# Preparation and Favorskii Reaction of Equatorial and Axial 2-Bromobenzo[6,7]bicyclo[3.2.1]oct-6-en-3-one[1]

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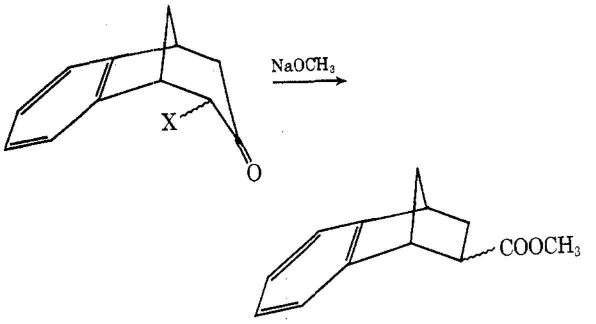
The title ketone was brominated to afford equatorial and axial 2-bromo ketones **6** and **7**, respectively, as well as the axial,axial 2,4-dibromo ketone **8**. Chlorination results were similar. Preparative routes to the individual brominated products were developed. The spectral characteristics of **6**, **7**, and **8** were quite like those of the nonbenzo analogs. The Favorskii reaction of either bromo ketone led to ring contraction and to the formation of the epimeric methyl benzonorbornene-2-carboxylates in good yield. The composition of the ester product did not depend significantly upon the reactant used but it did depend upon the solvent employed. The more polar solvent methanol (sodium methoxide was the base) largely favored the exo ester (exo:endo 80:20), whereas the less polar solvent glyme (same base) allowed an increase in the endo ester (exo:endo 58.5:41.5). The results are rationalized in terms of a cyclopropanone-mediated pathway from the bromo ketones to the esters. Subsequent base-catalyzed epimerization of the esters (solvent dependent) to the observed mixtures limited definitive conclusions about the Favorskii process.

Although monocyclic ring contraction by means of the Favorskii reaction is well known, such contraction in bicyclic molecules is less common.[2] In particular, this conversion in common bicyclic systems seems limited to bridgehead bromo ketones.[3] As part of a general program in benzonorbornene chemistry, it was of interest to investigate the reaction shown in eq 1.[4] Aside from the immediate question about the feasibility of reaction 1, two other specific points seemed worthwhile for investigation. First, would epimeric halo ketones yield epimerically related products, i.e., is reaction (1) stereospecific?[5] Second, could the solvent effect noted in earlier Favorskii reactions[7] be used to enhance the production of the endo 2-substituted product in eq 1—a type of compound generally less available than its exo counterpart?



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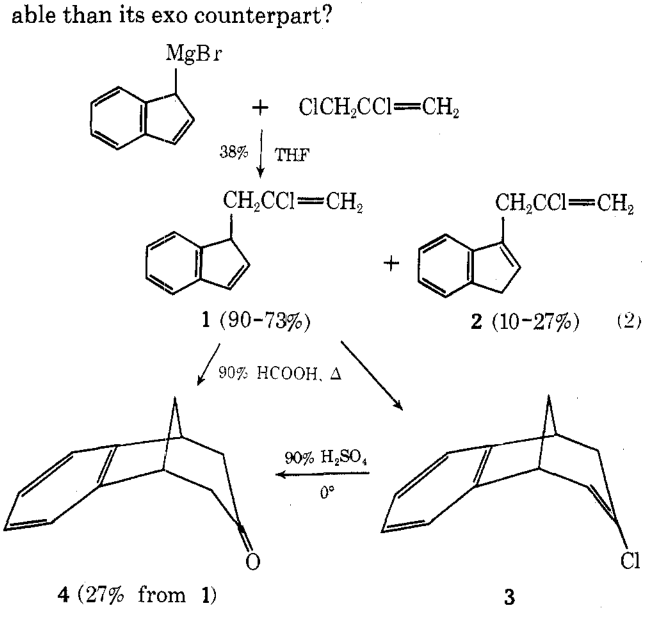

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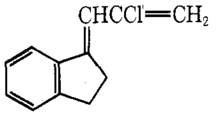
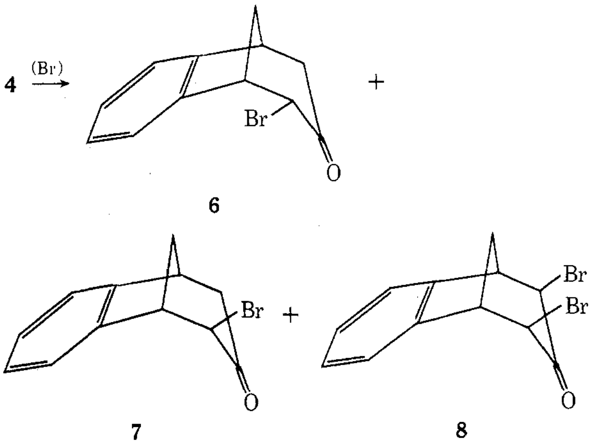
## Results

Benzo[6,7]bicyclo[3.2.1]oct-6-en-3-one (**4**) was prepared by the method of Lansbury and Nienhouse,[8] as shown in eq 2. The yields for the sequence were considerably below those reported. Moreover, in our preparations, the (chloroallyl)indene **2** accompanied the reported product **1**, making the separation of these isomers an additional complication.[9] Another isomeric possibility, compound **5**, was absent on the basis of both NMR and uv data.



**5**

Bromination of **4** under most conditions tried led to product mixtures of the equatorial 2-bromo ketone **6**, the axial 2-bromo ketone **7**, and the axial,axial 2,4-dibromo ketone **8**, shown in eq 3. *N*-Bromosuccinimide (NBS) was more selective, however, and its use constituted a good route to **7**. Some results are given in Table I.



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Chlorination of **4** was less satisfactory but quite analogous to bromination. When sulfuryl chloride was used, the axial,axial dichloro ketone (**8**-Cl) was isolable. Only crude samples of the axial chloro ketone **7**-Cl were obtained, and evidence for the equatorial isomer **6**-Cl was indirect. Use of *N*-chlorosuccinimide appeared to favor **7**-Cl.

The structure proofs for the bromo ketones **6–8** rest entirely upon their spectra. As may be seen in Table II, these bromo ketones were easily identified, nonetheless, because

Table I
Bromination of Benzobicyclooctenone 4

| Study | Reactants | Conditions | Products, % | | |
|---|---|---|---|---|---|
| | | | 6 | 7 | 8 |
| a | 4 + $Br_2$ | HOAc, 20° | 10–20 | 30–40 | 30–40 |
| b | 4 + $Br_2$ | HOAc, NaOAc, 20° | Trace | 40–50 | 40–50 |
| c | 4 + $PhN(CH_3)_3^+Br_3^-$ | THF, 20° | Trace | Trace | 40–50 |
| d | 4 + NBS + $Bz_2O_2$ | $CCl_4$, 76° | Trace | 90–98 | Trace |

Table II
Selected Spectral Characteristics of Bromo Ketones[a]

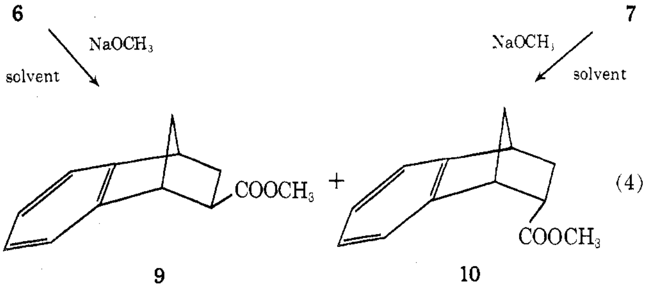
| Ketones | $\lambda_{max}$ (n,$\pi^*$), nm ($\epsilon$) | | $\nu_{C=O}$,[b] $cm^{-1}$ | | $\delta$H-2[c] | J, Hz | |
|---|---|---|---|---|---|---|---|
| | c-$C_6H_{12}$ | $CH_3CN$ | $CHCl_3$ | $CH_3CN$ | | 1,2 | 2, anti-8 |
| **4** | 288 (30) | | 1704 | | 2.38 (m) | | |
| **4a** | 280 (19) | | 1711 | | | | |
| **6** | 285 (29) | 283 (32) | 1727 | 1728 | 4.93 (d) | 3.6 | 0 |
| **6a** | | 284 (33) | 1733 | | (4.93) | 3.6 | 0 |
| **7** | 315 (188) | 308 (172) | 1720 | 1718 | 4.23 (m) | 3.2 | 1.6 |
| **7a** | 315 (105) | 313 (96) | 1715 | 1715 | (4.22) | 3.0 | 2.0 |
| **8** | 335 (105) | 332 (236) | 1722 | 1722 | 4.28 (dd) | 3.2 | 2.2 |
| **8a** | 342 (195) | 341 (190) | 1725 | 1722 | (4.28) | 3.0 | 1.8 |

[a] Ketone 4a is bicyclo[3.2.1]octan-3-one. Ketones 6a–8a are its bromo derivatives related to 6–8. Data for the ketones 4a and 6a–8a are taken from ref 10b. [b] Ca. 3% solutions in the given solvent. [c] $CDCl_3$ solvent. The values in parentheses are the observed values (ref 10b) + 0.25, an increment added to adjust these values taken in $CCl_4$ solvent to the $CDCl_3$ values.

their spectra closely resembled those of their nonbenzo analogs.[10]

As Table I indicates, the axial bromo ketone **7** was best synthesized using NBS. The dibromo ketone **8** was best obtained using phenyltrimethylammonium tribromide. The equatorial bromo ketone **6** was not easily producible from ketone **4**, however. Rather, epimerization of **7** with hydrogen bromide in acetic acid was employed. A mixture of **6** and **7** in a ca. 1:2 ratio was produced in this way. Separation by chromatography on silica gel then gave pure **6**. Epimerization of **7** to **6** with lithium bromide in acetone was unsuccessful. Characterization of **6** and **7** by their 2,4-DNP derivatives was complicated. Bromo ketone **6** afforded a product containing bromine, $\lambda_{max}$ ($CHCl_3$) 357 nm (log $\epsilon$ 4.35), which analyzed correctly for **6** 2,4-DNP. Thin layer chromatography showed that it was a mixture of two major and a number of minor components, however. Bromo ketone **7** produced an axial 2-ethoxy ketone 2,4-DNP derivative, $\lambda_{max}$ ($CHCl_3$) 359 nm (log $\epsilon$ 4.36).

Application of the Favorskii reaction on pure **6** or **7**, using sodium methoxide as the base, gave benzonorbornene products, as shown in eq 4. Moreover, the yields of esters **9** and **10** were good (70–94%) and the esters were separable. Two solvents were employed, methanol and 1,2-dimethoxyethane (glyme). Choice of solvent affected the reaction, as shown in Table III. Studies indicated, however, that this solvent effect involved *epimerization*. Placement of pure ester **9** in the basic medium used in each case gave comparable product mixtures of esters **9** and **10** as did the Favorskii reactions themselves.



(4)

**9** **10**

Table III
Favorskii Reaction on Bromo Ketones

| Bromo ketone | Solvent[a] | Ester yield, % | Composition by GLC[b] | |
|---|---|---|---|---|
| | | | % 9 | % 10 |
| **6** | $CH_3OH$ | 82 | 83.3 (90) | 16.7 (10) |
| **7** | $CH_3OH$ | 70 | 79.9 | 20.1 |
| **6** | Glyme | 94 | 58.5 (58) | 41.5 (42) |
| **7** | Glyme | 75 | 58.5 | 41.5 |

[a] Excess sodium methoxide was present in all cases. See Experimental Section. [b] Values in parentheses are the percentage compositions obtained by epimerization of pure ester 9 in the given solvent-base system.

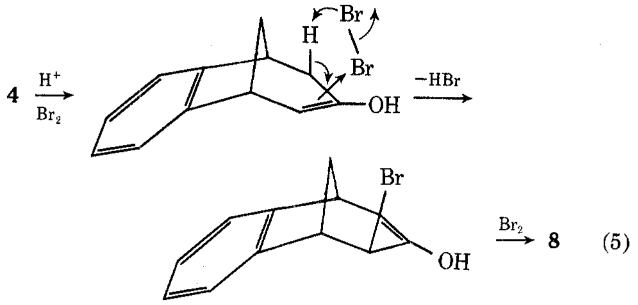
The exo ester **9** and its corresponding acid obtained by saponification were identical with samples available by another route.[11] Unreported at the outset of this study,[12a] endo ester **10** and its acid were initially characterized structurally only by spectra (see Discussion). In response to a referee's challenge on its structure, however, ester **10** (and its acid) were independently synthesized[12b] for comparison.

## Discussion

The structural evidence for and the origin of (chloroallyl)indene **2** in the sequence of eq 2 deserve comment. While there were slight differences between **1** and **2** in their ir and uv spectra, substantial structural evidence was best obtained from their NMR spectra. In **1**, the chloroallylic methylene protons were clearly nonequivalent because of the adjacent asymmetric center. An AB multiplet centered at $\delta$ 2.53 was evident.[13] In **2**, however, these methylene protons were equivalent as expected and a broad singlet resonance at $\delta$ 3.63 was observed. Additionally, **2** possessed another pair of methylene protons (benzylic), seen as a narrow doublet at $\delta$ 3.40. Finally, **1** exhibited four vinyl protons whereas **2** exhibited three. The origin of **2** probably was a base-promoted isomerization of **1** by excess indenyl Grignard reagent. The recommended procedure[8] utilized inverse addition (the Grignard reagent was *slowly added to* the dichloropropene). Such a procedure should minimize such an isomerization because locally high base (Grignard reagent) concentrations are avoided. Nonetheless, as **1** builds in concentration, opportunity for contact with the entering Grignard reagent increases. While not thoroughly investigated, the *rate of addition* of the Grignard reagent seemed important. Slow (ca. 10 min) addition gave 10% of **2**, while addition in toto gave 27% of **2**. In none of our tries, however, was the formation of some **2** avoided.[14]

The possibility that the by-product was **5** seems remote. The NMR spectrum of **5** should present an AA′BB′ pattern for the methylene protons and its uv spectrum should resemble that of 3-chloro-1-phenylbutadiene [lit.[16] $\lambda_{max}$ 283 nm ($\epsilon$ 20,400)]. However, the by-product showed no such NMR pattern and had $\lambda_{max}$ 250 nm ($\epsilon$ 6712).

The bromination of ketone **4** proceeded largely as anticipated. Axial bromination via enol intermediates is well documented[10] in **4a** and the preponderance of **7** over **6** is unexceptional. Comparison of studies a and b in Table I indicates that **6** is not a kinetic product. In the presence of a hydrogen bromide scavenger (sodium acetate), the formation of **6** was suppressed. Most likely, therefore, it formed in study a by an acid-catalyzed epimerization of **7**. Studies a–c do show one interesting feature: $\alpha,\alpha'$-dibromination to **8** is a serious side reaction in all cases, but particularly in tetrahydrofuran. The recent report[17] that dibromination follows a different mechanistic pathway than monobromination may find further exemplification here. If **8** had resulted from a *second* bromination of **7** (as has been customarily believed for such dibromo products), then about half of **7** was so changed in a and b. However, this same fate should have befallen **6**, and 5–10% of an equatorial, axial 2,4-dibromo ketone should have resulted. The absence of this product lends support to the idea that **4** is itself the source of **8** via a bromo enol as in eq 5. The improved formation of **8** in tetrahydrofuran in study c is in accord with the contention[17] that aprotic nonpolar media should assist dibromination relative to monobromination. Study d employed a radical bromination pathway. In the absence of benzoyl peroxide no reaction took place. The absence of **8** as a product is explicable because enols do not mediate such pathways. The formation of **7** must result from the lack of other easy reaction sites and the known exo (axial here) preference for chain transfer in related bicyclic systems.[18]

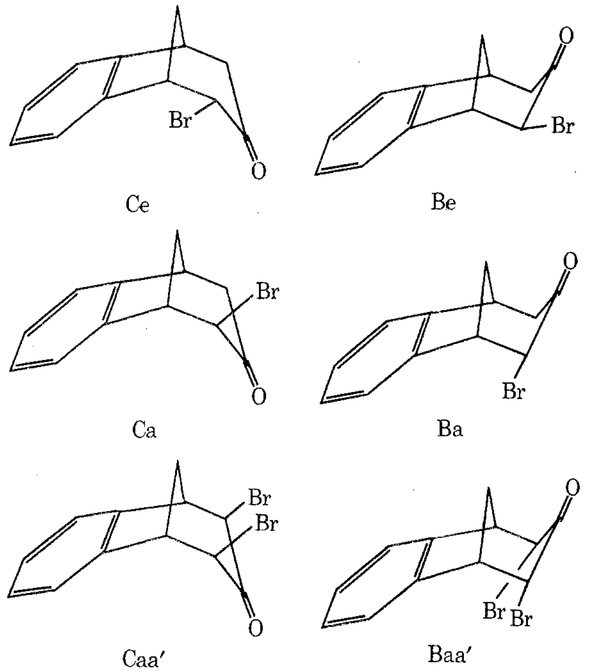


(5)

The structures for **6**–**8** that are based upon spectra seem secure.[19] In brief, equatorial $\alpha$-bromo substituents in ketones are known to cause little change in the n,$\pi$* absorption in the uv, either in $\lambda_{max}$ or in $\epsilon$, compared to the parent ketone. In contrast, a significant shift to higher frequency in the ir carbonyl stretch is observed. Bromo ketones **6** and **6a** show such behavior relative to **4** and **4a**. Essentially the reverse effects are caused by axial $\alpha$-bromo substituents, as illustrated by **7**, **7a**, **8**, and **8a** relative to the parent ketones. One point deserves more comment. The ir shift for the carbonyl stretch between **4** and **7** is greater than that between **4a** and **7a** (16 vs. 4 $cm^{-1}$) even though the bromo substituent is axial in both **7** and **7a**. This results from the more skewed axial position of the bromine in **7** caused by the [6,7]benzo ring. This skewing decreases the axial character at C-2 somewhat and increases the shift in the ir. The close similarity of the spectra of the benzo and nonbenzo ketones in Table II demonstrates that in these cases the aromatic $\pi$ system does not seriously perturb the situation, a point that had been a concern to others.[10c]

From the spectral data just discussed, an axial or an equatorial position for the bromide in the bromo ketones may be assigned. So **6** is either Ce or Be, **7** is either Ca or Ba, and **8** is either Caa′ or Baa′, as shown in Chart I, provided that only extreme chair or boat conformers are considered. Various data indicate that the chair conformers in Chart I predominate. The carbonyl stretching frequencies of these compounds remained essentially constant in either cyclohexane or acetonitrile, as did the molar absorptivities of the n,$\pi$* uv transition. Both of these features imply a high degree of conformational rigidity.[19] The symmetrical structure given for **8** (Caa′) was assigned from its revealing NMR spectrum. The bromomethine protons were identical and exhibited a doubled doublet at $\delta$ 4.28, with vicinal and long-range coupling constants in accord only with a chair conformer.[10] The similarity in those selected spectral characteristics presented in Table II between **8** and **7** clearly establish the chair conformation Ca for **7** as well. The bromomethine proton in **6** appeared as a sharp doublet at $\delta$ 4.93. Spin-decoupling experiments[20] showed that vicinal coupling alone was present. The value of $J_{1,2}$ here (3.6 Hz) was in better accord with the vicinal dihedral angle of 60° present in Ce than with one of 100° present in Be. The latter would be expected to have $J_{1,2} \simeq 0$ Hz, especially so because the bromine atom would nearly eclipse H-1 and contribute to the vanishing of the coupling.[21]

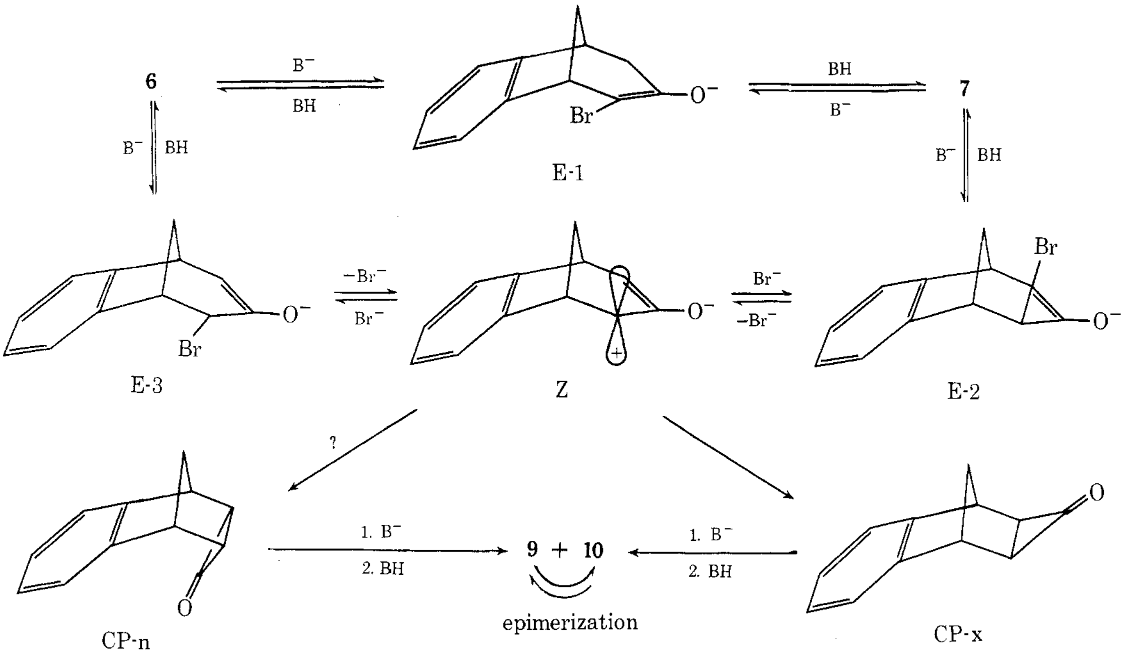
**Chart I**



The formation of an ethoxy ketone 2,4-DNP derivative from **7** is not unexpected.[22] Bromo ketone **7** was itself stable in acidic alcohol; so the derivative was probably formed from solvolysis of the **7** 2,4-DNP first formed. The mixture of derivatives formed from **6** may be *E,Z* isomers or skeletally rearranged products.[23] No work was done on this point, however.

Favorskii product **9** was identified by comparison with a

**Chart II**[a]



[a] $B^- = CH_3O^-$; BH = $CH_3OH$.

known sample.[11] The structure of ester **10** was most convincingly evidenced by comparison with **9**. In particular, three spectral features were sought and found that helped to distinguish the two. First, the exo methine proton H-2 in **10** was deshielded relative to the endo H-2 in **9** ($\delta$ 3.17 vs. 2.38, respectively). Second, the cis coupling for exo H-2 and the adjacent exo H-3 in **10** was greater[24] than the trans coupling for endo H-2 and the adjacent exo H-3 in **9** (10 vs. 5 Hz, respectively). Third, the methoxy protons in **10**, being closer to the aromatic ring, were upfield relative to those in **9**[25] ($\delta$ 3.49 vs. 3.72, respectively). Additionally, however, ester **10** was shown to be identical with a sample prepared by an unambiguous path.[12b]

The literature on the Favorskii reaction is voluminous. The current "normal" mechanism is a cyclopropanone-mediated pathway with intervening dipolar ion species.[26] "Abnormal" Favorskii reactions have been rationalized via a semibenzilic acid rearrangement mechanism.[27] The scheme given in Chart II is based on the more common "normal" mechanism as a guide. Because our studies do not bear significantly on the Favorskii pathway itself, particularly as kinetic control was absent owing to the ready epimerization of ester **9**,[28] it seems best to accommodate our results to the generally accepted mechanism. In dilute base (0.1 *M* sodium methoxide in methanol) **6** and **7** equilibrated rapidly, presumably via enolate E-1. The bromo ketones were additionally slowly consumed in the Favorskii process. The alternative enolates E-2 and E-3 formed from **7** and **6** should afford the zwitterion Z easily because the bromine in each is similarly positioned for departure. The disrotatory closure of Z to the exo cyclopropanone CP-x can then readily occur. Though symmetry-allowed, such analogous closure of Z to the endo cyclopropanone CP-n appears from molecular models to be somewhat unfavorable for steric reasons, although our data cannot exclude it. The carbonyl and ring $\pi$ systems are severely close and the transition state leading to CP-n should be disfavored for this reason. Also, some torsional strain between the bridgehead hydrogens and H-2,4 would develop as they pass by one another in the formation of CP-n. Nonetheless, either CP-x and CP-n would yield the esters **9** and **10** via base-promoted ring opening and subsequent epimerization. Finally, the different compositions of esters found in the two solvents used may reflect different solvation effects on the equilibria involved, but no further studies were made on this point.

## Experimental Section

Melting points and boiling points are uncorrected. The former were taken in capillaries in a Thomas-Hoover oil bath apparatus. All thin layer chromatography (TLC) was performed on Silicar-7GF coated plates or on commercial Analtech S. G. F. plates. Spectra were determined on the following instruments: NMR, Varian A-60, T-60, or HA-100 spectrometers; ir, Perkin-Elmer 421 or 521 spectrophotometers; and uv, Cary 11 or Beckman Octa V spectrophotometers. Gas chromatography (GLC) was conducted on a Varian Aerograph 1520 instrument with helium carrier gas. Microanalyses were done by Abbott Laboratories, North Chicago, Ill.

**Benzo[6,7]bicyclo[3.2.1]oct-6-en-3-one (4).** This ketone was obtained as reported, mp 66–67° (lit.[8b] mp 64–66°). Selected spectral features are given in Table II.[29]

**3-(2-Chloroallyl)indene (2).** In the preparation of **4**, reaction of indenylmagnesium bromide with 2,3-dichloropropene in tetrahydrofuran gave the reported product **1**[8] and varying amounts of **2**, depending upon the time of addition of the Grignard reagent (see Discussion). Indene **2** was isolated in one preparation by GLC on a column of fluorosilicone oil (QF-1, 15% on Chromosorb W) at 140°: $\nu$ ($CCl_4$) 1394 $cm^{-1}$ (trisubstituted alkene); $\delta$ ($CCl_4$) 7.40 (m, ArH), 6.43 (m, H-2), 5.33, 5.23 (m, $=CH_2$), 3.63 (broad s, allylic $CH_2$), 3.40 (narrow d, 1-$CH_2$); $\lambda_{max}$ (hexane) 250 nm ($\epsilon$ 6712).[30]

Anal. Calcd for $C_{12}H_{11}Cl$: C, 75.59; H, 5.82. Found: C, 75.45; H, 5.98.

**(a)-2-Bromobenzo[6,7]bicyclo[3.2.1]oct-6-en-3-one (7).** Ketone **4** (12 g, 70 mmol), *N*-bromosuccinimide (freshly recrystallized from water, 12.4 g, 70 mmol), benzoyl peroxide (0.96 g), and carbon tetrachloride (60 ml) were heated under reflux for 8 hr. The material was chilled and separated from the precipitate of succinimide. Evaporation under reduced pressure left a yellow oil (17.5 g, ca. 100%) which was indicated by TLC to be mainly **7**. The pure product was obtained by chromatography on silica gel using chloroform hexane mixtures as eluents as a colorless oil: 17.1 g (97%); $\nu$ ($CHCl_3$) 1720 $cm^{-1}$ (C=O); $\delta$ ($CDCl_3$) 7.22 (m, ArH), 4.23 (m, H-2), 3.31 (m, H-1, axial 4, 5), 2.48 (m, 8-$CH_2$, equatorial H-4); $\lambda_{max}$ (cyclohexane) 315 nm ($\epsilon$ 188). Other spectral data are in Table II.[29] The bromo ketone should be stored below 0°.

Anal. Calcd for $C_{12}H_{11}OBr$: C, 57.39; H, 4.42. Found: C, 57.58; H, 4.53.

Reaction of **7** (0.4 g) with 2,4-DNP reagent in alcohol–sulfuric acid slowly gave an orange precipitate (0.46 g, mp 74–84° dec). Recrystallization from acetone–water (no exchange to an acetone derivative occurred) gave a bromine-free pure product, mp 172.5–174.5° dec, 87 mg (14%), $\lambda_{max}$ ($CHCl_3$) 359 nm ($\epsilon$ 22,912). The presence of an ethoxy group was clear in the NMR spectrum, $\delta$ ($CDCl_3$) 3.58 (q), 1.26 (t). The derivative was presumably the 2,4-DNP derivative of the axial 2-ethoxybenzo[6,7]bicyclo[3.2.1]oct-6-en-3-one.

Anal. Calcd for $C_{20}H_{20}O_5N_4$: C, 60.60; H, 5.09; N, 14.13. Found: C, 60.73; H, 5.11; N, 14.32.

Bromo ketone **7** did not solvolyze in acidic alcohol under these conditions. Therefore the ethoxy derivative is believed to form from **7** 2,4-DNP by ethanolysis.

**(e)-2-Bromobenzo[6,7]bicyclo[3.2.1]oct-6-en-3-one (6).** Hydrogen bromide (8.75 g) was gently bubbled into bromo ketone **7** (17.5 g, 70 mmol) dissolved in acetic acid (875 ml). The solution was allowed to stand at room temperature. Analysis by TLC after 1.5 days indicated an epimeric mixture of **6** and **7**, together with small amounts of the parent ketone **4** and dibromo ketone **8**. No further change was observed in the time period 1.5–5 days. The mixture was poured into water and extracted with ether. Upon removal of the solvent from the dried extracts, a crude mixture of mostly **6** and **7** was obtained as a brown oil (16.1 g, 92%). Analysis by NMR indicated ca. two parts of **7** to one part of **6**. In chromatography on silica gel with chloroform–hexane, the elution order was **8**, **7**, **6**, and lastly **4**. In this way was isolated pure **6**, 3.77 g (21%), mp 108–109° from hexane: $\nu$ ($CHCl_3$) 1727 $cm^{-1}$ (C=O); $\delta$ ($CDCl_3$) 7.27 (m, ArH), 4.93 (d, H-2), 3.75 (m, H-1), 3.45 (m, H-5), 2.78 (finely structured m, 4-$CH_2$), 2.38 (m, 8-$CH_2$); $\lambda_{max}$ (cyclohexane) 285 nm ($\epsilon$ 28.8). Other spectral data are in Table II.[29]

Anal. Calcd for $C_{12}H_{11}OBr$: C, 57.39; H, 4.42. Found: C, 57.37; H, 4.48.

Use of catalytic amounts of hydrogen bromide in acetic acid, or formic acid, or carbon tetrachloride under various conditions was less effective in the epimerization. Pyridine failed to promote the reaction after 1 week at 25°. Under these last conditions lithium bromide in acetone was similarly ineffective. Sodium methoxide in methanol (0.1 *M*) at 25° rapidly isomerized **7** to **6** and vice versa. The process was complicated by loss of reactant to the Favorskii reaction, however.

Reaction of **6** (100 mg) with 2,4-DNP reagent in alcohol–sulfuric acid gave a precipitate, 160 mg, mp 138–143°. The orange solid was recrystallized from acetone (no exchange), mp 169–173° dec, $\lambda_{max}$ ($CHCl_3$) 357 nm ($\epsilon$ 22,514). Analysis by TLC indicated two major and several minor components. While no definite structures were assigned to these components, it is clear that no bromine loss occurred in this derivatization (cf. **7** above).

Anal. Calcd for $C_{18}H_{15}O_4BrN_4$: C, 50.13; H, 3.51; N, 12.99. Found: C, 50.18; H, 3.54; N, 13.04.

**(a,a)-2-4-Dibromobenzo[6,7]bicyclo[3.2.1]oct-6-en-3-one (8).** To a solution of ketone **4** (0.5 g, 2.9 mmol) in anhydrous tetrahydrofuran (20 ml) held at 20° there was added phenyltrimethylammonium tribromide (Aldrich, 1.6 g, 4 mmol). After 1 hr the solution was added to a saturated solution of sodium bicarbonate (12.5 ml) combined with sodium thiosulfate (0.1 *N*, 25 ml). The product was extracted with ethyl acetate. The extracts were dried and evaporated to afford crystalline **8**. Recrystallization from ether gave pure **8**, 0.44 g (46%), mp 166–169°: $\nu$ ($CHCl_3$) 1723 $cm^{-1}$ (C=O); $\delta$ ($CDCl_3$) 7.27 (s, ArH), 4.28 (dd, H-2, 4), 3.63 (m, H-1, 5), 3.27 (d, $J$ = 13 Hz, H-8 anti to aromatic ring), 2.42 (m, H-8 syn to aromatic ring); $\lambda_{max}$ (cyclohexane) 335 nm ($\epsilon$ 233). Other spectral data are given in Table II.[29]

Anal. Calcd for $C_{12}H_{10}OBr_2$: C, 43.67; H, 3.05. Found: C, 43.65; H, 3.21.

**Other Bromination Studies.** (1) Bromination of ketone **4** in glacial acetic acid (equimolar reactants at 20° with illumination from a 275-W sun lamp) gave a mixture of **6**, **7**, and **8**. See Table I. Analysis was by TLC, although crystalline **8**, which settled out upon completion of the reaction, could be isolated directly. This represented the fastest method to obtain **8**, but the yield was somewhat lower than the method described above. (2) Ketone **4** (0.5 g, 3 mmol) in glacial acetic acid (15 ml) containing 1 drop of acetic acid saturated with hydrogen bromide was treated dropwise with bromine (0.53 g) and anhydrous sodium acetate (0.27 g) in acetic acid (15 ml) over a 45-min period. Water (75 ml) was added and the crystalline precipitate was filtered off. The filtrate was extracted with ether thoroughly. Analysis by TLC of the precipitate and the solvent-free extracts indicated a ca. 1:1 ratio of **7**:**8**. Only a trace of **6** was detected. See Table I. (3) Bromination of ketone **4** in carbon tetrachloride as in part 1 led to a similar set of products but in ca. one-half the yield. (4) Attempted reaction of ketone **4** with NBS (equimolar, 1-hr reflux) gave an 80% recovery of **4** with no apparent bromination. (5) Attempted reaction as in 4 with NBS and a trace of benzoyl peroxide at 25° for 8 hr likewise was unsuccessful (94% recovery of **4**).

**Chlorination Studies.** (1) Ketone **4** (1.0 g, 5.8 mmol) in dry carbon tetrachloride (29 ml) was treated dropwise with sulfuryl chloride (5.2 ml, 6.4 mmol) in carbon tetrachloride (8 ml) at ambient temperature. After 2 hr the solution was poured into ice water. The organic layer was neutralized with sodium bicarbonate solution, separated, dried, and evaporated. The residue (1.42 g) was analyzed by TLC. By comparison of relative $R_f$ values with the bromo analogs, the product consisted principally of the axial chloro ketone **7**-Cl and the axial,axial′ dichloro ketone **8**-Cl, with a trace of the equatorial chloro ketone **6**-Cl. The dichloro ketone was the only pure product isolated: mp 153–155° from cyclohexane–hexane; $\delta$ ($CDCl_3$, partial spectrum) 4.15 (dd, H-2, 4).

Anal. Calcd for $C_{12}H_{10}OCl_2$: C, 59.78; H, 4.18. Found: C, 60.11; H, 4.31.

Impure **7**-Cl, mp 54–64° from hexane, was also isolated, $\delta$ ($CDCl_3$, partial spectrum) 4.02 (m, H-2). (2) Reaction of ketone **4** (0.5 g), benzoyl peroxide (40 mg), and *N*-chlorosuccinimide (0.4 g) in carbon tetrachloride under reflux for 8 hr gave crude **7**-Cl in quantitative yield (0.6 g). Only trace amounts of the other chloro ketones were evident by TLC analysis.

**Favorskii Reaction of Bromo Ketone 6. A. In Methanol.** A solution of sodium methoxide in methanol (2 *M*, 20 ml) was stirred with bromo ketone **6** (0.25 g, 1.0 mmol) at 25° for 4 hr. The solution was chilled to 0° and neutralized with glacial acetic acid. Ether (80 ml) was added and the precipitate of sodium acetate was separated. The ether was evaporated from the filtrate and the residual yellow oil (0.18 g) was analyzed by GLC on a silicone gum rubber column (10% SE-52 on Chromosorb W) at 180°. The chromatograms were calibrated with known samples. The yield of combined esters was 82%; the percentage composition was **9**:**10**, 88.3:16.7. Under these conditions endo ester **10** eluted before its exo isomer **9** (relative retention times 0.95:1).

**Methyl benzonorbornene-*exo*-2-carboxylate (9)** was identical with an authentic sample[11] as was the corresponding acid, mp 112–113° (lit.[11] mp 112–113°), obtained from it by saponification.

**Methyl benzonorbornene-*endo*-2-carboxylate (10)** was obtained as a colorless oil: $\nu$ ($CHCl_3$) 1728 $cm^{-1}$ (C=O); $\delta$ ($DCDl_3$) 7.11 (m, ArH), 3.65 (m, H-1), 3.49 (s, $COOCH_3$), 3.37 (m, H-4), 3.17 (doublet of triplets, H-2, $J_{2,exo\text{-}3}$ = 10, $J_{1,2}$ = $J_{2,endo\text{-}3}$ = 4 Hz), 2.10 (eight-line multiplet, exo H-3), 1.9–1.5 (m, endo H-3, 7-$CH_2$).

Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 76.89; H, 6.67.

Ester **10** was identical with a sample prepared in a totally independent fashion.[12b] Saponification of **10** with 1 *N* aqueous methanolic sodium hydroxide (25°, 20 hr) afforded benzonorbornene-*endo*-2-carboxylic acid: mp 131–132° from hexane; $\nu$ ($CHCl_3$) 3540, 3300–2500 (broad), 1750 (sh), 1710 $cm^{-1}$ (COOH); $\delta$ ($CDCl_3$) 9.03 (broad, COOH), 7.12 (m, ArH), 3.67 (m, H-1), 3.40 (m, H-4), 3.20 (doublet of triplets, H-2, $J$'s as in ester **10**), 2.10 (eight-line multiplet, exo H-3), 1.9–1.45 (m, endo H-3, 7-$CH_2$).

Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.52; H, 6.41.

Use of dilute sodium methoxide (0.1 *M*) in the above reaction for 52 hr was less satisfactory. The reaction led to ester **9** in only 44% yield and a number of uncharacterized by-products were observed. No endo ester **10** was detected although small amounts could have been overlooked in the complex GLC and NMR traces. Early stages of the reaction were followed by TLC. Partial isomerization of bromo ketone **6** to the axial isomer **7** was pronounced in the initial stages. Seemingly, the two were "equilibrated" in ca. 3 hr. Thereafter **7** afforded **9** while **6** slowly disappeared, at least partially, through isomerization to **7**.

**B. In 1,2-Dimethoxyethane (Glyme).** A suspension of sodium methoxide in glyme was prepared from sodium metal (0.12 g, 5 mg-atoms) and methanol (0.55 g) in hot solvent (7 ml). At 25°, bromo ketone **6** (0.25 g, 1.0 mmol) in glyme (1 ml) was added and the mixture was stirred for 1 hr. The reaction material was chilled to 0° and processed as described above. The yield of esters was 94.2% and the percentage composition was **9**:**10**, 58.5:41.5.

**Favorskii Reaction of Bromo Ketone 7.** These reactions were performed in exactly the same manner as described for **6**. The results are given in Table III.

**Epimerization Studies. A. In Methanol.** Ester **9** (1 mmol) was substituted for bromo ketone **6** in the procedure given above for the Favorskii reaction of the latter in methanol. The procedure used was identical and the recovered ester was analyzed by GLC as stated there. Recovery was essentially quantitative. The percentage composition determined by GLC was **9:10**, 90.2:9.8. The composition determined by NMR analysis was **9:10**, 87:13.

**B. In Glyme.** Ester **9** (1 mmol) was substituted for bromo ketone **6** in the procedure given above for the Favorskii reaction of the latter in glyme. The procedure used was identical and the recovered ester (~100%) was analyzed: by GLC, **9:10**, 58.1:41.9; by NMR, **9:10**, 60:40.

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**Registry No.**—**2**, 54143-19-0; **4**, 13351-26-3; **6**, 54143-20-3; **6** DNP, 54143-21-4; **7**, 54164-79-3; **7** DNP, 54164-80-6; **8**, 54143-22-5; **8** Cl, 54143-23-6; **9**, 54143-24-7; **10**, 54164-81-7; **10** free acid, 54274-40-7; 2,4-DNP derivative of (a)-2-ethoxybenzo[6,7]bicyclo[3.2.1]oct-6-en-3-one, 54143-25-8; phenyltrimethylammonium tribromide, 4207-56-1.

## References and Notes

(1) Taken from the M.S. Thesis of R.R.R., 1973. Portions of this work were presented at the 166th National Meeting of the American Chemical Society, Chicago, Ill., Aug 1973, Abstracts, No. ORGN 26.

(2) Reviews: (a) R. Jacquier, *Bull. Soc. Chim. Fr.*, **17**, 35 (1950); (b) A. S. Kende, *Org. React.*, **11**, 261 (1960).

(3) E. W. Warnhoff, C. M. Wong, and W. T. Tai, *J. Am. Chem. Soc.*, **90**, 514 (1968); W. C. Fong, R. Thomas, and K. V. Scherer, Jr., *Tetrahedron Lett.*, 3789 (1971).

(4) Dr. P. J. Chenier at the University of Wisconsin—Eau claire has found that *exo*-3-bromobenzonorbornenone-2 undergoes Haller–Bauer cleavage and not Favorskii ring contraction upon treatment with sodium hydroxide in tetrahydrofuran. We thank Dr. Chenier for this information prior to publication.

(5) Stereospecificity under certain conditions has been previously observed.[6]

(6) G. Stork and I. J. Borowitz, *J. Am. Chem. Soc.*, **82**, 4307 (1960).

(7) H. O. House and W. F. Gilmore, *J. Am. Chem. Soc.*, **83**, 3980 (1961).

(8) (a) P. T. Lansbury and E. J. Nienhouse, *J. Am. Chem. Soc.*, **88**, 4290 (1966); (b) P. T. Lansbury, E. J. Nienhouse, D. J. Scharf, and F. R. Hilfiker, ibid., **92**, 5649 (1970). We thank Professor Lansbury for detailed information on this synthesis early in our studies.

(9) The formation of **2** was first noticed in our work by F. Guziec, Senior Research Report, 1968. Lansbury and Nienhouse[8a] claimed its absence.

(10) (a) C. W. Jefford and B. Waegell, *Tetrahedron Lett.*, 1981 (1963); (b) B. Waegell and C. W. Jefford, *Bull. Soc. Chim. Fr.*, 844 (1964); (c) A. Baretta, J. P. Zahra, B. Waegell, and C. W. Jefford, *Tetrahedron*, **26**, 15 (1970).

(11) J. W. Wilt and P. J. Chenier, *J. Org. Chem.*, **35**, 1562 (1970).

(12) (a) An ethyl ester, possibly the ethyl ester analog of **10**, was reported by K. Alder and M. Fremery, *Tetrahedron*, **14**, 190 (1961), as the adduct of isoindene (generated in situ) and ethyl acrylate. A 20% yield was claimed, with support for structure from an unreported spectrum. Its configuration was not discussed. We have been unable to duplicate this work. (b) J. W. Wilt and V. Narutis, *J. Org. Chem.*, submitted for publication. In brief, the sequence involved the construction of a benzo ring onto the skeletal framework of norbornene-*endo*-2-carboxylic acid, followed by esterification to **10**.

(13) Lansbury and coworkers[8b] report the allylic methylene group at $\delta$ 2.48, with no mention of the AB multiplet.

(14) It has been our experience that small amounts of **2** can go undetected in **1**. The NMR differences reported[15] between 1- and 3-methylindene which were employed as corroborative evidence by Lansbury and Nienhouse[8a] for the absence of **2** do not relate well to the differences between **1** and **2**.

(15) A. Bosch and R. K. Brown, *Can. J. Chem.*, **42**, 1718 (1964).

(16) N. B. Kupletskaya, A. V. Dombrovskii, and A. P. Terent'ev, *Zh. Obshch. Khim.*, **27**, 3041 (1957).

(17) K. E. Teo and E. W. Warnhoff, *J. Am. Chem. Soc.*, **95**, 2728 (1973).

(18) J. W. Wilt, G. Gutman, W. J. Ranus, Jr., and A. R. Zigman, *J. Org. Chem.*, **32**, 893 (1967).

(19) For a pertinent, recent article with many leading references where the spectral features of cyclic $\alpha$-bromo ketones are developed in detail, see C. W. Jefford, R. McCreadie, P. Muller, and J. Pfyffer, *J. Chem. Educ.*, **50**, 181 (1973).

(20) We thank Dr. R. Egan and Ms. R. Stanaszek of Abbott Laboratories, North Chicago, Ill., for the decoupling experiments. Details of these experiments and of a LAOCN 3 computer-calculated spectrum of **6** are available in the thesis of R.R.R.

(21) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", Pergamon Press, Elmsford, N.Y., 1969, p 284. Cf. also K. G. R. Pachler, *Tetrahedron Lett.*, 1955 (1970).

(22) Cf. F. Ramirez and A. F. Kirby, *J. Am. Chem. Soc.*, **75**, 6026 (1953); **74**, 4331 (1954).

(23) For skeletal rearrangements in this system, see P. T. Lansbury and N. T. Boggs, III, *Chem. Commun.*, 1007 (1967); P. T. Lansbury and E. J. Nienhouse, ibid., 1009 (1967).

(24) Reference 21, p 289.

(25) The same effect has been observed for the methyl resonances of exo ($\delta$ 2.15) and endo ($\delta$ 1.87) 2-acetylbenzonorbornenes by R. R. Sauers and A. M. De Paolis, *J. Org. Chem.*, **38**, 639 (1973).

(26) Bordwell and coworkers have been largely responsible for the development of the detailed reaction sequence. For a recent paper, cf. F. G. Bordwell and J. G. Strong, *J. Org. Chem.*, **38**, 579 (1973).

(27) J. M. Conia and J. Salaün, *Tetrahedron Lett.*, 1175 (1963); *Bull. Soc. Chim. Fr.*, 1957 (1964).

(28) Our results do not *preclude* an "abnormal" pathway to the esters, but enolizable bromo ketones usually follow the "normal" pathway.

(29) Complete spectra may be found in the M.S. Thesis of R.R.R., 1973.

(30) Cf. (chloroallyl)indene **1**, $\lambda_{max}$ (hexane) 243 nm ($\epsilon$ 13,110).

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# Addition of Diphenyldiazomethane to 7-*tert*-Butoxynorbornadiene. Formation of *exo*- and *endo*-3,3-Diphenyltricyclo[3.2.1.0$^{2,4}$]octene Derivatives[1,2]

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Room temperature addition of the title two reactants (diene in excess) led to all of the monoadducts possible (40–55%) in roughly comparable amounts except for the exo-syn adduct, which was formed in very low yield. Minor amounts of bis adducts were observed. Some factors involved in this nonselective 1,3-dipolar cycloaddition are discussed. Pyrolysis of the adducts led to the corresponding tricyclic ethers in high yield. These ethers serve as convenient entries into the *exo*- and *endo*-3,3-diphenyltricyclo[3.2.1.0$^{2,4}$]octane systems. As examples of some transformations possible with these ethers, the exo-anti ether was converted via acetolysis and hydrolysis to its alcohol with complete retention of configuration. Similarly, the endo-syn ether was converted to its alcohol and eventually to the interesting parent hydrocarbon, *endo*-3,3-diphenyltricyclo[3.2.1.0$^{2,4}$]octene. The endo-anti and exo-syn ethers did not behave analogously. The former underwent an apparently deep-seated change upon acetolysis, whereas the latter smoothly rearranged to a bicyclo[3.2.1]octene derivative. The pathways of these reactions are discussed briefly, along with the presentation of confirmatory physical data for the structures assigned.

Work on another aspect of this general area[3] necessitated the synthesis of alcohol **6-OH** (vide infra). The first step in its preparation was the 1,3-dipolar cycloaddition of diphenyldiazomethane to 7-*tert*-butoxynorbornadiene. This addition resulted in a variety of adducts, all of which have potential utility in the study of 3,3-diphenyltricy-