Tetrahedron Letters No.54 pp.4743-4744, 1969. Pergamon Press. Printed in Great Britain

AN APPROACH TO THE SYNTHESIS OF 1,2-DIALKOXYACETYLENES VIA BENZYNE INTERMEDIATES

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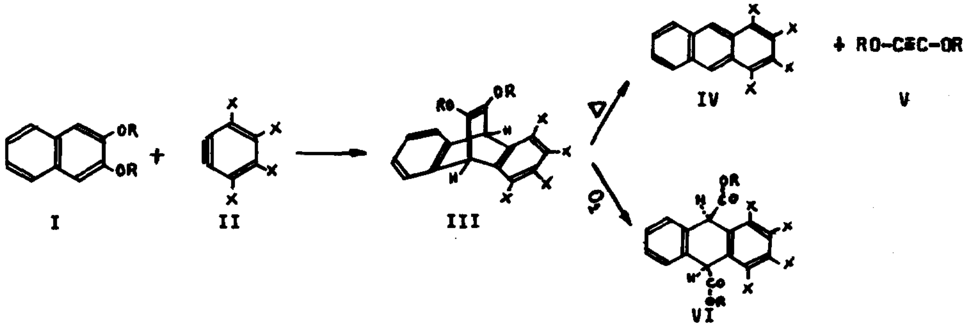
(Received in the U K 29th September 1969; accepted for publication 20th October 1969)



ADDUCTS of type III, which would afford the rather elusive 1,2-dialkoxyacetylenes V[1] by a retrodiene Diels-Alder reaction, have been prepared via benzyne intermediates.

The method is in fact a particular case of the more general synthesis of acetylenes by the "extrusion method"[2] and involves a transfer of the triple bond character of benzyne.[3]

As could be predicted, 2,3-dimethoxynaphtalene (I, R = CH_3) reacts with highly electrophilic benzynes (II) in the 1,4-position since the apparently more favored 2,5-addition[3,4] would destroy aromaticity in both rings (as would also do the 2,3-addition[5]). The reaction of 2,3-dimethoxynaphtalene with benzyne (II, X = H) generated by thermolysis of benzenediazonium carboxylate[6] gives no traces of the adduct III (R = CH_3; X = H). The more electrophilic tetrafluorobenzyne (II, X = F) (from tetrafluorobenzene magnesium chloride[4]) gives the adduct III (R = CH_3; X = F) which was isolated by preparative t.l.c. and characterised by i.r. ($\nu_{max}^{CCl_4}$ 1682, C=C st, and 1500 cm^{-1}, fluorinated aromatic ring) and n.m.r. spectroscopy (τ 6.3, singlet-6H; 4.95, singlet-2H; 2.7 and 2.95, AB system multiplets-4H, in CCl_4 solution), although pure product, free of fluorinated resins, was difficult to separate. However, 20% yield of pure adduct III (R = CH_3; X = Cl) could be obtained by the reaction of 2,3-dimethoxynaphtalene with tetrachlorobenzyne (II, X = Cl) generated according to the method of Heaney[7]: m.p. 169-172°; $\nu_{max}^{CCl_4}$ 1685 cm^{-1} (C=C st); τ 6.3 (singlet-6H), 4.83 (singlet-2H), 2.65 and 2.95 (AB system multiplets-4H) in CCl_4 solution; %C 53.5, %H 3.06 and %Cl 35.44.

Preliminary mass spectrometry studies on adduct III (R = CH_3; X = Cl) have confirmed its structure. In order to obtain physical evidence for thermal extrusion of dimethoxyacetylene (V,R = CH_3) the product was heated at 200° directly in the ion source and the spectrum recorded a few minutes later. The spectrum shows the molecular ion at m/e 400-408 (with the correct isotopic abundances due to the presence of four chlorine atoms); the base peak corresponds at m/e 357-365 (loss of mass 43: CH_3O-C) and the next more intense peak at m/e 314-322 (loss of mass 86 corresponding to 1,2,3,4-tetrachloroanthracene IV, X = Cl), both groups of peaks showing the same chlorine isotopic distribution pattern. The peak at m/e x 86, although it exists, has a very small intensity (5%), whereas the peak at m/e 43 is rather intense (42%). Since the spectrum also shows peaks at m/e 444-452 with the isotopic distribution pattern of four chlorine atoms, we suggest that "methoxycarbyne" rather than dimethoxyacetylene is formed in the probe. Carbynes have recently been generated and shown to add to double bonds with subsequent abstraction of hydrogen[8] , and a similar reaction on the highly nucleophilic double bond of adduct III would explain the presence of peaks at m/e 444-452.

The chemical behaviour of adduct III (R = CH_3; X = Cl or F) is also somewhat surprising and gives further evidence that the double bonded bridge breaks very easily under oxidative conditions. Adduct III (R =CH_3; X =Cl) in the open atmosphere is slowly transformed into a new substance (m.p. 266-268.5°; ν_{max} 1745 cm^{-1}; %C 49.56, %H 3.01, %Cl 32.22) for which the structure of a diester (VI, R = CH_3; X = Cl) is proposed, this would represent a reverse acyloin condensation induced by molecular oxygen.

Further mass spectrometry studies on the products obtained by thermolysis of addcut III (R = CH_3; X = Cl) and trapping experiments in order to get chemical evidence for the formation of dimethoxyacetylene (or other 1,2-dialkoxyacetylenes V,R $\neq$ CH_3) are being carried out and will be published elsewhere.

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