Registry No.—**5**, 15291-18-6; **6**, 25157-95-3; **7**, 54020-24-5; **8**, 20379-80-0; **9**, 20792-01-2; **10**, 53993-24-1; **11**, 53993-25-2; **12**, 54053-43-9; **13**, 53993-26-3; **14**, 54053-44-0; **15**, 53993-27-4; **16**, 53993-28-5; **17**, 53993-29-5; **18**, 53993-30-9; **19**, 53993-31-0; **20**, 53993-32-1; **21**, 53993-33-2; cyclooctatetraene, 629-20-9; dimethyl acetylenedicarboxylate, 762-42-5; 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene, 2207-27-4; oxalyl chloride, 79-37-8; trifluoroperacetic acid, 359-48-8; methanesulfonyl chloride, 124-63-0.

References and Notes

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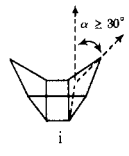

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Rearrangements of 1,2,3,4-Tetrachloropentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonan-9-one[1]

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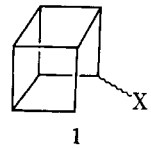
9,9-Dimethoxy-1,2,3,4-tetrachloropentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane (**2**) was found to rearrange to cage-opened ketone **4** on treatment with concentrated sulfuric acid, but, with hydrogen bromide in acetic acid, ketal **2** was hydrolyzed to tetrachlorohomocubane (**3**). Treatment of **3** with aqueous base gave rise to the oxahomocubane acid **6**, while treatment with sodium hydroxide in benzene gave tetrachlorosecocubane acid (**8**). The conversion of **3** to **6** was shown to proceed through **8** via a sequence of intramolecular chlorine displacements by the isolation of intermediate lactone **10**. These results are discussed in relation to reactions of similar compounds which have been previously described in the literature.

As part of an investigation of the tetracyclo[4.2.0.0^{2,5}.0^{4,7}]octane (secocubane) ring system, various chlorinated cage compound intermediates have been studied in an attempt to devise an efficient synthetic route to secocuban-5-yl derivatives (**1**). The chemistry of polycyclic cage compounds is altered a great deal owing to the electron-withdrawing inductive effects and to the steric effects of multiple chlorine substitution,[3] and in the present study attention has been directed toward the role of these two effects upon the rearrangement pathways of the cage system.

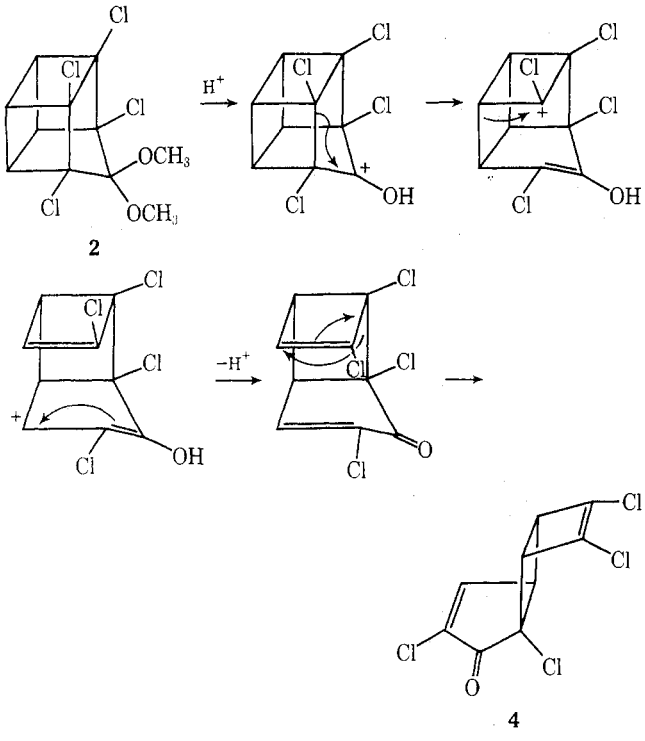


1

Tetrachlorohomocubanone ketal (**2**) was prepared in good yield by the method of Warrener and coworkers.[4] Attempts to hydrolyze ketal **2** with various concentrations of sulfuric acid (up to 75% acid at temperatures up to 80°) were unsuccessful, the ketal being recovered quantitatively. However, treatment of **2** with concentrated sulfuric acid at room temperature gave an unsaturated ketone **4**, which was isomeric with the expected cage ketone **3**, in 70% yield. The infrared absorption of the product at 1750, 1625, and 1590 cm^{-1} was compatible with an α-chloro conjugated carbonyl group and an additional chlorinated cyclobutene double bond.[5] The ultraviolet spectrum, λ_{max} 234 nm (ϵ 6700), also indicated a conjugated ketone. The NMR spectrum exhibited multiplets at δ 3.6 and 3.4 in a ratio of 2:1 in addition to a one-proton doublet at δ 7.7. Double irradiation of the signal at δ 3.6 caused the δ 7.7 doublet to collapse to a singlet.

The above data indicate cage-opening rearrangement of a hydrolysis intermediate with carbonium ion character at the carbonyl carbon to give the product, 3,4,6,8-tetrachlorotricyclo[4.3.0.0^{2,5}]nona-3,8-dien-7-one (**4**). One possible mechanism for the rearrangement to **4** is illustrated in Scheme I. The driving force behind the indicated 1,3-sigmatropic shift is not clear, but such a shift is necessary in

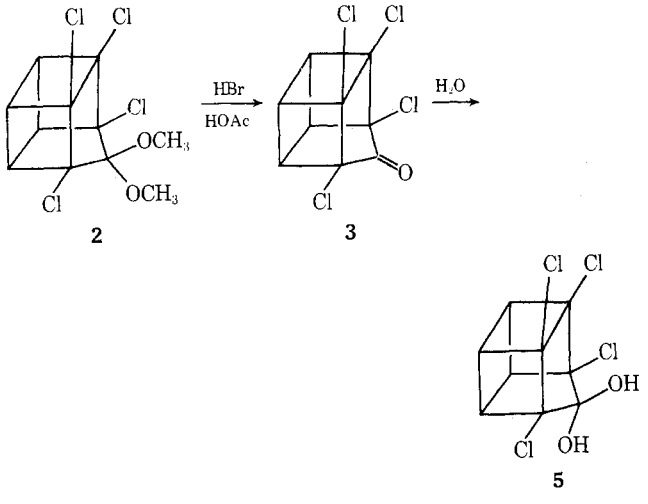
Scheme I



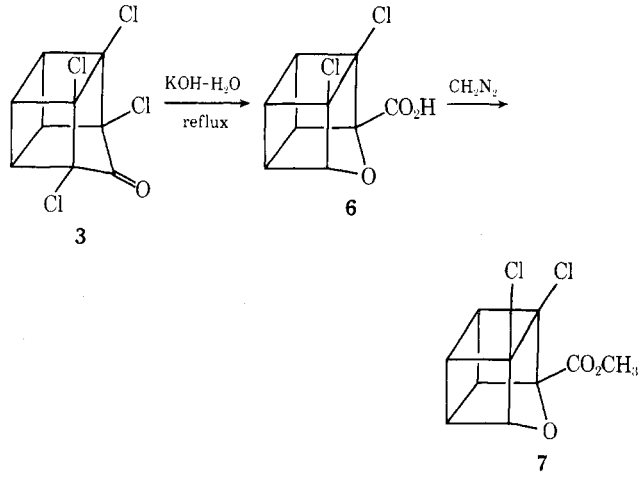
order to arrive at **4**, which has only one vinylic hydrogen. The exact nature of this rearrangement and the point at which the 1,3 shift occurs is an open point, and the sequence illustrated in Scheme I is purely arbitrary. In any event, generation of a very unstable carbonium ion at the carbonyl carbon and the great driving force due to strain release combine to bring about the observed rearrangement of **2** to **4**.

Acid-catalyzed hydrolysis of perchlorinated cage ketals generally requires quite vigorous conditions, usually concentrated or fuming sulfuric acid.[6] In such cases hydrolysis usually occurs without rearrangement and is due to the additional stability afforded to theex polycyclic systems by the presence of more than four chlorine substituents. Even though the perchlorinated cage ketals require more reactive conditions to initiate hydrolysis, they do not undergo the type of rearrangement pathway that is observed in the hydrolysis of **2**.

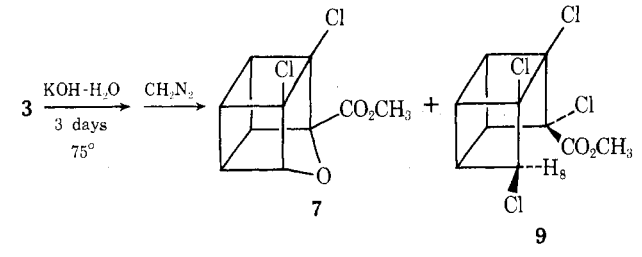
In an effort to hydrolyze ketal **2** without rearrangement, it was heated with 30% hydrogen bromide in acetic acid in a sealed tube. This procedure gave a quantitative yield of the desired ketone **3**, which hydrated rapidly to **5** on contact with the moisture in air. Pure **3** had a characteristic carbonyl absorption at 1800 cm^{-1}. This nucleophilic ketal cleavage reaction does not involve a carbonium ion intermediate and therefore rearrangement does not occur.[7]



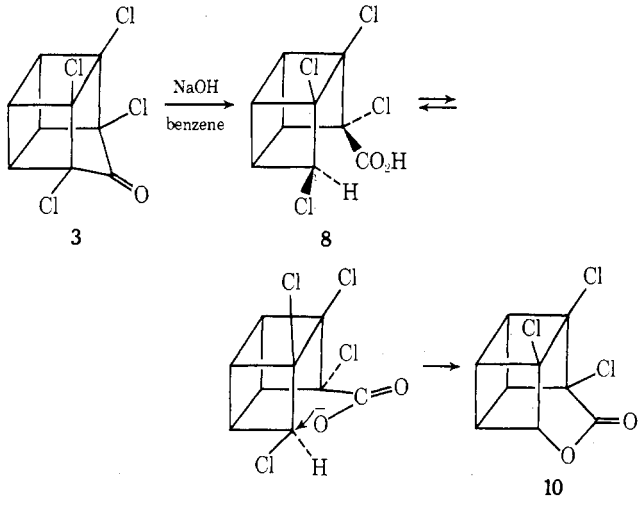
Treatment of ketone **3** or its hydrate **5** with an aqueous potassium hydroxide solution at reflux yielded oxahomocubanecarboxylic acid **6**, isolated as its methyl ester **7**. The structure of **7** was assigned on the basis of the following spectral evidence: NMR (CCl_4) δ 3.55 (m, 4 H), 3.9 (s, 3 H), 5.2 (m, 1 H); ir (CCl_4) 1760–1735 cm^{-1} (split carbonyl); mass spectrum *m/e* 231, 211. In addition, ester **7** gave correct elemental analysis for the molecular formula $C_{10}H_8O_3Cl_2$.



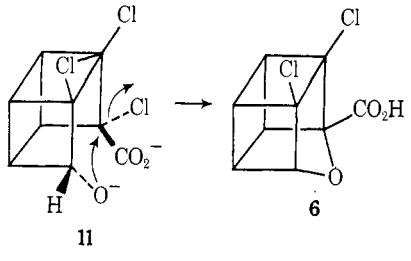
When **3** was treated with aqueous base at 75°, much longer reaction times were required for complete reaction. Esterification then gave an approximately equimolar mixture of **7** and the ester (**9**) of the desired cleavage product, tetrachlorosecocubanecarboxylic acid (**8**). Ester **9** had a single infrared carbonyl absorption at 1745 cm^{-1} and its NMR spectrum was similar to that of **7** with the exception of a sharp doublet (J = 2 Hz) at δ 4.5 for the endo α-chloro proton replacing the broad δ 5.2 multiplet for the exo α-oxy proton of **7**. The lack of complex splitting observed for the *endo*-secocubyl proton (H_8) of **9** is a rather general phenomenon which has been observed in other cage compounds.[8]



When ketone **3** was refluxed in benzene with solid, powdered sodium hydroxide, a quantitative yield of seco acid **8** was obtained. In an attempt to recrystallize **8**, the acid was dissolved in hot aqueous methanol; the solution upon concentration and cooling afforded a new compound, a crystalline solid which was not an acid. The new compound was assigned lactone structure **10** on the basis of its analysis for molecular formula $C_9H_5O_2Cl_3$, and the following spectral data: NMR ($CDCl_3$) δ 3.65 (m, 3 H), 4.1 (m, 1 H), 5.3 (doublet of doublets, J = 2 and 5 Hz, 1 H); ir ($CDCl_3$) 1780–1770 cm^{-1} (split carbonyl). Lactone **10** must be formed via intramolecular displacement of chlorine by carboxylate anion in the polar aqueous medium.

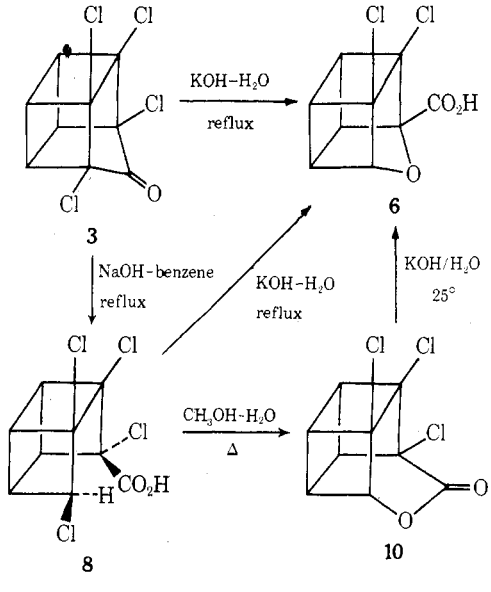


When lactone **10** was treated with aqueous potassium hydroxide at room temperature it was converted quantitatively to oxy acid **6**, indicating that the lactone is an intermediate in the conversion of ketone **3** to **6**. Thus, the saponification of the lactone must give ring-opened dianion **11**, which undergoes intramolecular chlorine displacement to yield the cyclic ether acid **6**.

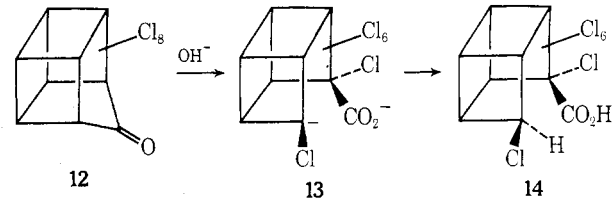


As a final proof that seco acid **8** is an intermediate in the conversion of **3** to **6**, it was also subjected to further treatment with aqueous potassium hydroxide solutions. At room temperature no reaction occurred, but at reflux **8** was rapidly and quantitatively converted to **6**. This result points out the necessity for a greater driving force and higher temperature in order to bring about the first intramolecular displacement to lactone **10**, and completes the cycle of intermediates capable of being converted into the end rearrangement product, oxy acid **6**. These results are summarized pn Scheme II.

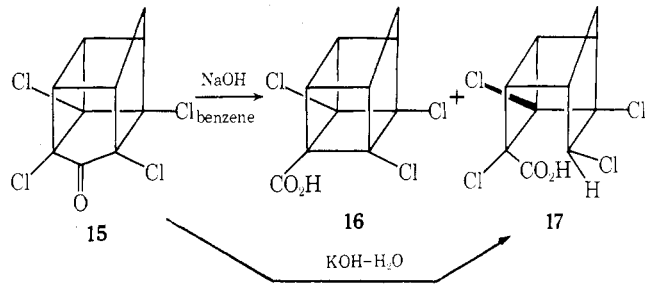
Scheme II



The reaction pathways for ketone **3** illustrated in Scheme II have been observed previously in related systems. Perchlorohomocubanone (**12**) was reported to give, stereospecifically, secocubane acid **14** in high yield when treated with either aqueous potassium hydroxide or sodium hydroxide in toluene.[9] Apparently the presence of four additional chlorine substituents stabilizes carbanion intermediate **13** sufficiently to prevent the further reactions observed in the tetrachloro compound.



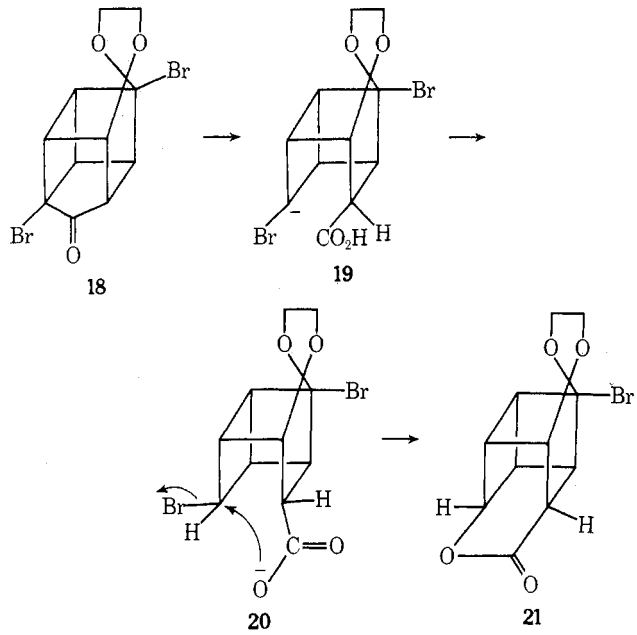
In a related study, tetrachloro ketone **15**, when heated with sodium hydroxide in benzene, was found to give a mixture of the ring-contracted product **16** and the ring-cleaved product **17** in a ratio of 3:2. However, on treatment with potassium hydroxide in either water or benzene, ketone **15** gave exclusively cleavage to **17** in near-quantitative yield.[10] While these results are less readily rationalized with the results of the present study, it is apparent that changes in steric and strain factors due to the extra one-carbon bridge in **15** must play a major role in determining what reaction pathways are open to the molecule.



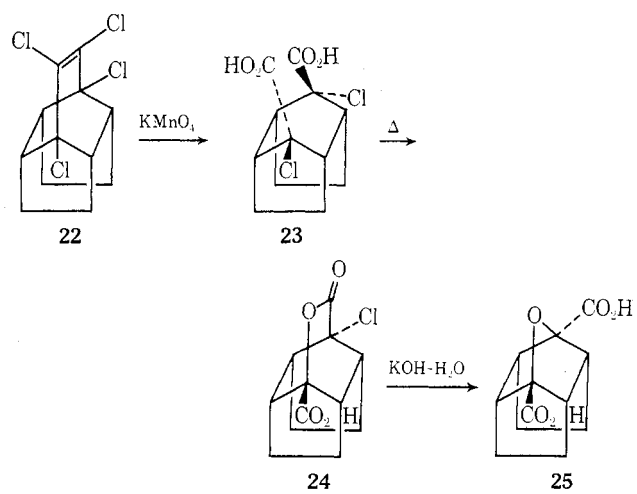
The formation of ring-cleaved products instead of the normal Favorskii-type contraction in these reactions can be attributed to a combination of factors due to ring strain and to the added stability of the chlorocarbanion intermediates. However, the less common intramolecular displacements occurring in the present study are most likely the result of severe steric interaction between the crowded endo substituents in the ring-opened intermediates. In both the formation of lactone **10** and its conversion to acid **6** the steric strain is relieved by closure of such an intermediate to the cyclic product.

The formation of lactone **10** is not without precedent; a similar intramolecular displacement to form lactone **20** has been observed in the attempted ring contraction of bromo ketone **18** in DMSO.[11] The absence of multiple halogen substituents to stabilize carbanion intermediate **19** inhibit the formation ringe cleavage products and permit the sequence of intramolecular proton transfer and subsequent bromine displacement to predominate (Scheme III). Also, the intramolecular displacement of halogen by alkoxide anion has been observed in the sequence outline in Scheme IV,[12] a result illustrating the generality of endo–endo-substituted cages undergoing intramolecular ring closure via chlorine displacement.

Scheme III



Scheme IV



Experimental Section

3,4,6,8-Tetrachlorotricyclo[4.3.0.0^{2,5}]nona-3,8-dien-7-one (4). A 125-mg (0.4 mmol) sample of ketal **2** was suspended in 5 ml of concentrated sulfuric acid and stirred at room temperature. The ketal gradually dissolved as the solution darkened in color. After 6 hr, the dark brown solution was poured into 60 ml of crushed ice and the precipitated yellow solid collected by filtration. The aqueous layer was extracted with ether and the combined ether layers were dried ($MgSO_4$). Rotary evaporation of the solvent afforded additional solid product. The combined crude product was chromatographed on 10 g of silica gel, eluted with 50% ether–pentane, and recrystallized from pentane to yield 70 mg (70%) of ketone **4**: mp 143–145°; NMR ($CDCl_3$) δ 3.4 (1 H, m) and 3.6 (2 H, m, bridgeheads), 7.7 (1 H, d, J = 3.5 Hz, vinylic) (irradiation of the δ 3.6 signal caused the vinylic signal at δ 7.7 to collapse to a singlet, and irradiation of the δ 7.7 signal greatly simplified the multiplet at δ 3.6); uv max (EtOH) 234 nm (ϵ 6700); ir ($CHCl_3$) 1750, 1625, and 1590 cm^{-1}; mass spectrum m/e 268 (M^+), 233 (M − Cl).

Anal. Calcd for $C_9H_4OCl_4$ (269.94): C, 40.04; H, 1.48; Cl, 52.60. Found: C, 40.13; H, 1.53; Cl, 52.38.

1,6,7,8-Tetrachloropentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonan-9-one (3). A 12.15-g (0.0385 mol) sample of ketal **2** was placed in a thick-walled Pyrex tube and 90 ml of 30% hydrogen bromide in acetic acid was added. The tube was sealed under nitrogen atmosphere and heated at 110° in a tube furnace for 10 days. The solvent was evaporated, carefully avoiding water, and the crude brown residue was chromatographed on 500 g of silica gel. Elution with 50% ether–pentane and recrystallization from hexane–methylene chloride yielded 10.0 g (96%) of **3** which hydrates readily on exposure to air: mp 175–178° (water loss at 100°); NMR (as hydrate **5**) ($CDCl_3$) δ 3.1 (2 H, broad, OH), 3.8 (4 H, s, cage protons); ir ($CHCl_3$) 1800 and 1150 cm^{-1} (after exposure to air a 360–3300-cm^{-1} absorption appears and the 1800-cm^{-1} peak is diminished); mass spectrum m/e 268 (M^+), 233 (M − Cl).

9-Oxa-2,3-dichloropentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane-1-carboxylic Acid (6). Treatment of ketone **3** or its hydrate **5** with various concentrations of aqueous potassium hydroxide at reflux afforded acid **6**, while at lower temperatures mixtures of acids **8** and **6** were obtained. Longer reaction times were required when lower base concentrations were employed. The procedures in all cases were similar and are illustrated by the following example.

A mixture of 0.52 g (2.0 mmol) of ketone **2** in 50 ml of 30% aqueous potassium hydroxide was refluxed under nitrogen for 6 hr. The solution was allowed to cool, poured into crushed ice, and acidified with concentrated hydrochloric acid, and the resultant precipitate was extracted with ether. The combined ether layers were washed with saturated salt solution, dried ($MgSO_4$), and rotary evaporated to yield 0.42 g (92%) of crude acid **6**. A pure sample of acid **6** was obtained by recrystallization from ether–pentane: mp 201.5–202.5°; NMR (acetone-d_6) δ 3.6 (4 H, m, cage protons), 5.35 (1 H, m, α-ether); ir (KBr) 3400–2500 and 1710 cm^{-1}; mass spectrum m/e 232 (M^+), 234 (M + 2), 197 (M − Cl), 199 (M + 2 − Cl).

Anal. Calcd for $C_9H_6O_3Cl_2$ (233.06): C, 46.30; H, 2.57; Cl, 30.45. Found: C, 46.18; H, 2.56; Cl, 30.62.

A portion of the acid was esterified with ethereal diazomethane and the crude ester was recrystallized from pentane, giving an analytical sample of methyl ester **7**: mp 86–88°; NMR (CCl_4) δ 3.3–3.7 (4 Hm m, cage protons), 3.9 (3 H, s, ester), 5.1–5.3 (1 H, m, α-ether proton); ir (CCl_4) 1760–1735 cm^{-1} (split carbonyl); mass spectrum m/e 231 (M − CH_3), 211 (M − Cl).

Anal. Calcd for $C_9H_6O_2Cl_4$ (287.99): C, 37.55; H, 2.10; Cl, 49.20. Found: C, 37.74; H, 2.13; Cl, 48.98.

1,2,3-*exo*-8-Tetrachlorotetracyclo[4.2.0.0^{2,5}.0^{4,7}]octane-*endo*-3-carboxylic Acid (8). Powdered sodium hydroxide (5.0 g, 0.125 mol) was added to a solution of 5.2 g (0.02 mol) of ketone **2** in 600 ml of benzene. The suspension was stirred magnetically and heated to reflux under nitrogen. After 21 hr, the mixture was cooled and extracted with water. The aqueous solution was acidified with concentrated hydrochloric acid and extracted several times with ether. The combined ether layers were washed with saturated salt solution, dried ($MgSO_4$), and rotary evaporated to give 4.8 g (92%) of crude acid **8**. Pure acid **8** was obtained by recrystallization from pentane: mp 216–220°; NMR (DMSO-d_6) δ 3.4–4.1 (4 H, m, cage protons), 4.8 (1 H, d, J = 2 Hz, α-chloro); ir ($CHCl_3$) 3500–2500 and 1720 cm^{-1}; mass spectrum m/e 241 (M − CO_2H), 215 (M − Cl − CO_2H), 217 (M + 2 − Cl − CO_2H).

Anal. Calcd for C_9H infn$6O_2Cl_4$ (287.99): C, 37.55; H, 2.10; Cl, 49.20. Found: C, 37.74; H, 2.13; Cl, 48.98.

A portion of acid **8** was esterified with ethereal diazomethane to give ester **9**. The ester was purified by recrystallization from pentane: mp 127–128°; NMR (CCl_4) δ 3.3–4.0 (4 H, m, cage protons), 3.95 (3 H, s, ester), 4.5 (1 H, d, J = 2 Hz, α-chloro proton); ir (CCl_4) 1745 cm^{-1}; mass spectrum m/e 264 (M − Cl).

Anal. Calcd for $C_{10}H_8O_2Cl_4$ (302.02): C, 39.75; H, 2.65; Cl, 47.00. Found: C, 40.04; H, 2.75; Cl, 46.74.

9-Oxa-1,2,3-trichloropentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decan-10-one (10). A solution of 1.0 g (3.5 mmol) of acid **8** in 150 ml of 10% aqueous methanol was refluxed for 24 hr and cooled, and the white precipitate was collected. The mother liquor was concentrated and a second crop was collected to yield a total of 8.7 g (100%) of lactone **10**. The product was recrystallized from ether–pentane to afford an analytical sample: mp 168–171°; NMR ($CDCl_3$) δ 3.5–4.0 (3 H, m) and 4.0–4.3 (1 H, m, cage protons), 5.3 (1 H, doublet of doublets, J = 2 and 5 Hz, α-oxy proton); ir ($CHCl_3$) 1780 and 1770 cm^{-1} (split carbonyl); mass spectrum m/e 215 (M − Cl), 217 (M + 2 − Cl), 219 (M + 4 − Cl).

Anal. Calcd for $C_9H_5O_2Cl_3$ (251.56): C, 42.90; H, 1.99; Cl, 42.30. Found: C, 43.02; H, 2.13; Cl, 42.09.

Conversion of Lactone 10 to Acid 6. A. At Reflux. A mixture of 62 mg (2.46 mmol) of lactone **10** in 20 ml of 20% aqueous potassium hydroxide was refluxed for 5 hr. The mixture was cooled, poured into crushed ice, and acidified with concentrated hydrochloric acid. The precipitate was extracted into ether, and the ether solution was washed with saturated salt solution and dried ($MgSO_4$). The solution was rotary evaporated to give crude **6**, which on esterification with ethereal diazomethane yielded 58 mg (95%) of methyl ester **7** identical with an authentic sample.

B. At Room Temperature. Lactone **10** (97.5 mg, 3.88 mmol) was suspended in 40 ml of 20% aqueous potassium hydroxide and stirred. The solid gradually dissolved, and after 5 days the clear, colorless solution was acidified, worked up as in A, and esterified to yield 80 mg of methyl esters. VPC examination (XF-1150 column, 200°) showed ester **7** and an unidentified by-product in a ratio of 5:1.

Acid 6 from Acid 8. A 66-mg (2.29 mmol) sample of acid **8** was stirred in 25 ml of 20% aqueous potassium hydroxide under nitrogen for several days. An aliquot worked up as described below yielded only unreacted starting material. The mixture was then refluxed for 5 hr and allowed to cool. The solution was poured into crushed ice and acidified with concentrated hydrochloric acid, and the resulting precipitate was extracted with three portions of ether. The ether extracts were washed with saturated salt solution, dried ($MgSO_4$), and rotary evaporated to yield 50 mg (88%) of acid **6**. The formation of acid **6** was confirmed by esterification of the acid with ethereal diazomethane, which gave methyl ester **7** identical with an authentic sample.

Registry No.—**2**, 20792-01-2; **3**, 54119-85-6; **4**, 54119-86-7; **5**, 54119-87-8; **6**, 54119-88-9; **7**, 54119-89-0; **8**, 54119-90-3; **9**, 54119-91-4; **10**, 54119-92-5.

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Synthesis of Some 4-Substituted Pentacyclo[4.3.0.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$]nonane Derivatives and Their Reactions. Cyclopropane Ring Expansion and Cleavage

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The direct photolysis of 8-cyanodeltacyclene (**1**) gave 4-cyanopentacyclo[4.3.0.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$]nonane (**2**) in a high yield. **2** was converted to the corresponding carboxylic acid **4**, carbinol **6**, and amine **10**. Buffered hydrolysis of **6** *p*-nitrobenzoate (**7**) and 3,5-dinitrobenzoate (**8**) afforded exclusively pentacyclo[5.3.0.$0^{3,6}$.$0^{2,10}$.$0^{5,9}$]decan-3-ol (**9**), a cyclopropylcarbinyl–cyclobutyl rearrangement product. Deamination of **10** in C_6H_6–AcOH gave unrearranged acetate **12** and rearranged acetate **13** in 7:13 ratio. Acid **4** was converted to isocyanate **18**, which gave the corresponding urea and urethane derivatives **19–22** on treatment with water, aniline, ethanol, and phenol, respectively. On refluxing with KOH in ethylene glycol, **19–22** afforded a ~1:9 mixture of *exo*-and *endo*-tetracyclo[4.3.0.$0^{2,9}$.$0^{4,8}$]nonan-3-ol (**23x** and **23e**) accompanied with a trace amount of ketone **24**. The formation of the alcohols was explained by base-catalyzed cyclopropylamine rearrangement, followed by the Meerwein–Ponndorf–Verley reduction.

The chemistry of small-ring compounds combined with cage structure has in recent years received a great deal of attention.[1] We were intrigued by the possibility of obtaining novel ring system by skeletal rearrangement of these systems. In this paper we wish to describe cyclopropylcarbinyl cation and cyclopropylamine anion rearrangements by using appropriately 4-substituted pentacyclo[4.3.0.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$]nonane derivatives.

Results and Discussion

Photolysis of 8-cyanodeltacyclene (**1**)[2] in ether afforded a photoisomer **2** in 88% yield and a trace amount of dimer **3**[3] (Scheme I). **2** was identified as 4-cyanopentacyclo[4.3.0.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$]nonane, an intramolecular $_{2\pi_s} + _{2\sigma_s}$ adduct, by spectral characteristics and the photochemical analogy.[4] Mass spectral molecular ion peak at *m/e* 143 and analysis indicated a formula $C_{10}H_9N$ for **2**. In the NMR ($CDCl_3$, 60 MHz) spectrum, **2** had characteristic signals as summarized in Table I. The lowest 4 H multiplet at δ 2.72 was assigned to H_1, H_8, H_2, and H_3 by comparison of the chemical shifts reported for 4,5-bismethoxycarbonyl[4a,d] and 4,5-dicarboxylic acid analogs[4a,b] as well as the parent pentacyclic compound.[4b] The broad triplet at δ 2.36 was assigned to H_5 because of its 1 H peak area and its signal pattern.[5] The complex multiplet at δ 2.17 and broad singlet at δ 1.88 were assigned to H_6 and H_7, and H_9 and $H_{9'}$, respectively. **3** had a molecular ion peak at *m/e* 286 ($C_{20}H_{18}N_2$) and ir (KBr) absorptions at 2250 (CN) and 814 and 790 cm^{-1} (nortricylene),[6] and hence **3** was characterized as an intermolecular $_{2\pi} + _{2\pi}$ photodimer.

On alkaline hydrolysis **2** afforded the corresponding carboxylic acid **4** in 90% yield. Esterification of **4** with diazomethane gave **5** quantitatively, which was reduced to carbinol **6** with lithium aluminum hydride (89%). The *p*-nitrobenzoate **7** and 3,5-dinitrobenzoate **8** were obtained in high yields by the usual method.[7] Lithium aluminum hydride reduction of **2** afforded the corresponding amine **10** (82%), which was characterized as its phenylurea derivative **11** (Scheme I). The structures of these derivatives were confirmed by the spectral and analytical data (Table I).[8]

On hydrolysis in 70% (v/v) aqueous dioxane in the presence of an excess amount of 2,6-lutidine at 170° for 24 hr, **7** afforded an alcoholic product **9** (40%, 77% based on **7** consumed), **6** (trace), and unreacted **7** (48%) after work-up on a