Table I

Melting Points (°C) of Sterols and Their Derivatives

Registry no.	Sterol	This work, *in vacuo*, corrected: Free sterol	Acetate	Registry no.	Benzoate	Registry no.	Literature[a]: Free sterol	Acetate	Benzoate
481-19-6	7-Dehydrostigmasterol	158.5–159.3	178.3–179	39533-73-8	184.5–185.5	39533-21-8	152–154[b]	172–173[c]	178.5–180[d]
481-18-5	α-Spinasterol	172–173	188.5–189	4651-46-1	204–205	39599-22-9	172.5[e]	187[e]	201–202[f]
521-03-9	Schottenol	151–151.5	159.5–160	14473-77-9	184–184.5	39533-21-6	148–150[g]	161–163[h]	183.5[g]
14291-38-4	5α-8(14)-Stigmasten-3β-ol	116.5–117	117.8–118.5	14291-39-5	87.5–88.5	39533-23-8	114[i]	119[e]	89[i]
39533-72-7	5α-8(14)-Stigmasten-3α-ol	176–176.5	84.5–85	39533-24-9	99–100	39533-25-0			

[a] Highest melting point reported. [b] Reference 4a,e. [c] Reference 4a. [d] Reference 4b. [e] D. Larsen and F. W. Heyl, *J. Amer. Chem. Soc.*, **56**, 2663 (1934). [f] M. C. Hart and F. W. Heyl, *J. Biol. Chem.*, **95**, 311 (1932). [g] C. Djerassi, G. W. Krakower, A. J. Lemin, H. H. Liu, J. S. Mills, and R. Villotti, *J. Amer. Chem. Soc.*, **80**, 6284 (1958). [h] G. Biglino, *Farmaco, Ed. Sci.*, **14**, 673 (1959); *Chem. Abstr.*, **54**, 6812*c* (1960). [i] E. Fernholz and W. L. Ruigh, *J. Amer. Chem. Soc.*, **62**, 2341 (1940).

α-Spinasterol. A. **Rh-Catalyzed Reaction.**[8]—7-Dehydrostigmasteryl acetate (25 g) in 1200 ml of 3:1 benzene–ethanol was hydrogenated at room temperature and 1 atm pressure over 1.6 g of tris(triphenylphosphine)chlororhodium (Strem Chemical Co.) for 18 hr. Solvent was evaporated, the dry residue was extracted with petroleum ether and filtered to remove catalyst, and solvent was again evaporated. The residue was crystallized from 2:1 ethanol–benzene and then from acetone to give 15.1 g of α-spinasteryl acetate, mp 188.5–189°. An additional 7.7 g, mp 187.5°, was recovered by work-up of the mother liquors. A portion of the product was hydrolyzed to α-spinasterol, and a benzoate was prepared (Table I).

B. **Raney Ni Catalyzed Reaction.**[9]—7-Dehydrostigmasteryl acetate (11.3 g) in 450 ml of dioxane and 5 ml of Et_3N was hydrogenated over 10 ml of catalyst for 23 hr at room temperature and 1 atm pressure. Removal of catalyst and evaporation of solvent to 120 ml deposited 7.5 g of α-spinasteryl acetate, mp 186–186.5°. Further cooling of the filtrate yielded an additional 2.6 g of product, mp 183.5–184°.

Schottenol. A.—7-Dehydrostigmasterol (15 g) in 750 ml of ethyl acetate and 5 ml of Et_3N was hydrogenated for 4 days over 25 ml of Raney Ni at room temperature and 1 atm pressure. The reaction was followed by glc of samples periodically removed. Catalyst was then filtered off and the solvent was reduced in volume to 150 ml to precipitate 9.15 g of schottenol, mp 149.5–151.5°. Work-up of the mother liquors gave no more pure material.

B.—The reaction as in A was repeated in a Parr stirred pressure vessel at 14 atm H_2 pressure. After 50 hr the product was worked up as before to yield 8.9 g of schottenol, mp 150–151.5°.

The products from several runs (24.5 g) were combined in 500 ml of hot ethyl acetate and cooled to room temperature to yield 18.5 g of schottenol, mp 151–151.5°. An acetate and a benzoate were prepared (Table I).

5α-8(14)-Stigmasten-3α- and -3β-ol.—7-Dehydrostigmasterol (17 g) in 700 ml of ethyl acetate and 5 ml of Et_3N was hydrogenated over 20 ml of Raney Ni at room temperature for 10 min at 14 atm and for 2 hr at 100° and 14 atm. The reaction was followed by glc. An additional 22 hr at 14 atm and 100° and 24 hr at 140 atm and 100° with fresh catalyst produced no changes in the glc pattern.

The autoclave was cooled, catalyst was removed, and the product (one peak on glc, two spots on tlc) was chromatographed on 1 kg of 2:1 10% $AgNO_3$–silica gel–Celite with 10% ether in petroleum ether. The two compounds were cleanly separated (tlc) to yield 4 g of the higher R_f material and 8 g of the lower R_f material.

The former was crystallized from methanol–benzene to yield 5α-8(14)-stigmasten-3α-ol, mp 176–176.5°, acetate, mp 84.5–85° (from methanol–benzene), and benzoate, mp 99–100° (from ethanol). The compound gave a fast blue color with the Liebermann–Burchard reagent, no precipitate with digitonin, and had an ir spectrum similar to that of 5α-cholestan-3α-ol.[12] The material last to emerge from the column was recrystallized from methanol–benzene and identified as 5α-8(14)-stigmasten-3β-ol, mp 116.5–117.0° (from ethanol), acetate mp 117.8–118.5° (from ethanol), and benzoate mp 87.5–88.5° (from acetone). It corresponded to the lower R_f spot on tlc, had the same retention time on glc as the 3α-ol, gave a precipitate with digitonin and a fast blue Liebermann–Burchard test, and had an ir spectrum similar to that of 5α-cholestan-3β-ol.[12]

Registry No.—NBS, 128-08-5.

Percyclophane-4

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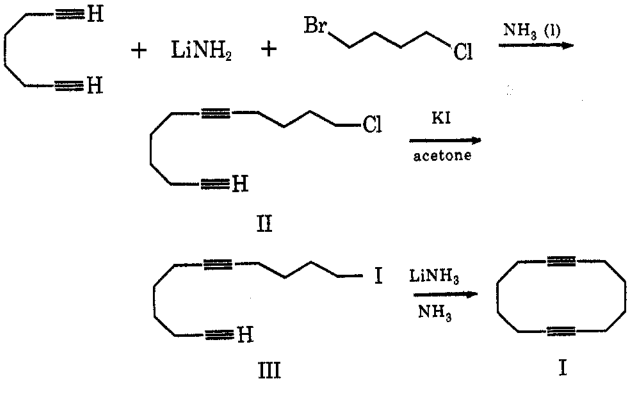
We wish to report the synthesis of an unusual new cage aromatic compound, percyclophane-4[1] (Figure 1). Percyclophane-4 was synthesized by the cyclic trimerization of cyclododecadiyne-1,7, catalyzed by organochromium and organocobalt compounds.

Cyclododecadiyne-1,7 (I) was synthesized from commercially available octadiyne-1,7 in the manner described below.



Overall yield of this synthesis was approximately 20%. This is a new synthesis of a previously reported compound.[2] Cyclododecadiyne-1,7 is a colorless, crystalline compound, mp 23 ± 2°, which on exposure

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[1] "Percyclophane" is a name coined by the author to describe this cage molecule. The name is derived from the word paracyclophane, which refers to molecules with a configuration of two benzene rings linked together in the para positions.

[2] (a) D. J. Cram, N. L. Allinger, and H. Steinberg, *J. Amer. Chem. Soc.*, **76**, 726 (1959); (b) D. J. Cram and N. L. Allinger, *ibid.*, 6132 (1954); (c) *ibid.*, **78**, 2518 (1956).

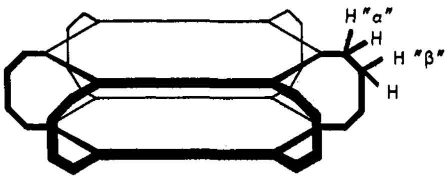

Figure 1.

to the air at room temperature slowly oxidizes to unknown products.[2]

Upon reaction of I with trimesitylchromium or dimesitylcobalt, a trimer was formed. The structure shown in Figure 1 of percyclophane-4 was assigned to the trimer. Elemental, infrared, nmr, and mass spectral analysis were consistent with this proposed structure.

Cyclododecadiyne was treated with either trimesitylchromium or dimesitylcoblat in a 5-10-fold molar excess in tetrahydrofuran solvent.[3] These reactions were generally run between −20 and 30°. These conditions, in the case of reaction with trimesitylchromium, gave a 10% yield of percyclophane-4 and in the case of dimesitylcobalt gave a yield of 70% of percyclophane-4. The percyclophane product was isolated and purified by sublimation. Elemental analysis was consistent with the formulation $C_{36}H_{48}$.

The nmr spectra of percyclophane-4 showed three broad resonances centered at δ 1.7, 2.3, and 2.9 with intensity ratios of 2:1:1, respectively. The resonances at δ 2.3 and 2.9 are attributed to the α hydrogens. The two hydrogens at each α position appear at different chemical shifts owing to rigidity of the structure. Models indicate that one α hydrogen is close to being in the plane of the aromatic ring while the other α hydrogen is close to being perpendicular to the ring. The broadness of the resonances must be due to unresolved complex spin-spin coupling and dipolar broadening. Anet and Brown[4] noted that the benzylic hydrogens in [3,3]percyclophane gave a singlet nmr resonance. The equivalence of the two benzylic hydrogens is attributed to a rapid equilibration between the pseudochair and boat configurations of the [3,3]paracyclophane. The energy barrier for this equilibrium was estimated at 11.7 kcal/mol. Models of percyclophane-4 indicate a tight packing of the six interring carbon bridges. This feature suggests a much higher barrier for equilibration. Actually the geometry of the molecule is such that the configurations of all the interring bridges must be changed simultaneously to avoid severe steric interactions. Such a simultaneous flipping of all six bridges would have a very high energy barrier indeed. Thus, the benzylic hydrogens are unique at nmr frequencies.

A second structure which might account for the observed nmr resonances would result from trimerization of only three acetylene moieties, giving rise to one fully substituted aromatic ring with three pendent cycloalkyne rings. For this structure an assignment could be made of the δ 2.9 resonance for the benzylic hydrogens and of the δ 2.3 resonance for the protons to the triple bond. We do note that these α hydrogens in cyclococedadiyne show a resonance at δ 2.1; however this resonance might well be shifted by shielding from the now present aromatic ring. The trimerization product failed, however, to show any reaction with bromine in carbon tetrachloride, which would have indicated the presence of the acetylenic linkages. This alternative structure must therefore be eliminated.

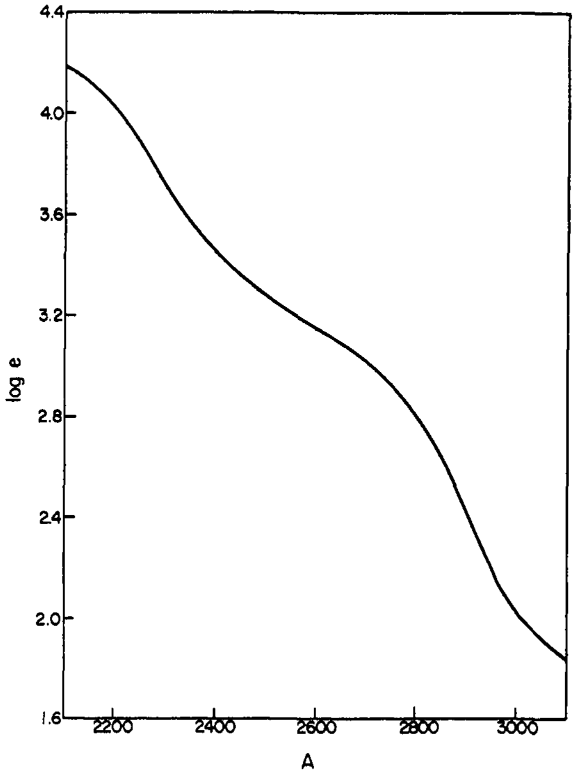

Figure 2.—Absorption spectra of percyclophane-4 in hexane.

The infrared spectrum of the percyclophane was characterized only by aliphatic C-H modes. No absorptions were noted which could be assigned to the aromatic part of the molecule. It is commonly noted that such highly substituted aromatic rings have very weak ring absorptions.[5]

Most conclusive of all the analytical data was the high-resolution mass spectrum, which showed a parent ion, *m/e* 480.78, which corresponds to an empirical formula of $C_{36}H_{48}$. In addition, 99% of the ion current was in the C_{36} fragment. Essentially no fragmentation of the molecular skeleton took place. Consistent with this data, it is unlikely that a trimer of cyclododecadyne $[(C_{12}H_{16})_3 = C_{36}H_{48}]$ could be assembled in any way except as the percyclophane-4, which would not show extensive fragmentation in the mass spectrum.

The ultraviolet spectrum of percyclophane-4 is shown in Figure 2. It is obvious that normal aromatic absorption is not present. This spectrum can be compared with those of [2.3]- and [4]paracyclophane shown in Figure 3. Cram[6] has shown that as two aromatic rings are brought close to one another a great deal of interaction between the rings takes place. This interring interaction results in a red shift of the major π-π^* band of the aromatic rings along with a loss of vibrational fine structure in the absorption band. It can be noted that percyclophane-4 has a λ_{max} (~2730 Å)

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(3) H. Zeiss, P. J. Whearley, and H. J. S. Winkler, "Benzenoid Metal Complexes," Ronald Press, New York, N. Y., 1966, and references cited therein.

(4) F. A. L. Anet and M. A. Brown, *J. Amer. Chem. Soc.*, **91**, 2389 (1969).

(5) L. J. Bellamy, "Infrared Spectra of Complex Molecules," Wiley, New York, N. Y., 1954.

(6) D. J. Cram, *Rec. Chem. Progr.*, **20**, 71 (1959).

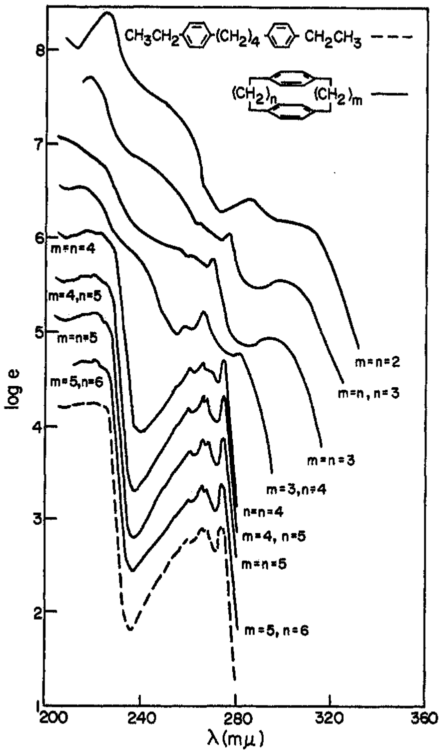

Figure 3.—Absorption spectra of paracyclophanes (each successive curve has been displaced upward by 0.5 log units, omitting the open-chair compounds).

and ϵ_{max} (~1000) very similar to that of [4,4]paracyclophane (λ_{max} 2630; ϵ_{max} 1300). The percyclophane-4 spectra, however, shows only the very broad absorption with no fine structure due to the steric strain and rigidity of the molecule.

Several attempts were made to synthesize similar trimers of commercially available[7] 1,6 cyclotridicadiyne and 1,8-cyclotetradecadiyne, but no tractable products could be isolated. We are presently investigating the chemical properties of this unusual molecule.

Experimental Section

Synthesis of Cyclododecadiyne.—In a 2-l., three-neck flask was placed 1 l. of liquid ammonia. To this was added 1.25 g of $Fe(NO_3)_3 \cdot 9H_2O$. The contents of the flask were blanketed with nitrogen at all times; 4.10 g (0.59 mol) of lithium wire was added in small chunks slowly to the flask. All of the lithium wire had dissolved within 15 min after addition was complete. Over a period of 10 min, 63 g (0.59 mol) of octadiyne-1,7 was added. The reaction mixture was stirred for 1.5 hr.

Into a second 2-l. flask was placed 125 ml of dry, distilled dioxane containing 102.5 g (0.59 mol) of $Br(CH_2)_4Cl$ (K and K Laboratories). The liquid ammonia solution from the first flask was pumped with nitrogen pressure through a filter stick into the second flask. This reaction mixture was allowed to warm with stirring overnight until all of the ammonia was evaporated. Upon evaporation of the ammonia, 500 ml of *n*-heptane was added, then 500 ml of water, and the phases were shaken and separated. The aqueous layer was extracted twice more with 200-ml portions of *n*-heptane. The combined *n*-heptane solutions were washed twice with 300-ml portions of 5% HCl solution and then dried over anhydrous Na_2SO_4. Removal of the *n*-heptane gave 100.2 g of crude product which upon distillation yielded 56 g (50%) of 1-chlorododecadiyne-5,11 (II): major infrared bands 3300, 2920, 2860, 2110, 1430, and 600–650 cm^{-1}; nmr triplet centered at δ 3.58 and complex multiplets centered at δ 2.13 and 1.60 with relative areas 2:7:8.

In a 60-ml glass ampoule was placed 5.0 g of II along with 7.60 g of NaI dissolved in 30 ml of dry acetone. The ampoule was sealed and heated at 80° for 17 hr. The ampoule was opened, and the NaCl was filtered off and washed with ether. Upon dilution of the acetone solution with ether the excess NaI precipitated and was filtered off. Removal of the solvent yielded 6.9 g (94%) of 1-iodododecadiyne-5,11 (III): major infrared bands 3300, 2920, 2860, 2110, 1430, and broad absorption centered around 500 cm^{-1}; nmr triplet centered at δ 3.20 and complex multiplets centered at δ 2.15 and 1.60 with relative areas of 2:7:8.

Into a 2-l., three-neck flask with air stirrer, cold trap, and inert gas head was placed 1 l. of liquid ammonia. $Fe(NO_3)_3 \cdot 9H_2O$ (0.1 g) and then 0.13 g (0.019 g-atom) of Li wire cut into small pieces were added. When the Li had dissolved, 4.28 g (0.015 mol) of III dissolved in 250 ml of dry ether was added dropwise over a period of 4.5 hr. Upon completion of the addition, the ammonia was allowed to evaporate. The product was worked up exactly as described for compound II and this work-up yielded 1.64 g of light yellow oil. This crude product contained residual compound II and III as well as cyclododecadiyne-1,7 (I). The crude product was chromatographed on Woelm neutral alumina, eluting with a gradient of hexane and benzene. Yield of purified cyclododecadiyne was 0.87 g (0.054 mol, 36%). The product crystallized upon refrigeration into large, colorless needles: mp 20 ± 2°;[2] major infrared bands 2900, 2820, 1430, 1330, 755 cm^{-1} (w); nmr showed broad multiplets centered at δ 2.10 and 1.70 with relative areas of 1:1.

Anal. Calcd: C, 90.0; H, 10.0. Found: C, 89.7; H, 10.1.

Percyclophane. Catalysis by Dimesitylcobalt.—Mesitylmagnesium bromide solution in THF was prepared and standardized by standard techniques. High-purity Mg (99.99%) was used in the preparation. Into a 25-ml, three-neck flask, with nitrogen purge, was placed 0.65 g (5.0 mmol) of anhydrous $CoCl_2$, then 58.5 ml (15.0 mmol) of a 0.0256 *M* solution of mesitylmagnesium bromide. The flask temperature was kept at −20° and the solution was stirred for 10 hr. In a second 200-ml flask was placed 1.60 g (10.0 mmol) of cyclododecadiyne dissolved in 50 ml of dry THF. To this was added 2.0 ml of the mesitylmagnesium bromide–$CoCl_2$ solution. The reaction mixture was allowed to stir at −30 to −40° for 2 hr, then allowed to warm to room temperature. The resulting solution was diluted with ether, and this ether phase was washed with water and 5% HCl solution, and then dried over anhydrous K_2CO_3. Removal of the solvent left 2.25 g of a greenish solid. This crude material was placed in a vacuum sublimation apparatus and heated at 150° (0.1 mm). A white, crystalline material, 1.1 g (70%), sublimed: mp 235°, mass spectral analysis showed parent ion of $C_{36}H_{48}$ (mol wt 480.78); major infrared bands 3000, 1450, 730 cm^{-1} (vw); nmr broad resonance centered at δ 2.90, 2.30, and 1.70 with relative areas of 1:1:2.

Anal. Calcd for $C_{36}H_{48}$: C, 90.0; H, 10.0. Found: C, 89.5; H, 9.6.

Registry No.—I, 4641-85-4; II, 39253-36-6; III, 39253-37-7; lithium amide, 7782-89-0; 1-bromo-4-chlorobutane, 6940-78-9; 1,7-octadiyne, 871-84-1; percyclophane-4, 39253-39-9.

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[7] Farchan Research Laboratories, Willouby, Ohio.

Methylation and Chlorination of Internal Olefins with Trimethylaluminum and Hydrogen Chloride

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In the course of our investigations on the fundamentals of cationic polymerizations initiated by alkylaluminum compounds, we are using small molecule model reactions to elucidate aspects of the polymerization mechanism. Since trialkylaluminums or dialkylaluminum halides (*e.g.*, Me_3Al, Et_3Al, Et_2AlCl) in conjunction with suitable cationogens (*e.g.*, HX or *t*-BuX) are most efficient initiator systems for the synthesis of high molecular weight polymers at relatively high temperatures,[1] we have been interested in exploring the chemis-