with no change in spectral properties: $\nu_{max}^{CCl_4}$ 1325, 1200, 1175, and 1130 cm^{-1} (SO_2); $\delta_{TMS}^{CCl_4}$ 1.90–2.83 (m, H_1 and H_2), 2.20, 2.34 (s, $N(CH_3)_2$), 3.33–3.74 and 4.00–4.62 (m, 2 H each, H_5 and α-sulfonyl), and 5.86 (broad s, 2 H, vinyl).

A methiodide of **18a** was obtained in 78% yield, mp 191° dec (methanol–water).

Anal. Calcd for $C_{10}H_{18}INO_2S$: C, 34.99; H, 5.29; N, 4.08. Found: C, 34.92; H, 5.35; N, 3.93.

5-Dimethylamino-8,8-dimethyl-7-thiabicyclo[4.2.0]oct-3-ene 7,7-Dioxide (18b).—A mixture of 5.0 g (0.038 mol) of **12** and 4.0 g (0.041 mol) of **17a** in 10 ml of dry benzene was left at room temperature under nitrogen for 1 week and then refluxed for 2 hr. The black solution was worked up and chromatographed as above to give an oily solid, recrystallization of which from ether–petroleum ether afforded 1.7 g (19.5%) of **18a**, mp 45–48°. An analytical sample was prepared through the hydrochloride salt, mp 215° dec (from methanol–ether), and regeneration of the free base: mp 59°; $\nu_{max}^{CCl_4}$ 1315, 1175, 1153, and 1112 cm^{-1} (SO_2); $\delta_{TMS}^{CDCl_3}$ 1.40 and 1.65 (s, *gem*-dimethyl), 2.28 (s, $N(CH_3)_2$), 2.17 (m, 2 H, H_2), 3.65–3.86 (m, H_5), 4.25–4.60 (m, H_6), and 5.88 (broads, 2 H, vinyl).

Anal. Calcd for $C_{11}H_{19}NO_2S$: C, 57.61; H, 8.35; N, 6.10; S, 13.98. Found: C, 57.62; N, 8.42; N, 5.99; S, 13.84.

A methiodide salt of **18b** was prepared, mp 211° dec (methanol–water).

Anal. Calcd for $C_{12}H_{22}INO_2S$: C, 38.82; H, 5.97; S, 8.64. Found: C, 38.62; H, 5.92; S, 8.42.

5-Diethylamino-8,8-dimethyl-7-thiabicyclo[4.2.0]oct-3-ene 7,7-Dioxide (18c).—A mixture of 1.0 g (7.6 mmol) of **12** and 0.94 g (7.6 mmol) of 1-diethylamino-1,3-butadiene (**17b**)[12] in 5 ml of dry xylene was refluxed under nitrogen for 12 hr. The dark reaction mixture was concentrated and the residue was chromatographed on Florisil. Elution of the column with petroleum ether containing increasing amounts of ether gave a yellow crystalline solid. Recrystallization of this substance from petroleum ether afforded 0.4 g (19.5%) of **18c**: mp 64°; $\nu_{max}^{CCl_4}$ 1312, 1165, 1150, and 1110 cm^{-1} (SO_2). Approximately one-fourth of the starting quantity of **12** was recovered.

Anal. Calcd for $C_{13}H_{23}NO_2S$: C, 60.66; H, 9.01; N, 5.44; S, 12.46. Found: C, 60.39; H, 8.88; N, 5.40; S, 12.36.

Registry No.—**7**, 23431-18-7; **8**, 23430-88-8; **11**, 23430-89-9; **14**, 23430-90-2; **15**, 23430-91-3; **16a**, 23431-19-8; **16b**, 23431-20-1; **18a**, 23430-92-4; **18a** (methiodide), 23430-93-5; **18b**, 23430-94-6; **18b** (methiodide), 23465-13-6; **18c**, 23430-95-7.

Acknowledgment.—This work was financed in part by the National Science Foundation, Grant GP5977, whom we thank.

[12] S. Hunig and H. Kahanek, *Chem. Ber.*, **90**, 238 (1957).

The Reaction of 6,6-Dibromobicyclo[3.1.0]hexane with Methyllithium. Efficient Trapping of 1,2-Cyclohexadiene by Styrene[1]

WILLIAM R. MOORE AND WILLIAM R. MOSER[2]

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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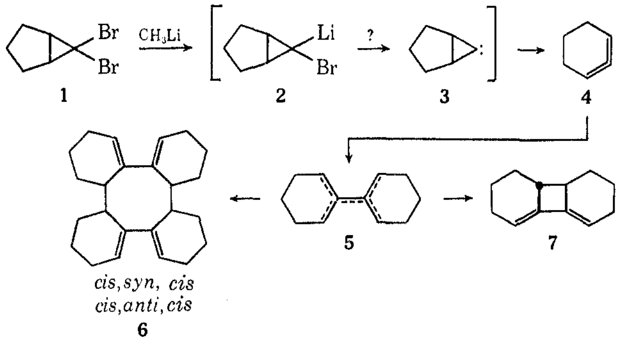
The reaction of 6,6-dibromobicyclo[3.1.0]hexane (1) with methyllithium in styrene affords a 76% yield of *exo*- and *endo*-7-phenylbicyclo[4.2.0]oct-1-ene (**8a** and **8b**) in a ratio of 2.2:1. The structures of **8a** and **8b** have been established by spectral methods, oxidative degradation, and hydrogenation to *exo*- and *endo*-7-phenylbicyclo[4.2.0]octane, which were synthesized independently. The formation of **8a** and **8b** is interpreted in terms of the generation of 1,2-cyclohexadiene, which adds to styrene to form a singlet biradical that closes to **8a** and **8b**.

The reaction of 6,6-dibromobicyclo[3.1.0]hexane (**1**) with methyllithium gives no evidence of products derived from carbene **3** (Scheme I). Rather, at −80° the major products are the stereoisomers **6**, while in refluxing ether diene **7** is formed in good yield.[3] We have interpreted[3] these results in terms of the generation of 1,2-cyclohexadiene (**4**) from either **2** or **3** (or both) and have suggested that dimerization of **4** first gives a diallylene **5**, which either cyclizes to **7** at "high" temperatures or dimerizes to **6** at low temperatures (Scheme I). In order to gain insight into the nature of 1,2-cyclohexadiene, we have investigated intercepting it with various reagents. In this paper we report the trapping of **4** with styrene and a rigorous proof of the structures of the adducts.

SCHEME I



The reaction of **1** with methyllithium in isobutylene, cyclohexene, and furan under a variety of conditions produced the same products, **6** and **7**, observed when ether was employed as the sole solvent; no evidence for any "trapping products" was obtained. However, addition of methyllithium in ether to a solution of **1** in pure styrene at −15° gave, after distillation, a 76% yield of a 1:1 styrene–C_6H_8 adduct **8**. A small amount (4–5%) of **7** was formed and the total distillation residue, *ca.* one-tenth the weight of **8**, was found to consist of **6** (along with small amounts of "trimeric" material[3]). No evidence was found for the formation of any styrene polymer. The product composition was the same with methyllithium made from methyl bromide or methyl iodide. Dilution of the styrene in ether lowered the yield of **8** somewhat.

The trapping product **8** was shown by glpc to be a mixture of two compounds, in a ratio of 2.2:1. Based on the detailed evidence presented below, the major product has been shown to be *exo*-7-phenylbicyclo-

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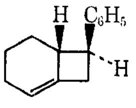
[1] Supported in part by the National Science Foundation (Grant GP-1306) and the Petroleum Research Fund administered by the American Chemical Society (Grant 1549-A4).

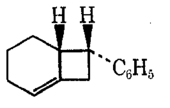
[2] National Institutes of Health Predoctoral Fellow, 1960–1964.

[3] W. R. Moore and W. R. Moser, *J. Amer. Chem. Soc.*, in press.

[4.2.0]oct-1-ene (**8a**) and the minor product to be *endo*-7-phenylbicyclo[4.2.0]oct-1-ene (**8b**). The major product **8a** could be isolated in a pure state by spinning-band distillation; the minor compound **8b** was isolated by preparative glpc. Elemental analysis and mass spectra established that both compounds were $C_{14}H_{16}$. Both showed infrared absorption characteristic of a monosubstituted benzene. The nmr spectra established that both compounds have five aromatic and one olefinic proton. The upfield portions of the spectra differ: **8a** shows four protons in a relatively sharp band at δ 2.99 with six protons in a broad band at δ 0.55–2.3; **8b** shows one proton as a triplet of doublets at δ 3.70 overlapping a complex three-proton pattern at δ 2.5–3.9 and six protons in a broad band at δ 0.35–2.5. These nmr differences serve as a basis for a structural and stereochemical assignment (below), confirmed by degradation.



8a

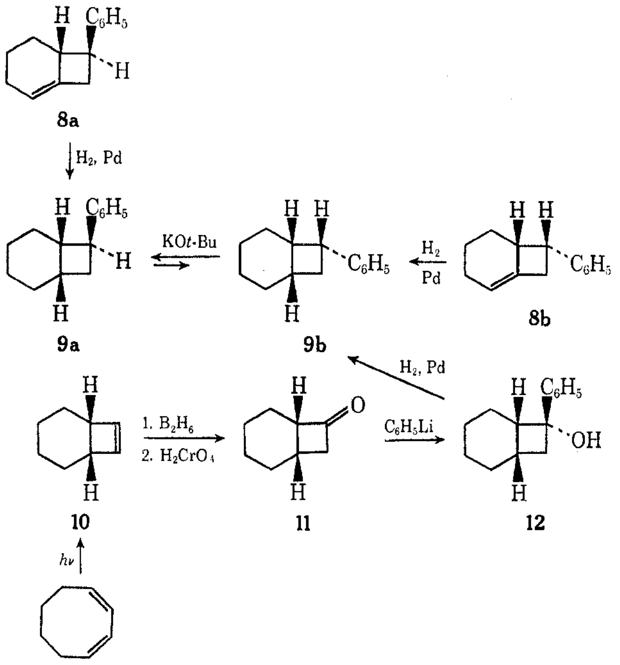


8b

Quantitative hydrogenation of **8a** over palladium on carbon established the presence of one double bond and gave a single product **9a** (no **9b**). Similarly, **8b** gave a single product **9b** (no **9a**) upon absorption of 1 mol of hydrogen. The two compounds, $C_{14}H_{18}$ by analysis and mass spectra, had similar, but different, ir and nmr spectra and the same glpc retention times on all columns employed except Craig polyester succinate. Heating either **9a** or **9b** with potassium *t*-butoxide in dimethyl sulfoxide[4] caused equilibration to a mixture of the two compounds containing about 90% **9a**, establishing that this isomer is the more stable. A similar mixture resulted from treatment of **9a,b** with potassium amide in liquid ammonia.

The structures **9a** and **9b** were established by the synthetic sequence outlined in Scheme II. *cis*-Bicyclo-[4.2.0]oct-7-ene (**10**), prepared by photolysis of *cis,cis*-1,3-cyclooctadiene,[5,6] was hydroborated and oxidized with chromic acid[7] to give *cis*-bicyclo[4.2.0]octan-7-one (**11**). Ketone **11** prepared in this way was shown to be identical with the ketone obtained by chromic acid oxidation of bicyclo[4.2.0]octan-7-ol.[8] Treatment of **11** with phenyllithium gave an 87% yield of 7-phenylbicyclo[4.2.0]octan-7-ol (**12**), which appeared to be a single epimer. Since the phenyl group should enter the molecule from the less hindered side, we assign the *exo*-phenyl configuration to **12**. Hydrogenolysis of **12** over palladium on carbon in acetic acid at 60° afforded only **9b**. The fact that base-catalyzed equilibration, which can only affect the configuration at the benzylic C-7 position, converts **9b** into **9a** establishes the structure of the latter. The assignment of the stereochemistry follows from consideration of the relative stabilities of these two isomers. An *endo*-phenyl group clearly suffers nonbonded repulsions absent in the *exo* isomer. Hence the less stable isomer, **9b**, must have the *endo*-phenyl configuration.

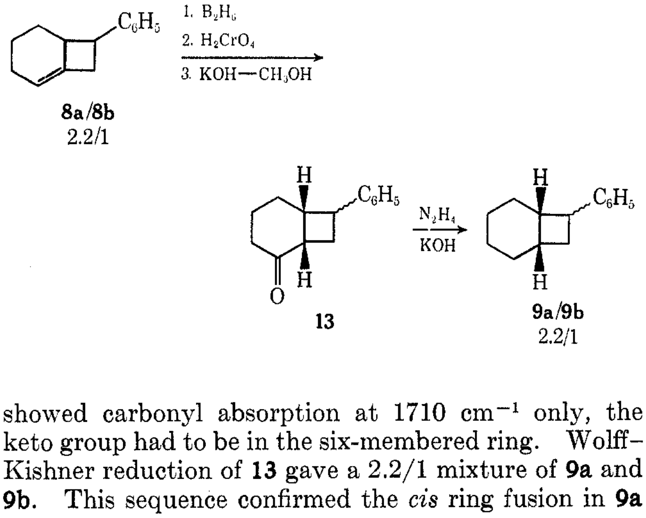
Scheme II



The hydrogenolysis of alcohol **12** thus proceeded with overall inversion of configuration at C-7. This result might be due to backside displacement of the protonated hydroxyl on the catalyst surface, but it is probable that the alcohol was catalytically dehydrated to 7-phenylbicyclo[4.2.0]oct-7-ene, which was then hydrogenated from the less hindered side, leading to the *endo* configuration for the phenyl group.

The data at this point established the carbon skeleton of **8a** and **8b** but not the position of the double bond. A 2.2/1 mixture of **8a**/**8b** was hydroborated and oxidized with chromic acid and the product was treated with dilute potassium hydroxide in methanol to ensure that only the more stable *cis*-fused bicyclic system was in hand. Since the resultant ketone **13** (Scheme III) showed carbonyl absorption at 1710 cm^{-1} only, the keto group had to be in the six-membered ring. Wolff–Kishner reduction of **13** gave a 2.2/1 mixture of **9a** and **9b**. This sequence confirmed the *cis* ring fusion in **9a**

Scheme III



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[4] D. J. Cram, C. A. Kingsbury, and B. Rickborn, *J. Amer. Chem. Soc.*, **83**, 3688 (1961).

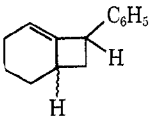
[5] (a) W. G. Dauben and R. L. Cargill, *J. Org. Chem.*, **27**, 1910 (1962). (b) S. F. Chappell and R. F. Clark, *Chem. Ind.* (London), 1198 (1962). (c) Both the direct[6a] and the photosensitized[6b] photolyses apparently involve *cis,trans*-1,3-cyclooctadiene. In both systems we observed quick formation of a glpc peak which apparently was this strained olefin.

[6] (a) W. J. Nebe and G. J. Fonken, *J. Amer. Chem. Soc.*, **91**, 1249 (1969); (b) R. S. H. Liu, *ibid.*, **89**, 112 (1967).

[7] H. C. Brown and C. P. Garg, *ibid.*, **83**, 2951 (1961).

[8] A. C. Cope and R. W. Gleason, *ibid.*, **84**, 1928 (1962).

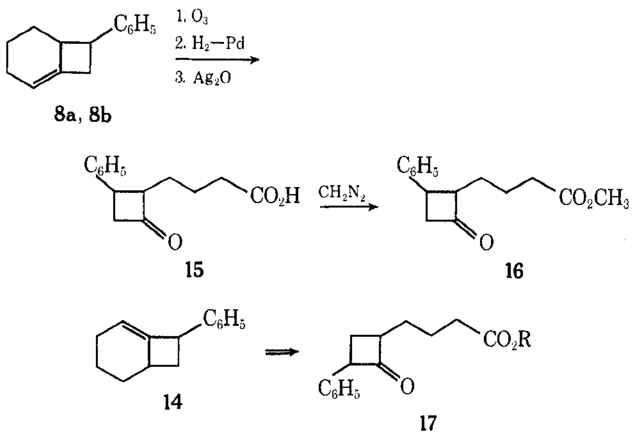
and **9b** and narrowed the possible alternate structures for **8a** and **8b** to the epimers of 8-phenylbicyclo[4.2.0]-oct-1-ene (**14**). Based on model compounds, we estimate that both epimers of **14** should show nmr signals for the benzylic proton (at C-8) at *ca.* δ 4.3.[9] Similarly, for **8b** we predict a value of *ca.* δ 3.5 for the benzylic proton (at C-7), close to the value of δ 3.70 observed. Molecular models show clearly that owing to the puckering of the four-membered ring the corresponding benzylic proton in **8a** lies in the shielding region of the double bond and consequently must fall upfield from the δ 3.70 signal of **8b**. This predication is confirmed by the observation that the signal from the C-7 proton of **8a** must fall in the band at δ 2.99 (along with the other three cyclobutane protons).[10] In addition, the C-7 proton of **8b** appears as a triplet of doublets ($J_1 = J_2 \cong 9$ Hz, $J_3 \cong 3$ Hz), a pattern consistent with structure **8b** ($J_{cis} \cong 9$ Hz, $J_{trans} \cong 3$ Hz), but totally inconsistent with structure **14**.



14

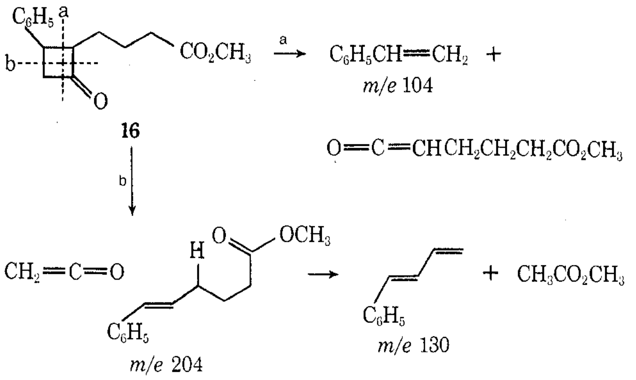
To confirm the spectral assignment of the position of the double bond, we investigated the oxidative degradation of **8a,b**. Ozonation of a 2.2:1 mixture of **8a,b** at −80° followed by catalytic hydrogenation of the ozonide and oxidation of the resultant aldehyde with silver oxide afforded keto acid **15** (71%) which was converted into the keto ester **16** with diazomethane (Scheme IV).

SCHEME IV



Both **15** and **16** show strong carbonyl absorption at 1780 cm^{-1} in the infrared, characteristic of cyclobutanones. The mass spectrum of the keto ester established that it was **16** and not the isomeric keto ester **17** which would result from **14**. Major fragments are found at *m/e* (rel intensity) 204 (13), 130 (60), and 104 (100). The base peak at *m/e* 104 represents styrene and supports either structure, but the *m/e* 204 and 130 peaks can come only from **16** and not from **17** (Scheme V).

SCHEME V

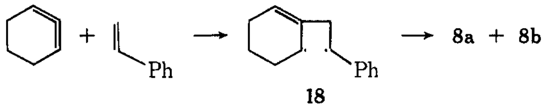


Further evidence supporting structure **16** rather than **17** came from deuterium-exchange studies. Keto acid **15** was treated with potassium carbonate in deuterium oxide for 17 hr and then washed with water to regenerate the CO_2H group, resulting in the incorporation of an average of 2.6 atoms of deuterium per molecule. Treatment of the deuterated **15** with diazomethane gave keto ester **16**, with the same deuterium content. Although the exchange had not quite reached the maximum for **15**, which has three protons adjacent to the keto group (protons adjacent to a carboxylate group do not exchange under these conditions), the observed incorporation of 2.6 atoms of deuterium per molecule clearly excludes structure **17**, which can incorporate a maximum of two atoms of deuterium per molecule.

Discussion

The formation of the adducts **8a** and **8b** in high yields substantiates our arguments[3] for the intermediacy of 1,2-cyclohexadiene. Although small amounts of **6** and **7** are formed, styrene clearly is an efficient trap. The orientation in this addition is similar to that observed for addition of normal allenes to activated olefins,[11] but, because **4** is by no means a normal allene, we felt that it was essential to provide unequivocal evidence for the structures of **8a** and **8b**.

Obviously the addition of **4** to styrene, a (2 + 2) cycloaddition, is very fast. A concerted thermal (2 + 2) cycloaddition must be suprafacial-antarafacial (*cis-trans*).[12] Since 1,2-cyclohexadiene can be looked upon as simply a badly twisted allene, any addition to it can be regarded as antarafacial. Yet the mode of dimerization of **4** (see Scheme I and ref 3) suggests that the addition of **4** to styrene is not concerted. We believe that this addition reaction is a two-step process involving formation of a biradical intermediate **18** which subsequently closes to both **8a** and **8b**.[13]



18

Addition of **4** to styrene to form **18** should occur with the plane of **4** approximately perpendicular to planar

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[9] The C-8 proton is on a cyclobutane ring, tertiary, allylic, and benzylic—all features causing a downfield shift.

[10] Models also suggest that the preferred rotational conformations of the phenyl group will lead to deshielding of the C-7 proton of **8b** but shielding of the C-7 proton of **8a**.

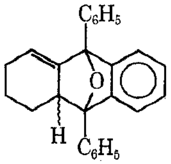
[11] (a) J. D. Roberts and C. M. Sharts, *Org. Reactions*, **12**, 1 (1962); (b) D. R. Taylor, *Chem. Rev.*, **67**, 317 (1967).

[12] R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).

[13] Based on the relative stabilities of **9a** and **9b** we assume that **8a** is more stable than **8b**.

styrene and oriented to minimize steric repulsions as depicted in Figure 1 (I). If closure follows from this conformation, models suggest that there should be at least a slight preference for formation of **8b** [closure along b, Figure 1 (I)] over **8a** [closure along a, Figure 1 (I)], but, if the biradical rotates to the sterically preferred conformation shown in Figure 1 (II), the two direct modes of closure are equivalent and give only **8a**. The fact that **8a** does predominate (2.2:1), provides some, if not compelling, support for the proposed intermediacy and mode of reaction of **18**.

Wittig and Fritze[14] have reported trapping 1,2-cyclohexadiene with 1,3-diphenylisobenzofuran and isolating a 4:1 ratio of adducts **19**. Based on infrared spectra, the major isomer was assigned the *endo* configuration. While this addition may be concerted, examination of models indicates that if a biradical were formed in this case, an analysis similar to that above predicts that formation of the *endo* isomer would be favored.



19

Finally, we wish to comment on the fact that, in the reactions which afforded **8a,b**, there was *no* polymerization of styrene (the solvent). Thus, if **18** is an intermediate, it cannot be a triplet; triplet **18** should be a highly efficient initiator for polymerization. Since triplet **4** would generate triplet **18**, it is clear that 1,2-cyclohexadiene, as generated from **1**, must be a singlet.

Experimental Section[15]

exo-**7-Phenylbicyclo[4.2.0]oct-1-ene (8a)** and *endo*-**7-Phenylbicyclo[4.2.0]oct-1-ene (8b).**—A solution of 65.6 g (0.273 mol) of 6,6-dibromobicyclo[3.1.0]hexene[3] (**1**) in 500 ml of styrene was cooled to −15° and 0.33 mol of 1 *M* methyllithium (prepared from methyl bromide and lithium) in ether was added dropwise with rapid stirring. After 15 min the mixture was warmed to room temperature and worked up in the usual way. Distillation afforded 36.1 g (74%) of olefins **8a,b**, bp 78° (0.04 mm), $n^{25}\mathrm{D}$ 1.5561, and a residue of 3.9 g. Glpc analysis (5% EGA, 150°) showed a ratio of **8a**:**8b** of 2.2:1. The distillation forerun showed 4.6% **7** and the residue (SE-30) was shown to consist of **6** along with small amounts of trimeric[3] material. A subsequent run gave a 76% yield of **8a,b**. The **8a,b** mixture showed only weak uv absorption (ethanol) at 250 mμ (log ε 2.51) which was due to the phenyl group, and the infrared spectrum showed bands which were due to **8a** and **8b** only.

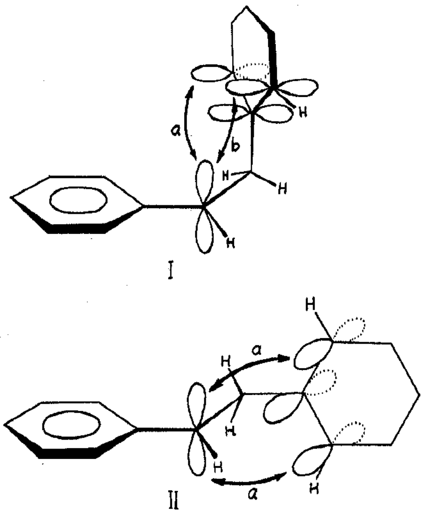


Figure 1.—Cyclization of the proposed biradical formed on addition of 1,2-cyclohexadiene to styrene: I, initial conformation; II, conformation after rotation. Closure in mode a gives **8a**, in mode b gives **8b**.

Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.08; H, 8.68.

Distillation through a 90-cm spinning-band column gave a pure sample of **8a** and a fraction enriched in **8b** from which **8b** was obtained by preparative glc (20% EGA, 140°).

Compound **8a** gave the following data: ir (neat) 3070, 3050, 3020, 1603, 1498, 770, 750, and 700 cm^{-1}; nmr (CCl_4) δ 7.31 (sharp, 5 H, C_6H_5), 5.41 (br, 1 H, C=CH), 2.99 (narrow, 4 H, C-6, C-7, C-8), and 0.5–2.3 (complex, 6 H, $CH_2CH_2CH_2$); mass spectrum *m/e* 184 (M^+).

Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.34; H, 8.76.

Compound **8b** gave the following data: ir (neat) 3070, 3050, 3020, 1603, 1498, 765, and 700 cm^{-1}; nmr (CCl_4) δ 7.32 (sharp, 5 H, C_6H_5), 5.46 (br, 1 H, C=CH), 2.5–3.9 (complex, 4 H, C-6, C-7, C-8, including a triplet of doublets at 3.70, C-7), and 0.4–2.5 (complex, 6 H, $CH_2CH_2CH_2$); mass spectrum *m/e* 184 (M^+).

Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.27; H, 8.79.

When the reaction was carried out using equal volumes of styrene and ether at −40° and methyllithium (made from methyl iodide) the ratio **8a**:**8b** was unchanged but the yield decreased.

exo-**7-Phenylbicyclo[4.2.0]octane (9a).**—Hydrogenation (25°, 1 atm) of 98.1 mg of **8a** over 30% palladium on carbon resulted in the rapid uptake of 1 equiv of hydrogen. Short-path distillation gave 94.2 mg (95%) of **9a**: ir (neat) 3070, 3050, 3020, 1603, 1498, 765, and 700 cm^{-1}; nmr (CCl_4) δ 7.37 (sharp, 5 H, C_6H_5), 3.55 (complex, 1 H, C-7), and 0.7–3.0 (complex, 12H); mass spectrum *m/e* 186 (M^+). Glpc on several columns showed only **9a** and no **9b**.

Anal. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74. Found: C, 90.33; H, 9.69.

Bicyclo[4.2.0]oct-7-ene (10).[5a]—Photolysis of 70 g of *cis,cis*-1,3-cyclooctadiene in 2.9 l. of anhydrous ether using a 500-W Hanovia high-pressure mercury arc (quartz probe) for 152 hr afforded 17 g (24%) of **10**, bp 129–135°, which was found to be 95% pure by glpc (12% TEG-12% C-20 M, 91°). Purification by preparative glpc (S-550, 104°) gave 11.6 g of pure **10** with infrared and nmr spectra identical with those obtained by Dauben and Cargill.[5a,16]

In the above photolysis as well as in an acetophenone-sensitized reaction, an unidentified peak (with a retention time 1.2 times that of 1,3-cyclooctadiene, TEG-C-20 M, 90°) appeared shortly after the photolysis began. Its concentration remained *ca.* one-third that of 1,3-cyclooctadiene during the remainder of the photolysis. This material apparently was *cis,trans*-1,3-cyclooctadiene.[6]

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[14] G. Wittig and P. Fritze, *Angew. Chem.*, **78**, 905 (1966); *Justus Liebigs Ann. Chem.*, **711**, 82 (1968). 1-Bromocyclohexene was treated with potassium *t*-butoxide in dimethyl sulfoxide in the presence of the isobenzofuran. The two adducts were formed in 41% combined yield.

[15] Spectral measurements were determined with the following instruments: ir, Perkin-Elmer Models 21, 237, and 337 spectrophotometers; nmr, Varian A-60 spectrometer; uv, Cary Model 14 spectrophotometer; mass spectrum, Consolidated Electrodynamics Model 21-130 mass spectrometer (ionizing potential of 70 eV). Glpc columns were generally 0.5 × 200 cm and 1.5 × 200 cm (homemade apparatus, thermal conductivity detector) or 0.2 × 150 cm and 0.2 × 300 cm (Wilkens A-600 flame ionization) employing acidic, basic, or neutral Chromosorb P or W and the following liquid phases: Carbowax 20M (C-20 M), silicone oil 550 (S-550), silicone oil 710 (S-710), tetraethylene glycol (TEG), SE-30 silicone rubber (SE-30), ethylene glycol adipate (EGA), Versamid 900 (V-900), silicone nitrile XF-1150 (XF-1150), silicone nitrile XE-60 (XE-60), and Craig polyester succinate (CPS). Internal standards were employed using appropriate response factors; peak areas were measured with a planimeter. Melting points are corrected and boiling points are uncorrected. All reactions employing organometallic reagents, active metals, alkoxides, hydrides, photolysis, pyrolysis, and diborane were conducted under a nitrogen atmosphere.

[16] We wish to thank Professor Dauben for providing spectra.

Bicyclo[4.2.0]octan-7-one (11).—Olefin **10** (7.3 g, 0.068 mol) was treated with a solution of 0.049 mol of diborane[17] in 85 ml of tetrahydrofuran at 0°. After addition of water and evaporation of most of the solvent, a solution of 16.5 g of sodium dichromate and 12 ml of concentrated sulfuric acid in 60 ml of water and 50 ml of ether were added. After 8 hr at 25° the usual work-up gave 5.0 g (60%) of **11**, bp 65° (6.5 mm), $n^{25}\text{D}$ 1.4742. The infrared spectrum was identical with that obtained by Cope and Gleason.[8]

Oxidation of bicyclo[4.2.0]octan-7-ol[8] in ether with chromic acid gave an 89% yield of **11** identical in every way with the sample prepared above.

7-Phenylbicyclo[4.2.0]octan-7-ol (12).—Addition of 28 mmol of phenyllithium in ether to 2.72 g (21.9 mmol) of **11** in ether at −80° followed by the usual work-up and short-path distillation (110°, 0.02 mm) gave 3.86 g (87%), $n^{25}\text{D}$ 1.5513, of **12** as a colorless liquid, $n^{25}\text{D}$ 1.5513. Glpc (15% V-900 at 220°, 2% EGA at 180°) showed only a single peak which appeared to be a single compound (based on plate values). Spectral data follow: ir (neat) 3400 (br), 3070, 3050, 3020, 1603, 1498, 765, and 700 cm^{-1}; nmr (CCl_4) δ 7.50 (5 H, C_6H_5) and 0.5–3.0 (complex, 13 H, OH at 2.20).

Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.08; H, 9.21.

***endo*-7-Phenylbicyclo[4.2.0]octane (9b). A. From 12.**—Alcohol **12** (161 mg) was stirred over 30% palladium on carbon in acetic acid at 58° under 1 atm of hydrogen. Hydrogen uptake was fairly rapid (25 min) up to 1 equiv and then became very slow, at which point the mixture was worked up to afford on short-path distillation 124 mg (84%) of **9b** as a colorless liquid, $n^{25}\text{D}$ 1.5332. Glpc analysis (CPS at 120°, EGA at 150°, XE-60) showed that the compound was pure and contained no **9a**. Spectral data follow: ir (neat) 3070, 3050, 3020, 1603, 1498, 760, and 700 cm^{-1}; nmr (CCl_4) δ 7.29 (5 H, C_6H_5), 3.55 (1 H, br, complex, C-7), and 0.5–2.9 (12 H, complex); mass spectrum *m/e* 186 (M^+).

Anal. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74. Found: C, 90.30; H, 9.69.

B. From 8b.—Hydrogenation of **8b** over 30% palladium on carbon in ethanol at 25° resulted in the rapid uptake of 1 equiv of hydrogen. Short-path distillation afforded a colorless liquid with glpc retention times (CPS, EGA, XE-60) and an infrared spectrum identical with that of **9b** prepared above. No **9a** was formed.

Equilibration of 9a and 9b.—Hydrocarbon **9b** (46 mg) was heated in a solution of potassium *t*-butoxide (prepared by adding 40 mg of potassium to anhydrous *t*-butyl alcohol followed by evaporation of the alcohol, ultimately at 0.01 mm for 8 hr) in 2 ml of anhydrous dimethyl sulfoxide at 58° for 19 hr. Glpc analysis (CPS, 120°, relative retention times **9a**, 1.05, **9b**, 1.00) established that **9a** and **9b** were present in a ratio of 86:14. The compounds were identified by glpc retention times and infrared spectra.

Hydrocarbon **9a** was treated in the same way, but heating was continued at 58° for 10 days. Glpc and infrared analysis established that **9a** and **9b** were present in a ratio of 90:10. Because of the much longer time, 90:10 must be closer to the equilibrium content than 86:14.

A sample of **8a** and **8b** (2.2:1) was stirred for 12 hr with 0.1 *M* potassium amide in liquid ammonia. The usual work-up yielded a mixture of **8a** and **8b** with an infrared spectrum nearly identical with that of the 90:10 mixture above.

Oxidative Hydroboration of 8a and 8b.—A 2.2:1 mixture of **8a** and **8b** (75 mg) was hydroborated in tetrahydrofuran with a 50% excess of diborane.[17] After 12 hr, water was added followed by a 25% excess of chromic acid in water and ether. After 48 hr at 25°, work-up yielded a ketone which showed a strong ir band at 1710 cm^{-1} only. This material was stirred with 10% potassium hydroxide in methanol at 25° for 40 hr. An aliquot showed only a 1710-cm^{-1} ir band. Diethylene glycol (25 ml) was added, the methanol was removed by distillation, and 4 ml of 68% aqueous hydrazine was added. The mixture was refluxed for 5 hr, the water was removed by distillation, and the mixture was then refluxed for 43 hr. Work-up and glpc analysis established that only **9a** and **9b** were present in a ratio of 2.2:1.

Ozonization of 8a,b.—A 2.2:1 mixture of **8a** and **8b** (2.2 g) was ozonized in 20 ml of ethyl acetate at −80°. The ozonide was hydrogenated in the same solvent over 5% palladium on carbon at 25° (90% of theoretical uptake). Filtration and evaporation of the solvent left a colorless oil: ir (neat) 1785, 1710, and 700 cm^{-1}; nmr (CCl_4) δ 9.67 (1 H, CHO), 7.28 (s, 5 H, C_6H_5), 2.59–3.75 (complex, 4 H, $C_6H_5\mathbf{CH}\mathbf{CH_2}CO\mathbf{CH}$), 2.32 (br, 2 H), and 1.70 (br, 4 H). The oil was treated with 2.0 g of silver oxide and 2.0 g of sodium hydroxide in 200 ml of 1:1 water–ethanol at 25° for 8 hr. The basic solution was filtered and washed with ether, affording 0.28 g of neutral material, ir (CCl_4) 3400 and 1780 cm^{-1} (no other carbonyl band). Acidification of the basic solution and extraction with ether afforded 1.95 g (71%) of **2-(3-carboxypropyl)-3-phenylcyclobutanone** (**15**) as a colorless oil, ir ($CHCl_3$) 1780 and 1710 cm^{-1} with a typical carboxyl band in the 3-μ region. This material could not be distilled without decomposition. Tlc and nmr of **15** and glpc of **16** indicated that **15** was at least 93% pure: ir (CCl_4) 1785, 1710, 1603, 1498, and 700 cm^{-1}; nmr ($CDCl_3$) δ 9.53 (s, 1 H, CO_2H), 6.90 (s, 5 H, C_6H_5), 3.03 (s, 2 H, $C_6H_5\mathbf{CH}\mathbf{CH}C{=}O$), 1.9–2.83 (complex, 4 H, t at 2.58, $\mathbf{CH_2}CO$, broad band at *ca.* 2.1, CH_2CO_2H), and 1.58 (br, 4 H, $\mathbf{CH_2CH_2}$). Keto acid **15** was treated with a slight excess of diazomethane in ether. Short-path distillation (0.08 mm, bath temperature 125°) left no residue and gave 2.05 g of an oil. Glpc analysis (2% EGA) showed one major and three minor peaks. The major peak (93%) was collected by glpc (10% EGA, 220°) and short-path distilled, giving **2-(3-carbomethoxypropyl)-3-phenylcyclobutanone** (**16**) as a colorless oil: $n^{25}\text{D}$ 1.5237; ir (CCl_4) 3070, 3050, 3020, 1785, 1740, 1140, 1175, and 700 cm^{-1}; nmr (CCl_4) δ 7.29 (s, 5 H, C_6H_5), 3.60 (s, 3 H, OCH_3), 3.21 (br s, 2 H, $C_6H_5\mathbf{CH}\mathbf{CH}C{=}O$), 1.92–3.05 (complex, 4 H, $CH_2C{=}O$ and $\mathbf{CH_2}CO_2CH_3$), and 1.2–1.96 (br, 4 H, $\mathbf{CH_2CH_2}$); mass spectrum *m/e* (rel intensity), 204 (13), 130 (60), 117 (13), 104 (100), 91 (16), 78 (26), 77 (24), no M^+ peak.

Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.14; H, 7.37. Found: C, 73.21; H, 7.23.

Keto acid **15** (85 mg) was dissolved in 25 ml of deuterium oxide containing 0.3 g of potassium carbonate. After 18 hr at 25°, the mixture was acidified with an acetic acid–sodium acetate buffer. The solution was washed with ether and the ether extract was washed with water. The solvent was evaporated under reduced pressure, leaving the deuterated keto acid **15**. Nmr analysis indicated a minimum of 2.6 atoms of deuterium per molecule. Treatment of the deuterated **15** with diazomethane gave deuterated **16**, which showed the same deuterium content as **15**.

Reaction of 1 with Methyllithium in the Presence of Isobutylene, Furan, and Cyclohexene.—Addition of methyllithium (1 *M* in ether) to **1** in 1:1 isobutylene–ether at −80°, 1:1 cyclohexene–ether at −80°, and furan (freshly distilled from sodium) at −80° followed by the usual work-up and glpc analysis (S-710, C-20 M, SE-30) showed no new products and also showed that the product composition was essentially the same[3] (**6** was the major peak) as that observed in the absence of the olefins.

Addition of 8 mmol of **1** to 10 ml of 1 *M* methyllithium in ether and 50 ml of isobutylene at −18° gave only products formed in the absence of the olefin. The yield of compound **7** was 21%.

Addition of 9 mmol of **1** in 10 ml of ether to 15 ml of 1 *M* methyllithium in 20 ml of cyclohexene at reflux gave a 60% of **7** and no new products.

Isomerization of 8a,b.—High-surface sodium on alumina, which has been utilized for isomerization of methylene cyclobutanes to cyclobutenes,[18] was prepared by shaking molten sodium (1 part) with anhydrous alumina (5 parts, Alcoa grade F) at 200° (0.1 mm). A 60 × 1.2 cm tube was packed with this sodium–alumina and maintained at 200° while a slow stream of nitrogen was passed through the tube. Passage of a 2.2:1 mixture of **8a** and **8b** through the pyrolysis tube gave a 50% recovery of a white solid. Glpc analysis (C-20M, 209°) showed four peaks, with relative retention times (per cent composition) of 0.61 (10), 0.71 (9), 1.00 (5), and 1.20 (76). The material with relative retention time 1.00 was shown to be starting material. The major component was identified as 1,2-diphenylethane by glpc retention times, melting points, and infrared spectra.

Registry No.—**1**, 2568-36-7; **8a**, 23115-89-1; **8b**, 23068-83-9; **9a**, 23068-84-0; **9b**, 23068-85-1; **12**, 23068-86-2; **15**, 23074-17-1; **16**, 23074-18-2; methyllithium, 917-54-4; 1,2-cyclohexadiene, 14847-23-5; styrene, 100-42-5.

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[17] H. C. Brown and P. A. Tierney, *J. Amer. Chem. Soc.*, **80**, 1552 (1958).

[18] E. Gil-Av and J. Herling, *Tetrahedron Lett.*, 27 (1961).