Reaction of *trans*-1-Cyclohexyl-2,3-dibenzoylaziridine (25) with Enedione 1.—A solution of 62 mg of enedione 1 in 5 ml of toluene containing 165 mg of aziridine **25** was heated at reflux for 2.75 hr. Concentration and filtration gave 181 mg (80%) of crude solid product. This was recrystallized several times from benzene to yield an analytical sample of adduct **27**: mp 175.5–177°; ir (KBr disk) 1765 (m), 1720 (s), 1675 (s), 1660 (s), 1230 (s) cm^{-1}; nmr ($CDCl_3$) δ 0.5–2.0 (m, 10 H, CH_2), 1.12 (s, 3 H, CH_3), 1.20 (s, 3 H, CH_3), 2.28–2.80 [broad, 1 H, C(1)H of cyclohexyl], 3.55 (dd, J_{BA} = 10.5 Hz, J_{BC} = 3 Hz, 1 H, $COCH_B$), 3.92 (dd, J_{AB} = 10.5 Hz, J_{AD} = 8 Hz, 1 H, $COCH_A$), 5.52 (d, J_{CB} = 3 Hz, 1 H, $ArCOCH_C$), 5.78 (d, J_{DA} = 8 Hz, 1 H, $ArCOCH_D$), 7.2–8.6 (m, 10 H, ArH).

Anal. Calcd for $C_{29}H_{31}O_4N$: C, 76.13; H, 6.84; N, 3.07. Found: C, 76.14; H, 6.91; N, 2.96.

Reaction of Diazomethane with Enedione 1.—A solution of 500 mg of enedione 1 in 20 ml of ether was treated with 30 ml of 0.14 *M* ethereal diazomethane. After 3 hr at room temperature excess diazomethane was distilled out on the steam bath and the solvent removed. The resulting crystals were washed with cyclohexane and filtered to give 514 mg (77%) of pyrazoline **28**. This was recrystallized by dissolution in benzene at room temperature, addition of cyclohexane, and subsequent cooling. Four such operations gave an analytical sample: mp 86–88°; ir 1770 (w), 1730 (s), 1545 (w) cm^{-1}; nmr ($CDCl_3$) δ 0.97 (s, 3 H, CH_3), 1.25 (s, 3 H, CH_3), 3.40 (six lines, 1 H, CH_2CH_BCO), 4.9–5.2 (m, 2 H, CH_XH_Y), 5.80 (broad dt, J_{AB} = 9 Hz, J_{AX} = 2.5 Hz, $J_{AY} \sim 0.5$ Hz, 1 H, NCH_ACO). This compound is light sensitive.

Anal. Calcd for $C_8H_{10}O_2N_2$: C, 57.82; H, 6.07; N, 16.86. Found: C, 57.91; H, 5.87; N, 16.76.

Pyrolysis of Pyrazoline 28.—A solution of 200 mg of adduct **28** in 10 ml of toluene was heated at reflux for 1.5 hr. The solvent was evaporated to leave 135 mg (81%) of crude product which was purified by preparative vpc to give an analytical sample of ketone **29**: ir 1750 (m), 1710 (s), 1620 (m), 1280 (m), 1120 (m) cm^{-1}; nmr δ 1.10 (s, 6 H), 2.10 (d, J = 1 Hz, 3 H), 6.84 (broad, 1 H).

Anal. Calcd for $C_8H_{10}O_2$: C, 69.54; H, 7.30. Found: C, 69.25; H, 7.25.

Photolysis of Pyrazoline 28.—A solution of 200 mg of adduct **28** in 400 ml of ether was photolyzed for 1 hr. Most of the solvent was removed and the product was purified by preparative vpc to give a small amount of **29** plus analytically pure cyclopropane **30**; ir 1763 (m), 1727 (s), 1265 (m), 1130 (m), 990 (m), 875 (m), 850 (m) cm^{-1}; nmr δ 1.03 (s, 3 H), 1.07 (s, 3 H), 1.17–1.92 (m, 2 H), 2.3–2.7 (m, 2 H).

Anal. Calcd for $C_8H_{10}O_2$: C, 69.54; H, 7.30. Found: C, 69.14; H, 7.22.

Registry No.—**1**, 26154-22-3; **3**, 3883-58-7; **4**, 25112-87-2; **6**, 26154-25-6; **9**, 26154-26-7; **10**, 26154-27-8; **11**, 26154-28-9; **12**, 26157-42-6; **14**, 26154-29-0; **21**, 26157-43-7; **22**, 26157-44-8; **23**, 26154-30-3; **26**, 26145-73-3; **27**, 26145-74-4; **28**, 26145-75-5; **29**, 15972-27-7; **30**, 15973-50-9; reaction product of 2,6-dimethylanthracene with **1**, 26154-33-6; reaction product of 2,6-dimethylanthracene with bishydrazone, 26154-34-7; 2,6-dichloroanthracene, 26154-35-8; reaction product of 2,6-dichloroanthracene with **1**, 26154-36-9.

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The Preparation and Properties of Cage Polycyclic Systems. I. Pentacyclo[5.3.0.$0^{2,5}$.$0^{3,9}$.$0^{4,8}$]decane and Pentacyclo[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]nonane Derivatives

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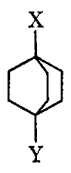
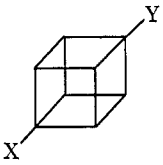
Reliable syntheses of some pentacyclo[5.3.0.$0^{2,5}$.$0^{3,9}$.$0^{4,8}$]decane (**22**) and pentacyclo[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]nonane (**23**) derivatives are described. The nmr spectra of several of them and the nmr spectra of the *endo*-dicyclopentadiene precursors are discussed; magnetic shielding of some of the cage methine protons is observed for certain ketones and ethylene ketals, a dimethyl ketal, and a hydrate, and even 5,9-dibromopentacyclo[5.3.0.$0^{2,5}$.$0^{3,9}$.$0^{4,8}$]decane has a two-proton absorption at higher field than that of the main group of protons. The cleavage of a nonenolizable α-bromo ketone, 5,9-dibromopentacyclo[5.3.0.$0^{2,5}$.$0^{3,9}$.$0^{4,8}$]deca-6,10-dione 6-ethylene ketal (**5**) to give a lactone (**17**), and several attempted Favorskii rearrangements on 5,9-dibromopentacyclo[5.3.0.$0^{2,5}$.$0^{3,9}$.$0^{4,8}$]-deca-6,10-dione (**6**) and 1-bromopentacyclo[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]nonan-9-one-4-carboxylic acid (**10**) are described.

Recently[1] we have prepared some 1,4-disubstituted bicyclo[2.2.2]octanes in order to study the polar effects of substituents X in a system such that they have no influence on the steric effect experienced by the reaction site Y. In these compounds the substituent is hidden from the reaction site by the bulk of the cyclic system and changing the substituent does not alter the steric effect at the reaction site. 1,4-Disubstituted cubanes[2] offer the same possibilities for studying polar effects without the intervention of steric effects,[3] and, after the preparation of 1,4-dimethoxy-





* Author to whom correspondence should be addressed.

(1) (a) S. Sotheeswaran, Ph.D. Thesis 1967, University of Hull, England; (b) N. B. Chapman, S. Sotheeswaran, and K. J. Toyne, *J. Org. Chem.*, **35**, 917 (1970).

(2) J. M. Key, Ph.D. Thesis, 1968, University of Hull, England.

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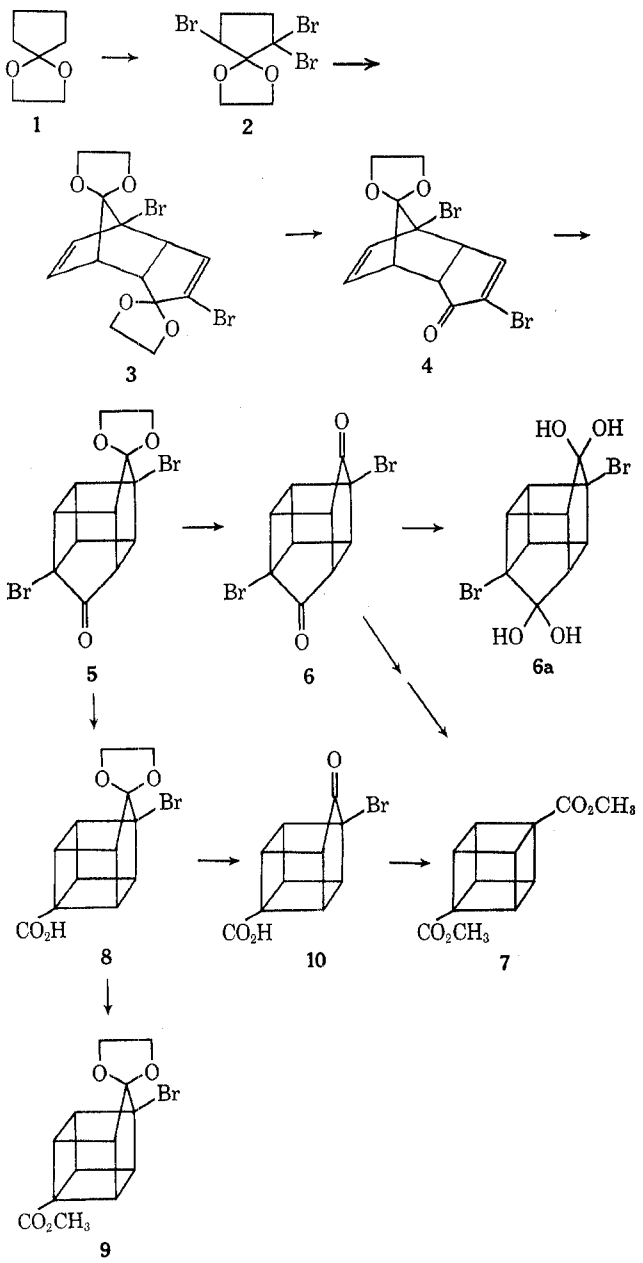
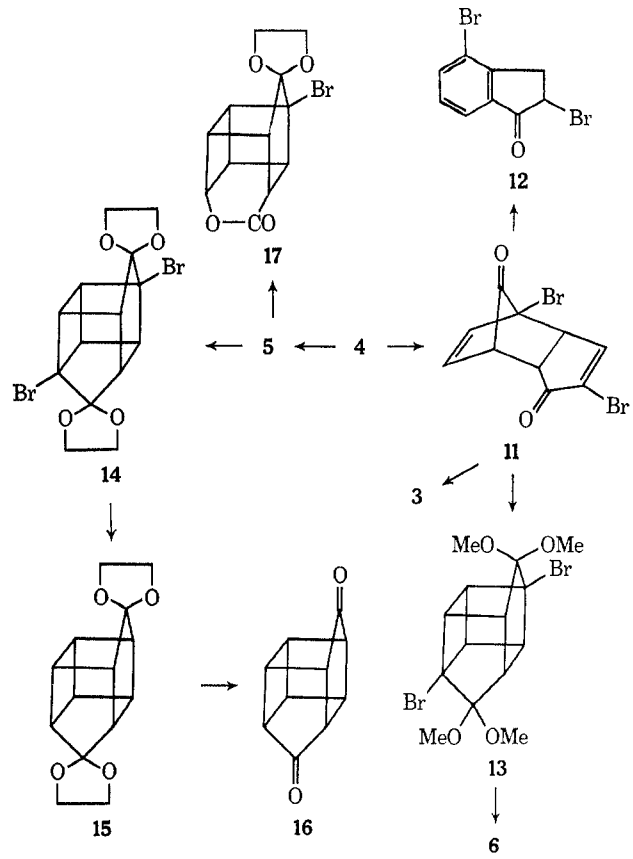
carbonylcubane was reported by Eaton and Cole,[4,5] we planned to prepare some 1,4-disubstituted cubanes for this purpose. However, we met numerous difficulties in following the preparative method reported by Eaton and Cole, arising from (a) the need to prepare cyclopent-2-en-1-one on a large scale, (b) the instability of the compounds leading to *endo*-2,4-dibromodicyclopentadiene-1,8-dione (**11**), which meant that many reactions gave tarry by-products, thus making purification difficult and causing low yields, and (c) the discovery that irradiation of **11** in 4% methanolic hydrogen chloride[6] gave the bisdimethyl ketal (**13**) and not the bishemimethyl ketal of **6** (see Schemes I and II).

SCHEME I



The Favorskii rearrangement of **6** gave variable yields; a 50% yield of **7** was isolated on one occasion but we were never able to repeat this and the usual yield was about 9%. The synthesis outlined in Scheme I was finally used as this avoids the difficulties a, b, and c mentioned above.

SCHEME II



Eaton and Hudson[7] brominated cyclopentanone ketals by using pyridinium bromide perbromide[8] in the alcohol from which the ketal had been derived; our attempts with this reagent failed. Various other established methods for the bromination of ketals were tried without success, *e.g.*, pyridinium bromide perbromide or trimethylphenylammonium perbromide in tetrahydrofuran,[9-12] and molecular bromine in a range of solvents. Dioxane dibromide, however, has been used[13] as a brominating agent and the initial isolation and purification of dioxane dibromide are unnecessary if bromine is added to the ketal in dioxane as solvent. This method proved successful and dibromination and tribromination of **1** gave good yields, and intermediates which were stable and relatively easy to purify (see Schemes I and III). This method is therefore a convenient way of preparing intermediates required for the synthesis of simple pentacyclodecane and pentacyclononane derivatives, and can be generalized to provide intermediates for the synthesis of complex substituted pentacyclodecanes[14] and pentacyclononanes, which

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(6) P. E. Eaton, personal communication.
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(8) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath, Boston, Mass., 1957, p 65.
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(10) A. Marquet and J. Jacques, *Tetrahedron Lett.*, 24 (1959).
(11) A. Marquet, M. Dvolaitzky, H. B. Kagan, L. Mamlok, C. Ouannes, and J. Jacques, *Bull. Soc. Chim. Fr.*, 1822 (1961).
(12) A. Marquet and J. Jacques, *ibid.*, 90 (1962).
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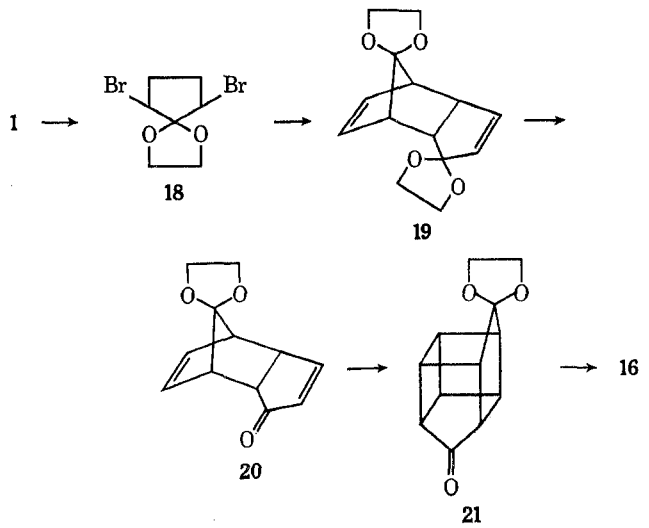
(14) W. L. Dilling and M. L. Dilling, *Tetrahedron*, **23**, 1225 (1967).

SCHEME III



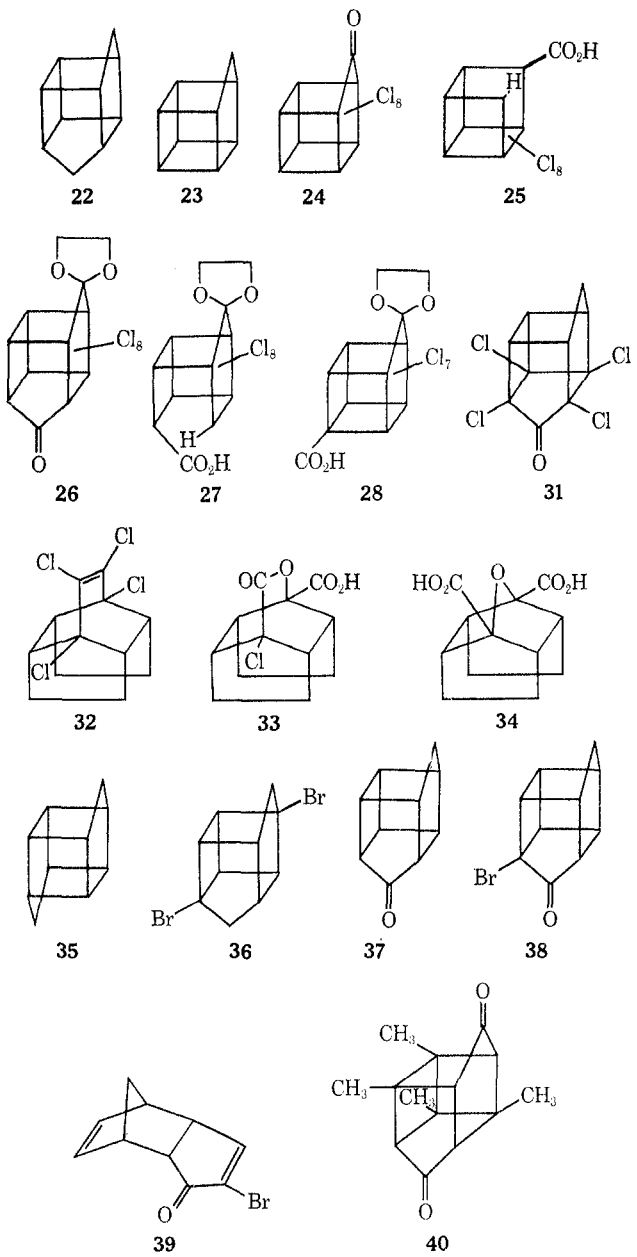
have attracted attention as potential antiviral agents.[15,16]

As we had obtained a poor yield of **7** from the Favorskii rearrangement of **6** by using the conditions recommended by Eaton and Cole,[4] we tried the reaction under various conditions as follows: aqueous potassium hydroxide 25–75% w/w, 90° up to reflux temperature, 20 hr–15 days, maximum yield 9%; powdered potassium hydroxide in xylene,[17,18] 25° up to reflux temperature, 1 day, no product; powdered potassium hydroxide in dimethyl sulfoxide, 50° up to 100°, 1 day, no product; powdered potassium hydroxide or sodium hydroxide in tetrahydrofuran,[19,20] 5° up to reflux temperature, 5 hr–2 days, no product; sodium methoxide in methanol, 25% w/w, reflux temperature, 1 day, no product; sodium methoxide–methanol in dimethyl sulfoxide, aqueous potassium hydroxide in dioxane, aqueous silver nitrate,[21] negligible yield.

Other workers[20,22,23] have experienced similar difficulties in the attempted Favorskii rearrangements of polychlorinated caged ketones. The attempted Favorskii rearrangement of **24** failed and the reaction gave a ring-cleaved product (**25**) which remained unchanged on treatment with base. Compound **26**, in a similar way, gave a ring-cleaved intermediate product (**27**), which in the presence of strong base gave the expected product (**28**).

The preparation[4] of **7** from **6** involves two successive Favorskii rearrangements and an alternative approach was to find the optimum conditions for each of these rearrangements by preparing **7** *via* **8** and **10**. The Favorskii rearrangement of **5** with 10% aqueous potassium hydroxide[4] was found to be unsatisfactory and the best yield (34%) was obtained by heating a 4% solution of **5** in 10% aqueous potassium hydroxide for 4 hr at 110°. It was more satisfactory to use a more concentrated base for a shorter time and a 4% solution of **5** in 25% aqueous potassium hydroxide for 2.5 hr at 110° gave consistent yields of **8** of 70–85%.

Compound **10** was subjected to a wide range of bases to see whether the yield of cubane-1,4-dicarboxylic acid could be improved. The use of aqueous potassium hydroxide, powdered potassium hydroxide in dimethyl sulfoxide or tetrahydrofuran, sodium methoxide in methanol or dimethyl sulfoxide, aqueous potassium hydroxide in dioxane, and aqueous silver nitrate, with a range of concentrations, reaction times and temperatures failed to improve the yield of **7**. A complication arising from the use of Pyrex vessels was the large amount of silicic acid formed on acidification of the reaction product, which made extraction of the cubane-1,4-dicarboxylic acid difficult. Reactions were tried in silica or 'Nalgon' tubes, or in sealed stainless steel tubes at high temperatures, but the optimum yield was still only 9%.



(15) British Patent 1,068,655 (1967); *Chem. Abstr.*, **68**, 2640m (1968).
(16) G. L. Dunn, V. J. DiPasquo, and J. R. E. Hoover, *J. Org. Chem.*, **33**, 1454 (1968).
(17) K. V. Scherer, Jr., R. S. Lunt, III, and G. A. Ungefug, *Tetrahedron Lett.*, 1199 (1965).
(18) R. J. Stedman, L. S. Miller, and J. R. E. Hoover, *ibid.*, 2721 (1966).
(19) K. V. Scherer, Jr., *ibid.*, 5685 (1966).
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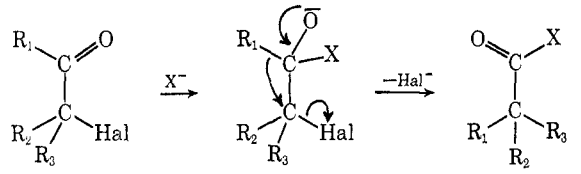
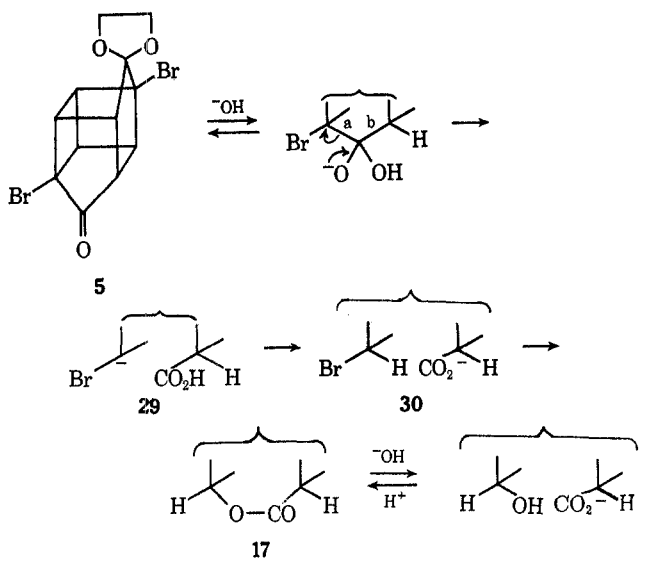
(21) A. C. Cope and E. S. Graham, *J. Amer. Chem. Soc.*, **73**, 4702 (1951).
(22) R. S. Lunt, III, Ph.D. Dissertation, University of California, Berkeley, Calif., 1968.
(23) G. A. Ungefug, Ph.D. Dissertation, University of California, Berkeley, Calif., 1968.

The proposed mechanism for the Favorskii rearrangement of nonenolizable α-halogeno ketones is similar to the mechanism of the benzilic acid rearrangement[4,24-26] and it seems reasonable that any nucleophile capable of producing the intermediate (I) may cause a Favorskii



I

rearrangement. A reaction which is mechanistically similar to the Favorskii reaction is the cleavage of nonenolizable ketones by potassium *tert*-butoxide–water in an aprotic solvent.[27-29] We decided to study this reaction to see whether a nonenolizable α-halogeno ketone would give a Favorskii rearrangement under these conditions. The Favorskii rearrangement of **5** gives acceptable yields and we tried its reaction with potassium *tert*-butoxide–water in dimethyl sulfoxide to see whether ring cleavage or Favorskii rearrangement occurred. The reaction gave the lactone **17** (see Scheme II) indicating that ring cleavage (breakage of bond a) rather than Favorskii rearrangement (breakage of bond b) had occurred, probably as shown. In



addition to the lactone produced, the cleavage of **5** leads to the acid **8** and possibly to the *tert*-butyl ester of **8**, which may arise from the reactions of **5** with hydroxide ion and *tert*-butoxide ion, respectively, to give a Favorskii rearrangement.

The action of alkali on cage chloro ketones has been reported to give several products. For example, Scherer, Lunt, and Ungefug[17] describe a normal Favorskii rearrangement, ring cleavage without displacement of chlorine, and ring cleavage followed by an olefin-forming elimination of chlorine; Stedman, Miller, and Hoover[18] describe a normal Favorskii product; and Dunn, DiPasquo, and Hoover[16] report the reaction of 4,5,7,8-tetrachloropentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decan-6-one (**31**) with solid sodium hydroxide in benzene to give ring cleavage and the Favorskii product, and to give ring cleavage almost exclusively with aqueous alkali or solid potassium hydroxide in benzene. In none of these reactions did the presence of the carboxylate anion group in the cleaved product lead to displacement of chlorine to yield the lactone, but Akhtar, Fray, and Yarrow[30] have recently shown that the oxidation of 9,10,11,12-tetrachlorotetracyclo[6.4.0.0^{4,12}.0^{5,9}]dodec-10-ene (**32**) with potassium permanganate in refluxing acetone leads to 9-carboxy-10-chlorotricyclo[4.2.1.1^{2,5}]-decane-9-hydroxy-10-carboxy lactone (**33**), which is formed by transannular nucleophilic displacement of chlorine. When this chlorolactone carboxylic acid (**33**) was heated with aqueous potassium hydroxide another internal nucleophilic substitution led to an oxygen-bridged dicarboxylic acid (**34**).

Lunt[22] attributes the formation of the ring-cleaved products in the attempted Favorskii reactions of the polychlorinated cage ketones (see above) to a combination of factors arising from the severe ring strain and from the stability of the chlorocarbanions. The difference in the type of ring-cleaved product obtained by Lunt and that reported here may be explained in the following way. The initial ring-cleaved anion (**29**) is a stronger base than the chlorocarbanion and will lead to **30** which is then capable of producing the lactone because bromine is more easily displaced than chlorine. The bromocarbanion (**29**) is not able to give a ring-closed product because of the absence of a leaving group on the carbon atom to which the carboxy group is attached. When the intermediate product (**27**) obtained by Lunt is treated with strong base it will give the chlorocarbanion, which is not susceptible to attack by the carboxylate anion group, and the alternative displacement of the chloride ion from the carbon atom to which the carboxy group is attached will give the ring-closed acid (**28**). Oxidation of **32**, however, does not lead to chlorocarbanion formation and the displacement of chloride ion by the carboxylate anion group is the only displacement possible.

The thermal decarbonylation of **11** gave 2,4-dibromoindanone. Baggiolini, *et al.*,[31] obtained *cis*-8,9-dihydroindenone from the thermal decomposition of *endo*-dicyclopentadiene-1,8-dione, and DePuy, *et al.*,[32] by decarbonylating the chloro compound analogous to the bromo compound **11**, have obtained the 8,9-dihydroindenone initially, which then aromatized at room temperature to give 2,4-dichloroindanone. The nmr spectrum of compound **12** agrees very closely with that reported by DePuy, *et al.*,[32] for 2,4-dichloroindanone.

Nmr Spectra.—One notable feature of the nmr spectra of cage compounds is that the presence of carbonyl or ethylene ketal groups causes shielding of some of the hydrogen atoms.[4,5,33-35] Stedman and Davis[33] have considered the nmr spectra of ketones and ketals of

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(26) J.-M. Conia and J.-L. Ripoll, *Bull. Soc. Chim. Fr.*, 755, 773 (1963).
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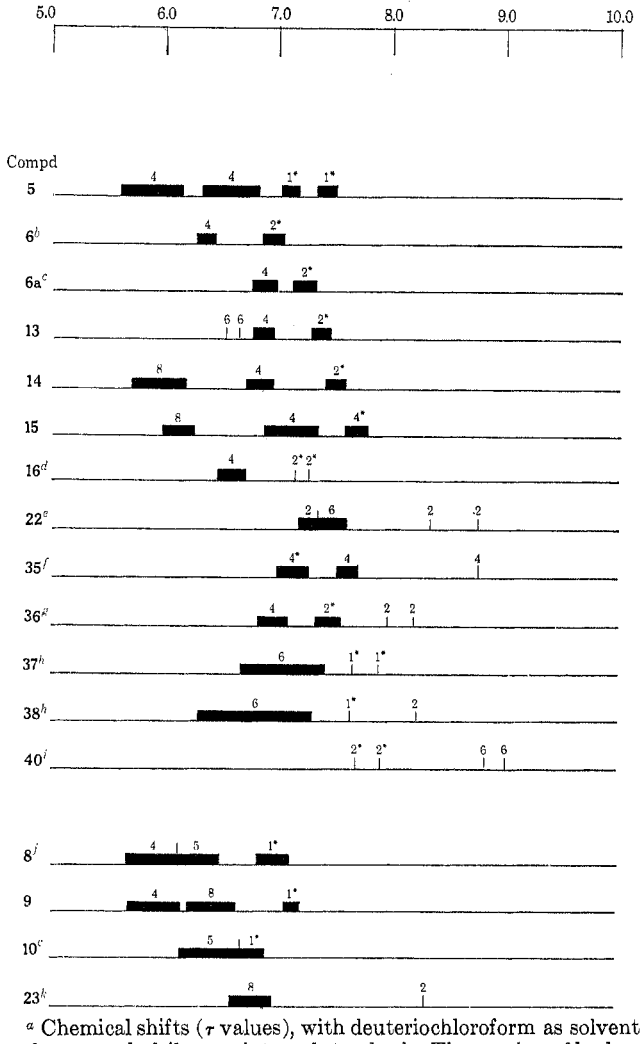
(30) I. A. Akhtar, G. I. Fray, and J. M. Yarrow, *J. Chem. Soc. C*, 812 (1968).
(31) E. Baggiolini, E. G. Herzog, S. Iwasaki, R. Schorta, and K. Schaffner, *Helv. Chim. Acta*, **50**, 297 (1967).
(32) C. H. DePuy, M. Isaks, K. L. Eilers, and G. F. Morris, *J. Org. Chem.*, **29**, 3503 (1964).
(33) R. J. Stedman and L. D. Davis, *Tetrahedron Lett.*, 1871 (1968).
(34) G. L. Dunn, V. J. DiPasquo, and J. R. E. Hoover, *ibid.*, 3737 (1966).
(35) R. J. Stedman and L. S. Miller, *J. Org. Chem.*, **32**, 35 (1967).

pentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane (**35**) and have concluded that for the ketones the α protons are held in the shielding zone of the carbonyl group[36,37] and for the ethylene ketals the shielding may arise from some long range anisotropic effect associated with the oxygen atom.[33] We have prepared several substituted pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decanes (**22**), all of which show the characteristic high-field resonance for protons at the position α to a carbonyl or ketal functional group, but the nmr results indicate that the high-field resonance is not confined to ketones and ethylene ketals, but also appears in the spectra of a dimethyl ketal (**13**), a hydrate (**6a**), and a halo compound (**36**). In Chart I are collected the bar diagrams for the nmr spectra of several pentacyclodecanes and their derivatives. For all derivatives shown the resonances for the hydrogen atoms at C_1, C_9, C_5, and C_7 (when present) appear at higher field than those of the remaining cage methine protons. As would normally be expected, the introduction of a carbonyl group into the molecule causes most of the cage protons to resonate at lower field [*e.g.*, **22**, **37**; and **36**, **6**] but the protons at the positions α to the carbonyl group appear at higher field than the main group. Compounds **36** and **6**, however, show that the carbonyl groups have little relative effect on cage protons, and the α protons and the remaining cage protons are moved downfield to approximately the same extent. Similarly, the ethylene ketal group causes the resonance of several protons to move to lower field but the α protons resonate at approximately the same position as in the parent hydrocarbon (see **22**, **15**, **14**). Bromine atoms cause all resonances to move to slightly lower field (**36**, **22**; **14**, **15**; **38**, **37**) but surprisingly **36** shows high-field methine protons although C_6 and C_{10} are unsubstituted. Compounds **14**, **5**, and **6** show that replacing the ethylene ketal group by a carbonyl group causes all the resonances to move to lower field, but the peculiar high-field behavior of the α proton remains. For a similar system, Stedman and Davis[33] have suggested that the shielding of α protons would only be observed for ketals when the ketal oxygen atoms form part of a rigid ring; indeed they found that for a dimethyl ketal none of the cage protons were greatly shielded with respect to those of the hydrocarbon. From Chart I it can be seen that a bisdimethyl ketal (**13**) and even a bishydrate (**6a**) still show 2 protons at higher field than the main group, as is observed for the bisethylene ketal **14**, although there is an indication that the separation of the high-field protons from the main group decreases from compounds **14** to **13** to **6a**.

CHART I

NMR SPECTRA OF PENTACYCLODECANE AND PENTACYCLONONANE DERIVATIVES[a]



[a] Chemical shifts (τ values), with deuteriochloroform as solvent and tetramethylsilane as internal standard. The number of hydrogen atoms responsible for each resonance is indicated and the probable assignments of resonances arising from protons α to the carbonyl or ketal groups are indicated by an asterisk. [b] See also ref 4. [c] In hexadeuterioacetone. [d] See also ref 31. [e] See also ref 43. [f] See also ref 33 and 43. [g] Preparation to be reported later (J. R. Bell, N. B. Chapman, and K. J. Toyne). [h] See ref 34. [i] See G. Maier and U. Mende, *Angew. Chem., Int. Ed. Engl.*, **8**, 132 (1969). [j] See also ref 5. [k] See ref 1b and 16.

It does not seem likely that the high-field resonances of the ethylene ketals arise because of a long-range anisotropic effect of oxygen since compound **36** shows the high-field resonances, although oxygen atoms are not present in the molecule, and compounds **13** and **6a**, in which rotation about the carbon–oxygen bonds is possible, still show high-field absorption.

In the formal conversion of the *endo*-dicyclopentadienes **3**, **4**, and **11** into the pentacyclodecane derivatives **14**, **5**, and **6**, respectively, the protons at positions C_7 and C_{7a} in the diene become the protons showing the high-field absorption. From Table I and Chart I it can be seen that the changes of chemical shift for this conversion are always to higher field, and for the formation of compound **14** are τ 0.11 and 0.47, for compound **5**, 0.11 and 0.53, and for compound **6**, 0.52 and 0.15. The methine resonance at highest field for **19** (see Table I) and for *endo*-2-bromodicyclopentadien-1-one (**39**)[16] is at τ 7.31 and 7.25, respectively, and for the cage compounds the high-field absorption is at τ 7.51 and 7.6,[16] respectively, which corresponds to a shift to high field of at least τ 0.20 and 0.35, respectively.

The nmr spectra of appropriately substituted pentacyclononanes, *e.g.*, compounds **8**, **9**, and **10**, also show a high-field proton resonance, which appears basically as a triplet because the symmetry of these molecules is such that the hydrogen atoms on C_3 and C_7 are chemically identical.

(36) J. W. ApSimon, W. G. Craig, P. V. Demarco, D. W. Mathieson, A. K. G. Nasser, L. Saunders, and W. B. Whalley, *Chem. Commun.*, 754 (1966).

(37) G. J. Karabatsos, G. C. Sonnichsen, N. Hsi, and D. J. Fenoglio, *J. Amer. Chem. Soc.*, **89**, 5067 (1967).

TABLE I

NMR SPECTRA OF *endo*-DICYCLOPENTADIENE DERIVATIVES[a]

Compd	Proton chemical shifts 1	2	3	3a	4	7	7a	5	6	8
endo-Dicyclopentadiene[b]	7.85									8.75
	8.40	——4.55——		6.82	——7.16, 7.27——		7.33	——4.08——		8.73
3			3.95	6.50		7.29	6.93	4.19	3.83	
4			2.38	6.35		6.95	6.81	4.09	4.00	
11			2.34	6.47		6.43	6.80	3.76	3.64	
19		4.43	4.23	——6.55, 7.13, 7.31, 7.31——				—3.85, 4.20—		
20		3.91	2.64	——6.43, 6.99, 7.07, 7.19——				—4.00, 4.14—		

[a] Chemical shifts (τ values) with deuteriochloroform as solvent and tetramethylsilane as internal standard. [b] See R. G. Foster and M. C. McIvor, *J. Chem. Soc. B*, 188 (1969).

It is clear from these observations that the anomalous high-field shift in the nmr spectra of these cage systems does not admit of a simple explanation and in any one case a number of opposing factors may be important. In an attempt to rationalise these results we are extending our studies to a wider range of cage compounds.

Experimental Section

Melting points and boiling points are uncorrected. Nmr spectra were recorded at 100 MHz with a Varian HA-100 or JEOL 4H-100 spectrometer, with tetramethylsilane as internal standard and deuteriochloroform as solvent; the chemical shifts and coupling constants were obtained by first-order analysis. The molecular ion peaks in the mass spectra are given for the bromine 79 isotope. Glpc analyses were achieved by using a Perkin-Elmer F11 gas-liquid chromatograph fitted with a column (72 in. × 1/8 in. o.d.) packed with 20% silicone gum rubber, SE-301, on Chromosorb W. Thin layer chromatography plates were spread with 0.1 mm of silica gel G, Merck 7731, and developed by spraying them with an ethanolic solution of phosphomolybdic acid and heating them to 180–200° for 30 min. Whenever a preparation leading to a useful yield of product is described, the reported yield was obtained reproducibly in several (up to 10) separate experiments.

Cyclopentanone Ethylene Ketal (1).—This compound was prepared by the method described by DePuy, *et al.*,[38] for the preparation of 2-chlorocyclopentanone ethylene ketal; it had bp 152–155° [lit.[39] 57–57.2° (18 mm)].

2,2,5-Tribromocyclopentanone Ethylene Ketal (2).—Cyclopentanone ethylene ketal (1) (128.0 g, 1.0 mol) in pure dioxane (1 l.) under a dry atmosphere was cooled to 10–15°. Bromine (480 g, 3.0 mol) was added dropwise with stirring during 1.5 hr, keeping the mixture below 15°. The mixture was then stirred at room temperature for 2 days and poured into 5% aqueous sodium bicarbonate (6 l.) and stirred, and the product was kept for 1 hr. The yellow solid was filtered off and washed with water, dried ($CaCl_2$) *in vacuo* overnight, and recrystallized twice (ethanol) to give 2,2,5-tribromocyclopentanone ethylene ketal (2) (253.7 g, 69.5%): mp 76–78°; nmr τ 5.21 (q, 1 H), 5.42–5.90 (m, 4 H), 6.77–8.33 (m, 4 H); ir (KCl) 1210, 1057, 1039, 950, 660 cm^{-1}; *m/e* 362 (M^+).

Anal. Calcd for $C_7H_9O_2Br_3$: C, 23.04; H, 2.49; Br, 65.70. Found: C, 23.06; H, 2.57; Br, 65.40.

***endo*-2,4-Dibromodicyclopentadiene-1,8-dione Bisethylene Ketal (3).**—For large scale preparations, the most convenient method involved the dehydrobromination of compound 2 with methanolic sodium methoxide.

Compound 2 (253.7 g, 0.73 mol) in pure dioxane (500 ml) was added dropwise at room temperature during 1.5 hr with stirring to sodium (92.0 g, 4.0 g-atoms) dissolved in methanol (1.1 l.). The mixture was heated under reflux with stirring for 2.5 hr and cooled, and water (3 l.) was added. The aqueous mixture was kept at room temperature for 1 hr and the solid was filtered off, dried ($CaCl_2$) *in vacuo*, and recrystallized twice (ethanol) to give *endo*-2,4-dibromodicyclopentadiene-1,8-dione bisethylene ketal (3) (106.6 g, 76%): mp 172–174°; nmr τ 3.83 (q, H_6), 3.95 (d, H_3), 4.19 (q, H_5), 5.68–6.21 (m, 8 H), 6.50 (q, H_{3a}), 6.93 (q, H_{7a}), 7.29 (m, H_7); $J_{3,3a}$ = 2.5, $J_{3,7}$ = 0.5, $J_{3a,7a}$ = 7.3, $J_{5,6}$ = 6.5, $J_{5,7}$ = 1.0, $J_{6,7}$ = 3.5, $J_{7,7a}$ = 4.8 Hz; ir (KCl) 3060, 3000, 1617, 1050, 1032, 1012 cm^{-1}; *m/e* 404 (M^+).

Anal. Calcd for $C_{14}H_{14}O_4Br_2$: C, 41.40; H, 3.48; Br, 39.36. Found: C, 41.50; H, 3.40; Br, 39.23.

The dehydrobromination of 2 with potassium *tert*-butoxide in dimethyl sulfoxide at 18–20°, potassium *tert*-butoxide in *tert*-butyl alcohol at 18–20°, or piperidine at reflux temperature gave compound 3 in 67, 63, and 89% yield, respectively. Compound 3 was also prepared (64% yield) by the reaction of 11 with ethylene glycol in benzene, with toluene-*p*-sulfonic acid as catalyst.

***endo*-2,4-Dibromodicyclopentadiene-1,8-dione 8-Ethylene Ketal (4).**—Concentrated hydrochloric acid (100 ml) was added dropwise at room temperature to a stirred solution of compound 3 (100 g, 0.246 mol) in tetrahydrofuran (1 l.). The mixture was stirred for 18 hr and then poured into 10% aqueous sodium bicarbonate (6 l.) and kept at room temperature for 1 hr. The product was filtered off, dried ($CaCl_2$) *in vacuo*, and recrystallized twice (toluene) to give compound 4 (81.4 g, 91%): mp 171–172° (lit.[4] 172–173°); nmr τ 2.38 (q, H_3), 4.00 (q, H_6), 4.09 (q, H_5), 5.68–6.13 (m, 4 H), 6.35 (q, H_{3a}), 6.81 (t, H_{7a}), 6.95 (m, H_7); $J_{3,3a}$ = 2.9, $J_{3,7}$ = 0.5, $J_{3a,7a}$ = 5.4, $J_{5,6}$ = 6.7, $J_{5,7}$ = 1.9, $J_{6,7}$ = 3.3, $J_{7,7a}$ = 5.3 Hz; ir (KCl) 2990, 1714, 1584, 1481 cm^{-1}; *m/e* 360 (M^+).

Anal. Calcd for $C_{12}H_{10}O_3Br_2$: C, 39.81; H, 2.78; Br, 44.15. Found: C, 40.01; H, 2.65; Br, 44.30.

5,9-Dibromopentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]deca-6,10-dione 6-Ethylene Ketal (5).—Compound 4 (17.0 g, 0.047 mol) in dry benzene (500 ml) in a Pyrex tube (40 × 5 cm) fitted with a condenser and nitrogen inlet tube was placed 1 cm from the quartz water-cooled jacket of a 450-W Hanovia medium-pressure mercury vapor lamp for 16–24 hr. The progress of the reaction was followed by using glpc (column temperature 220°) or tlc (benzene); compounds 4 and 5 have R_f values of 0.11 and 0.76, respectively. The benzene was removed and the residue was recrystallized twice (1:1 carbon tetrachloride–hexane) to give compound 5 (15.1 g, 89%): mp 148–150° (lit.[5] 148–150°); nmr τ 5.62–6.15 (m, 4 H), 6.31–6.81 (m, 4 H), 6.98–7.14 (m, 1 H), 7.26–7.42 (m, 1 H); ir (KCl) 2990, 2880, 1768 cm^{-1}; *m/e* 360 (M^+).

Anal. Calcd for $C_{12}H_{10}O_3Br_2$: C, 39.81; H, 2.78; Br, 44.15. Found: C, 39.80; H, 2.80; Br, 44.20.

5,9-Dibromopentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]deca-6,10-dione (6). Method 1.—A solution of compound 5 (10.0 g, 0.0276 mol) in concentrated sulfuric acid (100 ml) was stirred for 2 days. The reaction was followed by using tlc (1:19 methanol–benzene); compounds 5 and 6 have R_f values of 0.45 and 0.01, respectively. The dark solution was poured onto crushed ice and shaken with ether (three 50-ml portions). The ethereal extracts were discarded and the aqueous phase was diluted to 500 ml with water and washed continuously with ether (400 ml) for 20 hr. The ethereal solution was dried (Na_2CO_3) and the ether was removed to give the hydrate of 6 (7.3 g). Recrystallization (methylene chloride), followed by desiccation ($CaCl_2$) at 40° (1 mm), gave compound 6 (6.2 g, 71%): mp 230–232° dec (lit.[4] 232–233° dec); nmr τ 6.28–6.44 (m, 4 H), 6.86–7.02 (m, 2 H); ir (KCl) 3030, 1782 cm^{-1}; *m/e* 316 (M^+).

Method 2.—Compound 13 (0.5 g, 0.0012 mol) in tetrahydrofuran (5 ml) was heated under reflux overnight with hydrochloric acid (1 ml of concentrated acid, 1 ml of water). The solution was cooled, added to 10% aqueous sodium bicarbonate (20 ml), and shaken with ether (three 20-ml portions), and the ethereal solutions were dried ($MgSO_4$). Evaporation of the ether and crystallization (methylene chloride) of the residue gave the hydrate of

(38) C. H. DePuy, B. W. Ponder, and J. D. Fitzpatrick, *J. Org. Chem.*, **29**, 3508 (1964).

(39) E. J. Salmi, *Ber.*, **71**, 1803 (1938).

6. Desiccation (P_2O_5) at 48° (1 mm) for 24 hr gave compound **6** (0.21 g, 54%) with the physical properties given above.

1,4-Dimethoxycarbonylpentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane (7).—Compound **6** (1.0 g, 0.032 mol) or compound **10** (1.0 g, 0.00394 mol) in aqueous potassium hydroxide (30 ml of 50% w/w, *i.e.*, 20 g of potassium hydroxide in 20 g of water) was heated under reflux for 30 hr. The solution was poured into water (30 ml) and brought to pH 1 with hydrochloric acid. The solid was treated with ethereal diazomethane, the mixture was filtered, and the filtrate was washed with water and dried ($MgSO_4$). The ether was removed and the solid was crystallized (hexane) to give compound **7**, mp 161–162° (lit.[4] 161–162°). From compound **6** or compound **10** the yields were 0.072 g (10.4%) and 0.086 g (9.9%), respectively.

1-Bromopentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonan-9-one Ethylene Ketal 4-Carboxylic Acid (8).—A solution of compound **5** (44.0 g, 0.1255 mol) and potassium hydroxide (275.0 g) in water (1.1 l.) was stirred at room temperature for 20 min; most of the solid had then dissolved. During 45 min the temperature was raised to and then kept at 110–120° for 2 hr. The solution was cooled and acidified with hydrochloric acid, and the product was filtered off, washed, and crystallized twice (ethanol) to give compound **8** (28.6 g, 79%): mp 187–189° (lit.[5] 187–189°); nmr τ −0.98 (s, 1 H), 5.68–6.11 (sym m, 4 H), 6.12–6.50 (m, 5 H), 6.79–7.02 (m, 1 H); ir (CH_2Cl_2) 1730, 1688 cm^{-1}; *m/e* 298 (M^+).

Anal. Calcd for $C_{12}H_{11}O_4Br$: C, 48.18; H, 3.71; Br, 26.72. Found: C, 48.30; H, 3.60; Br, 26.50.

Methyl 1-Bromopentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonan-9-one Ethylene Ketal 4-Carboxylate (9).—Compound **8** (12.7 g, 0.0425 mol) was dissolved in ether (500 ml) and esterified with ethereal diazomethane. The ethereal solution was washed with water, sodium bicarbonate solution, water, and dried ($MgSO_4$). The ether was removed *in vacuo* and a solution of the solid in hot hexane was treated with decolorizing charcoal and allowed to cool to give methyl 1-bromopentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonan-9-one ethylene ketal 4-carboxylate (**9**) (11.6 g, 87%): mp 106–108°; nmr τ 5.69–6.11 (sym m, 4 H), 6.14–6.52 (m, includes a singlet at 6.33, 8 H), 6.92–7.01 (m, 1 H); ir (KCl) 2998, 2960, 2910, 2895, 1725, 1300, 1230, 650 cm^{-1}; *m/e* 312 (M^+).

Anal. Calcd for $C_{13}H_{13}O_4Br$: C, 49.86; H, 4.18; Br, 25.52. Found: C, 49.90; H, 4.00; Br, 25.60.

1-Bromopentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonan-9-one-4-carboxylic Acid (10).—A solution of compound **8** (20.0 g, 0.0669 mol) in aqueous sulfuric acid (360 ml of 75% w/w, *i.e.*, 143 ml of water and 252 ml of concentrated sulfuric acid) was stirred for 3 days at room temperature. The reaction was followed by using tlc [ethanol–water–ammonium hydroxide (2 *N*), 100:6:8], spraying with saturated aqueous ammonium bisulfate, and development at 200°. The mixture was poured onto crushed ice and diluted to 1 l. with water. The aqueous solution was shaken with ether (100 ml) to remove unchanged acid **8**. The aqueous phase was washed continuously with ether (400 ml) for 20 hr and then dried ($MgSO_4$). The ether was removed to give the crude hydrate of compound **10** (16.4 g) which was heated for 1 hr under reflux in toluene in an apparatus having a Dean–Stark separator. When cooled, the toluene solution gave 1-bromopentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonan-9-one-4-carboxylic acid (**10**) (15.1 g, 87%): mp 219–220°; nmr τ (CD_3COCD_3) 6.17–6.71 (m, 5 H), 6.72–6.86 (m, 1 H); ir (KCl) 3350, 3000, 2950, 1683, 1652, 1256, 1224 cm^{-1}; *m/e* 254 (M^+).

Anal. Calcd for $C_{10}H_7O_3Br$: C, 47.08; H, 2.77; Br, 31.33. Found: C, 47.03; H, 2.80; Br, 31.65.

***endo*-2,4-Dibromodicyclopentadiene-1,8-dione (11).**—A solution of compound **4** (2.65 g, 0.00736 mol) in concentrated sulfuric acid (10 ml) was stirred at room temperature for 2 days. The reaction mixture was poured onto crushed ice and the aqueous mixture was kept in the refrigerator overnight. The solid was filtered off and the filter cake was washed with water and dried ($CaCl_2$) *in vacuo* overnight. The solid was dissolved in hot carbon tetrachloride and treated with decolorizing charcoal. Compound **11** crystallized as fine white needles from the cold solution (1.71 g, 73%): mp 154–155° dec (lit.[4] 154–155° dec); nmr τ 2.34 (q, H_3), 3.64 (q, H_6), 3.76 (q, H_5), 6.43 (m, H_7), 6.47 (q, H_{3a}), 6.80 (q, H_{7a}); $J_{3,3a}$ = 3.0, $J_{3,7}$ = 0.5, $J_{3a,7a}$ = 6.5, $J_{5,6}$ = 7.0, $J_{5,7}$ = 1.5, $J_{6,7}$ = 3.5, $J_{7,7a}$ = 5.0 Hz; ir (KCl), 1795, 1722, 1585, 1556, 690 cm^{-1}; *m/e* 316 (M^+).

Anal. Calcd for $C_{10}H_6O_2Br_2$: C, 37.77; H, 1.90; Br, 50.27. Found: C, 37.70; H, 2.0; Br, 50.20.

2,4-Dibromoindanone (12).—Compound **11** (1.0 g, 0.00315 mol) in freshly distilled tetralin (50 ml) under nitrogen was heated slowly to and kept at 180° for 3 hr. The tetralin was removed *in vacuo* [42° (0.7 mm)] and the oily residue was dried ($CaCl_2$–paraffin wax) *in vacuo*. The solid in hot ethanol was treated with decolorizing charcoal and 2,4-dibromoindanone (**12**) crystallized from the cold solution (0.58 g, 64%): mp 80–82°; nmr τ 2.12–2.26 (m, 2 H), 2.62 (d, 1 H), 5.29 (q, H_2, $J_{H_2,H_{cis}}$ = 7.5 Hz, $J_{H_2,H_3\ trans}$ = 3.5 Hz), 6.26 [q, H_3 (cis to H_2), J_{gem} = 18.5 Hz], 6.66 [q, H_3 (trans to H_2)]; ir (KCl) 3037, 2960, 1728, 1600, 1572 cm^{-1}; *m/e* 288 (M^+).

Anal. Calcd for $C_9H_6OBr_2$: C, 37.27; H, 2.09; Br, 55.12. Found: C, 37.30; H, 2.05; Br, 54.92.

5,9-Dibromopentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]deca-6,10-dione Bisdimethyl Ketal (13).—A solution of compound **11** (5.0 g, 0.016 mol) in methanolic hydrogen chloride (72 g of a 4% w/w solution)[6] in a Pyrex tube (18.5 × 3.2 cm), fitted with a condenser and calcium chloride guard tube, was placed 1 cm from a 450-W Hanovia medium-pressure mercury vapor lamp and was irradiated for 24 hr, whereupon no olefinic stretching absorption (1585 cm^{-1}) could be detected. The solution was poured into 10% aqueous sodium bicarbonate (300 ml) and shaken with ether (three 100-ml portions) and the combined ethereal solutions were washed with water and dried ($MgSO_4$). The ether was removed and the residual brown oily solid was heated under reflux with water for 1 hr. The mixture was cooled, the water was decanted off, and the solid was dried ($CaCl_2$) *in vacuo*. Chromatography on a neutral alumina column (32 × 2.4 cm) and elution with petroleum ether (bp 40–60°) gave a white solid (2.9 g) which was crystallized (cyclohexane) to give 5,9-dibromopentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]deca-6,10-dione bisdimethyl ketal (**13**) (1.6 g, 25%): mp 123–124°; nmr τ 6.58 (s, 6 H), 6.61 (s, 6 H), 6.76–6.90 (m, 4 H), 7.22–7.35 (m, 2 H); ir (KCl) 2990, 2870, 650 cm^{-1}; *m/e* 408 (M^+).

Anal. Calcd for $C_{14}H_{18}O_4Br_2$: C, 41.00; H, 4.42; Br, 38.97. Found: C, 41.14; H, 4.46; Br, 38.60.

5,9-Dibromopentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]deca-6,10-dione Bisethylene Ketal (14).—Compound **5** (23.0 g, 0.064 mol), redistilled ethylene glycol (23.0 g, 0.37 mol) and toluene-*p*-sulfonic acid (0.1 g) in dry benzene (600 ml) were heated under reflux for 36 hr in an apparatus having a Dean–Stark water separator. The solution was cooled, washed with aqueous potassium hydroxide and water, and dried ($MgSO_4$). The benzene was removed *in vacuo* and the residue was crystallized twice (tetrahydrofuran) to give 5,9-dibromopentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]-deca-6,10-dione bisethylene ketal (**14**) (20.5 g, 80%): mp 188–190°; nmr τ 5.69–6.15 (m, 8 H), 6.68–6.85 (m, 4 H), 7.33–7.46 (m, 2 H); ir (KCl) 2990, 1304, 1035, 657 cm^{-1}; *m/e* 404 (M^+).

Anal. Calcd for $C_{14}H_{14}O_4Br_2$: C, 41.40; H, 3.48; Br, 39.36 Found: C, 41.30; H, 3.50; Br, 39.60.

Pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]deca-6,10-dione Bisethylene Ketal (15).—Compound **14** (13.1 g, 0.0323 mol) in tetrahydrofuran (250 ml) and *tert*-butyl alcohol (9.55 g, 0.130 mol) was stirred rapidly and finely cut pieces of lithium (1.34 g, 0.193 g-atom) were added in portions during 30 min. The mixture was heated under reflux for 2 hr and then allowed to cool. Water (50 ml) was added and the mixture was stirred vigorously for 4 hr. The solution was poured into water (1.1 l.), shaken with ether (three 150-ml portions) and the ethereal solutions were combined, washed with water, and dried ($MgSO_4$). The ether was evaporated off slowly through a Vigreux column (20 cm) to leave a residue which was crystallized twice (ethanol) to give pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]deca-6,10-dione bisethylene ketal (**15**) (7.3 g, 91%): mp 94–96°; nmr τ 5.96–6.22 (m, 8 H), 6.81–7.24 (m, 4 H), 7.44–7.59 (m, 4 H); ir (KCl) 2990, 1473, 1330, 948, 899 cm^{-1}; *m/e* 248 (M^+).

Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.72; H, 6.50. Found: C, 67.80; H, 6.50.

Pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]deca-6,10-dione (16). Method 1.—A solution of compound **21** (3.0 g, 0.0147 mol) in concentrated sulfuric acid (35.0 ml) was stirred at room temperature for 30 hr. The solution was then poured onto crushed ice and shaken with ether (three 150-ml portions), and the ethereal solutions were washed with water (three 50-ml portions) and dried ($MgSO_4$). The ether was removed and the residue was crystallized (1:1 acetic acid–water) to give compound **16** (1.76 g, 75%): mp 162–163° (lit.[31] 163°); nmr τ 6.50–6.70 (m, 4 H), 7.14 (s, 2 H), 7.24 (s, 2 H); *m/e* 160 (M^+).

Method 2.—A solution of compound **15** (3.0 g, 0.0121 mol) in concentrated sulfuric acid (35 ml) was stirred at room tempera-

ture for 24 hr. The extraction and isolation were similar to those described in method 1; the yield of **16** was 1.36 g (70%).

1-Bromotetracyclo[4.3.0.0^{2,5}.0^{3,8}]nonan-9-one Ethylene Ketal 4-Hydroxy-7-carboxy Lactone (17).—Compound **5** (1.08 g, 0.003 mol) in dry dimethyl sulfoxide (15 ml) was added during 1 hr, with ice-water cooling, to a stirred mixture of potassium *tert*-butoxide (3.36 g, 0.030 mol), water (0.162 g, 0.009 mol) and dimethyl sulfoxide (10 ml). The mixture was stirred overnight at room temperature and then poured into water (300 ml). The solution was saturated with salt and shaken with ether (three 50-ml portions) and the ethereal solutions (ethereal washings of the alkaline solution) were dried ($MgSO_4$). The aqueous solution was brought to pH 1 with hydrochloric acid and then shaken with ether (three 50-ml portions); the ethereal solutions (ethereal washings of the acidic solution) were dried ($MgSO_4$).

Ethereal Washings of the Alkaline Solution.—The ether was removed to give a pale yellow solid (0.18 g). Glpc analysis (column temperature 236°) showed the presence of three components (8:1:1) with retention times different from that of compound **5**. The solid was heated under reflux with potassium hydroxide (0.6 g) in water (0.6 ml) and methanol (6 ml) for 24 hr. The solution was cooled, poured into water (20 ml), and shaken with ether (three 10-ml portions), and the ethereal solutions were dried ($MgSO_4$). [Evaporation of the ether gave a solid (0.03 g) which was shown by glpc to contain the same distribution of components as the mixture before hydrolysis]. The aqueous solution was brought to pH 1 with hydrochloric acid and shaken with ether (three 10-ml portions), and the ethereal solutions were dried ($MgSO_4$). Evaporation of the ether gave a solid (0.11 g) which was treated with an ethereal solution of diazomethane. Analysis of the ethereal solution by glpc showed one main component (85%) which was identified with the methyl ester **9** by their identical retention times.

Ethereal Washings of the Acid Solution.—The ether was removed to give a colorless solid (0.53 g); glpc analysis showed the product to consist mainly of one component. However, when a small portion was dissolved in ether and treated with an ethereal solution of diazomethane, glpc showed the original major component and a small amount of another component which corresponded to the methyl ester **9** (identical retention times). The remaining solid (0.50 g) was purified by chromatography on a neutral alumina column (32 × 1.2 cm) (elution with ethyl acetate). The solvent was removed and the residue was crystallized (carbon tetrachloride) to give 1-bromotetracyclo[4.3.0.0^{2,5}.0^{3,8}]-nonan-9-one ethylene ketal 4-hydroxy-7-carboxy lactone (**17**) (0.29 g, 32%): mp 143–145°; nmr τ 4.65 (q, 1 H), 5.71-6.01 (m, 4 H), 6.76 (t, 1 H), 7.02 (q, 1 H), 7.46–7.86 (m, 3 H), 8.33 (q, 1 H); ir (KCl) 2978, 2905, 1786, 1775 cm^{-1}; ir (KCl disk of solid from reaction with LiOD–D_2O) 1555, 1500, 1440, 867, 500 cm^{-1}; *m/e* 298 (M^+), main peaks at 219 (100%, $C_{12}H_{11}O_4^+$), 191 ($C_{11}H_{11}O_3^+$), 175 ($C_{11}H_{11}O_2^+$), 156 ($C_8H_5Br^+$), 147 ($C_9H_7O_2^+$), 131 ($C_9H_7O^+$), 103 ($C_8H_7^+$), 98 ($C_5H_6O_2^+$); the formulas of all the ions in parentheses were confirmed by mass marking.

Anal. Calcd for $C_{12}H_{11}O_4Br$: C, 48.18; H, 3.71; Br, 26.72. Found: C, 47.92; H, 3.70; Br, 26.90.

2,5-Dibromocyclopentanone Ethylene Ketal (18).—This compound was prepared by the method described for compound **2**, using 2.0 mol of bromine. The mixture was allowed to attain room temperature and then stirred for a further hour. The colorless solution was poured into 5% aqueous sodium bicarbonate (5 l.) and shaken with ether (three 300-ml portions). The combined ethereal solutions were washed with water and dried ($MgSO_4$). Evaporation of the ether *in vacuo* gave a pale brown oil which usually solidified when kept in the refrigerator overnight. Recrystallization thrice (ethanol) gave 2,5-dibromocyclopentanone ethylene ketal (**18**) (194.7 g, 68.1%): mp 62–64°; nmr τ 5.75 (s, 6 H), 7.67–7.83 (m, 4 H); ir (KCl) 2980, 2954, 2892, 1304, 1212, 695 cm^{-1}; *m/e* 284 (M^+).

Anal. Calcd for $C_7H_{10}O_2Br_2$: C, 29.40; H, 3.52; Br, 55.89. Found: C, 29.65; H, 3.55; Br, 55.65.

Sometimes the product failed to solidify but the oil still gave satisfactory yields when used for the preparation of compound **19**. Garbisch[40] reported a method of brominating cycloalkanone ketals in ether which we found satisfactory for the preparation of 2,5-dibromocyclopentanone ethylene ketal (**18**), but which was not successful for the preparation of 2,2,5-tribromocyclopentanone ethylene ketal (**2**).

***endo*-Dicyclopentadiene-1,8-dione Bisethylene Ketal (19).**—A solution of compound **18** (190.0 g, 0.664 mol) in methanol (400 ml) was added dropwise with stirring to sodium (92.0 g, 4.0 g-atoms) in methanol (1.1 l.) cooled in ice water. The mixture was then heated under reflux for 9 hr, cooled, poured into water (5 l.), and shaken with ether (three 300-ml portions). The ethereal solutions were washed with water and dried ($MgSO_4$). The ether was removed and the residue was crystallized (ethanol) three times to give compound **19** (56.8 g, 69%): mp 91–92° (lit.[41] 92°); nmr τ 3.80–3.90 (m, 1 H), 4.15–4.27 (m, 2 H), 4.43 (q, 1 H), 5.98–6.13 (m, 8 H), 6.46–6.64 (m, 1 H), 7.13 (q, 1 H), 7.22–7.39 (m, 2 H); ir (KCl) 3040, 2982, 2888, 1695 cm^{-1}; *m/e* 248 (M^+).

Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.72; H, 6.50. Found: C, 67.70; H, 6.60.

***endo*-Dicyclopentadiene-1,8-dione 8-Ethylene Ketal (20).**—This compound was prepared by the partial hydrolysis of compound **19** at room temperature for 5 hr as described by Vogel and Wyes:[41] yield 92%; mp 93–94° (lit.[41] 94–95°); nmr τ 2.64 (q, 1 H), 3.91 (q, 1 H), 3.91-4.20 (m, 2 H), 5.94-6.24 (sym m, 4 H), 6.32–6.52 (m, 1 H), 6.91–7.25 (m, 3 H); *m/e* 204 (M^+).

Pentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]deca-6,10-dione 6-Ethylene Ketal (21).—This compound was prepared from compound **20** as described by Vogel and Wyes:[41] yield 50%; mp 58–60° (lit.[41] 58–60°).

Pentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane (22).—This compound was prepared as described by Schenck and Steinmetz,[42] and by Dilling, Braendlin, and McBee.[43] The residue was sublimed twice [90° (760 mm)] to give compound **22**: yield 14%; mp 139–141° (lit.[42] 134–136°,[43] 138–141°, and 142–143°); nmr τ 7.20–7.36 (m, 2 H), 7.38–7.58 (m, 6 H), 8.36 (d, 2 H), 8.79 (d, 2 H); *m/e* 132 (M^+).

Pentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane (35).—This compound was prepared by the dechlorination of dodecachloropentacyclo-[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane[44,45] as described by Dilling, Braendlin, and McBee.[43] The crude product was purified by chromatography on a neutral alumina column (elution with cyclohexane). The cyclohexane was removed *in vacuo* and the residue was sublimed [40° (40 mm)] to give compound **35**: yield 52%; mp 125–127° (sealed tube) (lit.[43] 125–127°); nmr τ 7.00–7.24 (m, 4 H), 7.43–7.57 (m, 4 H), 8.64 (s, 4 H); *m/e* 132 (M^+).

Registry No.—**2**, 25834-49-5; **3**, 25834-50-8; **4**, 25834-51-9; **5**, 25867-84-9; **6**, 25867-85-0; **6a**, 25834-60-0; **8**, 25867-86-1; **9**, 25867-87-2; **10**, 25867-88-3; **11**, 25834-52-0; **12**, 25834-53-1; **13**, 25834-54-2; **14**, 25867-89-4; **15**, 25834-55-3; **16**, 74725-77-0; **17**, 25915-60-0; **18**, 25834-57-5; **19**, 4576-45-8; **20**, 4576-44-7; **22**, 6707-86-4; **35**, 6707-88-6.

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