methylbicyclo[2.1.0]pentane (5b).—The above hydrazone, 12.8 g, as the salt, gave by the method described, 4.2 g (76%) of a liquid, almost pure by vpc, retention time 28 min. After fractionation, a middle cut, bp 67–68° (15 mm), was purified by preparative vpc: uv no absorption; ir no C=C; nmr[23] δ (CCl₄) 0.4 (m, 1), 0.7 (s, 3, Me), 1.0 (m, 1), 1.2 (s, 3, Me), 1.4 (s, 3, Me), 1.75 (m, 1), 3.4 (broad 1, -CHOH), 3.6 (broad, 1, OH); mass spectrum (70 eV) *m/e* (rel intensity) 126 (15), 125 (15), 111 (94), 43 (100). These spectra are consistent with structure **5b**.

Anal. Calcd for $C_8H_{14}O$: C, 76.15; H, 11.2. Found: C, 76.0; H, 11.0.

Propionylation of the Bicyclic Alcohol 5b Giving 6a.—Treatment of the alcohol **5b** with propionic anhydride in pyridine gave a product with the same retention time and ir spectrum as ester **6a**. This experiment was repeated and the result confirmed.

1,1,3,3-Tetramethylcyclobutan-2,4-dione Monobenzenesulfonylhydrazone (12).—The dione, 14 g (0.1 mol), and 8.6 g (0.05 mol) of benzenesulfonylhydrazine were dissolved in 150 ml of methanol and the solution left to stand 5 days. Filtration gave a small residue of bissulfonylhydrazone, mp 275° (recrystallized from dioxane–water), ir (Nujol) 1670 cm⁻¹ (C=N).

Anal. Calcd for $C_{20}H_{24}N_4O_4S_2$: C, 53.6; H, 5.4; N, 12.5; S, 14.3. Found: C, 53.75; H, 5.6; N, 12.4; S, 14.1.

Evaporation of the filtrate to dryness, followed by extraction of the residue with hot petroleum ether to recover unused dione left **12**: 9 g (61%); mp 141° (crystallized from aqueous methanol); ir (CH₂Cl₂) 1800 (CO), 1680 (C=N) cm⁻¹.

Anal. Calcd for $C_{14}H_{18}N_2SO_3$: C, 56.9; H, 5.7; N, 9.8; S, 11.3. Found: C, 57.1; H, 6.1; N, 9.5; S, 10.9.

Pyrolysis of the Salt of 12 Giving Bis-1,1,3,3-tetramethylcyclobutan-4-one Azine (15) and Methyl 2,5-Dimethyl-4-hexenoate (14).—**12** (34.5 g) was converted to its sodium salt and pyrolyzed as described above, giving 8 g (43%) of distillate plus a solid which collected in the condenser. The latter had mp 187°; uv max

(23) V. Rautenstrauch and F. Wingler, *Tetrahedron Lett.*, 4703 (1965).

227 mμ (log ε 4.0), 288 (2.26); ir (CCl₄) 1820 (C=O), 1800 (C=O), 1690 cm⁻¹ (C=N); nmr (CDCl₃) δ 1.45, 1.35 (1:1); mass spectrum (70 eV) *m/e* (rel intensity) 276 (21), 248 (35), 139 (12), 69 (100). These spectra support the proposed structure **15**.

Anal. Calcd for $C_{16}H_{24}N_2O_2$: C, 69.5; H, 8.8; N, 10.15. Found: C, 69.2; H, 8.6; N, 10.2.

The distillate had one major component on vpc with retention time 26.5 min. Fractionation gave 3 g of pure material: bp 72° (12 mm); n^{23}D 1.442; ir (CS₂) 2850 (OMe), 1740 (ester CO), 1160 (CO), 3020, 1670, 820 cm⁻¹ (Me₂C=CH-); nmr (CCl₄) δ 1.1 (d, 3, *J* = 6.5 Hz), 1.6 (d, 3, *J* = 1 Hz) and 1.7 (d, 3, *J* = 1 Hz, Me₂C=CH-), 2.3 (m, 2 + 1), 3.6 (s, 3, OMe), 5.1 (t, 1, Me₂C=CH-); mass spectrum (70 eV) *m/e* (rel intensity) 156 (32), 125 (11), 88 (83), 69 (100). The process M⁺ → *m/e* 88 (MeCH₂COOMe) + 66 was interpreted as a McLafferty rearrangement, in line with the proposed structure **14**.

Anal. Calcd for $C_9H_{16}O_2$: C, 69.2; H, 10.2. Found: C, 69.5; H, 10.25.

Registry No.—**4a**, 26308-71-4; 1-propionyloxy-2,2,-4,4-tetramethylcyclobutan-3-one, 1133-07-9; **4b**, 26308-73-6; **4b** dipropionate, 26308-74-7; **5b**, 26308-75-8; **6a**, 26308-76-9; **6b**, 26308-77-0; **7**, 15641-58-4; **8**, 26308-64-5; **12**, 26308-65-6; **14**, 26308-66-7; **15**, 26308-67-8; 2,2,4,4-tetramethylcyclobutane-1,3-diol monopropionate, 26308-68-9; 2,2,4,4-tetramethylcyclobutane-1,3-diol dipropionate, 26308-69-0; 1,1,3,3-tetramethylcyclobutane-2,4-dione bisbenzenesulfonylhydrazone, 26308-70-3.

Synthetic Studies Related to the Bird-Cage System. III.
Derivatives of Pentacyclo[5.4.0.0²,⁶.0³,¹⁰.0⁵,⁹]undecane, Tetracyclo[4.4.0.0³,⁹.0⁴,⁸]decane, and Pentacyclo[4.4.0.0²,⁵.0³,⁹.0⁴,⁸]decane[1]

R. John Stedman,[2] Libby S. Miller, Larry D. Davis, and John R. E. Hoover

Smith Kline and French Laboratories, Research and Development Division, Philadelphia, Pennsylvania 19101, and Temple University School of Pharmacy, Philadelphia, Pennsylvania 19140

Synthetic sequences leading to derivatives of the "one-winged" (pentacycloundecane) and "wingless" (tetracyclodecane) congeners of the bird-cage hydrocarbon and to representatives of the 1,3'-bishomocubane (pentacyclodecane) system are described. The chlorinated methanonaphthalenes 2, 8, and 11, prepared by stereoselective Diels–Alder condensation of appropriate precursors, were photochemically cyclized to the one-winged bird-cage structures 3, 9, and 12. Orthodox manipulation of the functional groups and dehalogenation with lithium led to the ketal 4, the ketone 5, the hydrocarbon 6, and the amine 15. The tetrachloro ketone 16 was subjected to a Favorskii-type contraction to enter the 1,3'-bishomocubane series 17, 18, 21, and 22. Base-catalyzed opening of 18 yielded the wingless bird-cage imine 19, which was hydrolyzed to the ketone 20. These are the first reported representatives of the wingless bird-cage system. Nmr and mass spectral characteristics of the compounds are discussed.

Previous reports from these laboratories have described the synthesis of a variety of derivatives of the bird-cage hydrocarbon.[1,3,4] Our continued interest in the possible biological activity of cage compounds led us to investigate the preparation of some representatives of the related "one-winged" (pentacyclo[5.4.0.0²,⁶.0³,¹⁰.-

0⁵,⁹]undecane) and "wingless" (tetracyclo[4.4.0.0³,⁹.-0⁴,⁸]decane) bird-cage systems (*e.g.*, 6 and 20, respectively) which lack one or both of the one-carbon bridges of the complete bird cage. In this paper we report the synthesis of the one-winged bird-cage hydrocarbon and some of its functionalized derivatives, and the extrusion of the single bridge with formation of a new cage bond to give representatives of the 1,3'-bishomocubane[5] (pentacyclo[4.4.0.0²,⁵.0³,⁹.0⁴,⁸]decane) system (*e.g.*, 22).

(1) Part II: R. J. Stedman and L. S. Miller, *J. Org. Chem.*, **32**, 3544 (1967).

(2) To whom inquiries should be addressed at Temple University School of Pharmacy.

(3) R. J. Stedman, A. C. Swift, and J. R. E. Hoover, *Tetrahedron Lett.*, 2525 (1965).

(4) R. J. Stedman and L. S. Miller, *J. Org. Chem.*, **32**, 35 (1967).

(5) See W. L. Dilling, C. E. Reineke, and R. A. Plepys, *ibid.*, **34**, 2605 (1969), for an explanation of the bishomocubane nomenclature.

Cleavage of the new highly strained bond provided an entry into the wingless bird-cage series.[6,7]

The key intermediates in the synthesis of the one-winged bird-cage derivatives were the hexahydro-*endo*-1,4-methanonaphthalenes, **2, 8,** and **11,**[8] which could be cyclized photochemically to the corresponding cage compounds. Our approach thus paralleled earlier syntheses of some 8,11-diketones of the one-winged system.[9] The methanonaphthalenes were prepared by the Diels–Alder reaction, the required endo geometry of the adducts being enforced by the operation of the principles which we have discussed previously in connection with the synthesis of the analogous hexahydrodimethanonaphthalenes.[4] Our use of highly chlorinated starting materials was dictated partly by stereochemical requirements and partly by consideration of the ease of handling of intermediates. We assumed that the chlorine atoms could ultimately be removed by lithium reduction, as in the full bird-cage system.[10]
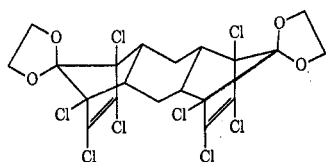
The syntheses of the one-winged bird-cage ketone **5** and the hydrocarbon **6** are shown in Scheme I. The ethylene ketal of tetrachlorocyclopentadienone (**1**), a reactive diene,[11] was condensed with 1,4-cyclohexadiene to give the Diels–Alder adduct **2.**[12] The endo configuration of **2** was anticipated from the operation of the endo addition rule for the genesis of norbornenes from cyclopentadienes[4] and was proved by its ready photochemical cyclization to **3.** We considered the possibility that, before reacting with **1,** the cyclohexadiene might have rearranged to the conjugated 1,3 isomer, which could then act either as diene or as dienophile in the Diels–Alder reaction. However, the product in either case would be less symmetrical than **2** and should give a more complex nmr spectrum than was, in fact, observed. Furthermore, the 1,4-cyclohexadiene, which was used in excess, could be recovered at the end of the reaction and was shown (glpc) to be free of the 1,3 isomer. The photocyclized cage compound **3** was dechlorinated with lithium and *tert*-butyl alcohol[10] to give the ketal **4.** Acid hydrolysis of **4** yielded the ketone **5,**

(6) Some of the compounds reported in this paper were described in a preliminary communication: R. J. Stedman, L. S. Miller, and J. R. E. Hoover, *Tetrahedron Lett.,* 2721 (1966).

(7) *Chemical Abstracts* names the one-winged system as 1,2,4-ethanylylidenecyclobuta[c,d]pentalenes. The other caged systems are named as in this paper. All chiral compounds were obtained as racemic mixtures.
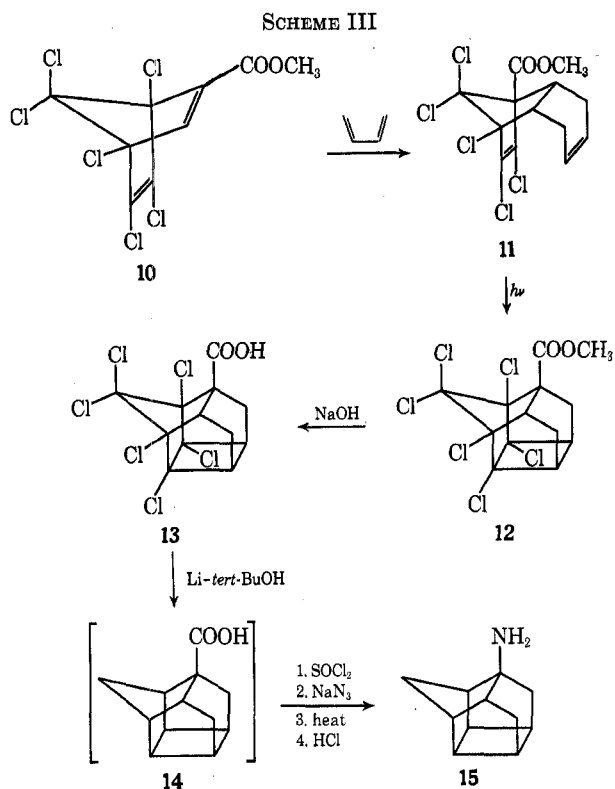
(8) For convenience, all the methanonaphthalenes are depicted in the conformation appropriate for cyclization.

(9) (a) R. C. Cookson, E. Crundwell, and J. Hudec, *Chem. Ind. (London),* 1003 (1958). (b) R. C. Cookson, E. Crundwell, R. R. Hill, and J. Hudec, *J. Chem. Soc.,* 3062 (1964). (c) D. F. O'Brien and J. W. Gates, Jr., *J. Org. Chem.,* **30,** 2593 (1965). (d) C. H. Krauch and W. Metzner, *Chem. Ber.,* **98,** 2106 (1965). (e) See also the recent synthesis of a triketone by C. M. Anderson, J. B. Bremner, H. H. Westberg, and R. N. Warrener, *Tetrahedron Lett.,* 1585 (1969). (f) G. R. Underwood and B. Ramamoorthy, *J. Chem. Soc. D,* 12 (1970), have recently reported the conversion of an 8,11 diketone to the hydrocarbon **6** in very low yield. No properties of **6** are given.

(10) P. Bruck, D. Thompson, and S. Winstein, *Chem. Ind. (London),* 405 (1960).

(11) (a) W.-H. Chang, *ibid.,* 709 (1964); (b) *J. Chem. Soc.,* 2305 (1965).

(12) A second, less soluble product was isolated from the reaction mixture and show t to be an adduct of 2 mol of **1** with one of 1,4-cyclohexadiene (see Experimental Section). Mechanistic considerations and the nmr spectrum suggest the structure

SCHEME I

which was converted to the hydrocarbon **6** by a Wolff–Kishner reduction.[9f] While this sequence was underway, an alternative approach to the hydrocarbon was undertaken as shown in Scheme II. The chlorinated

SCHEME II
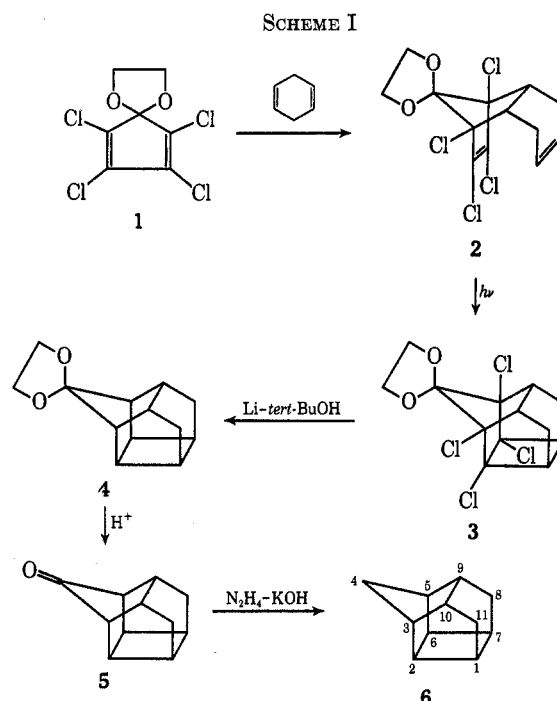
norbornene **7** was condensed with 1,3-butadiene to give the adduct **8.** In this reaction, the exo face of **7** is hindered by the bulky *gem*-dichloro group, and addition of the diene, therefore, occurs on its endo face.[4] Photochemical cyclization of **8** yielded the cage chlorocarbon **9.** Because of the success of the sequence of Scheme I, no attempt was made to dechlorinate **9** to the hydrocarbon.
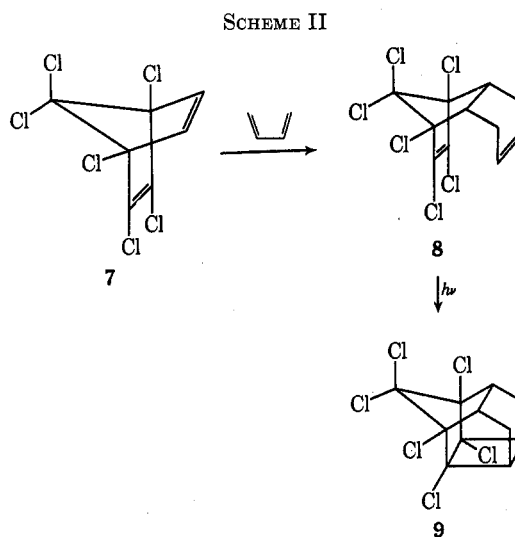
Scheme III shows the preparation of some derivatives of the one-winged cage substituted at the 9 position. The starting material in this case was the norbornadiene ester **10.**[1] The addition of 1,3-butadiene to **10,** sterically controlled by the *gem*-dichloro group, gave the endo adduct **11,** which was photochemically cyclized to the cage ester **12.** Alkaline hydrolysis gave the acid **13,** which was dechlorinated to **14;** the latter was not fully purified. A Curtius sequence converted **14** to the
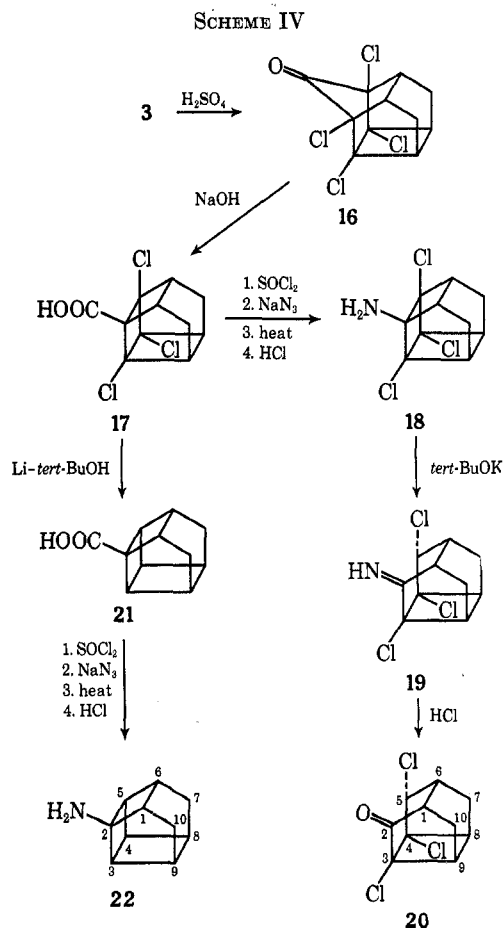
SCHEME III

SCHEME IV

amine **15**, which was purified as the hexamate and finally isolated as the hydrochloride.

Published literature indicated that the unknown wingless bird cage could not be synthesized in the same manner as the full and one-winged systems because the required unbridged hexahydronaphthalene precursors undergo photochemical dimerization or polymerization rather than cyclization;[9b] at least one bridge is necessary to bring the molecule into a conformation appropriate for closure.[13] Our approach was, therefore, to make the wingless cage indirectly, by excising the bridging carbon atom from a one-winged structure. The reaction sequence is shown in Scheme IV. The ketal **3** was hydrolyzed to the tetrachloro ketone **16** which, on heating with solid sodium hydroxide, underwent a Favorskii-type ring contraction[14] with extrusion of the carbonyl bridge to give the 1,3'-bishomocubane trichloro acid **17**. This was converted to the trichloroamine **18** by a Curtius sequence. Under basic conditions, **18** smoothly isomerized to the wingless bird-cage imine **19**, which was hydrolyzed by acid to the corresponding ketone **20**. The conversion of **18** to **19** is analogous to various known homoketonizations[15] and is the formal converse of the closure of an imine to a bird-cage amine previously reported from these laboratories.[3] Examination of models shows that, in the earlier case, the imine is highly congested and closure to the full cage is energetically favored despite the increase in angle strain. In the present case, the wingless imine is relatively uncongested[16] and the precursor bishomocubane cage is very highly strained; the reaction, therefore, proceeds in the direction of ring opening. At the time of our preliminary communication there was a slight doubt as to whether the 2–5 or the 2–3 bond of **18** was cleaved. Cleavage of the 1–2 bond was discounted since it was assumed that the favored transition state would carry a chlorine substituent at the developing carbanion center, and the nmr spectra of **19** and **20** showed the presence of a >CHCl group. We favored cleavage of the 2–5 bond, which appears to offer the greater relief of strain.[17] This view was supported by the carbonyl stretching frequency (5.66 μ) of **20**; cleavage of the 2–3 bond would lead to a cyclobutanone derivative with a nearly coplanar α-chlorine substituent, which should have a shorter wavelength absorption.[18] Final confirmation of the course of the cleavage reaction has been supplied by an X-ray crystallographic analysis[19] of **20**, which also disclosed the stereochemistry at C-5. The orientation of the C–Cl bond away from the carbonyl group avoids both congestion and an unfavorable dipole–dipole interaction.

(13) W. B. Avila and R. A. Silva, *J. Chem. Soc. D*, 94 (1970), have very recently reported the sucessful photocyclization of a hexahydronaphthalene with a five-membered anhydride ring bridging the 4a and 8a positions.

(14) (a) P. E. Eaton and T. W. Cole, Jr., *J. Amer. Chem. Soc.*, **86**, 3157 (1964); (b) K. V. Scherer, Jr., R. S. Lunt III, and G. A. Ungefug, *Tetrahedron Lett.*, 1199 (1965); (c) K. V. Scherer, Jr., G. A. Ungefug, and R. S. Lunt III *J. Amer. Chem. Soc.*, **88**, 2859 (1966); (d) G. L. Dunn, V. J. DiPasquo, and J. R. E. Hoover, *J. Org. Chem.*, **33**, 1454 (1968).

(15) (a) A. Nickon, J. H. Hammons, J. L. Lambert, and R. O. Williams, *J. Amer. Chem. Soc.*, **85**, 3713 (1963); (b) C. H. DePuy and L. R. Mahoney, *ibid.*, **86**, 2653 (1964); (c) R. Howe and S. Winstein, *ibid.*, **87**, 915 (1965); (d) T. Fukunaga, *ibid.*, **87**, 916 (1965).

(16) The relative ease of hydrolysis of **19**, presumably through a tetrahedral intermediate at C-2, is evidence of the lack of congestion in comparison with the imino compounds of ref 3, which are totally resistant to hydrolysis.

(17) This reasoning supposes either that partial relief of strain is important in stabilizing the transition state, or that the reaction is under thermodynamic control.

(18) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed. Wiley, New York, N. Y., 1958, pp 139–141, 149.

(19) D. Schwarzenbach, *Acta Crystallogr., Sect. B*, **24**, 238 (1968).

The trichloro acid 17 was one of the first representatives of the 1,3'-bishomocubane system.[20] As shown in Scheme IV, we were able to dechlorinate 17 in the usual way with lithium and tert-butyl alcohol and to convert the resulting acid 21 to the amine 22 by the Curtius procedure. The acid was purified through its cyclohexylamine salt and the amine through its hexamate.

Nmr Spectra.—We have previously discussed the shielding of α protons by a carbonyl or cyclic ethylene ketal group in cage compounds.[4,21] This phenomenon was seen again in the ketone 5 and the ketal 4, both of which have a two-proton methine resonance at δ 1.8 in chloroform, overlapping the methylene signals. The assignment of the upfield methine signals to the 3 and 5 protons was confirmed in the ketone by observing the benzene-induced solvent shift.[22] In the ketal the assignment was strengthened by a spin-decoupling experiment.[23,24] In the hydrocarbon 6, the methine protons appear as two equal groups, at δ 2.2 and 2.55; spin-decoupling established that the 3 and 5 protons are in the group at δ 2.2.[24,25] Thus the upfield shift caused by the carbonyl and ethylene ketal groups is 0.4 ppm. By contrast, the dimethyl ketal of 5[26] has its highest field methine signals at δ 2.1, and no significant shielding effect relative to the hydrocarbon is apparent. This is consistent with our previous speculation that the shielding by the ethylene ketal group is dependent on the oxygen nonbonding orbitals being appropriately oriented by the cyclic structure.[4,21]

Comparison of the nmr spectra of the esters 11 and 12 with those of the corresponding unsubstituted compounds 8 and 9 showed that the carbomethoxy group deshields the β proton in the 8a or 10 position by about 0.8 ppm. Similar deshielding was seen in the acid 13 in pyridine solution,[27] the 10 proton being displaced 1.2 ppm downfield from the other methine signals. The same effect was noted in the analogous compounds of the full bird-cage system[1] and is indicative of strong

constraints on the rotation of the ester or carboxylate group, probably arising from interaction with the nearby chlorine atoms. The 1 proton in the acid 17 showed this effect to a much smaller extent.[28]

The signals of the 8- and 11-methylenes of the one-winged bird-cage system and of the corresponding 7- and 10-methylenes of the bishomocubane and wingless bird-cage systems were all easily recognizable as modified AB quartets. In the chlorinated derivatives J_{gem} (J_{AB}) is 13.5–14.5 Hz, while in the nonchlorinated compounds it is 12–13 Hz (presumably all negative). In all cases, one proton of the geminal pair appeared as a fairly slim doublet and the other, as a doublet either markedly broadened or split into multiplets with 2–4 Hz line separation. We assigned the slim signals to the endo protons and the broad ones to their exo partners,[29] on the basis of their dihedral relationships to the vicinal methine protons.[30] Inspection of molecular models suggested that the endo protons have dihedral angles of $\sim$75° with both neighbors and the exo protons $\sim$45°.[31] In the spectra of all the nonchlorinated cages (one-winged or bishomocubane systems) the exo members of the methylene pairs resonate at least 0.5 ppm to higher field than their endo partners. In the one-winged series it was possible to compare the chemical shifts (in chloroform) of the 8- and 11-methylenes in the chlorinated and unchlorinated pairs 3:4, 9:6, and 16:5. The presence of four or six chlorine atoms causes a small (0.2–0.3 ppm) downfield shift of the endo protons and a very much greater downfield shift (0.8–1.1 ppm) of the exo protons; the exo protons in the chlorinated compounds thus resonate, in some cases, at lower field than the endo protons.

Mass Spectra.—The one-winged bird-cage derivatives undergo three major (sometimes concurrent) modes of fragmentation, each involving the rupture of four bonds (Figure 1a–c). The charge can reside on either fragment. Fragmentation according to 1a or 1b may be regarded as reversal of the photochemical ring closure of the methanonaphthalenes, followed by two alternative retro-Diels–Alder reactions; the methanonaphthalenes themselves show these retro-Diels–Alder reactions as important fragmentation pathways.

Fragmentation of the wingless bird-cage compounds (19 and 20) occurs predominantly by the cleavage of three bonds (Figure 1d), with transfer of a hydrogen atom onto the portion having the heteroatom X; this fragment carries the charge. The 1,3'-bishomocubanes (17, 18, 21, and 22) show major fragments arising from cleavage of four bonds (Figure 1e). Both pathway 1d and pathway 1e may be rationalized as yielding two cyclopentadiene fragments.[32] The bishomocubanes show very weak molecular ion peaks, presumably because of their ability to cleave to the stable cyclopentadiene fragments without hydrogen rearrangement. Some

(20) Other representatives of this cage system have been reported by W. G. Dauben and D. L. Whalen, J. Amer. Chem. Soc., 88, 4739 (1966), and by J. C. Barborak, L. Watts, and R. Pettit, ibid., 88, 1328 (1966).

(21) R. J. Stedman and L. D. Davis, Tetrahedron Lett., 1871 (1968).

(22) See J. Ronayne and D. H. Williams, J. Chem. Soc. B, 540 (1967); R. G. Wilson, D. E. A. Rivett, and D. H. Williams, Chem. Ind. (London), 109 (1969), and references given therein, and also ref 4. In the present case, the high-field methine signal was displaced 0.15 ppm upfield on changing from chloroform to benzene, while all other signals moved 0.3 ppm upfield. The small solvent shift for the high-field signal is consistent with its assignment to protons located near the plane perpendicular to the C–O bond axis and passing through the trigonal carbon atom. Solvent shifts are referenced to internal TMS. See J. K. Becconsall, G. D. Daves, Jr., and W. R. Anderson, Jr., J. Amer. Chem. Soc., 92, 430 (1970), for calculation of the reference-independent shifts.

(23) The decoupling experiment was carried out in benzene solution using a Varian HA-100 spectrometer. Benzene gave better resolution of the overlapping methine signals than chloroform, although the general appearance of the spectrum was the same. A spectrum was run in the mixed solvents to establish that there was no crossover of signals. The upfield methine protons were shown to be coupled with two pairs of downfield methines, but not with the 8- or 11-methylenes. We thank Mr. W. Jankowski of Varian Associates for this experiment.

(24) The assumption was made that long-range couplings do not contribute appreciably to the appearance of the spectrum.

(25) The nmr work on 6 was performed by Mr. W. W. Simons of Sadtler Research Laboratories using a Varian HA-100D instrument. Coupling was shown between the 4-methylene protons and the higher field methines, but not the lower field methines.

(26) Prepared by refluxing 5 with methanolic HCl and 2,2-dimethoxypropane. The dimethyl ketal had mp 50–54° and was characterized by its mass spectrum (molecular ion at m/e 206), and by the appearance of methyl peaks at δ 3.22 and 3.33 (CDCl₃) in the nmr spectrum.

(27) 13 presumably exists as the anion in pyridine solution. In DMSO-d₆ the 10-proton resonates 0.55 ppm downfield from the other methine signals.

(28) In pyridine the signal assigned to the 1-proton of 17 appeared 0.4 ppm to lower field than the other methine resonances. In DMSO-d₆ all the methine signals were approximately coincident.

(29) The methylene proton oriented toward the other methylene group is here designated endo.

(30) N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, San Francisco, Calif., 1964, p 49.

(31) For compound 20, the dihedrals were calculated from the X-ray crystallographic data (ref 19): H_exo–C₇–C₆–H, 46°; H_exo–C₇–C₈–H, 45°; H_endo–C₇–C₆–H, 72°; H_endo–C₇–C₈–H, 85°; H_exo–C₁₀–C₁–H, 44°; H_exo–C₉–C₉–H, 39°; H_endo–C₁₀–C₁–H, 64°; H_endo–C₁₀–C₉–H, 74°. We thank Dr. D. E. Zacharias for performing these calculations.

(32) Cf. W. L. Dilling and M. L. Dilling, Tetrahedron, 23, 1225 (1967).

novel derivatives were prepared in order to get reliable values for their molecular weights (see Experimental Section).[33]

The substituents on all the cage compounds undergo their expected fragmentations (*e.g.*, loss of COOH from the acids, CO from the ketones, and Cl and HCl from the chlorinated compounds); these losses are superimposed on the cage fragmentations. The nonchlorinated compounds show additional minor peaks indicative of rearrangement processes, including loss of methyl and ethyl radicals and apparent formation of the tropylium ion (peaks at m/e 91, 65, and 39).[34]

Experimental Section

General.—Corrected capillary melting points are reported. Spectra were determined with the following instruments: Perkin–Elmer Infracord (infrared in mull or film); Perkin–Elmer Model 521 grating spectrophotometer (infrared in solution); Varian A-60 or Jeolco C-60H spectrometer (nmr, 5–10% solutions where solubility permitted, TMS or sodium 2,2-dimethyl-2-silapentane-5-sulfonate as internal standards);[35] Hitachi Perkin–Elmer RMU-6E mass spectrometer (70 eV). Molecular weights were determined with a Mechrolab 301A vapor pressure osmometer.

Irradiations were carried out under a nitrogen atmosphere with a 450-W Hanovia medium-pressure mercury vapor lamp contained in a water-cooled quartz immersion well. Petroleum ether refers to the fraction with bp 30–60°. *tert*-Butyl alcohol was dried over Linde 4A molecular sieve, and tetrahydrofuran over a mixture of 4A and 13X sieves; MgSO₄ was the drying agent in other cases.

1,2,3,4-Tetrachloro-1,4,4a,5,8,8a-hexahydro-*endo*-1,4-methanonaphthalen-9-one, Cyclic Ethylene Ketal (2).—A solution of 100 g (0.382 mol) of 1 in 350 ml of 1,4-cyclohexadiene was refluxed for 1 hr. The cyclohexadiene was evaporated to leave a solid residue.[36] This was stirred with 1.5 l. of cyclohexane at room temperature. The filtered solution (see below for treatment of solid) was evaporated to dryness, and the crystalline residue was washed with methanol to give 108 g (83%) of product, mp 94–101°, suitable for use in the next step. A pure sample of 2 was obtained by recrystallization from methanol and sublimation at 90° (0.05 mm): mp 100–102°; ir (mull) 6.24 μ (C=C); nmr (CDCl₃) AB pattern, $J \sim$ 16 Hz, $\delta_A \sim$1.85, $\delta_B \sim$2.30 (all peaks m, 4 H, allylic CH₂), $\delta \sim$2.85 (m, 2 H, CH), 4.23 (br s, 4 H, OCH₂CH₂O), 5.85 (m, 2 H, CH=CH); mass spectrum, molecular ion at m/e 340 (4 Cl).

Anal. Calcd for C₁₃H₁₂Cl₄O₂: C, 45.65; H, 3.54. Found: C, 45.46; H, 3.40.

The material[12] insoluble in cyclohexane (10.5 g, 9%) was recrystallized from ethyl acetate: no melting point below 300°; ir (mull) 6.27 μ (C=C); nmr (pyridine-d_5) δ 0.5– 1.2 (m) and ∼2.1 (d of t) (2 H each, skeleton CH₂, J_{gem} = 13 Hz), 2.5–3.0 (m, 4 H, CH), 4.0–4.4 (A₂B₂ pattern, 8 H, OCH₂CH₂O); mass spectrum, molecular ion at m/e 600 (8 Cl).

Anal. Calcd for C₂₀H₁₆Cl₈O₄: C, 39.77; H, 2.67. Found: C, 39.76; H, 2.75.

2,3,5,6-Tetrachloropentacyclo[5.4.0.0²,⁶.0³,¹⁰.0⁵,⁹]undecan-4-one, Cyclic Ethylene Ketal (3).—A solution of 20 g of 2 in 1.6 l. of acetone was irradiated for 1 hr. The acetone was evaporated to leave a tan solid. The total product from five such irradiations (0.292 mol of 2) was recrystallized from methanol to give 70 g (70%) of 3 with mp 210–218°, suitable for use in the next step. Recrystallization from ethanol raised the melting point to 219–221°: no ir (mull) in C=C stretching region; nmr (CDCl₃) δ

(33) A number of aromatic derivatives of the 1,3′-bishomocubane acids and amines were investigated in the search for products with low ionization potentials which would give stable molecular ions. This work will be reported elsewhere.

(34) The appearance of tropylium ions in the fragmentation patterns of cage compounds has been reported previously: see ref 14d and literature cited therein.

(35) The following abbreviations are used in describing the nmr spectra: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad; env, envelope.

(36) It was convenient to carry out the first part of the evaporation under atmospheric pressure to collect the cyclohexadiene for reuse. The recovered material was shown by glpc to be free from 1,3-cyclohexadiene.
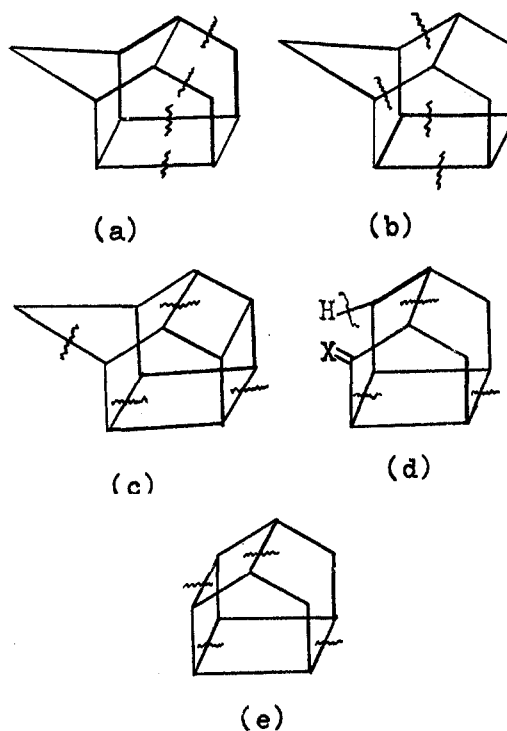

Figure 1.

∼1.8 (br s, 4 H, cage CH₂),[37] ∼2.9 (br s, 4 H, CH), 4.28 (s, 4 H, OCH₂CH₂O); mass spectrum, molecular ion at m/e 340 (4 Cl).

Anal. Calcd for C₁₃H₁₂Cl₄O₂: C, 45.65; H, 3.54; mol wt, 342. Found: C, 45.64; H, 3.56; mol wt (osmometric), 337.

Pentacyclo[5.4.0.0²,⁶.0³,¹⁰.0⁵,⁹]undecan-4-one, Cyclic Ethylene Ketal (4).—To a solution of 35 g (0.102 mol) of 3 in 600 ml of dry tetrahydrofuran were added 76.8 ml (0.816 mol) of dry *tert*-butyl alcohol and 11.3 g (1.63 g-atoms) of lithium wire cut into small pieces. The reaction mixture was kept under nitrogen. A vigorous reaction started after a few minutes and was moderated by cooling as necessary; as the reaction subsided, the mixture was heated to maintain the reflux for a total of 1 hr. The reaction mixture was poured into 2 l. of ice–water; the product was extracted into ether, and the ether phase was washed with water and dried. The solid left on evaporation was triturated with petroleum ether at −30° to give 14.0 g (67%) of 4 with mp 53–56°. Recrystallization from methanol–water and sublimation at 45° (0.1 mm) raised the melting point to 55–57°; nmr (CDCl₃) AB pattern, J = 12.5 Hz, δ_A 0.97 (br d), δ_B 1.62 (d) (4 H, cage CH₂), δ 1.80 (m, 2 H, CH), 2.5–3.0 (env, 6 H, CH), and 3.90 (s, 4 H, OCH₂CH₂O); mass spectrum, molecular ion at m/e 204.

Anal. Calcd for C₁₃H₁₆O₂: C, 76.44; H, 7.90. Found: C, 76.21; H, 7.88.

Pentacyclo[5.4.0.0²,⁶.0³,¹⁰.0⁵,⁹]undecan-4-one (5).—To a stirred mixture of 55 ml of concentrated H₂SO₄ and 50 ml of water at room temperature was added 10 g (0.0490 mol) of 4. After 15 min the dark solution was poured into ice–water, and the resulting yellow precipitate was extracted into ether. The ethereal solution was washed with water, dried, and evaporated to a brown solid residue. This was recrystallized (charcoal) from petroleum ether to give 4.6 g (59%) of 5, mp 200–204°. Sublimation at 65° (0.1 mm) gave material with mp 204–206°; ir (CH₂Cl₂) complex band centered at 5.68 μ (C=O);[38] nmr (CDCl₃) AB pattern, J = 12.5 Hz, δ_A 1.03 (br d), δ_B 1.89 (d) (4 H, CH₂), δ ∼1.8 (br s, 2 H, CH), and 2.7–3.2 (env, 6 H, CH); mass spectrum, molecular ion at m/e 160.

Anal. Calcd for C₁₁H₁₂O: C, 82.46; H, 7.55. Found: C, 82.66; H, 7.40.

Pentacyclo[5.4.0.0²,⁶.0³,¹⁰.0⁵,⁹]undecane(6).—A mixture of 0.56 g (3.50 mmol) of 5 and 0.41 ml (8.5 mmol) of hydrazine hydrate in 20 ml of triethylene glycol was kept overnight at room temperature, and then heated for a few minutes on the steam bath.

(37) In benzene this signal was seen as an AB pattern, J = 13.5 Hz, downfield peaks broad.

(38) The full bird-cage ketone (ref 4) also shows a complex carbonyl region. For discussion of this phenomenon in related cases, see ref 5 and 9b.

After cooling, 2.4 g of KOH pellets was added.[39] The reaction mixture was slowly heated in an oil bath while a gentle stream of nitrogen was blown over its surface and then through a receiver cooled in CO_2–acetone. The crystalline product collected in the receiver while the bath temperature was raised from 150 to 195° during 1.5 hr. It was dissolved in a small volume of pentane, washed with water, and dried over molecular sieve, and the solvent removed under slightly reduced pressure. The crystalline residue amounted to 0.35 g (68%), mp 207–208° (sealed capillary, totally immersed), unchanged by recrystallization from methanol and sublimation at 100° (atmospheric pressure): nmr (CDCl₃, 100 MHz)[25] AB pattern, $J = 12$ Hz, δ_A 0.98 (br d), δ_B 1.45 (d) (4 H, 8- and 11-CH₂), AB pattern, $J = 10$ Hz, δ_A 1.18, δ_B 1.64 (all peaks somewhat br, 2 H, 4-CH₂), δ 2.1–2.3 (env, 4 H,·CH) and ~2.55 (br s, 4 H, CH); mass spectrum, molecular ion at m/e 146.

Anal. Calcd for C₁₁H₁₄: C, 90.35; H, 9.65. Found: C, 90.31; H, 9.78.

1,2,3,4,9,9-Hexachloro-1,4,4a,5,8,8a-hexahydro-*endo*-1,4-methanonaphthalene (8).—A mixture of 32.8 g (0.10 mol) of **7**,[40] 16.6 ml (0.20 mol) of 1,3-butadiene, 16 ml of toluene, and 0.2 g of hydroquinone was heated at 135° for 9 hr in a glass-lined autoclave. The mixture was evaporated and the dark residue was distilled at 110–120° (0.05 mm) to give a colorless oil which solidified on standing. Trituration with a small volume of methanol at −30° followed by recrystallization from methanol gave 8.3 g (24%) of **8** with mp 92–93°. Further recrystallization raised the melting point to 94–95°:[41] ir (mull) 6.20 μ (C=C); nmr (CDCl₃) AB pattern, $J \sim 16$ Hz, $\delta_A \sim 1.9$, $\delta_B \sim 2.35$ (all peaks m, 4 H, CH₂), $\delta \sim 3.0$ (m, 2 H, CH), and 5.82 (m, 2 H, CH=CH); mass spectrum, molecular ion at m/e 350 (6 Cl).

Anal. Calcd for C₁₁H₈Cl₆: C, 37.44; H, 2.28. Found: C, 37.76; H, 2.43.

2,3,4,4,5,6-Hexachloropentacyclo[5.4.0.0²,⁶.0³,¹⁰.0⁵,⁹]undecane (9).—A solution of 3.0 g (8.50 mmol) of **8** in 500 ml of acetone was irradiated for 1 hr. The solvent was evaporated and the solid residue was recrystallized twice from methanol to give 0.73 g (24%) of **9**: no melting point below 300°; no ir (mull) in C=C stretching region; nmr (CDCl₃) AB pattern, $J = 14$ Hz, δ_A 1.73 (d), δ_B 2.05 (br d) (4 H, CH₂), and $\delta \sim 3.05$ (br s, 4 H,CH); mass spectrum, molecular ion at m/e 350 (6 Cl).

Anal. Calcd for C₁₁H₈Cl₆: C, 37.44; H, 2.28; mol wt, 353. Found: C, 37.54; H, 2.37; mol wt (osmometric), 353.

Methyl 1,2,3,4,9,9-Hexachloro-1,4,4a,5,8,8a-hexahydro-*endo*-1,4-methanonaphthalene-4a-carboxylate (11).—A mixture of 60 g (0.168 mol) of **10**, 27.8 ml (0.336 mol) of 1,3-butadiene, 30 ml of toluene, and 0.3 g of hydroquinone was heated for 9 hr at 140° in a glass-lined autoclave. The solvent was evaporated, and the residue was recrystallized from hexane to give 46.5 g (67%) of product, mp 84–87°, suitable for use in the next step. Recrystallization from methanol and sublimation at 85° (0.1 mm) gave material with mp 92–94°: ir (mull) 5.85 μ (C=O) and 6.22 (C=C); nmr (CDCl₃) δ 2.2–2.5 (env, 4 H, CH₂), 3.73 (s, 3 H, OCH₃), ~3.8 (m, 1 H, CH),[42] and 5.5–6.0 (m, 2 H, CH=CH); mass spectrum, molecular ion at m/e 408 (6 Cl).

Anal. Calcd for C₁₃H₁₀Cl₆O₂: C, 37.99; H, 2.45. Found: C, 38.20; H, 2.42.

Methyl 2,3,4,4,5,6-Hexachloropentacyclo[5.4.0.0²,⁶.0³,¹⁰.0⁵,⁹]-undecane-9-carboxylate (12).—A solution of 45 g (0.110 mol) of **11** in 1.5 l. of acetone was irradiated for 1 hr. Evaporation gave a dark solid, which was recrystallized from ethanol (charcoal) to give 25.2 g (56%) of product, mp 148–150°, suitable for use in the next step. Further recrystallization from methanol gave material with mp 153–155°: ir (mull) 5.80 μ (C=O); nmr (CDCl₃) AB pattern, $J = 14$ Hz, δ_A 1.79 (d of d), δ_B 2.17 (d of m) (2 H, 11-CH₂), AB pattern, $J = 14$ Hz, δ_A 1.85 (d), δ_B 2.38 (d of t) (2 H, 8-CH₂), $\delta \sim 3.05$ (m, 2 H, 1- and 7-CH), ~3.8 (br s, 4 H, 10-CH and OCH₃);[43] mass spectrum, molecular ion at m/e 408 (6 Cl).

Anal. Calcd for C₁₃H₁₀Cl₆O₂: C, 37.99; H, 2.45. Found: C, 37.93; H, 2.41; mol wt (osmometric), 399.

2,3,4,4,5,6-Hexachloropentacyclo[5.4.0.0²,⁶.0³,¹⁰.0⁵,⁹]undecane-9-carboxylic Acid (13).—A mixture of 25 g (0.0608 mol) of **12** with 400 ml each of 2.5 N aqueous NaOH and ethanol was refluxed for 3 hr and then evaporated to half volume. The solid which precipitated was redissolved by adding 1 l. of water. Acidification with HCl gave 22 g (91%) of crystalline **13**, suitable for use in the next step. The compound could be recrystallized from methanol–water: no melting point below 300°; ir (mull) 5.85 μ (C=O); nmr (pyridine)[44] AB pattern, $J = 14.5$ Hz, δ_A ~1.9 (somewhat br d), δ_B ~2.1 (br d) (2 H, 11-CH₂), AB pattern, $J = 14$ Hz, δ_A 2.06 (d), δ_B 2.64 (br d) (2 H, 8-CH₂), $\delta \sim 3.15$ (br s, 2 H, 1- and 7-CH), 4.32 (br s, 1 H, 10-CH); mass spectrum, molecular ion at m/e 394 (6 Cl).

Anal. Calcd for C₁₂H₈Cl₆O₂: C, 36.31; H, 2.03. Found: C, 36.36; H, 2.00.

Pentacyclo[5.4.0.0²,⁶.0³,¹⁰.0⁵,⁹]undecan-9-amine (15).—A solution of 20 g (0.0504 mol) of **13** in 350 ml of dry tetrahydrofuran was dehalogenated with 8.38 g (1.21 g-atoms) of lithium and 56.9 ml (0.605 mol) of dry *tert*-butyl alcohol under the conditions used to convert **3** to **4**. A second treatment with the same quantities of reagents was required for complete dechlorination, as judged by glpc.[45] The reaction mixture was poured into 2 l. of ice–water, acidified with HCl, and extracted with benzene–ether. The extracts were washed with dilute HCl and evaporated to dryness. The semisolid residue was dissolved in 150 ml of ethyl acetate and treated with cyclohexylamine until the pH (test paper) reached 8. The crude cyclohexylamine salt of **14** which crystallized weighed 12.3 g. It was dissolved in water, acidified with HCl, and extracted with benzene–ether. Evaporation of the extracts gave 7.5 g of the free acid. This was recrystallized from methanol–water to give 3.8 g of **14**, mp 119–127°, suitable for use in the next step.[46] A 3.0-g (15.8 mmol) sample of **14** was stirred overnight with 30 ml of SOCl₂. The excess reagent was evaporated, benzene was added, and the evaporation was repeated to give the acid chloride (ir in film 5.65 μ) as an amber oil. This was dissolved in 150 ml of acetone, cooled to 0°, and treated with a solution of 1.20 g (18.5 mmol) of sodium azide in 12 ml of water. The mixture was stirred for 15 min at 5° and then diluted with 200 ml of ice-cold water, and the acyl azide was extracted into 250 ml of toluene in three portions. The toluene solution was well washed with water, dried, and heated first for 20 min on the steam bath (gas evolution) and then for 1 hr at reflux. Evaporation gave the brown oily isocyanate (ir in film 4.40 μ), which was refluxed for 1 hr with 100 ml of acetone and 25 ml of concentrated HCl. The acetone was evaporated and replaced with water. The acidic solution was washed with benzene and made basic with NaOH, and the free amine was extracted into benzene. The benzene solution was washed with water and evaporated. The residue of crystalline **15** was dissolved in 35 ml of acetonitrile and treated with a solution of a slight excess of cyclohexylsulfamic (hexamic) acid in 16 ml of acetonitrile and 2 ml of water. The crystalline hexamate which precipitated amounted to 3.0 g; recrystallization from acetonitrile containing 5% of water gave 2.5 g of pure material (glpc). This was partitioned between 0.5 N NaOH and benzene–ether and the organic phase was washed with water and evaporated to a crystalline residue, which was dissolved in 25 ml of 2-propanol and 75 ml of ethyl acetate and acidified with a little ethereal HCl. The hydrochloride of **15** which crystallized amounted to 1.09 g (14% from **13**): no melting point below 300°; ir (mull) 3.9, 4.95, 6.24, and 6.33 μ (NH₃⁺); nmr (D₂O–DCl)[47] δ 1.0–2.0 (m of s and br s, 6 H, CH₂),[48] ~2.35 and ~2.65 (br s, 3 H and 4 H, respectively, CH); mass spectrum, molecular ion at m/e 161.

(39) *Cf.* W. L. Dilling, H. P. Braendlin, and E. T. McBee, *Tetrahedron*, **23**, 1211 (1967).

(40) Shell technical grade, 91% purity.

(41) In some cases, recrystallization lowered the melting point to *ca.* 85° (unsharp). We attribute this to the occurrence of a second crystalline form.

(42) This signal was partially obscured by the OCH₃ singlet. In benzene it was seen as an approximate triplet, separation of the outermost peaks 12 Hz.

(43) In benzene the 10-CH resonance was well separated from the OCH₃ signal, and appeared as a multiplet, separation of the outermost peaks 6 Hz.

(44) The spectrum in DMSO-d_6 established the absence of signals in the low field region.

(45) A small sample was worked up and esterified with BF₃–methanol for glpc.

(46) We were unable to obtain a sample of **14** of high purity. The broad-melting material described here gave a molecular ion at m/e 190 as expected and showed a carbonyl stretching band at 5.90 μ (mull). However, the nmr spectrum showed the presence of an olefinic impurity. Hindsight suggests that treatment with permanganate might have been beneficial: *cf.* R. J. Stedman, L. D. Davis, and L. S. Miller, *J. Org. Chem.*, **33**, 1280 (1968).

(47) The nmr in trifluoroacetic acid showed the absence of resonances in the region obscured by the HOD peak.

(48) The pattern was consistent with three overlapping AB quartets, but no unique assignments could be made. The broader peaks were in the high field region.

Anal. Calcd for $C_{11}H_{16}ClN$: C, 66.83; H, 8.16; Cl, 17.93; N, 7.08. Found: C, 66.83; H, 8.11; Cl (ionic), 18.20; N, 7.10.

2,3,5,6-Tetrachloropentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-4-one(16).—A suspension of 70 g (0.204 mol) of **3** in 350 ml of concentrated H_2SO_4 was stirred for 100 hr at room temperature. The reaction mixture, still containing suspended solid, was poured into 2.5 l. of ice–water, and the product collected and dried *in vacuo.*[49] The yield of **16** was 54 g (89%), mp 172–190°, suitable for use in the next step. Recrystallization from CCl_4 gave material with mp 199–201°: ir (CH_2Cl_2) 5.53 μ (C=O); nmr $(CDCl_3)$ δ ~2.1 (br s, 4 H, CH_2),[50] 3.09 and 3.22 (br s, 2 H each, CH); mass spectrum, molecular ion at m/e 296 (4 Cl).

Anal. Calcd for $C_{11}H_8Cl_4O$: C, 44.34; H, 2.71. Found: C, 44.42; H, 2.67.

3,4,5-Trichloropentacyclo[4.4.0.0^{2,5}.0^{3,9}.0^{4,8}]decane-2-carboxylic Acid (17).—A solution of 50 g (0.168 mol) of **16** in 1.2 l. of toluene was stirred for 20 min at reflux with 160 g of crushed NaOH pellets. The cooled reaction mixture was poured into 6 l. of ice–water, the phases separated, and the aqueous layer acidified with HCl to precipitate the crude product. This was recrystallized from methanol–water to give 32.0 g (68%) of **17**, mp 246–249° dec, suitable for use in the next step. Further recrystallization raised the melting point to 249–251° dec: ir (mull) 5.88 μ (C=O); nmr (pyridine)[51] δ ~1.65 and ~1.8 (br s, 2 H each, CH_2), ~3.1 (br s, 2 H, 8- and 9-CH), and AB pattern, J ~ 10 Hz, δ_A ~3.05, δ_B ~3.5 (all peaks m, 2 H, 6- and 1-CH, respectively); mass spectrum of *p-tert*-butylphenyl ester, molecular ion at m/e 410 (3 Cl).[52]

Anal. Calcd for $C_{11}H_9Cl_3O_2$: C, 47.26; H, 3.25. Found: C, 47.55; H, 3.14.

3,4,5-Trichloropentacyclo[4.4.0.0^{2,5}.0^{3,9}.0^{4,8}.]decan-2-amine (18).—A sample of 25 g (0.0894 mol) of **17** was refluxed with 150 ml of $SOCl_2$ for 2.5 hr to convert it to the solid acid chloride (ir in mull 5.60 μ), which was taken through a Curtius sequence (isocyanate, solid, ir in mull 4.40 μ) as in the conversion of **14** to **15**. In this case the free amine was precipitated from the benzene-washed acid solution by adding NH_4OH. The yield was 17.0 g (76%): mp 166–168° dec, unchanged by recrystallization from methanol–water and sublimation [75° (0.05 mm)]; ir (mull) 2.95, 3.03 and 6.23 μ (NH_2); nmr $(CDCl_3)$ δ ~1.8 (br s, 6 H, reduced to 4 H by equilibration with D_2O, NH_2, and CH_2), ~2.9 and ~3.1 (br s, 2 H each, CH);[53] mass spectrum of *p*-dimethylaminophenylthiocarbamoyl derivative,[54] molecular ion at m/e 427 (3 Cl).

Anal. Calcd for $C_{10}H_{10}Cl_3N$: C, 47.94; H, 4.02; N, 5.59. Found: C, 48.04; H, 4.08; N, 5.29.

3,4,5-Trichlorotetracyclo[4.4.0.0.^{3,9}0^{4,8}]decan-2-imine (19).—To a stirred suspension of 5.01 g (0.020 mol) of **18** in 50 ml of dry *tert*-butyl alcohol was added 5 g of potassium *tert*-butoxide. After 15 min, the resulting clear solution was poured into ice–water to precipitate 4.96 g (99%) of **19**, mp 106–109° dec. Recrystallization from hexane and sublimation at 90° (0.1 mm) raised the melting point to 107–109° dec; ir (mull) 5.95 μ (C=N); nmr $(CDCl_3)$ AB pattern, J = 13.5 Hz, δ_A 1.49 (d of m) δ_B 2.00 (somewhat br d) (2 H, CH_2), AB pattern, J = 13.5 Hz, δ_A 1.96 (somewhat br d), δ_B 2.31 (d of m) (2 H, CH_2), δ 2.7–3.3 (env, 4 H, 1-, 6-, 8- and 9-CH), 4.10 (somewhat br s, 1 H, 5-CH); mass spectrum, molecular ion at m/e 249 (3 Cl).

The compound slowly decomposed on exposure to air.

Anal. Calcd for $C_{10}H_{10}Cl_3N$: C, 47.94; H, 4.02; N, 5.59. Found: C, 47.75; H, 3.99; N, 5.43.

3,4,5-Trichlorotetracyclo[4.4.0.0^{3,9}.0^{4,8}]decan-2-one (20).—A solution of 4.01 g (0.0160 mol) of **19** in 65 ml of 3 N HCl was heated at 55° for 5 hr. The ketone which slowly precipitated from solution amounted to 3.74 g (93%), mp 113–115°, unchanged by recrystallization from methanol and sublimation at 100° (0.05 mm); ir (CH_2Cl_2) complex band centered at 5.66 μ

(C=O);[38] nmr $(CDCl_3)$ AB pattern, J = 13.5 Hz, δ_A 1.69 (d of t), δ_B 2.10 (somewhat br d) (2 H, CH_2), AB pattern, J = 13.5 Hz, δ_A 2.10 (somewhat br d), δ_B 2.41 (d of q) (2 H, CH_2), δ 2.7–3.5 (m, 4 H, 1-, 6-, 8- and 9-CH), 4.08 (somewhat br s, 1 H, 5-CH); mass spectrum, molecular ion at m/e 250 (3 Cl).

Anal. Calcd for $C_{10}H_9Cl_3O$: C, 47.75; H, 3.61. Found: C, 47.86; H, 3.58.

Pentacyclo[4.4.0.0^{2,5}.0^{3,9}.0^{4,8}]decane-2-carboxylic Acid (21).—A solution of 30 g (0.107 mol) of **17** in 650 ml of dry tetrahydrofuran was dehalogenated by two treatments each with 8.90 g (1.28 g-atom) of lithium and 60.4 ml (0.642 mol) of *tert*-butyl alcohol, and the resulting **21** was precipitated as its cyclohexylamine salt (26.4 g, 89%) (*cf.* the conversion of **13** to **14**). The crude salt was satisfactory for use in the preparation of **22**. A sample of the salt was recrystallized from methanol–ethyl acetate, dissolved in water, and acidified with HCl to precipitate the free acid, mp 100–108°. Recrystallization from petroleum ether and sublimation at 90° (0.1 mm) gave **21** with mp 111–114°; ir (mull) 5.95 μ (C=O); nmr $(CDCl_3)$ δ 0.9–1.5 (m), ~1.8 and ~2.0 (br s) (4 H, CH_2),[55] 2.8–3.5 (env, 7 H, CH), and 11.11 (s, 1 H, COOH); mass spectrum of *p-tert*-butylphenyl ester,[56] molecular ion at m/e 308.

Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 75.00; H, 6.67.

Pentacyclo[4.4.0.0^{2,5}.0^{3,9}.0^{4,8}]decan-2-amine (22).—A sample of 25 g (0.0908 mol) of the crude cyclohexylamine salt of **21** was converted to the free acid and taken through a Curtius sequence (acid chloride, ir in film 5.65 μ; isocyanate, ir in film 4.40 μ) using the same conditions as in the conversion of **14** to **15**; in the present case the free acid was not recrystallized. The crude **22** obtained was converted to the crystalline hexamate (10.1 g) by treatment with a slight excess of cyclohexylsulfamic acid in acetonitrile containing 10% of water. Recrystallization from the same solvent mixture gave 7.3 g of the pure salt (glpc as trifluoroacetyl derivative of the amine). The hexamate was converted to the hydrochloride as in the case of **15**. The yield of **22** hydrochloride was 3.2 g (19% overall): mp 255–257° dec; ir (mull) 3.7, 4.0, 4.85, and 6.25 μ (NH_3^+); nmr $(D_2O$-DCl)[47] overlapping AB patterns, both J = 13 Hz, upfield portions δ ~1.1 and ~1.3 (both br d), downfield portions ~1.85 and ~1.9 (both d) (4 H, CH_2),[57] 2.8–3.6 (m, 7 H, CH); mass spectrum of *p*-dimethylaminophenylthiocarbamoyl derivative,[54] molecular ion at m/e 325.

Anal. Calcd for $C_{10}H_{14}ClN$: C, 65.39; H, 7.68; Cl, 19.30; N, 7.63. Found: C, 65.31; H, 7.69; Cl (ionic), 19.37; N, 7.55.

---

(49) This electrophilic ketone slowly formed a hydrate (*gem*-diol) on exposure to air, as shown by the mass spectrum.

(50) In benzene this signal was seen as an AB pattern, J = 14 Hz, downfield peaks broad.

(51) The spectrum in DMSO-d_6 showed the absence of low field signals, and displayed one of the methylene resonances as an AB pattern of broad (upfield) and narrow (downfield) peaks, J = 13.5 Hz.

(52) The ester was prepared by method B of R. C. Parish and L. M. Stock, *J. Org. Chem.,* **30**, 927 (1965).

(53) In benzene there was partial separation of some of the coincident resonances, and a J_{gem} ~ 14 Hz and a J_{vic} ~ 10 Hz could be described.

(54) The free amine was warmed with excess *p*-dimethylaminophenyl isothiocyanate at 60° for 20 min to give the derivative.

(55) This pattern was consistent with two overlapping AB quartets, J ~ 13 Hz, upfield protons split into multiplets, but no unique assignments could be made.

(56) The underivatized compound showed evidence of the presence of a dihydro impurity, presumably arising from reductive cleavage of one of the cage bonds. In view of the very low abundance of the molecular ions of the 1,3'-bishomocubanes compared with the less strained cages, the quantity of the impurity was probably much less than was indicated by the relative intensities of the M and M + 2 peaks. In the derivatives, which showed much greater molecular ion abundances, the intensity of M + 2 was scarcely greater than that required for the ^{13}C isotopic content of M.

(57) The patterns appeared as four sharp peaks downfield and three broad peaks upfield. Unambiguous correlation of the portions of the AB patterns was not possible.