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SYNTHESIS OF o-ETHYNYLBENZALDEHYDE AND AN APPROACH TO DIBENZO-[18]ANNULENE

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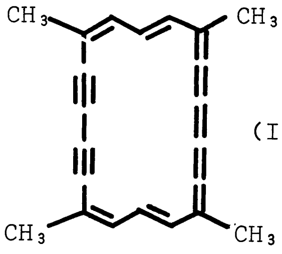
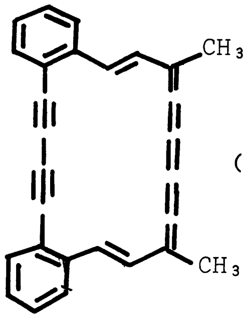
A convenient synthesis of o-ethynylbenzaldehyde (VIII) has been developed. An approach to dibenzo[18]annulene from VIII has also been described.

In 1968, one of the authors (J.O.) reported the synthesis and its aromatic properties of 1,5,10,14-tetramethyl-6,8,15,17-tetradehydro[18]annulene(I).$^{1)}$ It promted us to synthesize the corresponding dibenzo[18]annulene(II) in order to realize the effect of annelation of benzene nuclei on the conjugated 18-membered ring system containing a diacetylene and a hexapentaene linkages.



(I)

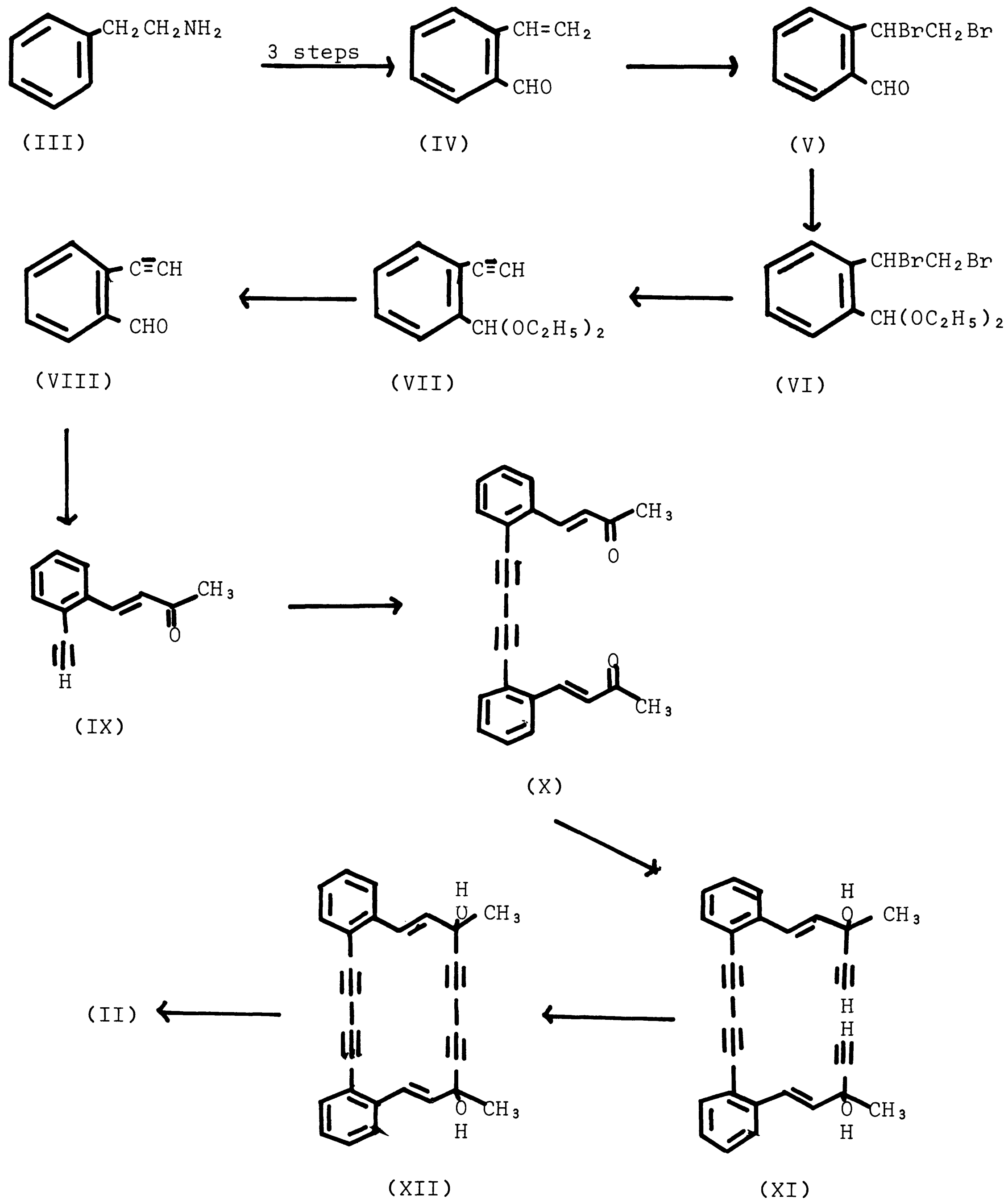


(II)

For this aim the synthesis of o-ethynylbenzaldehyde(VIII) was required, and VIII appeared to be a valuable intermediate for other conjugated macrocyclic compounds containing fused benzene nuclei.

We now describe a convenient synthesis of VIII, and an approach to [a,m]dibenzo-5,10-dimethyl-6,8,15,17-tetradehydro[18]annulene(II).

o-Vinylbenzaldehyde(IV) was prepared by three steps from phenethylamine(III) as described by Dale et al.$^{2)}$ The reaction of IV with 1 molar equivalent of bromine gave o-(1,2-dibromoethyl)benzaldehyde(V) [white cubes, m.p.78∿79°C, Found:C,37.17; H,2.69%. Calcd.for $C_9H_8OBr_2$:C,37.02;H,2.76%] in a 74% yield,which was converted



with triethyl orthoformate in the presence of p-toluenesulfonic acid into diethyl acetal(VI) in an 88% yield.

Dehydrobromination of VI by potassium hydroxide in boiling methanol gave acetylenic acetal(VII), which after removal of the protecting group under acidic condition afforded the expected o-ethynylbenzaldehyde(VIII) [white needles, m.p. 60.0∿60.5°C, Found:C,82.80;H,4.58%. Calcd.for C_9H_6O:C,83.06;H,4.65%. IR:3250

(-C≡CH), 2090(-C≡C-), 1760(>C=O) cm^{-1}. NMR in $CDCl_3$[a]: -0.47 s (1H) aldehyde, 6.6 s (1H) ethynyl, 1.85∿2.55τ m (4H) aromatic].

Conversion of VIII to II according to the reaction sequence developed in the synthesis of tetradehydro[18]annulene(I)[1] was attempted.

Condensation of VIII with acetone gave the ketone (IX) [pale yellow cubes, m.p.106∿107°C] in a 56% yield, which was oxidatively coupled to yield diketone (X) [yellow cubes, m.p.144∿145°C, Found:C,84.93;H,5.26%. Calcd.for $C_{24}H_{18}O_2$: C,85.18;H,5.36%] in an 80% yield by use of cupric acetate in pyridine-methanol.[3] The reaction of the diketone (X) with lithium acetylide ethylenediamine complex in tetrahydrofuran gave diethynyl glycol (XI) in a 63% yield.[4]

Intramolecular oxidative coupling of the glycol (XI) was performed under a high dilution condition using ether as an entraining agent by Eglinton's method.[3] Cyclic glycol (XII) [pale yellow cubes, m.p. ca. 160°C (decom.)][b] was obtained after chromatographic purification on alumina in a 33% yield.

In the event, the dehydroxylative reaction of cyclic glycol (XII) could be effected by use of stannous chloride in concentrated hydrochloric acid, though only in poor yield.[c] Rapid color change of the resulting red oil seemed to reflect the unstable nature of the annelated annulene (II). The substance could be kept at room temperature only in relatively dilute solution for less than half an hour. Accordingly, all attempts to obtain II in the neat state or in concentrated solution resulted in decomposition, and it was not possible to determine

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a). T.M.S. was used as an internal standard. The s, d and m are the abbreviation of singlet, doublet and multiplet, respectively.

b). Its structure was determined by IR, NMR and mass spectra [M^+=388, Calcd. for $C_{28}H_{20}O_2$:388.44], although the elemental analysis gave unsatisfactory result. The authors wish to thank Prof. M. Nakagawa in Osaka university for mass spectra measurement.

c). The full hydrogenation of the reaction product over platinum catalyst in ethyl acetate gave the brownish mixtures, and significant results were not obtained.

the IR, NMR, UV, or mass spectra clearly.

The UV spectra [λ_{max} (>300mμ) 350 (relative optical density, 0.50), 418 (0.93), 437 (1.00), 510mμ sh in cyclohexane] were similar to that of 1,6-dimethyl-1,6-diphenylhexapentaene [λ_{max} 352 (0.27), 419 (0.60), 443mμ (1.00) in benzene], and it seemed that the product obtained essentially was II.

But in NMR spectrum only multiplet at 2.55 τ (center) was observed probably due to benzene ring protons.

Hence it seems that peripheral conjugation in II does not occur, but we can not discuss the aromaticity of II by these spectral data conclusively.

The extreme unstability of II may be reduced by introduction of substituent groups bulkier than methyl group. The synthesis of phenyl derivative is now under investigation.

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