Tetra-t-butyldidehydro[22]annulene

By Masahiko Iyodo and Masazumi Nakagawa*

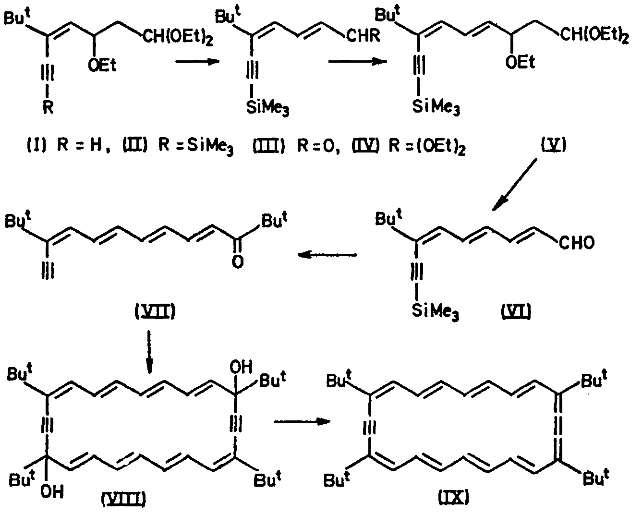
(*Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan*)

Summary The synthesis of aromatic 3,11,14,22-tetra-t-butyl-1,12-didehydro[22]annulene by reductive dehydroxylation of cyclodocosaoctaenediynediol is described.

We recently reported the cyclic dimerization of polyenynic ketones by the Favorskii reaction and the conversion of the resulting cyclic glycols into didehydro-[14]-[1] and -[18]-annulenes.[2] An analogous reaction sequence has been applied to the synthesis of tetra-t-butyldidehydro[22]-annulene (IX).

The ether acetal (I)[3] in tetrahydrofuran was treated with ethylmagnesium bromide and then with chlorotrimethylsilane at room temperature. Distillation of the product gave the trimethylsilyl derivative (II) (92%). The latter was treated with aqueous acetic acid containing sodium acetate to give the trimethylsilyldienyne aldehyde (III) (89%), [2,4-dinitrophenylhydrazone, m.p. 201—203° (dec.)] which was converted into the diethyl acetal (IV) (94%) by the usual method. The reaction of ethyl vinyl ether with (IV) in benzene in the presence of BF_3-etherate[4] afforded

(V) (86%). Treatment of (V) with acetic acid-sodium acetate gave (VI) (87%), (2,4-dinitrophenylhydrazone, m.p. 208—211°). Condensation of pinacolone with (VI) under alkaline conditions afforded the tetraenynic ketone (VII) m.p. 133·5—134·0° (60%), accompanyied by hydrolysis of the protective group. A solution of (VII) in tetrahydrofuran was added to a suspension of powdered potassium hydroxide in liquid ammonia to yield the 22-membered cyclic glycol (VIII) as a mixture of diastereomers which could be separated into (VIIIa) m.p. 252° (dec.), (31%), and (VIIIb) m.p. 220—221°, (58%) on chromatography on alumina. The two compounds gave identical u.v. and n.m.r. spectra, but a slight difference was observed in the i.r. spectra.



Finely powdered tin(II) chloride dihydrate was added to a suspension of the cyclic glycol (VIIIa—b) in ether containing hydrogen chloride at −60° under a nitrogen atmosphere. The resulting dark-violet solution was worked-up in the usual way and the product chromatographed on alumina to give tetra-t-butyldidehydro[22]annulene (IX), dark-violet crystals, m.p. *ca.* 230° (dec.) (94%), M^+ 506. Calc. mol. wt., 506·8]. Hydrogenation of (IX) in ethyl acetate–acetic acid over a platinum catalyst at −15– −20° afforded tetra-t-butylcyclodocosane as a mixture of stereoisomers (92%), M^+ 532, m.p. 104—112° and m.p. 91—95°. The annulene (IX) gave a 1:1 π-complex with trinitrofluorenone, m.p. *ca.* 260° (dec.)†. The u.v. spectrum of (IX) in tetrahydrofuran resembled closely that of tetra-t-butyltetradehydro[22]annulene.[3] The n.m.r. spectrum of (IX) clearly indicates the aromatic nature and conformational stability of the didehydro[22]annulene system.

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† The elemental analyses, except for unstable free aldehydes (III) and (IV), n.m.r., i.r., and mass spectra for all new compounds were consistent with the assigned structures.

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[4] *Cf.*, R. Rüegg, M. Montavon, G. Ryser, G. Saucy, U. Schwiter, and O. Isler, *Helv. Chim. Acta*, 1959, **42**, 854, and preceding papers.

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