that the quantity of n-butyllithium was adjusted to be 0.040 mmol. Cyclohexane was used as a solvent for **1a**; 1:9 cyclohexane–THF was used for **7a** and **8a**. The progress of the reaction was again followed by scanning the methylsilyl region of the nmr, but the peaks observed were those of the protonated ethylenediamines rather than their anions. Rearrangements were generally much slower than with 1 equiv of base (Figure 2).

N,N-Bis(trimethylsilyl)-N′-methyl-N′-phenylethylenediamine (11). To a solution of 5.0 g (0.018 mol) of **7b** in 20 ml of ether was added 11 ml of 1.6 M n-butyllithium–hexane solution, at −30°. The reaction mixture was allowed to warm to room temperature and stirred for 24 hr, turning to a red color. Methyl iodide (5.2 g, 0.036 mol) was added and the mixture was stirred for an additional 4 hr. Work-up in the usual way gave 4.7 g (72%) of colorless **11**, bp 134–137° (1 torr), n^{22}D 1.5127.

Anal. Calcd for $C_{15}H_{30}N_2Si_2$: C, 61.15; H, 10.27; N, 9.51; Si, 19.07. Found: C, 61.40; H, 10.11; N, 9.72; Si, 18.79.

1,1,2-Trimethyl-5-trimethylsilyl-1-sila-2,5-diazacyclopentane (12). To a solution of 8.0 g (0.037 mol) of **2b** in 30 ml of tetrahydrofuran, cooled in a −70° bath, was added 21 ml of 1.6 M n-butyllithium–hexane solution (0.037 mol of n-BuLi). The reaction mixture was warmed to room temperature and then heated to reflux for 48 hr. Pyrrole (2.5 g, 0.037 mol) was added, and half of the solvent was removed by distillation. The residue was distilled twice under reduced pressure, yielding 6.5 g (81%) of colorless liquid **12**, bp 80–84° (22 torr), n^{22}D 1.4413. The nmr spectrum showed sharp resonances at τ 9.98, 9.94, and 7.55, with relative intensities 2:3:1 respectively, assigned to the dimethylsilyl, trimethylsilyl, and N-methyl protons, and a complex pattern at τ 6.84–7.35 due to the methylene protons.

The infrared spectrum showed bands at 680 (w), 712 (w), 750 (w), 775 (m), 798 (m), 833 (s), 939 (s), 1010 (s), 1055 (s), 1090 (w), 1183 (m), 1218 (w), 1253 (s), 1345 (m), 1450 (w), 1470 (w), 2800 (w), 2880 (w), and 2960 (m) cm⁻¹.

Anal. Calcd for $C_8H_{22}N_2Si_2$: C, 47.49; H, 10.88; N, 13.85; Si, 27.77. Found: C, 47.35; H, 10.86; N, 13.76; Si, 27.76.

When an identical reaction was carried out, but stirred 48 hr at room temperature instead of refluxed, only the starting material (**2b**) was found after work-up.

A reaction on the same scale, but with only 2.1 ml of the 1.6 M n-butyllithium–hexane (0.0036 mol of n-BuLi), produced 5.6 g (76%) of **12**, as well as 75% of the theoretical volume of methane.

1,1-Dimethyl-2,5-bis(trimethylsilyl)-1-sila-2,5-diazacyclopentane (13). The method of synthesis was similar to that for **12**, except that **3** was used as the starting material. The product (94%) was a colorless liquid, bp 119–120° (23 torr), n^{25}D 1.4452 (lit.[9] bp 63–64° (4 torr), $n^{21.5}$D 1.4438). The nmr spectrum showed sharp resonances at τ 9.94 (Me_3Si), 9.89 (Me_2Si), and 7.03, with relative intensities of 9:3:2, respectively. The infrared spectrum contained bands at 675 (w), 748 (w), 773 (m), 787 (m), 827 (s), 855 (w), 943 (s), 1020 (s), 1074 (s), 1110 (m), 1250 (s), 1332 (w), 1400 (w), 1430 (w), 1465 (w), 2830 (w), 2900 (w), and 2960 (m) cm⁻¹.

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Unsaturated Macrocyclic Compounds. LV.[1] The Synthesis of 1-Bromocyclotrideca-1,2-diene-4,8,10-triyne, a Highly Unsaturated 13-Membered Ring Cyclic Allene

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Abstract: The synthesis of trideca-1,5,8,12-tetrayn-7-ol (**2**) from hexa-1,5-diyne (**1**) is described. Oxidative coupling of **2** with oxygen, cuprous chloride, and ammonium chloride gave the cyclic "monomer" **3** in 80% yield, as well as the cyclic "dimer" **5**. Treatment of **3** with phosphorus tribromide led to 1-bromocyclotrideca-1,2-diene-4,8,10-triyne (**8**), a highly unsaturated 13-membered ring cyclic allene.

Fully conjugated carbocyclic systems incorporating an allene grouping, containing an odd number of carbon atoms in the ring, are an interesting class of compound.[3] No such conjugated cyclic allene has been prepared yet, although a number of simple cyclic allenes are known.[4] We now report the synthesis of 1-bromocyclotrideca-1,2-diene-4,8,10-triyne (**8**), a highly unsaturated 13-membered ring cyclic allene. Although it has not been possible to rearrange this substance to a fully conjugated system, the method employed should serve as a model for the synthesis of the related fully conjugated cyclic bromo allenes **12a** and **12b**.

Treatment of hexa-1,5-diyne (**1**)[5] with 1 molar equiv of ethylmagnesium bromide, followed by 0.5 molar equiv of ethyl formate,[6] gave trideca-1,5,8,12-tetrayn-7-ol (**2**) in 23% yield. Oxidative coupling of the alcohol **2** with oxygen, cuprous chloride, and ammonium chloride in aqueous ethanol and benzene[7] then led to the 13-membered ring cyclic monomer **3** in 80% yield. The remarkably high yield is unusual for this type of coupling reaction, not involving high-dilution conditions. The structure of **3** was based on the analytical and spectral data, and confirmation was provided by

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(1) Part LIV: R. H. Mitchell and F. Sondheimer, *J. Amer. Chem. Soc.*, 90, 530 (1968).

(2) Author to whom inquiries may be addressed at the Chemistry Department, University College, London W.C.1, England.

(3) Molecular orbital calculations of "odd" annulenes have been reported: E. Heilbronner, *Tetrahedron Letters*, 1923 (1964); see also H. E. Zimmerman, *J. Amer. Chem. Soc.*, **88**, 1564 (1966); M. J. S. Dewar, *Tetrahedron Suppl.*, **8**, 75 (1966).

(4) A. T. Blomquist, R. E. Burge, and A. C. Sucsy, *J. Amer. Chem. Soc.*, **74**, 3636 (1952); A. T. Blomquist, L. H. Liu, and J. C. Bohrer, *ibid.*, **74**, 3643 (1952); W. R. Moore and H. R. Ward, *J. Org. Chem.*, **25**, 2073 (1960); L. Skatteböl, *Tetrahedron Letters*, 167 (1961); *Acta Chem. Scand.*, **17**, 1683 (1963); W. J. Ball and S. R. Landor, *Proc. Chem. Soc.*, 143 (1961); *J. Chem. Soc.*, 2298 (1962).

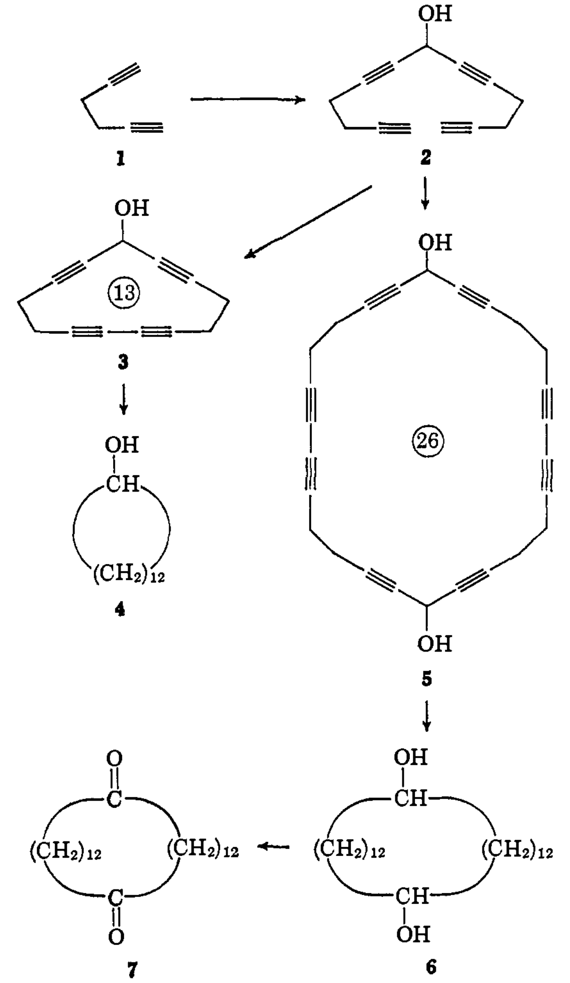
(5) R. A. Raphael and F. Sondheimer, *ibid.*, 120 (1950).

(6) See E. R. H. Jones, L. Skatteböl, and M. C. Whiting, *ibid.*, 4765 (1956).

(7) The benzene serves to keep the products in solution (see R. Wolovsky and F. Sondheimer, *J. Amer. Chem. Soc.*, **87**, 5720 (1965)).

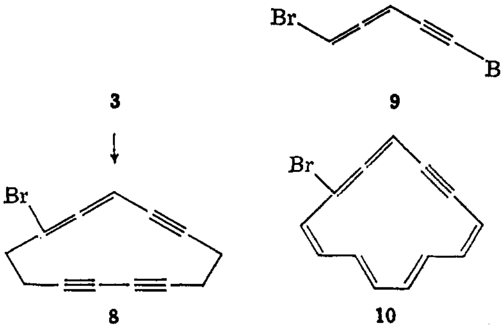
catalytic hydrogenation to the known cyclotridecanol (4).[8]

The oxidative coupling of **2** also gave 4% of the 26-membered ring cyclic dimer **5**. The structure of this compound was confirmed by catalytic hydrogenation to cyclohexacosane-1,14-diol (**6**). Oxidation with chromium trioxide (Jones reagent) then furnished the known cyclohexacosane-1,14-dione (**7**),[9] identified by direct comparison with a sample prepared by another route.[10] The fact that the saturated diol **6** did not show a sharp melting point indicated that this substance (and hence the cyclic dimer **5**) consisted of a mixture of *cis* and *trans* isomers.



The cyclic monomer **3** was subjected to a number of reactions (reduction with lithium aluminum hydride, treatment with methanesulfonyl or *p*-toluenesulfonyl chloride under various conditions), but in no case could a pure product be isolated. Substance **3** was also treated with thionyl chloride in pyridine in order to obtain the corresponding chloro compound, which on reduction with a zinc–copper couple should have given cyclotrideca-1,2-diene-4,8,10-triyne (**8**, H instead of Br).[11] However, the thionyl chloride reaction also did not proceed smoothly.

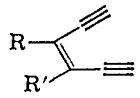
On the other hand, treatment of the cyclic monomer **3** with phosphorus tribromide in tetrahydrofuran led to 20% of a very unstable crystalline substance, to which the bromo allene structure **8** is assigned. The related transformation of α-hydroxyethynyl compounds to the corresponding bromo allenes by means of concentrated hydrobromic acid, with or without cuprous bromide, has been reported[12] (in the present case, reaction of **3** with hydrobromic acid did not give the bromo allene **8**). The structure **8** was established by the analytical and spectral data. The infrared spectrum (KBr) exhibited bands at 2250 (w) and 2210 (w) cm^{-1} (acetylene), as well as at 1948 (m) (allene).[13] The ultraviolet spectrum (ether) showed λ_{max} 258 mμ (ε 19,500);[14] this is in excellent agreement with the data (λ_{max} 254 mμ) reported for 1-bromo-6,6-dimethylhepta-1,2-dien-4-yne (**9**),[12] containing one less alkyl substituent than the main chromophore of **8**. The nmr spectrum (deuteriochloroform) of **8** exhibited a finely split peak at τ 4.54 (allene proton) and a multiplet at 7.2–7.6 (methylene protons).



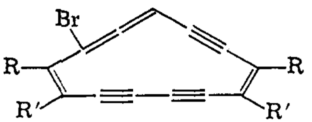
The monocyclic nature of the bromo allene **8** was confirmed by catalytic hydrogenation in ethyl acetate over platinum oxide, which resulted in hydrogenolysis and led mainly to cyclotridecane. The position of the bromine atom in **8** follows from the mechanism of the reaction (see ref 12).

Substance **8** is isomeric with a fully conjugated cyclic allenic bromo hexaenyne (*e.g.*, **10**), and might be convertible to such a system (or its dehydrobromination product) by treatment with base. However, this transformation could not be effected with potassium *t*-butoxide in *t*-butyl alcohol and benzene (at room temperature or at reflux), despite the fact that similar rearrangements have been carried out under these conditions in other cases.[15]

Syntheses of *cis*-hex-3-ene-1,5-diyne (**11a**)[16] and of 1,2-diethynylcyclohexene (**11b**)[17] have been carried out



11a, R = R′ = H
b, R, R′ = $(CH_2)_4$



12a, R = R′ = H
b, R, R′ = $(CH_2)_4$

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[8] *Inter al.*, L. Ruzicka, P. A. Plattner, and H. Wild, *Helv. Chim. Acta*, **28**, 395 (1945).

[9] *Inter al.*, L. Ruzicka, M. Stoll, H. W. Huyser, and H. A. Boekenoogen, *ibid.*, **13**, 1152 (1930).

[10] C. C. Leznoff and F. Sondheimer, *J. Amer. Chem. Soc.*, **89**, 4247 (1967).

[11] The analogous transformation of penta-1,4-diyn-3-ol *via* 3-chloropenta-1,4-diyne to penta-1,2-dien-4-yne has been described: E. R. H. Jones, H. H. Lee, and M. C. Whiting, *J. Chem. Soc.*, 341 (1960).

[12] D. K. Black, S. R. Landor, A. N. Patel, and P. F. Whiter, *Tetrahedron Letters*, 483 (1963).

[13] *Inter al.*, see J. H. Wotiz and D. E. Mancuso, *J. Org. Chem.*, **22**, 207 (1957).

[14] The ε value is approximate, and is based on the weight of material obtained after evaporation of the solvent to dryness.

[15] *Inter al.*, F. Sondheimer and R. Wolovsky, *J. Amer. Chem. Soc.*, **84**, 260 (1962); F. Sondheimer and Y. Gaoni, *ibid.*, **84**, 3520 (1962).

[16] W. H. Okamura and F. Sondheimer, *ibid.*, **89**, 5991 (1967).

[17] G. M. Pilling and F. Sondheimer, unpublished experiments.

recently in these laboratories. It will be of interest to investigate whether these compounds can be converted to the fully conjugated cyclic bromo allenes **12a** and **12b** by reaction sequences analogous to the one described in this paper for the transformation of hexa-1,5-diyne (**1**) to the bromo allene **8**.

Experimental Section

Melting points were taken on a Fisher-Johns apparatus and are uncorrected. Ultraviolet spectra were determined with a Cary 14 spectrophotometer and infrared spectra with a Perkin-Elmer 257 or a Unicam SP-200 spectrophotometer. Nmr spectra were measured with a Perkin-Elmer R-10 or a Varian HA-100 spectrometer, and mass spectra with an AEI MS9 spectrometer. Thin layer chromatography was carried out on silica gel.

Trideca-1,5,8,12-tetrayn-7-ol (2). A solution of ethylmagnesium bromide [prepared from ethyl bromide (5.45 g, 0.05 mol) and magnesium (1.215 g, 0.05 g-atom)] in tetrahydrofuran (40 ml) was added under nitrogen during 15 min to a stirred solution of hexa-1,5-diyne (**1**)[5] (3.9 g, 0.05 mol) in tetrahydrofuran (70 ml). The mixture was stirred for 2 hr, and a solution of ethyl formate (1.85 g, 0.025 mol) in tetrahydrofuran (40 ml) was then added during 30 min. The mixture was stirred for a further 16 hr, and the complex was then decomposed by addition of saturated ammonium chloride solution. Ether was added, and the ether layer was washed with dilute hydrochloric acid and saturated sodium chloride solution. The dried ether extract was evaporated, and the oily residue was repeatedly extracted with boiling hexane (total volume, 3–4 l.). Concentration of the hexane solution and cooling in Dry Ice–acetone yielded the alcohol **2** (1.04 g, 23%) as needles, mp 58–60°. Recrystallization from aqueous ethanol gave a pure sample, mp 60–61°; $\lambda_{max}^{CHCl_3}$ 3560 (OH), 3300 (HC≡), and 2290, 2230, 2120 ($C{\equiv}C$) cm^{-1}; nmr spectrum ($CDCl_3$), 1 H singlet at τ 4.83 (>C*H*OH), 1 H singlet at 7.20 (O*H*), 8 H finely split peak at 7.49 (CH_2), and a 2 H triplet (J = 2 cps) at 7.90 (≡C*H*); mass spectrum, molecular ion at *m/e* 184.086 (calcd for $^{12}C_{13}{}^{1}H_{12}{}^{16}O$: 184.089).

Anal. Calcd for $C_{13}H_{12}O$: C, 84.75; H, 6.57. Found: C, 84.36; H, 6.54.

Oxidation of 2 to Cyclotrideca-2,6,8,12-tetrayn-1-ol (Cyclic Monomer) (3) and Cyclohexacosa-2,6,8,12,15,19,21,25-octayne-1,14-diol (Cyclic Dimer) (5). A solution of **2** (3 g) in ethanol (25 ml) was added to a mixture of cuprous chloride (20 g), ammonium chloride (64 g), and water (170 ml), containing concentrated hydrochloric acid (0.4 ml). The stirred mixture was placed in a water bath at 60°, and after 5 min more ethanol (25 ml) and benzene (100 ml) was added. A vigorous stream of oxygen was then bubbled into the well-stirred mixture, which was kept at 60°. The reaction was allowed to proceed at this temperature for 1 hr, the volume being maintained by periodic addition of benzene. The cooled mixture was extracted with ethyl acetate, and the organic layer was washed with dilute hydrochloric acid and water. The dried extract was evaporated, and the solid residue was triturated with a small volume of ethyl acetate. The residue was powdered and again extracted with a little ethyl acetate. The resulting solid on crystallization from dioxane–pentane gave the cyclic dimer **5** (0.12 g, 4%) as chunky crystals, explosion point *ca.* 215°;[18] λ_{max}^{EtOH} 228 mμ (ϵ 1210), 240 (1140), and 256 (720); ν_{max}^{KBr} 3430 (OH) and 2270, 2230 ($C{\equiv}C$) cm^{-1}.

Anal. Calcd for $C_{26}H_{20}O_2$: C, 85.69; H, 5.53. Found: C, 85.30; H, 5.58.

Evaporation of the combined ethyl acetate extracts and crystallization from ethyl acetate–hexane yielded the cyclic monomer **3** (2.37 g, 80%) as chunky crystals, explosion point *ca.* 112°;[18] λ_{max}^{EtOH} 230 mμ (ϵ 420), 243 (440), and 257 (340); ν_{max}^{KBr} 3370 (OH) and 2280 ($C{\equiv}C$) cm^{-1}; nmr spectrum ($CDCl_3$), 1 H singlet at τ 4.84 (>C*H*OH), 9 H multiplet at *ca.* 7.4 (CH_2 and O*H*); mass spectrum, molecular ion *m/e* 182.073 (calcd for $^{12}C_{13}{}^{1}H_{10}{}^{16}O$: 182.073).

Anal. Calcd for $C_{13}H_{10}O$: C, 85.69; H, 5.53. Found: C, 85.46; H, 5.73.

Cyclotridecanol (4) from 3. The cyclic monomer **3** (130 mg) in ethyl acetate (20 ml) was stirred for 2 hr in hydrogen in the presence of platinum oxide. Removal of the catalyst and solvent, followed by distillation at 80° (bath temperature, 1 mm), yielded cyclotridecanol (81 mg, 75%), mp 56–58°. Preparative tlc gave a sample, mp 59–60° (lit.[8] mp 58.5°); mass spectrum, peak at *m/e* 180 (M − H_2O).

Cyclohexacosane-1,14-diol (6) and Cyclohexacosane-1,14-dione (7) from 5. The cyclic dimer **5** (100 mg) in dioxane (50 ml) was stirred for 2 hr in hydrogen over platinum oxide. Removal of the catalyst and solvent gave cyclohexacosane-1,14-diol (106 mg), mp 83–98°, presumably as a mixture of stereoisomers. This material was dissolved in acetone (5 ml), and oxidized with 8 *N* chromium trioxide (Jones reagent)[19] (2 ml) at 20° for 10 min. Isolation with ether and crystallization from pentane yielded cyclohexacosane-1,14-dione (61 mg, 57% over-all), mp 67–68° (lit.[9] mp 68–69°); $\nu_{max}^{CCl_4}$ 1701 cm^{-1} (saturated C=O); mass spectrum, molecular ion at *m/e* 392. Identity with a sample (mp 66–68°) prepared by another route[10] was established by mixture melting point determination and infrared spectral comparison.

1-Bromocyclotrideca-1,2-diene-4,8,10-triyne (8). Phosphorus tribromide (0.1 ml) was added to a solution of the cyclic monomer **3** (130 mg) in dry tetrahydrofuran (2 ml) at *ca.* −80° (Dry Ice–acetone bath). The bath was removed, and the solution was allowed to stand for 30 min. Pentane was then added, and the solution was washed with water and dried. Examination of an aliquot by tlc showed that three products had been formed. Only the fastest moving could be isolated in pure form. The extract was chromatographed directly on alumina (200 g; Woelm, activity II–III). The fractions eluted with pentane, which contained only one product by tlc examination, were combined and evaporated to dryness in nitrogen under reduced pressure at room temperature. This procedure yielded the bromo allene **8** (35 mg, 20%) as colorless crystals, explosion point *ca.* 65°;[18] ultraviolet, infrared (rapid scan), and nmr spectra, see Discussion section; mass spectrum, molecular ions at *m/e* 246 and 244.

Anal. Calcd for $C_{13}H_9Br$: C, 63.70; H, 3.70. Found: C, 63.54; H, 4.02.

The crystalline compound on standing at room temperature rapidly turned brown and decomposed (the KBr disk used for determination of the infrared spectrum after 30 min no longer showed any allene or acetylene bands). The substance also slowly decomposed in ether solution at *ca.* 0° in the dark, but *ca.* 50% could be recovered after 3 days.

Hydrogenation of 8. The bromo allene **8** (25 mg) in ethyl acetate (10 ml) was stirred for 2 hr in hydrogen over platinum oxide. The catalyst and solvent was removed, and the residue was subjected to preparative tlc. The liquid (15 mg) eluted with pentane showed peaks in the mass spectrum at *m/e* 260, 258, and 182 (ratio *ca.* 1:1:20), indicating it to be mainly cyclotridecane (molecular ion 182) admixed with a small amount of 1-bromocyclotridecene (molecular ions at *m/e* 260, 258).

Acknowledgment. C. C. L. is indebted to the National Research Council of Canada for the award of a Postdoctoral Overseas Fellowship, 1965–1967.

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(18) Placed on a block on an open cover slide just below this temperature; only gradual decomposition occurred when the melting point was determined in the usual way.

(19) *Inter al.*, K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946); P. Bladon, J. M. Fabian, H. B. Henbest, H. P. Koch, and G. W. Wood, *ibid.*, 2402 (1951); R. G. Curtis, I. M. Heilbron, E. R. H. Jones, and G. F. Woods, *ibid.*, 457 (1953).