

SYNTHESIS OF A [14]ANNULENO[18]ANNULENE

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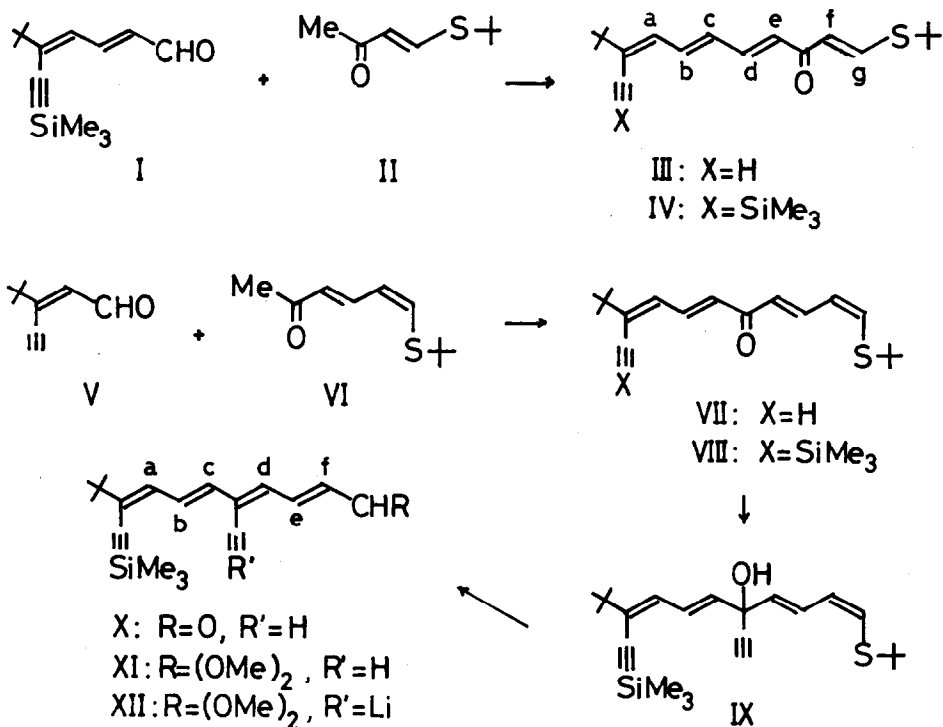
In the previous papers, we have reported the synthesis of annulenoannulenes consisting of two same size 'acetylene-cumulene'-dehydroannulenes, *i.e.*, tetra-*t*-butylhexakisdehydro[12.12.4][18]annuleno[18]annulene (1), tetra-*t*-butyltrisdehydro[10.10.2][14]annuleno[14]annulene (2) and tetra-*t*-butyltrisdehydro[14.14.2][18]annuleno[18]annulene (3).

Because the NMR spectral behavior of these 'acetylene-cumulene'-annulenoannulenes seemed to afford fundamental informations on the induction of diamagnetic ring current in bicyclic system, we have decided to prepare annulenoannulenes of this series consisting of two different (4n+2)-membered rings. The sole instance of this type is an ortho fused [14]annuleno[18]annulene reported recently by T. M. Cresp and F. Sondheimer (4).

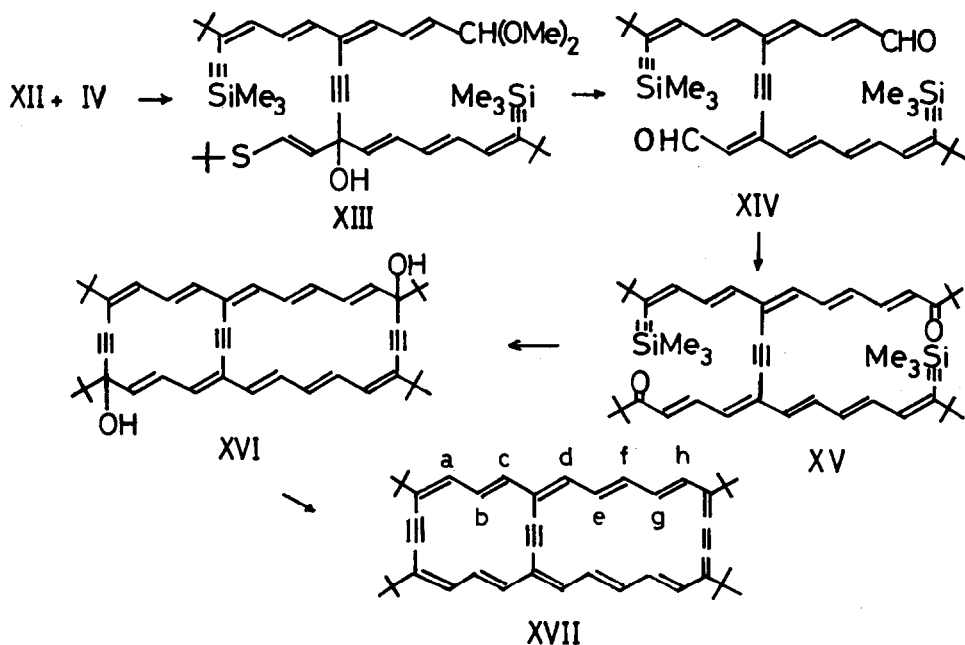
This communication is concerned with the synthesis of trisdehydro[14.10.2]-[14]annuleno[18]annulene (XVII).

The product of the aldol condensation of methyl vinyl ketone (II) (2) with the trimethylsilyldienyne aldehyde (I) (5) was chromatographed on alumina (Merck, Akt. II-VIII) and eluted with hexane-benzene to yield slightly impure tetraenyne ketone (III, orange red liquid, 82%). The ketone (III) in tetrahydrofuran was treated successively with lithium diethylamide at -78°C and trimethylchlorosilane to give trimethylsilyl derivative (IV, pale yellow needles, mp 107.5~109.5°C, M^+ 374, 61%, NMR(100 MHz, $CDCl_3$): H^g τ 2.14 (d, J=15, 1H); H^b or H^d 2.64 (dd, J=11,15, 1H); H^d or H^b 2.86 (dd, J=11,15, 1H); H^f 3.46 (d, J=15, 1H); H^c 3.55 (dd, J=11,15, 1H); H^a 3.59 (d, J=11, 1H); H^e 3.72 (d, J=15, 1H); *t*-Bu-S 8.75 (s, 9H); *t*-Bu-C 8.84 (s, 9H); $SiMe_3$ 9.75 (s, 9H)). The aldol condensation of the enyne aldehyde (V) (7) with 6-*t*-butylthio-3,5-hexadien-2-one (VI) (3) yielded tetraenyne ketone (VII, orange red liquid, M^+ 302, 91%, NMR(60 MHz, CCl_4): olefinic τ 2.15~3.93 (m, 7H); $-C\equiv CH$ 6.46 (s, 1H); *t*-Bu-S 8.62 (s, 9H); *t*-Bu-C 8.83 (s, 9H)). The ketone (VII) in tetrahydrofuran was treated at -60°C with lithium diethylamide and then with trimethylchlorosilane to give VIII (orange red liquid, M^+ 374, 79%, NMR(60 MHz, CCl_4): olefinic τ 2.14~3.87 (m, 7H); *t*-Bu-S 8.62 (s, 9H); *t*-Bu-C 8.84 (s, 9H); $SiMe_3$ 9.75 (s, 9H)). The product (IX) obtained by the reaction of VIII at -60°C with lithium acetylide in tetrahydrofuran (8)

was mixed without isolation with 2N sulfuric acid to yield tetraene aldehyde (X, yellow cryst., mp 115.0~115.5°C, M^+ 310, 81%, NMR(100 MHz, $CDCl_3$): CHO τ 0.34 (d, $J=8$, 1H); H^b or H^e 2.31 (dd, $J=11,15$, 1H); H^e or H^b 2.48 (dd, $J=11,15$, 1H); H^a or H^d 3.35 (d, $J=11$, 1H); H^d or H^a 3.56 (d, $J=11$, 1H); H^c 3.61 (d, $J=15$, 1H); H^f 3.76 (dd, $J=8.15$, 1H)). Dimethyl acetal (XI, yellow cryst., mp 52.5~54.5°C,



M^+ 356, 97%) obtained from X in the usual way was converted into the lithio derivative (XII) on treatment at *ca.* -10°C with butyllithium in tetrahydrofuran. A solution of IV in tetrahydrofuran was added at -10~-15°C into the solution of XII. To the stirred reaction mixture containing XIII was added 2N sulfuric acid. Chromatography of the product on silica gel (Merck) followed by elution with benzene-ether (98:2) yielded dialdehyde (XIV, yellow cryst., mp 116.0~118.5°C, M^+ 594, 68%, NMR(100 MHz, $CDCl_3$): CHO τ -0.24 (d, $J=8$, 1H), 0.34 (d, $J=8$, 1H); olefinic 2.22~3.80 (m, 12H); *t*-Bu 8.82 (s), 8.83 (s) (18H); SiMe₃ 9.81 (s), 9.88 (s) (18H)). The reaction of the dialdehyde (XIV) with the carbanion derived from diethyl 3,3-dimethyl-2-oxo-butylphosphonate (*t*-BuCOCH₂(O)P(OEt)₂) (2,9) on treatment with lithium yielded diketone (XV, orange cryst., mp 180.0~180.5°C, 57%, NMR(100 MHz, $CDCl_3$): olefinic τ 2.00~3.72 (m, 16H); *t*-Bu 8.83 (s), 8.84 (s) (36H); SiMe₃ 9.82 (s), 9.92 (s) (18H)). A solution of XV in tetrahydrofuran was added to a suspension of potassium hydroxide in liquid ammonia. The crude crystals obtained by working up the reaction mixture were passed through a short column of alumina (Merck, Akt. II~III) to give bicyclic glycol (XVI, brownish



yellow cryst., mp $>270^{\circ}\text{C}$ (dec.), 88%). A solution of XVI in ether was mixed at -55°C with a solution of stannous chloride dihydrate in the same solvent saturated with hydrogen chloride. Deep violet solid obtained on working up the reaction mixture was dissolved in dichloromethane and chromatographed on alumina (Woelm, Super I) to give 7,10,20,23-tetra-*t*-butyl-8,21,23-trisdehydro[14.10.2]-[14]annuleno[18]annulene (XVII, deep violet cryst., mp $>280^{\circ}\text{C}$ (dec.), 90%).

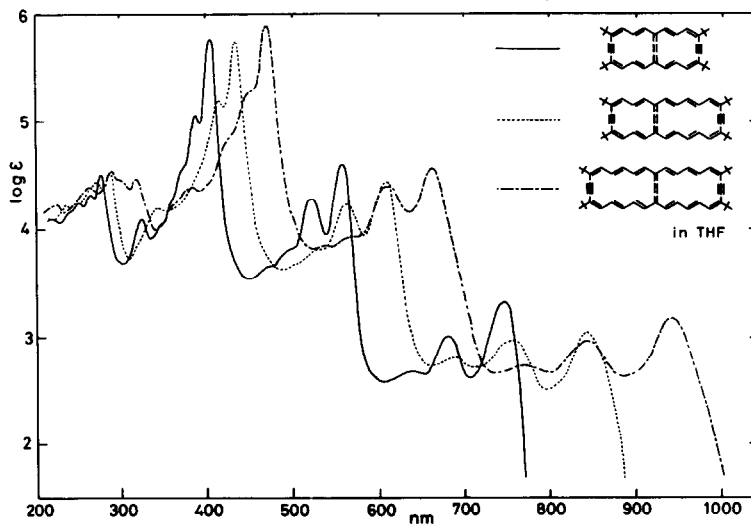


Fig. Electronic spectra of XVII and related annulenoannulenes in THF.

Table. 100 MHz NMR Parameters of XVII in CDCl_3 (τ -value)

		Outer-H	Inner-H	t-Bu
[14]-membered ring	H ^a	0.37 (d, J=13.5, 2H)	H ^b 13.19 (dd, J=13.5, 14.5, 2H)	7.98 (s, 36H)
	H ^c	-0.10 (d, J=14.5, 2H)		
[18]-membered ring	H ^d	0.26 (t, J=14.5, 2H)	H ^e 10.30 (dd, J=13.5, 14.5, 2H)	8.11 (s, 36H)
	H ^f	0.48 (t, J=13.5, 2H)	H ^g 11.24 (dd, J=12.5, 13.5, 2H)	
	H ^h	1.00 (d, J=12.5, 2H)		

The annulenoannulene (XVII) was found to be a quite stable compound in contrast to the corresponding tetra-*t*-butylbisdehydro[26]annulene (10) which had been found to be a quite unstable. XVII forms 1:1 CT complex (deep green cryst., mp >280°C (dec.)) with 2,4,7-trinitrofluorenone.

As illustrated in the figure, the annulenoannulene (XVII) showed an electronic spectrum closely related with those of this series of annulenoannulenes. The NMR parameters summarized in the table revealed that the annulenoannulene (XVII) is strongly diatropic. The most remarkable feature of the NMR spectrum is the gradual high-field shift of outer protons as the distance from the bridge is increased. The same trend is observed in the chemical shifts of inner protons in the 18-membered ring. It should be also noted that the signal of inner protons in the 14-membered ring appeared in a much higher field as compared with those of the 18-membered ring. These facts seem to be difficult to understand if the ring current of the annulenoannulene is confined to the periphery.

The NMR spectral characteristics of this series of annulenoannulenes will be discussed elsewhere in near future.

References and Note

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