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SYNTHESIS OF A [18]ANNULENO[18]ANNULENE

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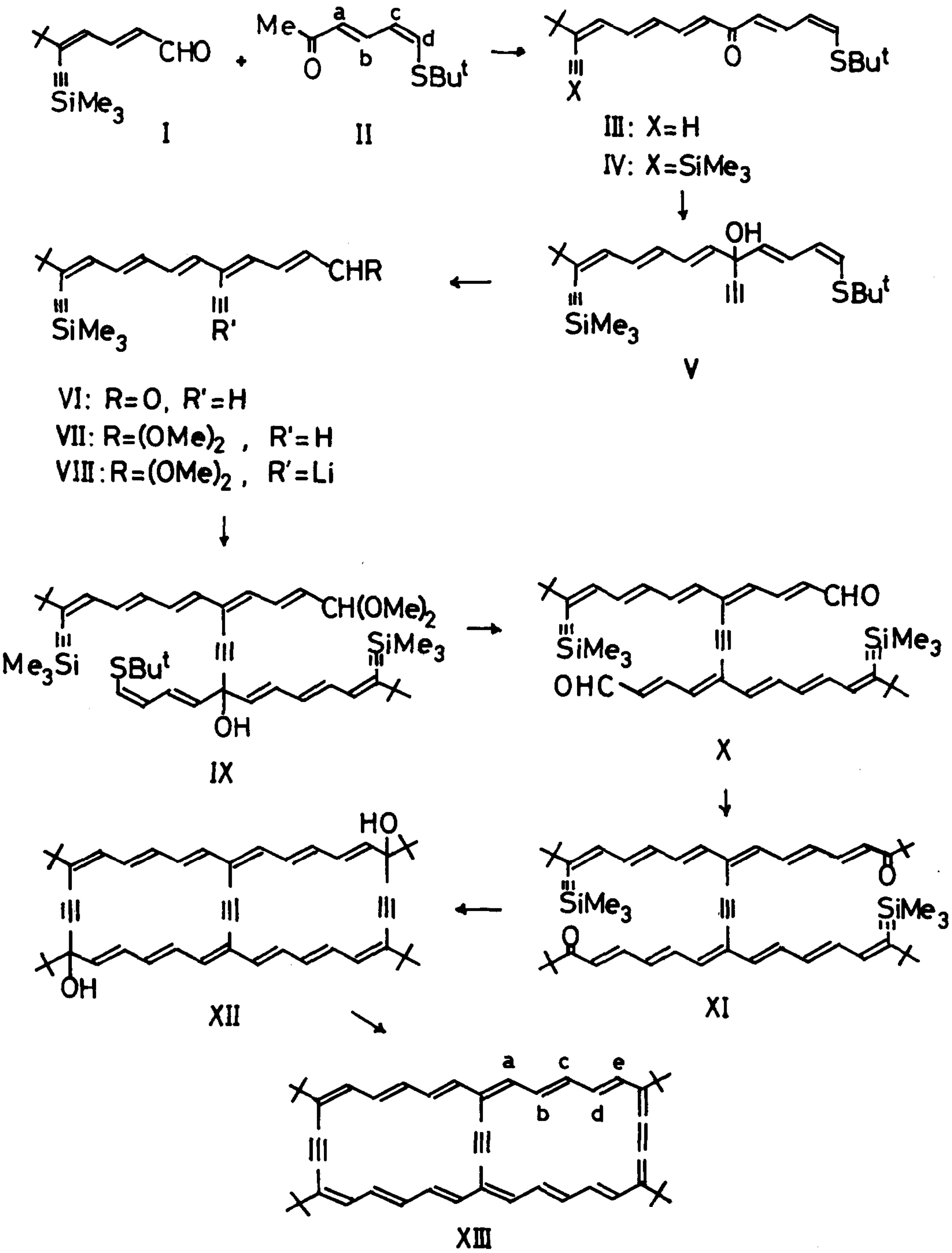
Recently bicyclic systems consisting of two fused annulene rings (annulenoannulenes) have received considrable attention. We have reported the synthesis of tetra-*t*-butylhexakisdehydro[12.12.4][18]annuleno[18]annulene (1) and tetra-*t*-butyltrisdehydro[10.10.2][14]annuleno[14]annulene (2) consisting of two tetrakisdehydro[18]- and bisdehydro[14]annulenes, respectively. Also the synthsis of annulenoannulenes made up of two ortho fused bisdehydroannulene derivatives has been reported by T. M. Cresp and F. Sondheimer (3).

We have extended our work to the synthesis of trisdehydro[4m-2.4n-2.2]-[4n+2]annuleno[4m+2]annulenes. In this communication, we wish to report the synthesis of trisdehydro[14.14.2][18]annuleno[18]annulene (m=n=4, XIII) and the synthesis of trisdehydro[14.10.2][14]annuleno[18]annulene (m=3, n=4) will be reported in the following paper.

The addition of *t*-butylmercaptan (4) to hexen-5-yn-2-one (5) in ethanol in the presence of Triton B yielded 6-*t*-butylthio-3,5-hexadien-2-one (II, pale yellow needles, mp 58.7∿59.5°C, 70%, NMR(60 MHz, CCl_4): H^a τ 4.05 (d, J_{ab}=15); H^b 2.72 (q, J_{ab}=15, J_{bc}=10); H^c 3.84 (t, J_{bc}=10); H^d 3.42 (d, J_{cd}=10); CH_3 7.81 (s); *t*-Bu 8.61 (s)). The *cis*-configuration of 5,6-double bond was revealed by the NMR spectroscopy. Product of the aldol condensation of trimethylsilyl derivative of diennye aldehyde (I) (6) with II was chromatographed on silica gel (Merck), and eluted with ether-benzene (3:97) to give slightly crude pentaenyne ketone (III). The ketone (III) was treated with lithium diethylamide at -82°C in tetrahydrofuran and then with trimethylchlorosilane to yield the trimethylsilyl derivative (IV, yellow cryst., mp 114.0∿114.7°C (dec.), M^+ 400, 58% based on II, NMR(100 MHz, $CDCl_3$): olefinic τ 2.13∿3.82 (m); *t*-Bu 8.57 (s), 8.84 (s); $SiMe_3$ 9.75 (s)). The ethynyl alcohol (V) obtained by the reaction of IV with lithium acetylide in tetrahydrofuran (8) was treated without isolation with an aqueous sulfuric acid to give the aldehyde (VI, orange cryst., mp 105.3∿106.7°C (de.), M^+ 336, 83%, NMR(60 MHz, CCl_4): CHO τ 0.34 (d); olefinic 2.18∿3.88 (m); $-C{\equiv}CH$ 6.34 (s); *t*-Bu 8.84 (s); $SiMe_3$ 9.75 (s)). The dimethyl acetal (VII) obtained from VI in the usual way was converted into lithio derivative (VIII) on treatment with butyllithium in tetrahydrofuran at -7∿-8°C.



The lithio derivative (VIII) was allowed to react with the trimethylsilyl ketone (IV). Treatment of the product (IX) without isolation with an aqueous sulfuric acid gave dialdehyde (X, orange needles, mp 162.5 163.1°C (dec.), M^+ 646, 56%, NMR(100 MHz, $CDCl_3$): CHO τ 0.37 (d, J=8, 2H); olefinic 2.3∿2.8 (m, 14H); *t*-Bu 8.85 (s, 18H); $SiMe_3$ 9.83 (s, 18H)). The reaction of caranion derived from diethyl 3,3-dimethyl2-oxo-butylphosphonate (tBuCOCH$_2$(O)P(OEt)$_2$) on treatment with sodium hydride in dimethoxyethane (9) with the dialdehyde (X) gave bis-trimethylsilyl diketone (XI, orange cryst., mp 181.0∿181.4°C, M^+ 810, 65%, NMR(100 MHz, $CDCl_3$): olefinic τ 2.60∿3.68 (m); *t*-Bu 8.82 (s); $SiMe_3$ 9.84 (s)). A solution of the diketone (XI) in tetrahydrofuran was added to a suspension of potassium hydroxide in liquid ammonia. The bicyclic glycol (XII, orange yellow cryst., mp >280°C (dec.), M^+ 666, 69%, NMR(100 MHz, acetone-d_6-CS_2 (1:1)): olefinic τ 2.69∿4.06 (m); OH 5.93 (s); *t*-Bu 8.82 (s), 8.94 (s)) was formed accompanying the cleavage of the trimethylsilyl groups (2). A diluted solution of the bicyclic glycol (XII) in dichloromethane-tetrahydrofuran (20:1) was added to a stirred solution of stannous chloride dihydrate in concentrated hydrochloric acid at *ca.* -10°C resulting in a deep green solution. The reaction mixture was worked up to give crude deep green crystals which were dissolved in tetrahydrofuran and chromatographed on alumina (Woelm, Super I). Elution with the same solvent gave pure 7,10,22,25-tetra-*t*-butyl-8,23,30-trisdehydro-[14.14.2][18]annuleno[18]annulene (XIII, deep green cryst., mp >280°C (dec.), M^+ 632, 89%) (10).

The annulenoannulene (XIII) was found to be rather sparingly soluble and fairly stable compound. The periphery of XIII is 30π-electron system. However, the corresponding monocyclic 3,15,18,30-tetra-*t*-butyl-1,16-bisdehydro[30]-annulene (11) has been found to be weakly diatropic and highly unstable. The electronic spectrum of XIII showed close similarity with that of analogous trisdehydro[10.10.2][14]annuleno[14]annulene (3), except for a bathochromic shift in XIII (For the absorption curves of XIII and related compounds, see the following paper). A strong diatropicity of the annulenoannulene (XIII) was revealed by the NMR spectrum shown in the figure. The NMR parameters are summarized in the table.

Table. The 100 MHz NMR Parameters of XIII
τ-Values in $CDCl_3$

H^a	0.17 (d, J=14);	H^c	0.29 (t, J=13);	H^e	0.83 (d, J=12)
H^b	11.07 (dd, J=13, 14)	H^d	11.90 (dd, J=12, 13)		
t-Bu		8.13 (s)			

The most remarkable characteristics of the NMR spectrum of XIII is the gradual high-field shift of all signals as the distance from the central bridge to the respective protons is increased. The NMR spectral characteristics will be

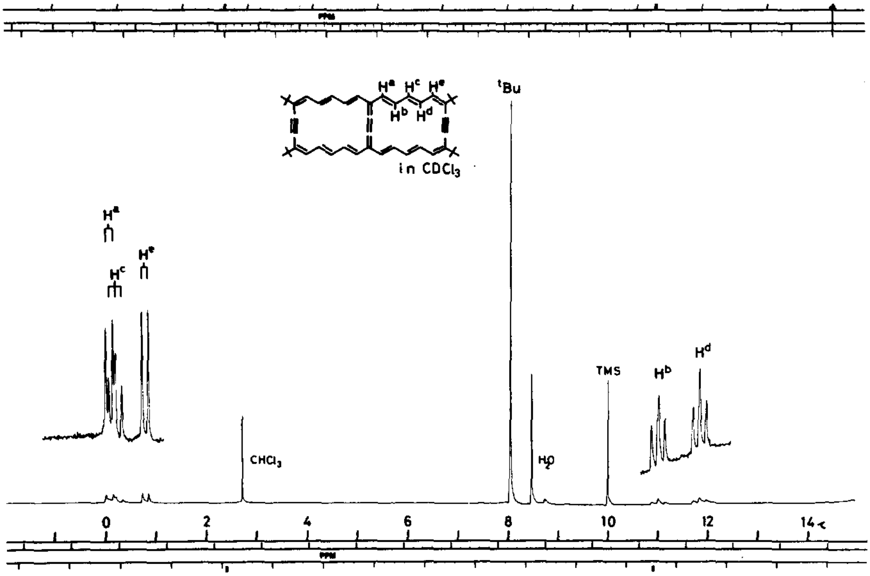


Fig. 100 MHz NMR spectrum of XIII in $CDCl_3$

discussed elsewhere in comparison with those of the other members of this type of annulenoannulenes.

References and Notes

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