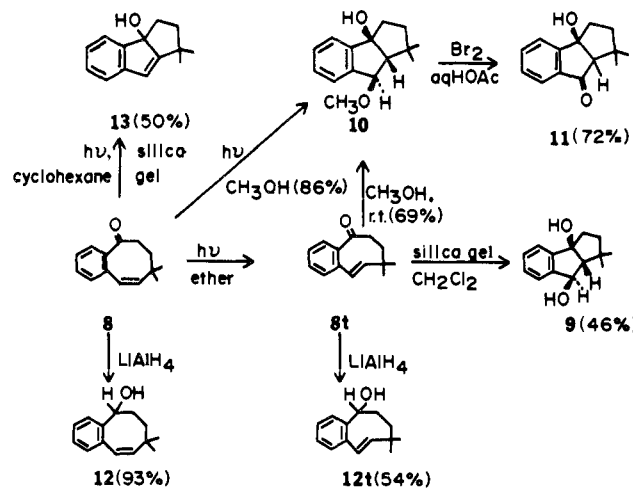
20 (R_6 = R_8 = H)

activity varies enormously with methyl substitution. Also, α-cleavage competes with double bond isomerization in **14** (although similar competition did not occur in the seven-membered analogue[1]). Finally, interesting stereospecific reactions of the $\Delta^{4,5}$-trans isomers of **8**, **14**, and **20** are described.

Results and Discussion

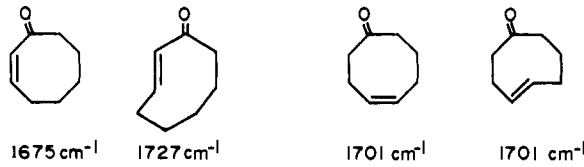
Irradiation of 8. When an ether solution of **8** (the synthesis of **8** is described below) was irradiated through Pyrex, changes occurred in the IR and NMR spectra which suggested that a mixture of **8** (13%) and **8t** (87%) was formed (Scheme I). The

Scheme I

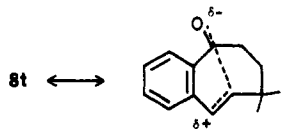


$\nu_{C=O}$ shifted from a pair of bands at 1696 (m) and 1671 (s) cm^{-1} for **8**[8] to a single band at 1657 cm^{-1} for **8t**. This shift of

the carbonyl band to *lower* frequency is remarkable, particularly if compared with the spectra of *cis*- and *trans*-2- or -4-cyclooctenones.[2a,6] The shift to higher frequency in going from



cis- to *trans*-2-cyclooctenone is attributed to deconjugation as a consequence of steric strain. The reported[6] lack of change in carbonyl frequency in the 4-octenones was not commented on. We attribute the low frequency carbonyl band in **8t** to a



strong transannular interaction between the double bond and the carbonyl group. The reactions of **8t** with water and methanol (vide infra) support this view.

Also striking was the decrease in intensity of the singlet at δ 1.02 due to the C(6) *gem*-dimethyl group in **8** and the appearance of two three-proton singlets at δ 1.18 and 1.23 due to the same methyls in **8t.** Since **8t** is chiral[9] the methyls at C(6) are no longer equivalent. Simultaneously, the vinyl protons shift to slightly lower field (δ 5.50 and 6.32 in **8**, δ 5.62 and 6.67 in **8t**) and have a somewhat larger coupling constant (13 Hz in **8**, 15 Hz in **8t**).

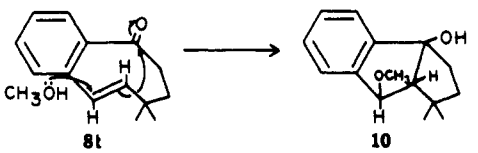
Attempts to purify **8t** by column chromatography on silica gel gave the crystalline diol **9**, formed by transannular addition of water to **8t.** The structure of **9** followed from its spectra. There was no carbonyl, but intense hydroxyl absorption in the infrared, showing that **9** was not a 1,2-adduct of water to **8t.** The UV spectrum was similar to that of indane. The NMR spectrum showed no vinyl protons, but a pair of doublets at δ 4.70 and 2.00 (J = 3 Hz) corresponding to the trans relationship between the methine protons at C(4) and C(5), respectively. This same relationship was observed in the methanol adduct **10** (vide infra).

Treatment of **8t** with methanol at room temperature for 2 h gave (69%) a single methanol adduct assigned structure **10.** The same product was obtained (86%) by irradiation of **8** in methanol. The structure of **10** was clear from its spectra. The IR showed no carbonyl, but strong hydroxyl absorption, and the UV spectrum was similar to that of **9.** The NMR spectrum showed doublets at δ 4.30 and 2.00 (J = 2.5 Hz) for the trans methine protons at C(4) and C(5). Other features of the NMR spectrum were consistent with the assigned structure. The mass spectrum of **10** showed a small $M^+ - H_2O$ and a large $M^+ - CH_3OH$ peak.

It was difficult to obtain **10** analytically pure (this was also true of its analogues **18** and **21**). Oxidative cleavage of **10** with bromine in aqueous acetic acid gave the hydroxyindanone **11**, which was obtained analytically pure. The IR and UV spectra of **11** were typical for an indanone and the IR also showed a hydroxyl band. The NMR spectrum of **11** showed the C(5) methine proton as a singlet at δ 2.23 (somewhat lower field and different multiplicity than in **9** or **10**).

The facile and stereospecific formation of a single water (**9**) or methanol (**10**) adduct of **8t** deserves comment. The addition of methanol and other nucleophiles to *trans*-2-cyclooctenones is well known.[2b,d,4a,d,10] However, we found that methanol does not add at room temperature to *trans*-4-cyclooctenone (**7**).[6] Consequently the 2,3-benzo group markedly increases the reactivity of **8t** (compared to **7**) toward nucleophiles. The striking effect on the carbonyl absorption frequency of **8t**, but not **7**, has already been mentioned (vide supra). It is clear from these results that the polarity of the carbon–carbon double bond must be reversed in **8** and **8t.** In **8** we would expect C(5) to be δ^+ and C(4) to be δ^- due to conjugation of the double bond with the carbonyl group *through* the aromatic ring. In **8t** direct transannular conjugation causes C(4) to be δ^+ and C(5) to be δ^-. Consequently nucleophilic attack occurs at C(4). This is not the case with 2-cyclooctenones where nucleophilic attack occurs at C(3) independent of whether the double bond is cis or trans.

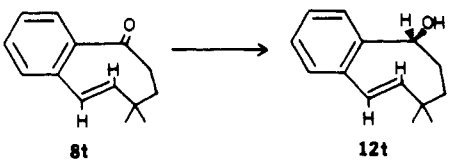
We regard the addition of methanol or water to **8t** as essentially concerted processes (similar to the seven-membered ring analogue[1]). One could in principle obtain four products from the transannular addition of methanol to **8t;** the two



8t **10**

five-membered rings could be fused cis or trans, and the methoxyl or hydroxyl groups could in either case be cis or trans to one another. Only one stereoisomer is formed, suggesting that ring closure is concerted with or rapidly follows nucleophilic attack. Only one face of the double bond is accessible to attack in a *trans*-cyclooctene,[11] since the other face is blocked by the ring carbons. Thus the only observed product is **10.**

Lithium aluminum hydride reduction of **8** gave the corresponding alcohol **12,** but irradiation of **8** in ether followed by similar reduction gave a different alcohol **12t.** Alcohol **12** was an oil, whereas **12t** was crystalline. Reduction of **8t** occurred in a 1,2 manner, not transannularly, since **12t** had two trans vinyl protons in the NMR (δ 5.72 and 6.28, J = 16 Hz). Since **8t** is chiral and a new chiral center is created in the reduction, two diastereomers of **12t** could be formed. However, the reduction was stereospecific and gave only one diastereomer. The product had a sharp melting point, and had only one set of NMR peaks. Particularly sensitive to the possible presence of a second isomer were the methyl peaks; there were only two (δ 1.08, 1.17) as expected for a single diastereomer. Clearly the ring carbons block one face of the carbonyl group from hydride attack. We believe that **12t** is the *RS*(*SR*) diast-



8t **12t**

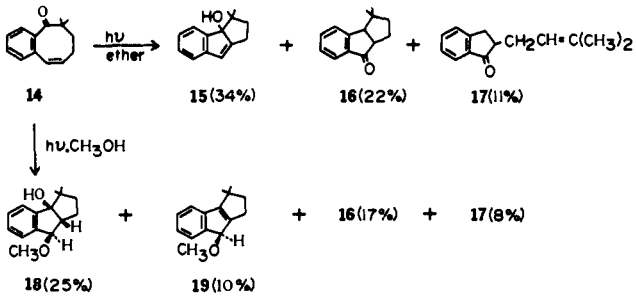
ereomer (shown for only one of the two enantiomers); the hydroxyl group should project "in" toward the carbon–carbon double bond.

Finally, irradiation of **8** absorbed on silica gel and suspended in cyclohexane gave the indenol **13.** The structure of **13** follows from its spectra. It showed a hydroxyl band at 3300 cm^{-1} and a typical indene UV spectrum. The NMR spectrum showed only one vinyl proton as a singlet at δ 5.95 and two methyl singlets (δ 1.18, 1.35) in addition to other expected peaks. We suspect that **13** is formed directly and not through dehydration of **9,** since **9** is not dehydrated by silica gel (compare with the formation of **15** from **14,** vide infra).

Irradiation of 14. In sharp contrast with **8,** irradiation of **14** in ether gave no NMR or IR evidence for the formation of a stable trans intermediate, although one product (**15**) was isolated which was clearly derived from such an intermediate (Scheme II). The irradiation of **14** was stopped after about 50% conversion because secondary photoproducts were formed on prolonged irradiation.

The structures of **15–17** were deduced from their spectra. The properties of **15** and **13** were similar, but differed in ways

Scheme II



which are explicable due to the different positions of the *gem*-dimethyl group. In particular, the vinyl proton in **15** (δ 6.06) was a doublet of doublets with small homoallylic coupling (J = 1 and 2 Hz) with the C(6) methylene protons, whereas in **13** the vinyl proton appeared as a sharp singlet (δ 5.95). Also the difference in chemical shifts of the methyl singlets (δ 0.59, 1.30 in **15**, but δ 1.18, 1.35 in **13**) is a consequence of shielding of the *endo*-methyl in **15** by the aromatic ring.

Compounds **16** and **17** had carbonyl bands at 1715 cm^{-1} and UV spectra characteristic of indanones. Compound **16** was saturated (no vinyl protons in the NMR) and had two methine protons, one a doublet at δ 3.27 (J = 7 Hz) and the other a d × d × d at δ 3.00 (J = 9,7, and 4.5 Hz) corresponding to the ring juncture protons α to the aromatic ring and carbonyl group, respectively. The mass spectrum of **16** showed a strong parent peak (*m/e* 200, 42%) and a base peak at *m/e* 131 corresponding to the plausible loss of a dimethylallyl radical following γ-hydrogen abstraction.[12]

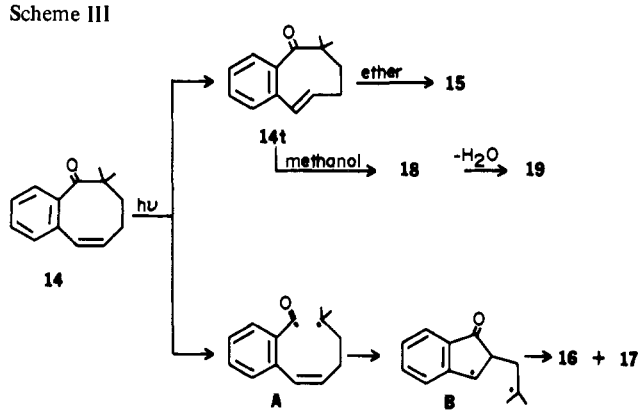
Compound **17** had a vinyl proton at δ 5.11 which was a triplet × septet (J = 6.5 and 1 Hz) and two allylic methyls at δ 1.63 and 1.67 (each a doublet, J = 1 Hz). Irradiation at δ 5.11 collapsed the methyl signals to singlets, whereas irradiation in the methyl region converted the vinyl signal to a triplet, J = 6.5 Hz, thus confirming the $-CH_2CH{=}C(CH_3)_2$ moiety. The mass spectrum of **17** showed in addition to the parent peak (*m/e* 200, 13%) a base peak at *m/e* 132 corresponding to the loss of the side chain (presumably as isoprene).

Irradiation of **14** was more efficient in methanol than in ether; only 4% of **14** was recovered after 3 h, compared to 45% after 4.5 h in ether. The major product from NMR examination of the crude product was the methanol adduct **18**, although isolation was difficult and some of the product was dehydrated to **19** on the chromatography column. Indanones **16** and **17** were still formed. The NMR spectrum of **18** was analogous to that of **10** with differences predictable as a consequence of the different locations of the *gem*-dimethyl group. For example the *endo*-methyl at C(8) in **18** was shielded more by the aromatic ring than the comparable methyl at C(6) in **10** (δ 0.50 vs. 0.77). The C(4) methine protons in **10** and **18** had nearly identical chemical shifts and coupling constants with the adjacent methine proton, supporting the same trans relationship between these protons in both compounds.

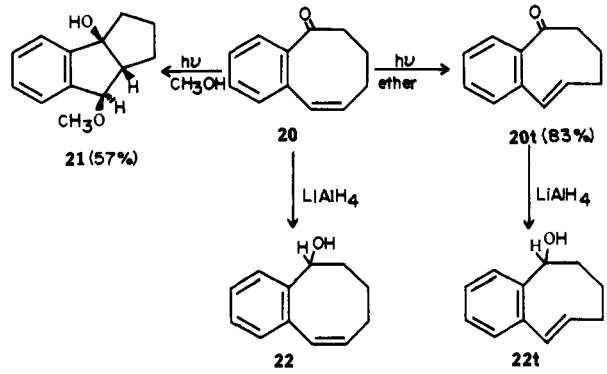
Compound **19** was derived from **18** by loss of water (M^+ 214). The base peak in the mass spectrum of **19** (*m/e* 158) corresponded to loss of isobutylene, as with **15**. The UV spectrum of **19** was consistent with an indene moiety more planar than that in **15**. The methine proton adjacent to the methoxyl group in **19** appeared as a singlet (δ 4.67) at lower field than the corresponding proton in **18**, due to the adjacent double bond.

A plausible mechanism for formation of the photoproducts of **14** is shown in Scheme III. Excitation results either in isomerization of the $\Delta^{4,5}$ double bond to give **14t** or in α-cleavage to give A. By analogy with the addition of methanol to **8t**, we presume that **14t** is the logical precursor of **18**. However, we could obtain no direct evidence for **14t**, which is

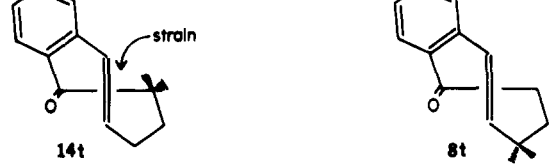
Scheme III



Scheme IV



clearly much more reactive than **8t**. We can only guess at the reasons for this reactivity difference. Models show that in **14t**



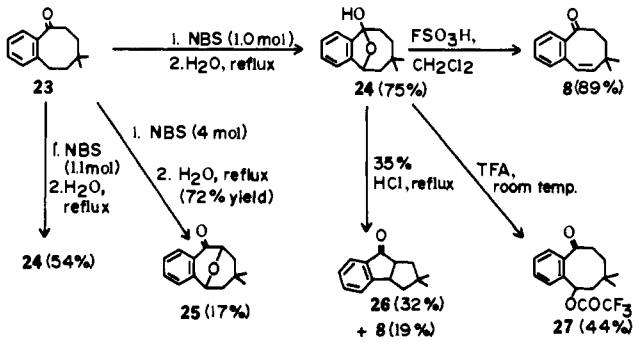
one of the two methyl groups projects directly in toward the trans double bond, undoubtedly increasing the strain. In **8t**, on the contrary, both methyl groups project out, in directions which do not appear to substantially increase the ring strain. This could account for the reactivity difference between the two compounds.

Compound **15** was formed directly in the irradiation of **14**; the vinyl proton at δ 6 .06 was readily apparent in the crude reaction mixture, showing that **15** was not formed by dehydration of a water adduct of **14t** on chromatographic workup. We cannot say with certainty whether **15** is formed directly from an excited state of **14** or whether it is formed from **14t**, but the latter possibility seems more likely since all of this material is diverted to the methanol adduct **18** when the irradiation is carried out in methanol.

α-Cleavage of **14** to A is followed by cyclization to B, which then either closes to give **16** or gives **17** by γ-hydrogen abstraction. We cannot explain why α-cleavage competes with double bond isomerization in the eight-membered ring series, but does not compete in the seven-membered ring analogue.[1]

Irradiation of 20. The photochemistry of **20** (Scheme IV) paralleled closely that of **8**. In ether a mixture of **20** (17%) and **20t** (83%) was produced; the chemical shifts and coupling constants of **8t** and **20t** were nearly identical. In methanol the crystalline adduct **21** was formed. Consistent with **10** and **18**, the C(4) methine proton in **21** appeared at δ 4.15 as a doublet, J = 3 Hz (the C(5) methine proton was not discretely visible).

Scheme V



We presume that **20t** is an intermediate in the formation of **21.**

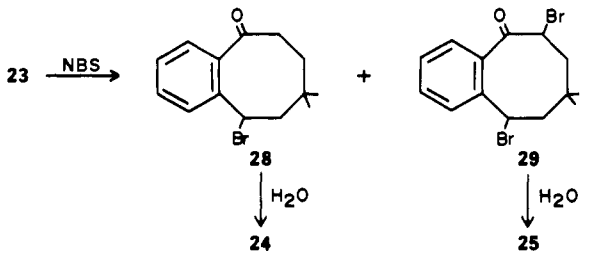
Reduction of **20t** gave the trans alcohol **22t** whose vinyl protons had nearly the same chemical shifts (δ 5.80, 6.31) and coupling constant (J = 15 Hz) as those of **12t.**

A Comparison. Irradiation of **8, 14,** and **20** converts them to the corresponding $\Delta^{4,5}$-trans isomers. With **14,** however, α-cleavage competes with double bond photoisomerization. The trans isomers of **8** and **20** have comparable stabilities; each can be readily detected (NMR, etc.) and is stable for some time at room temperature in solution. In contrast, **14t** could not be detected physically, though it was trapped by reaction with methanol. Thus the location of methyl groups on the *trans*-cyclooctenone ring can substantially alter the strain and hence reactivity of the double bond.

All three trans intermediates react stereospecifically and transannularly with methanol, in a manner which suggests that addition and ring closure are essentially concerted. The polarity of the 4,5-double bonds is reversed in the cis and trans isomers of **8, 14,** and **20,** with C(4) clearly δ^+ and subject to nucleophilic attack in the trans isomers.

Synthetic Procedures. The synthesis of **8** was not trivial and has some interesting features. The most successful route, which was only arrived at after many attempts, is shown across the top of Scheme V. It involved benzylic bromination of **23** with *N*-bromosuccinimide (NBS) followed by careful hydrolysis of the resulting bromide with water (no base; vide infra). This gave the hemiketal **24** as a pale yellow oil. The structure of **24** is based on its spectra and conversion to **8, 26,** and **27.** It showed hydroxyl but no carbonyl absorption in the IR, only aromatic UV absorption, and had an NMR spectrum with two methyl singlets (δ 0.62, 1.08) and a doublet at δ 4.67 (J = 8 Hz) for the methine proton, apparently coupled to only one of the two adjacent methylene protons.

The amount of NBS used in the bromination of **23** was critical to the synthesis of **24.** For example, if only a 10% excess was used, the yield of **24** decreased to 54% and the keto ether **25** was also formed; indeed the latter became the major product (72%) when a large excess of NBS was used. This result must



be a consequence of introducing a second bromine α to the carbonyl group of **23.** The structure of **25** was deduced from its spectra. There was a strong carbonyl band at 1683 cm^{-1}; the NMR spectrum showed singlets at δ 0.48 and 0.94 for the methyls and two doublets of doublets for the bridgehead methine protons, at δ 4.27 (J = 3 and 5 Hz) and at δ 4.90 (J = 1 and 6 Hz) for the C(1) and C(5) protons, respectively.

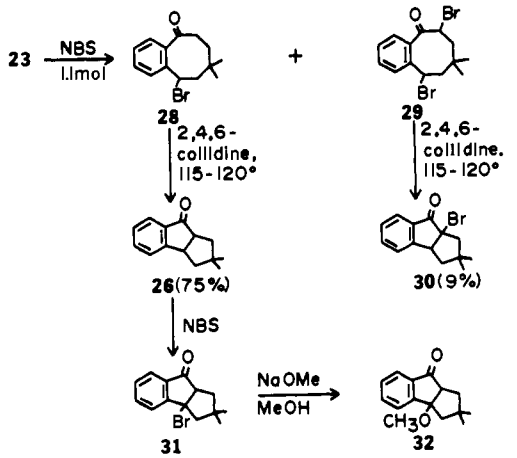
The conversion of **24** to **8** also depended strongly on the reagent. Fluorosulfonic acid gave the desired product in good yield. However, concentrated hydrochloric acid gave low yields of **8** and higher yields of the indanone **26,** and trifluoroacetic acid gave the trifluoroacetate **27.** The structure of **8** was evident from its spectra, as already described in the section on its irradiation.

The structure of **26** followed from its spectra, alternate synthesis, and reactions (vide infra). It had an IR ($\nu_{C=O}$ 1700 cm^{-1}) and UV spectrum characteristic of an indanone. The ring juncture methine protons appeared as two quartets (J = 8 Hz) at δ 3.17 (C(1)) and 3.88 (C(5)); treatment of **26** with sodium methoxide in CH_3OD removed the δ 3.17 signal, and converted the peak at δ 3.88 to a triplet.

The structure of **27** was also clear from its spectra. There were two carbonyl bands in the IR (1773, 1692 cm^{-1}), two methyl singlets for groups cis and trans to the trifluoroacetate function (δ 1.00, 1.12), and the C(4) methine proton was a doublet of doublets, J = 4 and 10 Hz, at δ 6.10.

The seven-membered ring analogue of **8** was synthesized[13] by bromination of the saturated precursor with NBS and elimination of HBr with 2,4,6-collidine. When this approach was applied to **8** (Scheme VI), we obtained instead of **8** the

Scheme VI



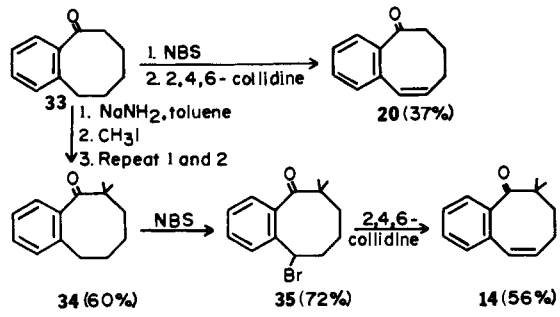
transannular elimination product **26** (75%). In addition, a bromo ketone **30** was obtained (9%) as a consequence of dibromination to **29** in the first step. The yield of **30** could be increased by using excess NBS. The position of the bromine in **30** was indicated in the following ways. NBS bromination of **26** gave **31,** which readily reacted with dilute sodium methoxide in methanol to give a methyl ether (**32**). Bromo ketone **30,** however, was inert toward sodium methoxide in methanol under the same conditions. This difference would be expected for a tertiary benzylic bromide (**31**) compared with an α-bromo ketone (**30**). Also, the methine proton (C(5)) in **30** appeared at lower field (δ 4.14) than the methine proton (C(1)) in **31** (δ 3.52).

The aqueous hydrolysis of **28** to **24** (Scheme V) provides an interesting method for avoiding the undesired transannular elimination (**28** to **26,** Scheme VI) observed with base, and may provide a general path for selecting between these alternatives.

Finally, in Scheme VII we show the synthesis of **14** and **20,** which were simpler than the synthesis of **8.** Bromination of **33**[14] and collidine elimination gave **20** in moderate yield. Apparently the *gem*-dimethyl group at C(6) in **23** must be responsible for preventing the desired 1,2-elimination in that case by sterically hindering attack of base at C(5); when these methyls are absent, as in **33,** the desired elimination occurs.

Methylation of **33** gave **34,** which could then easily be con-

Scheme VII



verted to **14** by bromination and elimination. In this case the intermediate bromo ketone **35** was nicely crystalline and could be purified prior to the elimination step. The structures of **20**, **34**, **35**, and **14** (Scheme VII) were all certain from their spectra and method of synthesis (see Experimental Section).

Experimental Section[15]

3,4-Benzo-7,7-dimethylbicyclo[3.3.0]oct-3-en-2-one (26). To a solution of 4.0 g (0.02 mol) of 2,3-benzo-6,6-dimethylcyclooct-2-en-1-one (**23**)[16] in 100 mL of carbon tetrachloride was added 3.6 g (0.02 mol) of freshly recrystallized *N*-bromosuccinimide and 0.1 g of azobisisobutyronitrile. The mixture was heated at reflux for 2 h, then cooled. The succinimide was removed by filtration and the solvent was evaporated to leave a residue which showed (NMR) a doublet of doublets at δ 5.40 assigned to the C(4) methine proton of 2,3-benzo-4-bromo-6,6-dimethylcyclooct-2-en-1-one (**28**). The NMR spectrum also showed a small triplet at δ 4.37 due to the C(8) methine proton of 2,3-benzo-4,8-dibromo-6,6-dimethylcyclooct-2-en-1-one (**29**), formed as a minor reaction product. The crude bromination product was heated with 4.9 g (0.04 mol) of 2,4,6-collidine at 115–120 °C for 12 h. The cooled reaction mixture was triturated with carbon tetrachloride, and the CCl_4 layer was washed with 10% hydrochloric acid, water, and dried ($MgSO_4$). Removal of the solvent under reduced pressure gave the crude product as an oily residue which by analytical GLC (5 ft × 0.125 in. column, 3% SE-30 on 100–120 mesh Raroporl, 30 mL/min N_2, 180 °C) consisted of two products, **26** (retention time 4.4 min) and **30** (retention time 8.3 min). Column chromatography[15] gave as the first fraction 3.0 g (75%) of **26** as a pale yellow oil. The second fraction gave 0.5 g (9%) of a bromine-containing pale yellow oil considered to be 3,4-benzo-1-bromo-7,7-dimethylbicyclo[3.3.0]-oct-3-en-2-one (**30**). Both products could also be purified by preparative GLC (5 ft × 0.25 in. column, 20% SE-30 on Chromosorb W, 80–100 mesh, 190 °C).

For **26**: IR (neat) $\nu_{C=O}$ 1700 cm^{-1}; λ_{max} (cyclohexane) 294 nm (ϵ 3610), 285 (3350), 247 (14 350), 239 (17 030);[17] NMR[18] (CCl_4) δ 0.85 (s, 3 H, syn-C(7) methyl, 1.7), 1.07 (s, 3 H, anti-C(7) methyl, 1.0), 1.13–2.33 (m, 4 H, methylenes), 3.17 (q, 1 H, J = 8 Hz, C(1) methine, 5.7), 3.88 (br q, 1 H, J = 8 Hz, C(5) methine, 2.0), 7.15–7.78 (m, 4 H, arom); mass spectrum, *m/e* (rel intensity) 200 (72), 185 (46), 167 (57), 145 (42), 144 (100), 131 (24), 116 (24), 115 (47); treatment of **26** (150 mg) with a solution of sodium methoxide (250 mg) in methanol-d_1 (3.5 mL) at room temperature for 4 h gave 129 mg of **26**-d_1 lacking the 1 H signal at δ 3.17 and with the signal at δ 3.88 converted to a broad triplet.

Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 84.15; H, 8.10.

For **30**: IR (neat) $\nu_{C=O}$ 1706 cm^{-1}; λ_{max} (cyclohexane) 301 nm (ϵ 2970), 292 (3320), 248 (16 580); NMR (CCl_4) δ 0.75 (s, 3 H, syn-C(7) methyl, 1.1), 1.27 (s, 3 H, anti-C(7) methyl, 1.0), 1.43 (dd, 1 H, J = 6, 12.5 Hz, syn-C(6) methylene, 2.0), 2.27 (dd, 1 H, J = 10, 12.5 Hz, anti-C(6) methylene, 1.3), 2.32 (s, 2 H, C(8) methylene, syn 3.7, anti 2.7), 4.14 (dd, 1 H, J = 6, 10 Hz, C(5) methine, 3.4), 7.20–7.88 (m, 4 H, arom); mass spectrum, *m/e* (rel intensity) 280 (15), 278 (16), 200 (79), 199 (100), 185 (15), 183 (23), 181 (15), 167 (20), 145 (17), 144 (43), 143 (53), 115 (62). Treatment of **30** with sodium methoxide in CH_3OD did not result in any deuterium incorporation.

Anal. Calcd for $C_{14}H_{15}BrO$: C, 60.23; H, 5.42. Found: C, 60.04; H, 5.60.

When the reaction was repeated using, in the bromination step, 207 mg (1.0 mmol) of **23**, 900 mg (5.0 mmol) of NBS, 25 mg of AIBN, and 15 mL of CCl_4, the yields were 96 mg (48%) of **26** and 95 mg (34%) of **30**.

3,4-Benzo-7,7-dimethyl-5-methoxybicyclo[3.3.0]oct-3-en-2-one (32). A mixture containing 1.0 g (5 mmol) of **26**, 1.8 g (10 mmol) of *N*-bromosuccinimide, and 25 mg of azobisisobutyronitrile in 30 mL of carbon tetrachloride was heated at reflux for 4 h. The succinimide was removed by filtration and the solvent was evaporated. The crude residue (3,4-benzo-5-bromo-7,7-dimethylbicyclo[3.3.0]oct-3-en-2-one, **31**) had an NMR spectrum which showed a doublet of doublets at δ 3.52 (C(1) methine). This residue was treated with a solution of sodium methoxide (2.5 g) in methanol (50 mL) at room temperature for 4 h. Evaporation of the solvent under reduced pressure gave a reddish oil which was triturated with carbon tetrachloride. The CCl_4 layer was washed with water and dried ($MgSO_4$). Removal of the solvent under reduced pressure gave an oily residue which, on analytical GLC (5 ft × 0.125 in. column, 5% FFAP on Chromosorb G, 100–120 mesh, 30 mL/min of N_2, 195°C) showed a single product, retention time 10.2 min. Column chromatography[15] gave 0.93 g (82%) of **32** as a pale yellow oil. The product could be further purified by preparative GLC (5 ft × 0.25 in. column, 20% FFAP on Chromosorb W, 80–100 mesh, 205 °C): IR (neat) $\nu_{C=O}$ 1707 cm^{-1}; λ_{max}^{MeOH} 290 nm (ϵ 1820), 283 (1820), 244 (13 210); NMR (CCl_4) δ 0.70 (s, 3 H, methyl), 1.12 (s, 3 H, methyl), 1.47–2.30 (m, 4 H, C(6) and C(8) methylenes), 2.87 (s, 3 H, methoxyl), 3.05 (dd, 1 H, J = 6, 9 Hz, C(1) methine), 7.07–7.65 (m, 4 H, arom); mass spectrum, *m/e* (rel intensity) 230 (60), 215 (27), 202 (26), 183 (36), 174 (95), 173 (90), 159 (100), 115 (32).

Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.22; H, 7.89.

Similar treatment of **30** with sodium methoxide in methanol gave no reaction.

7,8-Benzo-4,4-dimethyl-9-oxabicyclo[4.2.1]non-7-en-1-ol (24). A mixture containing 2 g (0.01 mol) of 6,6-dimethyl-2,3-benzocyclooct-2-en-1-one (**23**),[16] 1.8 g (0.01 mol) of *N*-bromosuccinimide, and 0.03 g of azobisisobutyronitrile in 50 mL of carbon tetrachloride was heated at reflux for 2 h. The succinimide was removed by filtration and the solvent was evaporated. The residue was refluxed with 150 mL of water for 20 h. The oil which separated was extracted with chloroform, and the chloroform layer was washed with water and dried ($MgSO_4$). Removal of the solvent under reduced pressure and column chromatography[15] of the residue gave as the first fraction 90 mg (4.5%) of recovered **23** and as the second fraction 1.64 g (75%) of **24** as a pale yellow oil. The product could also be purified by GLC (5 ft × 0.25 in. 20% SE-30 on Chromosorb W, 200 °C): IR (neat) ν_{OH} 3375 cm^{-1}; λ_{max}^{MeOH} 268 nm (ϵ 690), 261 (790), 255 (600); NMR (CCl_4) δ 0.62 (s, 3 H, methyl), 1.08 (s, 3 H, methyl), 1.2–2.5 (m, 6 H, methylenes), 4.33 (br s, 1 H, hydroxyl), 4.67 (d, 1 H, J = 8 Hz, bridgehead), 6.63–6.87 (m, 1 H, arom), 6.93–7.17 (m, 3 H, arom); mass spectrum, *m/e* (rel intensity) 218 (9.5), 200 (25), 185 (21), 172 (16), 169 (23), 167 (35), 157 (23), 147 (100), 145 (30), 144 (49), 141 (21), 131 (81), 129 (46), 128 (59), 115 (52), 105 (26), 91 (26), 77 (43).

Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.02; H, 8.33.

3,4-Benzo-7,7-dimethyl-9-oxabicyclo[3.3.1]non-3-en-2-one (25). A mixture containing 1 g (5.0 mmol) of 6,6-dimethyl-2,3-benzocyclooct-2-en-1-one (**23**),[16] 3.6 g (20 mmol) of *N*-bromosuccinimide, and 0.02 g of azobisisobutyronitrile in 50 mL of carbon tetrachloride was heated at reflux for 2 h. The succinimide was removed by filtration and the solvent was evaporated. The residue was refluxed with 100 mL of water for 20 h. Workup as in the preparation of **24** and column chromatography gave 0.78 g (72%) of **25** as a colorless oil. Purification could also be accomplished by GLC (5 ft × 0.125 in. 20% SE-30 on Chromosorb W, 200 °C): IR (neat $\nu_{C=O}$ 1683 cm^{-1}; λ_{max}^{MeOH} 300 nm (ϵ 1080), 291 (1170), 250 (10 820); NMR (CCl_4) δ 0.48 (s, 3 H, methyl), 0.94 (s, 3 H, methyl), 1.37–2.27 (m, 4 H, methylenes), 4.27 (dd, 1 H, J = 3, 5 Hz, C(1) methine), 4.90 (dd, 1 H, J = 1, 6 Hz, C(5) methine), 6.87–7.50 (m, 3 H, arom) 7.67–7.88 (m, 1H, arom); mass spectrum, *m/e* (rel intensity) 216 (9), 160 (12), 132 (16), 131 (100), 103 (26), 77 (26).

Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.79; H, 7.35.

The ratio of **23** to *N*-bromosuccinimide is critical in the preparation of **24** and **25**. When the above procedure was repeated, but with a mole ratio of **23** to NBS of 1:1.1, the products were 54% of **24** and 17% of **25**. The two compounds could be separated by GLC (5 ft × 0.125 in.

column, 3% SE-30 on Raroporl, 30 mL/min of N_2, 160 °C). The retention times were 8.2 min for **24** and 5.9 min for **25.**

2,3-Benzo-6,6-dimethyl-2,4-cyclooctadienone (8). A three-necked flask was modified by having a narrow exit tube at the base that followed the curve of the flask to the top, and was then bent down in a U shape. To 1 mL of fluorosulfonic acid placed in the flask, swept with dry nitrogen and cooled to −78 °C, was added dropwise a solution of 200 mg (0.916 mmol) of **24** in 3 mL of CH_2Cl_2. The mixture was stirred at −35 °C for 2 h. The resulting yellow solution was forced by nitrogen pressure out the exit tube into a vigorously stirred slurry of ice and water. The CH_2Cl_2 layer, combined with CH_2Cl_2 washings of the aqueous layer, was washed with 5% sodium carbonate solution, water, and dried ($MgSO_4$). Removal of the solvent gave a pale yellow oil, which was subjected to column chromatography[15] to give 164 mg (90%) of **8** as a pale yellow oil. The product could also be purified by GLC (5 ft × 0.25 in. column, 20% SE-30 on Chromosorb W, 80–100 mesh, 100 mL/min He flow, 205 °C, retention time 15.4 min): IR (neat $\nu_{C=O}$ 1696 (m), 1671 (s) cm^{-1}; λ_{max} (cyclohexane) 306 nm (ϵ 2150), 248 (sh, 7720), 229 (21 740); NMR (CCl_4) δ 1.02 (s, 6 H, *gem*-dimethyl), 1.72–2.00 (m, 2 H, C(7) methylene), 2.52–2.75 (m, 2 H, C(8) methylene), 5.50 (d, 1 H, J = 13 Hz, C(5) vinyl), 6.32 (d, 1 H, J = 13 Hz, C(4) vinyl), 6.83–7.45 (m, 4 H, arom); mass spectrum, *m/e* (rel intensity) 200 (46.5), 185 (30), 172 (63), 158 (31), 157 (70), 144 (34), 143 (49), 129 (100), 128 (76), 127 (29), 115 (56); treatment of **8** (200 mg) with sodium methoxide (250 mg) in deuteriomethanol (5 mL) gave the 8,8-dideuterio ketone (190 mg) in which the multiplet at δ 2.5–2.75 (C(8) methylene) was absent and the multiplet at δ 1.72–2.00 became a broad singlet at δ 1.87 (C(7) methylene).

Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.88; H, 8.09.

Treatment of **24** (0.23 g, 1.05 mmol) with 5 mL of 35% hydrochloric acid (reflux, 19 h) gave, after workup as above, but with chloroform in place of methylene chloride, only 40 mg (19%) of **8** and 67 mg (32%) of **26.**

2,3-Benzo-6,6-dimethyl-4-trifluoroacetoxy-2-cyclooctenone (27). A solution containing 0.24 g (1.1 mmol) of **24** in 1 mL of trifluoroacetic acid prepared at ice temperature was stirred at room temperature for 20 h, then poured into ice water. The resulting brown oil was extracted with chloroform, and the chloroform layer was washed with 5% sodium carbonate solution, water, and dried ($MgSO_4$). Removal of the solvent under reduced pressure and column chromatography of the oily residue gave 0.16 g (44%) of **27** as a colorless oil. The product could also be purified by GLC (5 ft × 0.25 in. column, 20% SE-30 on Chromosorb W, 80–100 mesh, 200 °C; for analysis, 5 ft × 0.125 in. column, 3% SE-30 on Raroporl 30, 100–120 mesh, 30 mL/min of N_2, 170 °C; retention time 94 s): IR (neat) $\nu_{C=O}$ 1773, 1692 cm^{-1}; λ_{max}^{MeOH} 268 nm (ϵ 960); NMR (CCl_4) δ 1.00 (s, 3 H, methyl), 1.12 (s, 3 H, methyl), 1.33–1.67 (m, 2 H, C(7) methylene), 1.82 (d, 1 H, J = 4 Hz, C(5) proton), 2.00 (d, 1 H, J = 10 Hz, C(5) proton), 2.40–2.73 (m, 2 H, C(8) methylene), 6.10 (dd, 1 H, J = 4, 10 Hz, C(4) methine), 6.82–7.40 (m, 4 H, arom); mass spectrum, *m/e* (rel intensity) 314 (5), 243 (5), 200 (13), 185 (10), 167 (10), 157 (10), 147 (16), 144 (19), 133 (22), 131 (100). The compound was not analyzed.

Irradiation of 8 in Methanol; 2,3-Benzo-6,6-dimethyl-*anti*-4-methoxybicyclo[3.3.0]oct-2-en-1-ol (10). A solution containing 60 mg (1.3 mmol) of **8** in 7 mL of methanol was degassed and irradiated (Pyrex) for 2 h. Evaporation of the solvent and column chromatography of the residue gave 55 mg (82%) of **10** as a pale yellow oil: IR (neat) ν_{OH} 3425 cm^{-1}; λ_{max}^{MeOH} 270 nm (ϵ 580), 262 (600), 256 (580); NMR (CCl_4) δ 0.77 (s, 3 H, C(6) methyl), 1.17 (s, 3 H, C(6) methyl), 0.95–2.23 (m, 4 H, methylenes), 2.00 (d, 1 H, J = 2.5 Hz, C(5) methine), 3.15 (s, 3 H, methoxyl), 3.23 (s, 1 H, hydroxyl, exchanges in D_2O), 4.30 (d, 1 H, J = 2.5 Hz, C(4) methine), 7.00–7.25 (m, 4 H, arom); mass spectrum, *m/e* (rel intensity) 232 (4), 214 (7), 200 (83), 185 (32), 172 (33), 167 (82), 162 (46), 161 (100), 158 (46), 147 (33), 145 (38), 144 (36), 131 (28), 129 (29), 128 (33), 115 (28), 91 (18), 77 (26). Similar irradiation of **8**-d_2 (50 mg, deuterium at C(8)) in 6.5 mL of methanol gave **10**-d_2 (45 mg, deuterium at C(8)), whose NMR spectrum differed from that of **10** in that the 4 H multiplet at δ 0.95–2.23 was converted to two 1 H doublets at δ 1.10 and 1.58, J = 12 Hz, due to the methylene at C(7). Compound **10** was sensitive and could not be obtained analytically pure.

2,3-Benzo-6,6-dimethylbicyclo[3.3.0]oct-2-en-1-ol-4-one (11). To a solution containing 100 mg (0.43 mmol) of **10** in 10 mL of 60% aqueous acetic acid was added 1 mL of bromine with ice cooling, and the resulting solution was stirred at room temperature for 2 days. The reaction mixture was diluted with 50 mL of water, neutralized with 10% sodium bicarbonate solution, and extracted with chloroform. The chloroform layer was washed with water, dried ($MgSO_4$), and concentrated to leave a yellow oil which was subjected to column chromatography (chloroform eluent) to give 67 mg (72%) of **11** as a viscous yellow oil. The product could be further purified by preparative GLC (5 ft × 0.25 in. column, 20% SE-30 on Chromosorb W, 80–100 mesh, 100 mL/min of He, 205 °C, retention time 28 min): IR (neat) ν_{OH} 3458, $\nu_{C=O}$ 1704 cm^{-1}; λ_{max}^{MeOH} 290 nm (ϵ 2000), 283 (2040), 245 (12 260); NMR (CCl_4) δ 0.82 (s, 3 H, methyl), 1.20 (s, 3 H, methyl), 1.25–1.67 (m, 2 H, C(7) methylene), 1.90–2.33 (m, 2 H, C(8) methylene), 2.23 (s, 1 H, C(5) methine), 3.73 (br s, 1 H, hydroxyl), 7.15–7.53 (m, 4 H, arom); mass spectrum, *m/e* (rel intensity) 216 (53), 198 (43), 187 (22), 183 (93), 173 (26), 155 (33), 148 (61), 147 (100), 146 (35), 129 (18), 128 (18), 115 (27), 105 (35), 91 (15), 77 (40).

Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.84; H, 7.34.

Irradiation of 8 in Ether; Formation of 8t. A solution containing 50 mg (0.25 mmol) of **8** in 5 mL of ether was degassed and irradiated (Pyrex) for 2 h. NMR analysis (using vinyl proton peaks at δ 6.32 for **8** and 6.67 for **8t**) showed that the solution contained 13% of **8** and 87% of a new ketone assigned structure **8t.** Evaporation of the solvent gave crude **8t** as a pale yellow oil from which the following properties were deduced: IR (neat) $\nu_{C=O}$ 1657 cm^{-1}; λ_{max} (cyclohexane) 287 nm (ϵ 1880, sh), 228 (16 030); NMR (CCl_4) δ 1.18 (s, 3 H, methyl), 1.23 (s, 3 H, methyl), 1.80–2.45 (m, 4 H, methylenes), 5.62 (d, 1 H, J = 15 Hz, C(5) vinyl), 6.67 (d, 1 H, J = 15 Hz, C(4) vinyl), 6.83–7.47 (m, 4 H, arom); mass spectrum, *m/e* (rel intensity) 200 (52), 185 (32), 172 (58), 157 (54), 144 (100). Upon standing at room temperature, **8t** gradually reverted to **8** (monitored by NMR, half-life 2 days).

Reaction of 8t with Methanol. A solution of 50 mg (0.25 mmol) of **8** in 6 mL of ether was degassed and irradiated (Pyrex) for 1.5 h. The resulting solution of **8t** (NMR) was evaporated and the residue was dissolved in 5 mL of methanol and stirred at room temperature for 2 h. Workup gave 39 mg (67%) of **10,** identical (spectra) with the material obtained by irradiating **8** in methanol.

2,3-Benzo-6,6-dimethylbicyclo[3.3.0]oct-2-en-1,4-diol (9). A solution of 30 mg (0.15 mmol) of **8** in 3 mL of ether was irradiated (Pyrex) for 2 h. The resulting solution of **8t** (NMR) was column chromatographed to give 15 mg (46%) of **9,** which was further purified by recrystallization from hexanes to give colorless needles, mp 150–151 °C: IR (Nujol) ν_{OH} 3320 cm^{-1}; λ_{max}^{MeOH} 270 nm (ϵ 930), 263 (960), 256 (830), 250 (710); NMR ($CDCl_3$) δ 0.88 (s, 3 H, methyl), 1.20 (s, 3 H, methyl), 1.03–2.25 (m, 4 H, methylenes), 2.00 (d, 1 H, J = 3 Hz, C(5) methine), 2.85 (br s, 2 H, hydroxyls), 4.70 (d, 1 H, J = 3 Hz, C(4) methine), 7.00–7.37 (m, 4 H, arom); mass spectrum, *m/e* (rel intensity) 218 (6), 200 (19), 148 (73), 147 (100), 144 (21).

Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.98; H, 8.33.

2,3-Benzo-6,6-dimethyl-2,4-cyclooctadienol (12). To a suspension of 11.4 mg of lithium aluminum hydride in 4 mL of ether at 0–5 °C was added dropwise with stirring a solution of 80 mg (0.4 mmol) of **8** in 2 mL of ether. The mixture was refluxed for 2 h. After cooling to room temperature, excess hydride was destroyed with water and the ether layer and extracts were washed with saturated sodium chloride solution and dried ($MgSO_4$). Removal of the solvent gave a pale yellow oil which, on column chromatography, gave 75 mg (93%) of nearly pure **12** as an oil: IR (neat) ν_{OH} 3400 cm^{-1}; λ_{max} (cyclohexane) 239 nm (ϵ 7580), 217 (sh, 4290); NMR (CCl_4) δ 0.88 (s, 3 H, methyl), 1.03 (s, 3 H, methyl), 1.12–2.28 (m, 4 H, methylenes), 2.90 (s, 1 H, hydroxyl), 4.87 (dd, 1 H, J = 6, 11 Hz, C(1) methine), 5.33 (d, 1 H, J = 12 Hz, C(5) vinyl), 5.98 (d, 1 H, J = 12 Hz, C(4) vinyl), 6.68–7.40 (m, 4 H, arom); mass spectrum, *m/e* (rel intensity) 202 (22), 184 (5), 173 (12), 169 (14), 159 (17), 146 (100), 145 (52), 141 (25), 132 (23), 131 (75), 129 (30), 128 (49), 115 (33), 91 (34), 77 (33). The compound was analyzed as its acetate, as attempts to further purify it by GLC failed because of its thermal instability.

2,3-Benzo-6,6-dimethyl-2,4-cyclooctadienyl Acetate (36). A solution containing 60 mg (0.3 mmol) of **12** in 6 mL of acetic anhydride and 20 mL of acetic acid was heated at 100 °C for 2 h. The reaction mixture was concentrated under reduced pressure to leave a yellow oil, which was triturated with chloroform. The chloroform layer was washed with water and dried ($MgSO_4$). Removal of the solvent and

column chromatography of the residue gave 67 mg (92%) of **36** as a colorless oil which could be further purified by GLC (5 ft × 0.25 in. column, 6% SE-30 on Chromosorb G, 80–100 mesh, 180 °C): IR (neat) $\nu_{C=O}$ 1732 cm^{-1}; λ_{max} (cyclohexane) 241 nm (ϵ 7760), 217 (sh, 4300); NMR (CCl_4) δ 0.95 (s, 3 H, C(6) methyl), 1.17 (s, 3 H, C(6) methyl), 2.00 (s, 3 H, acetyl), 1.0–2.3 (m, 4 H, methylenes), 5.43 (d, 1 H, J = 12 Hz, C(5) vinyl), 5.88 (dd, 1 H, J = 5, 11 Hz, C(1) methine), 6.10 (d, 1 H, J = 12 Hz, C(4) vinyl), 6.80–7.27 (m, 4 H, arom); mass spectrum, *m/e* (rel intensity) 244 (10), 202 (72), 173 (19), 169 (18), 159 (18), 146 (100), 145 (28), 141 (29), 132 (24), 131 (35), 129 (26), 128 (40), 115 (23), 91 (14), 77 (13).

Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.53; H, 8.31.

(4*E*)-2,3-Benzo-6,6-dimethyl-2,4-cyclooctadienol (12t). A solution of 100 mg (0.5 mmol) of **8** in 20 mL of ether was degassed and irradiated (Pyrex) for 1.5 h. The conversion to **8t** was followed by NMR. The solvent was evaporated and the residue was taken up in 3 mL of ether and added dropwise at 0–5 °C to a suspension of 11.4 mg of lithium aluminum hydride in 5 mL of ether. This mixture was refluxed for 2 h. Workup as in the preparation of **12** and column chromatography gave 56 mg (54%) of **12t** as colorless prisms (pentane), mp 85–87 °C: IR (Nujol) ν_{OH} 3300, $\nu_{C=C}$ 1645 cm^{-1}; λ_{max} (cyclohexane) 243 nm (ϵ 7030), 225 (sh, 5920); NMR (CCl_4) δ 1.08 (s, 3 H, methyl), 1.17 (s, 3 H, methyl), 1.35–2.25 (m, 4 H, methylenes), 2.42 (br s, 1 H, hydroxyl), 4.62 (dd, 1 H, J = 1.5, 7.5 Hz, C(1) methine), 5.72 (d, 1 H, J = 16 Hz, C(5) vinyl), 6.28 (d, 1 H, J = 16 Hz, C(4) vinyl), 6.95 (s, 4 H, arom); mass spectrum, *m/e* (rel intensity) 202 (14), 184 (34), 169 (74), 159 (27), 142 (29), 141 (100), 131 (35), 129 (40), 128 (72), 115 (33), 91 (23), 77 (22).

Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.95; H, 8.89. In addition, 7 mg (7%) of **12** was isolated from the column chromatography.

2,3-Benzo-6,6-dimethylbicyclo[3.3.0]octa-2,4-dien-1-ol (13). A solution of 30 mg (0.15 mmol) of **8** in 4 mL of cyclohexane was shaken with 0.4 g of Davidson 950 60–200 mesh silica gel (activated at 150 °C for 10 h), and the degassed mixture was irradiated (Pyrex) for 2 h. The tube contents were filtered and the silica gel was slurried with portions of methylene chloride and filtered. Combined organic layers were evaporated and the resulting yellow residue, after column chromatography, gave 15 mg (50%) of **13** as colorless prisms (pentane), mp 120–121 °C: IR (Nujol) ν_{OH} 3300 cm^{-1}; λ_{max} (cyclohexane) 307 nm (ϵ 1060, sh) 295 (sh, 2670), 285 (sh, 4390), 276 (4790), 233 (4880); NMR (CCl_4) δ 1.18 (s, 3 H, methyl), 1.35 (s, 3 H, methyl), 1.73–2.65 (m, 4 H, methylenes), 5.95 (s, 1 H, vinyl), 6.70–7.25 (m, 4 H, arom); mass spectrum, *m/e* (rel intensity) 200 (12), 185 (5), 182 (9), 172 (40), 169 (12), 167 (26), 157 (13), 152 (15), 145 (17), 144 (100), 129 (17), 128 (21), 116 (14), 115 (20).

Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.96; H, 8.03.

Irradiation of 4-Cyclooctenone in Methanol. A solution of 37 mg (0.3 mmol) of *cis*-4-cyclooctenone[6] in 7 mL of methanol was irradiated (Pyrex) for 20 h. The mixture, analyzed by GLC (5 ft × 0.125 in. column, 5% FFAP on Chromosorb G, 100–120 mesh, 115 °C) contained only *cis*- (25%) and *trans*-4-cyclooctenes (75%).

2,3-Benzo-8,8-dimethyl-2,4-cyclooctadienone (14). 2,3-Benzo-2-cyclooctenone[14] (13.05 g, 75 mmol) was methylated twice (toluene, sodamide, methyl iodide) by the procedure used to synthesize the seven-membered ring homologue[1] and gave 9 g (60%) of 2,3-benzo-8,8-dimethyl-2-cyclooctenone (**34**) as an oil, bp 93–95 °C (0.5 Torr): IR (neat) $\nu_{C=O}$ 1680 cm^{-1}; NMR (CCl_4) δ 1.10 (s, 6 H, methyls), 1.60–1.80 (m, 6 H, C(5), C(6), and C(7) methylenes), 2.65–2.90 (m, 2 H, C(4), methylene), 6.80–7.10 (m, 4 H, arom).

Bromination of **34** (9 g, 44.5 mmol) with 8.85 g (50 mmol) of *N*-bromosuccinimide and 0.2 g of benzoyl peroxide in 110 mL of refluxing carbon tetrachloride gave, after recrystallization from hexane, 9 g (72%) of 2,3-benzo-4-bromo-8,8-dimethyl-2-cyclooctenone (**35**), mp 109–110 °C: IR (Nujol) $\nu_{C=O}$ 1675 cm^{-1}; NMR ($CDCl_3$) δ 1.08 (s, 3 H, methyl) 1.21 (s, 3 H, methyl), 1.50–1.90 (m, 4 H, C(6) and C(7) methylenes), 2.20–2.60 (m, 2 H, C(5) methylene), 5.28 (t, 1 H, J = 7 Hz, C(4) methine), 6.75–7.50 (m, 4 H, arom); mass spectrum, *m/e* (rel intensity) 282, 280 (3), 201 (36), 41 (100).

Dehydrobromination of **35** (7.5 g, 27 mmol) with 10 mL of 2,4,6-collidine at 135–145 °C overnight gave 3 g (56%) of **14,** bp 100–115 °C (0.5 Torr). Column chromatography (50 g of silica gel-60) gave 2.2 g (41%) of pure **14** (solidifies in the refrigerator): IR (neat) $\nu_{C=O}$ 1685 cm^{-1}; λ_{max} (cyclohexane) 300 nm (ϵ 250, flat) 246 (sh, 16 000), 230 (19 500); NMR (CCl_4) δ 1.13 (s, 6 H, methyls), 1.60–1.90 (m, 2 H, C(7) methylene), 2.00–2.50 (m, 2 H, C(6) methylene), 5.50 (dt, 1 H, J = 11, 5 Hz, C(5) vinyl), 6.25 (br d, 1 H, J = 11 Hz, C(4) vinyl), 6.70–7.20 (m, 4 H, aryl); mass spectrum, *m/e* (rel intensity) 200 (8), 144 (100). An analytical sample was prepared by GLC (6 ft × 0.25 in. column, 10% XF 1150 on Chromosorb W, 180 °C).

Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 84.01; H, 7.91.

Irradiation of 14 in Ether. A solution of **14** (500 mg, 2.5 mmol) in 50 mL of ether (freshly distilled from lithium aluminum hydride) was irradiated (Pyrex) for 4.5 h. The solvent was evaporated and the residue was chromatographed on 50 g of silica gel and collected as three main fractions. Fraction 1 (225 mg, 45%) was recovered **14.** Fraction 2 (124 mg) was a mixture of two compounds which could be separated by GLC (5 ft × 0.25 in. column, 10% XF 1150 on Chromosorb W, 190 °C). The ratio of these compounds, assigned structures 2,3-benzo-8,8-dimethylbicyclo[3.3.0]octa-2,4-dien-1-ol (**15**) and 2-(3-methyl-2-butenyl)-1-indanone (**17**), was approximately 3:1 (GLC, NMR), and the yields based on consumed **14** were 34 and 11%, respectively. Compound **15** solidified after GLC purification, mp 59–60 °C.

For **15:** IR (neat) ν_{OH} 3540 (sh), 3440 cm^{-1}; λ_{max} (cyclohexane) 298 nm (ϵ 800, sh), 278 (1640), 230 (8000), 224 (8180); NMR ($CDCl_3$) δ 0.59 (s, 3 H, *endo*-methyl), 1.30 (s, 3 H, *exo*-methyl), 1.70 (br s, 1 H, hydroxyl, exchanges with D_2O), 1.80–2.60 (m, 4 H, C(6) and C(7) methylenes), 6.06 (dd, 1 H, J = 1, 2 Hz, vinyl), 6.80–7.30 (m, 4 H, arom); mass spectrum, *m/e* (rel intensity) 200 (7), 144 (100).

Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.92; H, 7.95.

For **17:** IR (neat) $\nu_{C=O}$ 1715 cm^{-1}; λ_{max} (cyclohexane) 290 nm (ϵ 3880), 281 (3550), 247 (17 200), 240 (18 880), 234 (sh, 16 200), 212 (8100); NMR ($CDCl_3$) δ 1.63 (d, 3 H, J = 1 Hz, methyl), 1.67 (d, 3 H, J = 1 Hz, methyl), 2.30–3.50 (m, 5 H, methylenes and methine), 5.11 (t × m, 1 H, J = 6.5, ~ 1 Hz, vinyl), 7.10–7.70 (m, 4 H, arom); mass spectrum, *m/e* (rel intensity) 200 (13), 132 (100).

Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.91; H, 8.13.

Fraction 3 from column chromatography gave 60 mg (22%) of 2,3-benzo-8,8-dimethylbicyclo[3.3.0]oct-2-en-4-one (**16**): IR (neat) $\nu_{C=O}$ 1715 cm^{-1}; λ_{max} (cyclohexane) 294 nm (ϵ 3090), 284 (2730), 247 (15 270), 239 (15 820), 234 (sh, 14 090), 213 (9270); NMR (CCl_4 δ 0.70 (s, 3 H, *endo*-methyl), 1.18 (s, 3 H, *exo*-methyl), 1.30–1.60 (m, 2 H, C(7) methylene), 1.80–2.10 (m, 2 H, C(6) methylene), 3.00 (ddd, 1 H, J = 4.5, 7, 9 Hz, C(5) methine), 3.23 (d, 1 H, J = 7 Hz, C(1) methine), 7.00–7.60 (m, 4 H, arom); mass spectrum, *m/e* (rel intensity) 200 (42), 131 (100). An analytical sample of **16** was collected by GLC (6 ft × 0.25 in. column, 10% XF 1150 on Chromosorb W, 180 °C).

Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.88; H, 8.11.

Irradiation of 14 in Methanol. A solution of **14** (600 mg, 3 mmol) in 60 mL of methanol was irradiated (Pyrex) for 3 h. The solvent was evaporated and the residue was column chromatographed (50 g of silica gel-60) to give five main fractions. Fraction 1 was recovered **14** (25 mg, 4%). Fraction 3 gave 48 mg (8%) of **17.** Fraction 4 gave 101 mg (17%) of **16.** Fraction 2 gave 66 mg (10%) of 2,3-benzo-8,8-dimethyl-4-methoxybicyclo[3.3.0]octa-1(5),2-diene (**19**): λ_{max} (cyclohexane) 310 nm (ϵ 780, sh), 279 (sh, 7690), 273 (8140), 244 (3060), 230 (10 700); NMR (CCl_4) δ 1.25 (s, 3 H, methyl), 1.30 (s, 3 H, methyl), 2.00–2.25 (m, 2 H, C(7) methylene), 2.40–2.60 (m, 2 H, C(6) methylene), 2.95 (s, 3 H, methoxyl), 4.67 (s, 1 H, C(4) methine), 6.90–7.30 (m, 4 H, arom); mass spectrum, *m/e* (rel intensity) 214 (14), 158 (100). An analytical sample of **19** was prepared by GLC (6 ft × 0.25 in. column, 10% XF 1150 on Chromosorb W, 180 °C).

Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 84.08; H, 8.46.

Fraction 5 (210 mg) was obtained by using 10% methanol in methylene chloride as eluent. It was shown by NMR to contain at least 80% of 2,3-benzo-8,8-dimethyl-4-methoxybicyclo[3.3.0]oct-2-en-1-ol (**18**), 25% yield. This material contained a carbonyl impurity which could not be entirely removed by additional chromatography: IR (neat) ν_{OH} 3400 cm^{-1} (impurity, 1700 cm^{-1}); NMR ($CDCl_3$) δ 0.50 (s, 3 H, *endo*-methyl), 1.18 (s, 3 H, *exo*-methyl), 1.20–2.50 (m, 5 H, C(6) and C(7) methylenes, C(5) methine), 2.73 (br s, 1 H, hydroxyl, exchanges with D_2O), 3.25 (s, 3 H, methoxyl), 4.25 (d, 1 H, J = 3 Hz,

C(4) methine), 7.18 (br s, 4 H, arom); mass spectrum, *m/e* (rel intensity) 232 (7), 214 (0.5), 200 (10), 132 (100).

2,3-Benzo-2,4-cyclooctadienone (20). A mixture containing 4.8 g (27.6 mmol) of 2,3-benzo-2-cyclooctenone,[14] 7.4 g (39 mmol) of *N*-bromosuccinimide, and 0.2 g of benzoyl peroxide in 300 mL of carbon tetrachloride was refluxed under nitrogen for 2 h, cooled, and filtered. The solvent was removed under reduced pressure and the residue was heated with 4 g of 2,4,6-collidine at 100 °C for 4 h. The cooled solution was washed successively with dilute hydrochloric acid, salt solution, and dried (Na_2SO_4). The solvent was evaporated and the residue was chromatographed to give as the second fraction 1.75 g (37%) of **20:** IR (neat) $\nu_{C=O}$ 1681 cm^{-1}; λ_{max}^{EtOH} 310 nm (ϵ 2280), 258 (5650), 237 (6840); NMR (CCl_4) δ 1.9–2.2 (m, 4 H, C(6) and C(7) methylenes), 2.6–2.9 (m, 2 H, C(8) methylene), 5.8–6.2 (m, 1 H, C(5) vinyl), 6.67 (d, 1 H, J = 11 Hz, C(4) vinyl), 6.93–7.5 (m, 3 H, arom), 7.7–7.9 (m, 1 H, arom); mass spectrum, *m/e* (rel intensity) 172 (14), 145 (15), 144 (100), 131 (15), 129 (14), 116 (33), 115 (50), 63 (10).

Irradiation of 20 in Methanol. A solution of 280 mg (1.63 mmol) of **20** in 50 mL of anhydrous methanol was irradiated (Uranium glass filter). The reaction was followed by GLC (6 ft × 0.25 in. column, 10% FFAP on Chromosorb G, 80 mL/min He, 225 °C). The peak due to starting material (retention time 5 min) gradually decreased in favor of a single product peak (retention time 7.5 min). Reaction was complete in 26 h. The solvent was removed by rotary evaporation and the residual yellow oil was subjected to preparative thin layer chromatography (2 mm silica gel, methylene chloride eluent) to give 191.5 mg (57%) of 2,3-benzo-4-methoxybicyclo[3.3.0]oct-2-en-1-ol (**21**), mp 108–109 °C. Several minor products (TLC) were not further purified or identified. For **21:** IR (KBr) ν_{OH} 3450 cm^{-1}; λ_{max}^{EtOH} 269 nm (ϵ 6110), 262 (6310), 255 (4460), 220 (6620); NMR ($CDCl_3$) δ 1.2–2.4 (m, 7 H, methylenes and C(5) methine) 3.23 (s, 3 H, methoxyl), 3.42 (br s, 1 H, hydroxyl), 4.15 (d, 1 H, J = 3 Hz, C(4) methine), 7.2 (s, 4 H, arom); mass spectrum, *m/e* (rel intensity) 204 (8), 189 (16), 186 (5), 175 (22), 172 (59), 161 (67), 144 (95), 128 (31), 115 (39), 91 (16), 77 (18), 59 (100).

Irradiation of 20 in Ether. A solution of 110 mg of **20** in 50 mL of ether (freshly distilled over lithium aluminum hydride) was irradiated (Uranium glass filter) for 1.5 h. NMR examination showed the doublet at δ 6.67 (J = 11 Hz) in **20** nearly disappeared in favor of a new doublet at δ 6.77 (J = 15 Hz) assigned to the trans isomer **20t.** Integration showed about 83% **20t** and 17% **20.** For **20t:** NMR ($CDCl_3$) δ 1.0–3.0 (br m, 6 H, methylenes), 5.71 (distorted t or dd, 1 H, J = 15, 12 Hz, C(5) vinyl), 6.77 (d, 1 H, J = 15 Hz, C(4) vinyl), 7.0–7.45 (m, 4 H, arom). Irradiation of the signal at δ 5.71 collapsed the signal at δ 6.77 to a singlet.

(4*Z*)-2,3-Benzo-2,4-cyclooctadienol (22). A mixture of 80 mg (0.46 mmol) of **20** and 23 mg of lithium aluminum hydride in 10 mL of ether was refluxed for 2.5 h. Workup and purification by GLC (6 ft × 0.25 in. column, 5% SE-30 on Chromosorb W, 80 mL/min He, 140 °C, retention time 10 min) gave 48 mg (59%) of **22** as a colorless oil: IR (neat) ν_{OH} 3400 cm^{-1}; λ_{max}^{EtOH} 246 nm (ϵ 9100); NMR ($CDCl_3$) δ 1.2–2.3 (m, 6 H, methylenes), 2.32 (d, 1 H, J = 3 Hz, hydroxyl, exchanges with D_2O), 5.00 (m, 1 H, C(1) methine), 5.68 (dt, 1 H, J = 12, 4.5 Hz, C(5) vinyl), 6.23 (d, 1 H, J = 12 Hz, C(4) vinyl), 6.8–7.5 (m, 4 H, arom); mass spectrum, *m/e* (rel intensity) 174 (35), 156 (14), 145 (94), 132 (39), 131 (68), 129 (40), 128 (100), 117 (35), 115 (64), 91 (41), 77 (39).

(4*E*)-2,3-Benzo-2,4-cyclooctadienol (22t). A solution of 140 mg (0.81 mmol) of **20** in 50 mL of ether (freshly distilled from lithium aluminum hydride) was irradiated (Uranium glass filter) for 1.5 h. The volume of ether was reduced by rotary evaporation to about 10 mL, 20.4 mg of lithium aluminum hydride was added, and the mixture was refluxed for 2 h. Workup and purification of the products by preparative thin layer chromatography (2 mm silica gel, methylene chloride) gave 26 mg (18%) of **22** and 37 mg (26%) of **22t;** the latter product moved faster on TLC. For **22t:** IR (neat) ν_{OH} 3450 cm^{-1}; NMR (CCl_4) δ 1.20–2.40 (m, 6 H, methylenes), 3.20 (br s, 1 H, hydroxyl), 4.60 (br d, 1 H, J = 8 Hz, C(1) methine), 5.80 (m, 1 H, C(5) vinyl), 6.31 (d, 1 H, J = 15 Hz, C(4) vinyl), 6.95 (s, 4 H, arom); mass spectrum, *m/e* (rel intensity) 174 (20), 156 (31), 145 (80), 144 (36), 141 (32), 132 (32), 131 (54), 129 (43), 128 (100), 127 (24), 119 (32), 117 (36), 115 (62), 91 (35), 77 (36).

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