# Synthetic Studies Related to the Bird-Cage System. II. 1- and 2-Substituted Derivatives of Hexacyclo[5.4.1.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$.$0^{8,11}$]dodecane[1]

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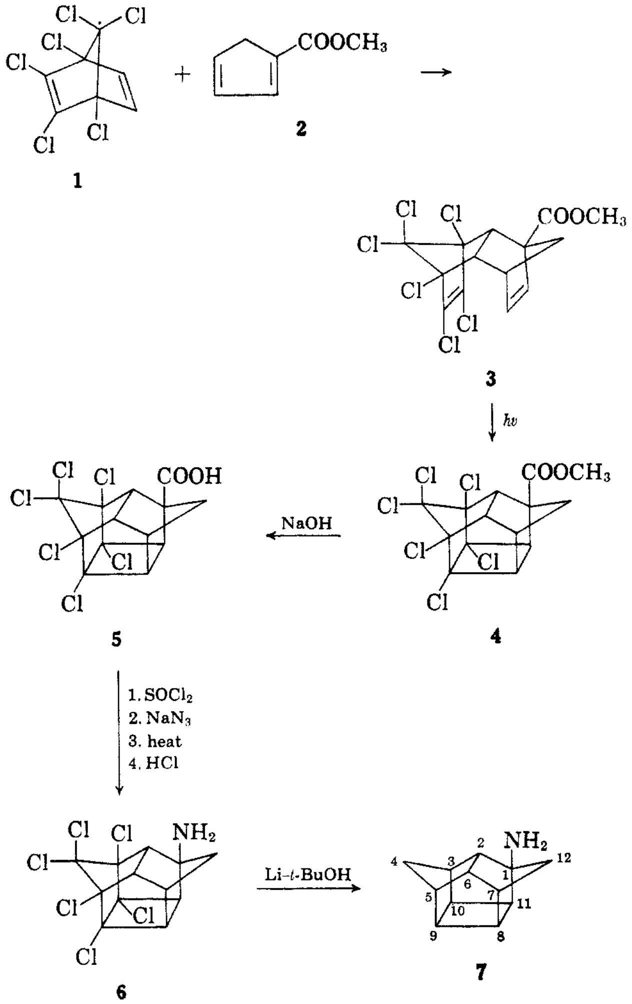
*Received May 29, 1967*

Synthetic sequences leading to the amino derivatives **7** and **13** of the bird-cage hydrocarbon are described. The key intermediates were the hexahydro-1,4-*endo,endo*-5,8-dimethanonaphthalene esters **3** and **9**, which were cyclized photochemically to the caged esters **4** and **10**. These were converted *via* the acids **5** and **11** to the chlorinated amines **6** and **12**, which were dehalogenated to give **7** and **13**.

Our interest in the possible biological activity of cage compounds led us to undertake the synthesis of the 1- and 2-amino derivatives (**7** and **13**) of the bird-cage hydrocarbon.[2,3] Functionalization (except by halogen atoms) of the bird-cage system has hitherto been restricted to the 4 and 8 positions.[1,3,4] The work described in this paper provides access to bird-cage derivatives with carboxyl and amino groups in the 1 and 2 positions; these should be flexible intermediates for the synthesis of other functional derivatives.[5]

A promising approach to the amines **7** and **13** seemed to be through the construction and cyclization of appropriately substituted hexahydro-1,4-*endo,endo*-5,8-dimethanonaphthalenes (isodrins), a procedure similar to that used in the synthesis of the bird-cage ketone.[1] The key to the success of this process is the Diels–Alder addition of a norbornadiene to a cyclopentadiene to give a dimethanonaphthalene skeleton with the *endo,endo* configuration. The required stereoselectivity in this reaction is dependent on the presence of appropriate bulky substituents in the norbornadiene component.[6] Conveniently, these are chlorine atoms, which, after they have performed their function of stereochemical guidance, can be removed by reduction with lithium.[7] Consideration of the availability of starting materials and the ease of handling of intermediates led us to select the carbomethoxy group as a precursor for the amino function, effecting the conversion at a late stage in the synthetic sequence. Our key intermediates were therefore the carbomethoxy-substituted isodrins **3** and **9**.

SCHEME I



The initial step in the synthesis of **7** (Scheme I) was the addition of the hexachloronorbornadiene **1** to methyl cyclopentadienecarboxylate (**2**). The *endo,-endo* geometry of the product could confidently be predicted, since there was no reason to expect the carbomethoxy substituent to affect the stereochemical course of the reaction. However, although **2** is believed to exist with the carbomethoxy group mainly in the 1 position as shown,[8] the facile rearrangement of substituted cyclopentadienes[9] left open the possibility that it might react in a different isomeric form. When dimeric **2** was heated with **1** under conditions where partial monomerization would occur, a single adduct was isolated. Its nuclear magnetic resonance (nmr) spectrum showed the presence of a methylene group and two vinylic protons, and was thus consistent only with structure **3**. This finding is in accord with the limited information available in the literature[10]

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[1] Part I: R. J. Stedman and L. S. Miller, *J. Org. Chem.*, **32**, 35 (1967).

[2] The numbering of the bird-cage system used in this paper is shown in structure **7**. *Chemical Abstracts* indexes the hydrocarbon as decahydro-1,5,2,4-ethanediylidenecyclopenta[*c,d*]pentalene.

[3] Approaches to the 4- and 8-amino derivatives have been reported in ref 1 and in a preliminary communication by R. J. Stedman, A. C. Swift, and J. R. E. Hoover, *Tetrahedron Letters*, 2525 (1965).

[4] (a) S. B. Soloway, A. M. Damiana, J. W. Sims, H. Bluestone, and R. E. Lidov, *J. Am. Chem. Soc.*, **82**, 5377 (1960); (b) P. Carter, R. Howe, and S. Winstein, *ibid.*, **87**, 914 (1965); (c) T. Fukunaga, *ibid.*, **87**, 916 (1965).

[5] All new compounds described except **13** are asymmetric, and were obtained as racemic mixtures.

[6] Reference 1 has a fuller discussion of the stereochemistry of this reaction.

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

[8] D. Peters, *J. Chem. Soc.*, 1761 (1959).

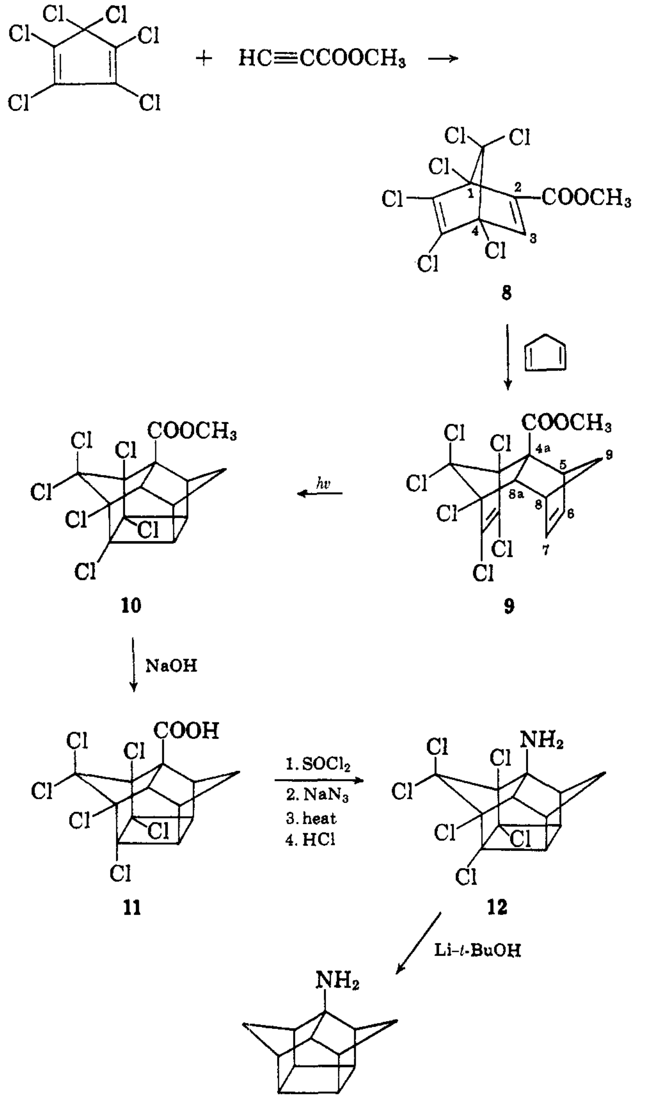
[9] (a) V. A. Mironov, E. V. Sobolev, and A. N. Elizarova, *Tetrahedron*, **19**, 1939 (1963); (b) S. McLean and P. Haynes, *ibid.*, **21**, 2329 (1965).

[10] (a) K. Alder, F. H. Flock, A. Hausweiler, and R. Reeber, *Ber.*, **87**, 1752 (1954); (b) G. Kresze, G. Schultz, and H. Walz, *Ann.*, **666**, 45 (1963); (c) K. Wiesner and A. Philipp, *Tetrahedron Letters*, 1467 (1966). These reports all refer to the reactions of **2** with good dienophiles under much milder conditions than were necessary in the present case.

about the reactions of **2** as a diene. Ultraviolet irradiation of **3** in acetone gave the ester **4** which was hydrolyzed to the acid **5**. This was converted to the amine **6** by a Curtius sequence and dechlorinated with lithium and *t*-butyl alcohol to yield **7**.

In the synthesis of the amine **13** (Scheme II), the first step was the condensation of hexachlorocyclopentadiene with methyl propiolate to give the norbornadiene ester **8**.[11] The condensation of **8** with cyclopentadiene was the stereochemical crux of the sequence. Under kinetic control, substituents on a dienophile reacting with cyclopentadiene favor the *endo* side of the developing norbornene ring. However, it was not clear whether the C-1 to C-2 and C-3 to C-4 bonds or the carbomethoxy group of **8** would win the *endo* situation with respect to the new (unchlorinated) norbornene ring in the adduct. In the latter event, the adduct would have the *endo,exo* configuration. In fact, the only product isolated was **9**, whose *endo,endo* geometry was proven by its ready photochemical cyclization to **10**. This result supports the view that it is the size of the substituents on the dienophile rather than their electronic interactions with the diene which is responsible for their preference for the *endo* location.[12] The conversion of **10** to the amine **13** exactly paralleled that of **4** to **7** in Scheme I.

SCHEME II



**Nmr Spectra.**—The proton resonance spectra of the dimethanonaphthalenes **3** and **9** were sufficiently well resolved to allow assignment of most of the signals by consideration of their chemical shifts and splitting patterns. The spectra of the fully closed-cage systems were so complex that only the geminal coupling constants of the 4- and 12-methylene groups could be precisely determined. These varied between 10.5 and 12.5 cps, being noticeably greater (probably in the negative sense) than the corresponding values (8.5 and 9 cps) in the dimethanonaphthalenes. The change in $J_{gem}$ on cyclization to the full-cage system may reflect a decrease in angle strain at the methylene group and consequent modification of the hybridization at the carbon atom.[13] A further difference between the cages and the dimethanonaphthalenes was the greater coupling in the latter between the methylene and flanking methine protons.[14]

Comparison of the spectrum of **9** with that of isodrin[15] showed that the carbomethoxy group strongly deshields the adjacent proton on C-8a but not that on C-5. Similar selective deshielding of one methine proton was seen in the derived caged compounds **10** and **11**.[16] It is likely that the selective deshielding in **9** arises from hindrance of the rotation of the carbomethoxy group caused by the nearby chlorine atoms, and that, since the geometry of the molecule in this region is not much affected by cyclization to the cage system, the corresponding proton (*i.e.*, that on C-6) is the one strongly deshielded in **10** and **11**. It is probable that the constraints upon the carbomethoxy group which produce this effect in **10** are also responsible for its great resistance to alkaline hydrolysis in comparison with **4**. No highly selective deshielding of a single proton was seen in **4** or any of the other compounds of Scheme I.

## Experimental Section

**General.**—Corrected capillary melting points are reported. Infrared spectra were determined in Nujol mull with a Perkin-Elmer Infracord. Nmr spectra were determined with a Varian A-60 spectrometer, using 5–10% solutions when solubility permitted; chemical shifts are reported in parts per million downfield from tetramethylsilane (organic solvents) or sodium 3-trimethylsilyl-1-propanesulfonate (water) as internal standards. Molecular weights were measured with a Mechrolab Model 301A vapor pressure osmometer. Determination of $pK_a$ values was carried out by potentiometric titration, using a Sergent Model D automatic titrator (glass–calomel electrodes). 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.

**Methyl 5,6,7,8,9,9-Hexachloro-1,4,4a,5,8,8a-hexahydro-1,4-*endo,endo*-5,8-dimethanonaphthalene-1-carboxylate (3).**—A

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(11) P. J. Graham, E. L. Buhle, and N. Pappas [*J. Org. Chem.*, **26**, 4658 (1961)] have prepared the ethyl ester by an analogous reaction.

(12) J. G. Martin and R. K. Hill, *Chem. Rev.*, **61**, 537 (1961).

(13) J. A. Pople and A. A. Bothner-By, *J. Chem. Phys.*, **42**, 1339 (1965).

(14) Comparison of the spectra of isodrin and the related cyclic ethylene ketal[1] with those of the corresponding closed cages showed the same changes in coupling constants on cyclization.

(15) In $CDCl_3$ isodrin showed 5- and 8-CH signals at $\delta$ 2.99 and 4a- and 8a-CH at 3.37 (numbering as in **9**).

(16) The parent hexachloro bird-cage-compound formed by cyclization of isodrin[7] showed methine proton resonances in deuteriochloroform as a broad singlet at $\delta$ 3.18, and in pyridine as a complex multiplet at $\delta$ 2.7–3.2.

mixture of 460 g (1.40 moles) of **1**[17] and 174 g (0.70 mole) of dimeric **2**[18] was heated for 5.5 hr in a bath at 150°. The dark reaction mixture was dissolved in 500 ml of methanol and cooled to −50° to precipitate the crude crystalline product. Recrystallization from methanol–water gave 218 g (37%) of **3**: mp 99–101°; infrared absorptions at 5.78 μ (C═O) and 6.22 μ (C═C); nmr signals ($CDCl_3$) at $\delta$ 1.98 (2H partially resolved doublet, central peaks of AB pattern, 10-$CH_2$)[19] 3.12 (1 H partially resolved multiplet, 4-CH), 3.70 (2 H AB pattern, $J$ = 9.5 cps, $\delta_A-\delta_B \simeq 13$ cps, upfield portion split into doublets with 3.5-cps separation, downfield portion sharp singlets, 4a- and 8a-CH, respectively), 3.82 (3 H singlet, $OCH_3$), and 6.19 (2 H AB pattern, $J$ = 6 cps, $\delta_A-\delta_B \simeq 8.5$ cps, upfield portion split into doublets with 3-cps separation, downfield portion slightly broadened singlets, 3- and 2-CH═, respectively).

*Anal.* Calcd for $C_{14}H_{10}Cl_6O_2$: C, 39.75; H, 2.38. Found: C, 39.95; H, 2.33.

**Methyl 3,4,4,5,9,10-Hexachlorohexacyclo[5.4.1.0$^{2,6}$.0$^{3,10}$.0$^{5,9}$.0$^{8,11}$]dodecane-1-carboxylate (4).**—A solution of 50 g (0.118 mole) of **3** in 500 ml of acetone was irradiated for 1 hr. Evaporation of the acetone and recrystallization of the residue from ethanol gave 38.9 g (78%) of **4**: mp 154–156°; infrared absorption at 5.80 μ (C═O); nmr signals ($CDCl_3$) at $\delta$ 2.14 (2 H AB pattern, $J$ = 11.5 cps, $\delta_A-\delta_B = 14$ cps, 12-$CH_2$), 3.0–3.8 (5 H complex multiplet, methine CH), and 3.80 (3 H singlet, $OCH_3$).

*Anal.* Calcd for $C_{14}H_{10}Cl_6O_2$: C, 39.75% H, 2.38; mol wt, 423. Found: C, 39.77; H, 2.29; mol wt (osmometric), 420.

**3,4,4,5,9,10-Hexachlorohexocyclo[5.4.1.0$^{2,6}$.0$^{3,10}$.0$^{5,9}$.0$^{8,11}$]dodecane-1-carboxylic Acid (5).**—Compound **4** (30 g, 0.0709 mole) was refluxed for 2.5 hr with 400 ml each of ethanol and 2.5 $N$ aqueous sodium hydroxide. The resulting clear solution was evaporated to *ca.* 300 ml, diluted with 600 ml of water to dissolve the sodium salt of the product, and acidified with HCl to precipitate 28.2 g (97%) of **5** (mp 288–291° dec) suitable for use in the next step. Recrystallization from acetonitrile gave material with mp 291–293° dec; infrared absorptions at 3.75 (broad, OH) and 5.85 μ (C═O); nmr signals (pyridine)[20] at $\delta$ 2.23 (2 H AB pattern, $J$ = 11.5 cps, $\delta_A-\delta_B = 17$ cps, 12-$CH_2$), and 2.9–3.6 and 3.7–4.1 (3 H and 2 H, respectively, complex multiplets, methine CH).

*Anal.* Calcd for $C_{13}H_8Cl_6O_2$: C, 38.18; H, 1.97. Found: C, 38.18; H, 2.25.

**3,4,4,5,9,10-Hexachlorohexacyclo[5.4.1.0$^{2,6}$.0$^{3,10}$.0$^{5,9}$.0$^{8,11}$]dodecan-1-amine (6).**—A mixture of 20 g (0.0489 mole) of **5** and 250 ml of thionyl chloride was refluxed for 2 hr. The excess reagent was evaporated, benzene was added, and the evaporation was repeated to give the acid chloride (C═O absorption at 5.7 μ) as a brown oil. This was dissolved in 500 ml of acetone, cooled to 0°, and treated with a solution of 3.70 g (0.057 mole) of sodium azide in 35 ml of water. The mixture was stirred for 15 min at 5°, and then diluted with 600 ml of water. The solid azide which was precipitated was extracted into 700 ml of toluene. This solution was washed with water, dried ($MgSO_4$), and then heated for 1 hr on the steam bath (nitrogen evolution). Evaporation gave the isocyanate (N═C═O absorption at 4.42 μ) as a tan solid. This was hydrolyzed by refluxing for 20 hr with a mixture of 400 ml of acetic acid and 100 ml of concentrated HCl. Evaporation gave a solid residue of the product hydrochloride which was dissolved in 800 ml of very dilute HCl and 200 ml of ethanol. After removal of a small amount of insoluble solid, the solution was brought to pH 9 with concentrated $NH_4OH$ to precipitate 14.1 g (76%) of **6**, suitable for use in the next step. Recrystallization from methanol–water gave material with mp 295–297° dec after previous darkening; infrared absorptions at 2.98, 3.03, 6.13, and 6.36 μ ($NH_2$); nmr signals ($CF_3COOH$) at $\delta$ 2.44 (2 H AB pattern, $J$ = 11 cps, $\delta_A-\delta_B = 10$ cps, 12-$CH_2$), 3.25 and 3.60 (1 H and 4 H, respectively, broad singlets, methine CH), and 7.80 (3 H hump, $NH_3^+$).

*Anal.* Calcd for $C_{12}H_9Cl_6N$: C, 37.93; H, 2.39; N, 3.69. Found: C, 37.88; H, 2.25; N, 3.74.

**Hexacyclo[5.4.1.0$^{2,6}$.0$^{3,10}$.0$^{5,9}$.0$^{8,11}$[dodecan-1-amine (7).**—To a solution of 14.0 g (0.0368 mole) of **6** in 250 ml of dry tetrahydrofuran were added 41.5 ml (0.442 mole) of dry *t*-butyl alcohol[21] and 6.13 g (0.883 g-atom) of lithium wire, cut into small pieces. The reaction mixture was kept under nitrogen. A vigorous reaction commenced after a few minutes and was moderated by cooling as necessary. As it subsided, heat was supplied to maintain the reflux for a total of 1 hr. The reaction mixture was poured into 1 l. of ice water, the product was extracted into benzene–ether (1:1), and the extracts were washed with water and evaporated to an oil. The crystalline hexamate of the product was obtained by adding a solution of 6.60 g (0.0368 mole) of cyclohexylsulfamic (hexamic) acid in a mixture of 60 ml of acetonitrile and 20 ml of isopropyl alcohol. The hexamate was recrystallized from isopropyl alcohol–acetonitrile until the amine component was pure by gas–liquid partition chromatography (glpc).[22] Usually two recrystallizations gave material of 99% purity.[23] The yield of purified hexamate averaged 5 g. This material was partitioned between 0.5 $N$ NaOH and ether–benzene (1:1), and the organic phase was washed with water and evaporated to a partially crystalline residue which was dissolved in isopropyl alcohol and made acidic with ethereal HCl. Excess ethyl acetate was added to precipitate 2.28 g (30% over-all) of the **hydrochloride** of **7**; shrinks and darkens but does not melt below 350°; infrared absorptions at *ca.* 3.9 (broad), 4.89, 6.26, and 6.30 μ ($NH_3^+$); nmr signals ($D_2O$–DCl)[24] at $\delta$ 1.70 and 2.09 (two overlapping 2 H AB patterns, both with $J$ = 10.5 cps, $\delta_A-\delta_B = 21$ and 18.5 cps for upfield and downfield patterns, respectively, 4- and 12-$CH_2$), and 2.45 and 2.72 (9 H as two overlapping broad singlets, methine CH); p$K_a$ (water, 25°), 10.61.

*Anal.* Calcd for $C_{12}H_{16}ClN$: C, 68.72; H, 7.69; Cl, 16.91; N, 6.68. Found: C, 68.65; H, 7.66; Cl (ionic), 16.91; N, 6.68.

**Methyl 1,4,5,6,7,7-Hexachlorobicyclo[2.2.1]hepta-2,5-diene-2-carboxylate (8).**—A mixture of 150 g (1.78 mole) of methyl propiolate and 444 g (1.63 mole) of hexachlorocyclopentadiene was heated under reflux in a bath at 140° for 20 hr. Treatment of the resulting dark oil with 400 ml of methanol gave 410 g (71%) of **8** as light tan crystals (mp 81–84°) suitable for use in the next step. Recrystallization from methanol and sublimation at 60° (0.05 mm) gave material with mp 87–89°; infrared absorptions at 3.27 (CH═), 5.80 (C═O), 6.20 and 6.28 μ (C═C); nmr signals ($CDCl_3$) at $\delta$ 3.84 (3 H singlet, $OCH_3$) and 7.42 (1 H singlet, CH═).

*Anal.* Calcd for $C_9H_4Cl_6O_2$: C, 30.29; H, 1.13. Found: C, 30.30; H, 1.05.

**Methyl 1,2,3,4,10,10-Hexachloro-1,4,4a,5,8,8a-hexahydro-1,4-*endo*,*endo*-5,8-dimethanonaphthalene-4a-carboxylate (9).**—A mixture of 200 g (0.560 mole) of **8** and 100 ml of cyclopentadiene[25] was heated under reflux in a bath at 65°. Three further 100-ml portions of cyclopentadiene were added at intervals of 1.5 hr, the total reaction time being 6 hr. The crude crystalline product was obtained by adding 500 ml of petroleum ether (bp 30–60°) and chilling to −30°. Recrystallization from ethanol gave 81.5 g (34%) of **9** with mp 147–149°. Further recrystallization gave material with mp 148–150°; infrared absorptions at 5.80 (C═O) and 6.22 μ (C═C); nmr signals ($CDCl_3$) at $\delta$ 1.86 (2 H AB pattern, $J$ = 9 cps, $\delta_A-\delta_B \simeq 23$ cps, upfield portion split into triplets with 1.5-cps separation, downfield portion broad singlets, 9-$CH_2$), 3.1–3.35 (2 H complex multiplet, 5- and 8-CH), 3.87 (3 H singlet, $OCH_3$), 4.17 (1 H doublet, $J$ = 4 cps, 8a-CH), and 6.28 (2 H broad singlet, CH═CH).

*Anal.* Calcd for $C_{14}H_{10}Cl_6O_2$: C, 39.75; H, 2.38. Found: C, 39.99; H, 2.50.

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[17] Shell technical grade, 91% purity.

[18] Crude Thiele's acid was esterified,[8] and the neutral product was used without further purification.

[19] In benzene solution, this pattern was expanded and showed $J$ = 8.5 cps. The downfield portion was split into doublets with 1.5-cps separation.

[20] The nmr was also run in DMSO-$d_6$ to establish the absence of vinylic proton signals.

[21] Tetrahydrofuran was dried over a mixture of Linde 4A and 13X Molecular Sieves; *t*-butyl alcohol over 4A only.

[22] Samples of the hexamate were partitioned between aqueous alkali and benzene, and the benzene phase was chromatographed on a column packed with 60–80 mesh Diatoport S loaded with 15% Carbowax 20M and 5% terephthalic acid. The major impurity (*ca.* 15%) present in the crude material ran somewhat more slowly than the product. No separation was achieved on a column loaded with silicone gum rubber.

[23] Recrystallization of the hydrochloride did not effect the required purification.

[24] The spectrum was also run in $CF_3COOH$ to prove the absence of vinylic proton signals at $\delta \sim 5$, the region obscured by the HOD peak.

[25] R. B. Moffett in "Organic Syntheses," Coll. Vol. IV, N. Rabjohn, Ed., John Wiley and Sons, Inc., New York, N. Y., 1963, p 238. The total monomer used was 400 ml (4.87 moles).

**Methyl 1,7,8,11,12,12-Hexachlorohexacyclo[5.4.1.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$.$0^{8,11}$]dodecane-2-carboxylate (10).**—Two 25-g batches (0.118 mole in total) of **9** in 500 ml of acetone each were irradiated for 1 hr, and the resulting solutions were combined and evaporated. Recrystallization of the residue from methanol gave 41.5 g (83%) of **10**: mp 165–167°; infrared absorption at 5.77 μ (C=O); nmr signals ($CDCl_3$) at δ 1.78 (2 H AB pattern, $J$ = 11.5 cps, $\delta_A-\delta_B$ = 17 cps, 4-$CH_2$), 3.15 and 3.9 (partially resolved multiplets, 4 H and 1 H, respectively, methine CH), and 3.77 (3 H singlet, $OCH_3$).

*Anal.* Calcd for $C_{14}H_{10}Cl_6O_2$: C, 39.75; H, 2.38, mol wt, 423. Found: C, 39.99; H, 2.27; mol wt (osmometric), 426.

**1,7,8,11,12,12-Hexachlorohexacyclo[5.4.1.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$.$0^{8,11}$]dodecane-2-carboxylic Acid (11).**—Compound **10** (30 g, 0.0709 mole) was refluxed for 32 hr with 400 ml each of ethanol and 2.5 *N* aqueous NaOH. The resulting clear solution was evaporated to *ca.* 300 ml, diluted with 600 ml of water, and acidified with HCl to precipitate 28.3 g (98%) of **11**, suitable for use in the next step. Recrystallization from ethyl acetate–hexane gave material which darkened but did not melt below 350°; infrared absorptions at 3.75 (broad, OH) and 5.87 μ (C=O); nmr signals (pyridine)[20] at δ 1.79 (2 H AB pattern, $J$ = 11.5 cps, $\delta_A-\delta_B$ = 31.5 cps, 4-$CH_2$) and 3.14, 3.41, and 4.22 (3 H, 1 H, and 1 H, respectively, partially resolved multiplets, methine CH).

*Anal.* Calcd for $C_{13}H_8Cl_6O_2$: C, 38.18; H, 1.97. Found: C, 38.16; H, 2.00.

**1,7,8,11,12,12-Hexachlorohexahydro[5.4.1.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$.$0^{8,11}$]-dodecan-2-amine (12).**—Compound **11** (20 g, 0.0489 mole) was subjected to the Curtius reaction sequence exactly as in the conversion of **5** to **6**. In this case both the acid chloride (C=O absorption at 5.71 μ) and the isocyanate (N=C=O absorption at 4.42 μ) were crystalline solids. The yield of **12** precipitated at pH 9 was 14.0 g (75%), suitable for use in the next step. Recrystallization from ethanol–water gave material which darkened but did not melt below 350°; infrared absorptions at 2.95, 3.01, and 6.17 μ ($NH_2$); nmr signals ($CF_3COOH$) at δ 2.24 (2 H AB pattern, $J$ = 12.5 cps, $\delta_A-\delta_B$ = 28 cps, 4-$CH_2$), 3.1–3.8 (5 H as overlapping broad singlet and partially resolved multiplet, methine CH), and 7.8 (3 H hump, —$NH_3^+$).

*Anal.* Calcd for $C_{12}H_9Cl_6N$: C, 37.93; H, 2.39; N, 3.69. Found: C, 38.18; H, 2.38; N, 3.48.

**Hexacyclo[5.4.1.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$.$0^{8,11}$]dodecan-2-amine (13).**—A 14.0-g (0.0368 mole) sample of **12** was dehalogenated and the product purified[23] by the procedure which was used for the conversion of **6** to **7**. Three recrystallizations were required to give hexamate (5 g) of 99% purity. This yielded 1.45 g (19%) of the **hydrochloride** of **13**: darkens and shrinks but does not melt below 350°; infrared absorptions at 3.9 (multiplet), 4.96, 6.20, and 6.30 μ ($NH_3^+$); nmr signals ($D_2O$–DCl)[24] at δ 1.78 (4 H AB pattern, $J$ = 11 cps, $\delta_A-\delta_B$ = 30 cps, 4- and 12-$CH_2$), and 2.53 and 2.66 (9 H as two overlapping broad singlets, methine CH); p$K_a$ (water, 25°), 9.69.

*Anal.* Calcd for $C_{12}H_{16}ClN$; C, 68.72; H, 7.69; Cl, 16.91; N, 6.68. Found: C, 68.88; H, 7.80; Cl (ionic), 16.62; N, 6.65.

**Registry No.**—**3**, 14128-62-2; **4**, 14154-65-5; **5**, 14128-63-3; **6**, 14171-90-5; hydrochloride of **7**, 14128-64-4; **8**, 14128-65-5; **9**, 14171-91-6; **10**, 14128-66-6; **11**, 14128-67-7; **12**, 14128-68-8; hydrochloride of **13**, 14128-69-9.

**Acknowledgments.**—We wish to thank Dr. J. R. E. Hoover for his interest and encouragement during the course of this work and Mr. J. J. Taggart for his skilled and cheerful technical assistance. We are indebted to Miss M. A. Carroll and her associates for the microanalytical data, Dr. W. E. Thompson and his staff for the nmr spectra, Mr. J. W. Lockard for the gas chromatograms, and Mr. J. W. Hamill for the p$K_a$ determinations.

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# Molecular Rearrangements during Solvolyses of Pentaoxyphosphoranes. Polyketones Derived from Phthalaldehyde and Terephthalaldehyde[1]

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*Received May 24, 1967*

Methanolysis of the trimethylbiacetyl-benzaldehyde-phosphite adduct (2,2,2-trimethoxy-4β-methyl-4α-acetyl-5α-phenyl-1,3,2-dioxaphospholane) gave trimethyl phosphate and 3-phenyl-2,4-pentanedione. This new type of molecular rearrangement involved the 1,2 shift of an acetyl group during the loss of phosphate. 1-Phenyl-2-acetylpropylene oxide was not an intermediate in the rearrangement. The bispentaoxyphosphorane derived from the reaction of two molecules of 2,2,2-trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholene with phthalaldehyde gave two molecules of trimethyl phosphate and one molecule of 1,2-bis-(diacetylmethyl)benzene. This tetraketone was obtained in the dienol diketo and the monoenol triketo tautomers. The bispentaoxyphosphorane, made from two molecules of 2,2,2-trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholene and one molecule of terephthalaldehyde, underwent methanolysis to trimethyl phosphate and 1,4-bis(diacetylmethyl)benzene, which was obtained as the dienol diketo tautomer. The corresponding 1,2-bis-4′- and 1,4-bis-4′-(3′,5′-dimethyl)pyrazolylbenzene were made from the tetraketones and hydrazine.

The nucleophilic addition of 2,2,2-trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholene, I, to the carbonyl function of benzaldehyde gave the two diasteromeric forms of 2,2,2-trimethoxy-4-methyl-4-acetyl-5-phenyl-1,3,2-dioxaphospholane,[3] II. The isomers IIa and IIb with the *cis-* and *trans*-$CH_3$/H configurations were formed in about 90:10 proportion, respectively. The pentavalency of the phosphorus was based on the large positive value of the $P^{31}$ nmr shift.[4] The configurations were assigned from the $H^1$ nmr data.

The condensation of two molecules of the phospholene I with phthalaldehyde gave the three possible diastereomers of a bispentaoxyphosphorane,[5] IIIa,

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(2) This investigation was supported by Public Health Service Grant CA-04769-08 from the National Cancer Institute, and by the National Science Foundation, Grant GP 6690-Y.

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