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NOVEL 1,6-CYCLOADDITION PRODUCTS OF DEHYDROBENZENE

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In the course of our study of photochemical decomposition of benzenediazonium o-carboxylate in some solvents (1), we isolated two new products when benzenediazonium o-carboxylate was decomposed thermally in acetone. The structure of these compounds were studied and determined as follows.

Benzenediazonium o-carboxylate, prepared from 5.0 gr. of anthranilic acid, was suspended in acetone and warmed to a temperature which caused gas evolution. After one hour, the gas evolution had almost ceased. From the reaction mixture, we isolated benzoic acid (15%), o-biphenylene (7%) and two new products, i.e., a yellow crystalline product A, mp. 195-196° (350 mg.) and colourless needles B, mp. 200-200.5° (400 mg.).*

The molecular weight determination (found 220) and analytical data (Found; C 69.71%, H 3.82%, N 12.13%) of compound A show that it has a molecular formula $C_{13}H_8O_2N_2$ (Calc.; C 69.64%, H 3.60%, N 12.50%) corresponding to the one composed of each one molecule of dehydrobenzene and benzenediazonium o-carboxylate. This compound was hydrolysed by refluxing with 0.2N aq. sodium hydroxide giving a red crystalline product, mp. 212.5-213°, whose ultraviolet spectrum (λ_{max}^{EtOH} (log. e) 247 (4.03), 328 (4.19), 386 mμ (3.90). Elementary analysis: Found; C 63.88%, H 4.16%, N 11.21%. Calc. for $C_{13}H_{10}O_3N_2$; C 64.46%, H 4.16%, N 11.57%) was similar to that of o-hydroxyazobenzene ($\lambda_{max}^{C_6H_6}$ (log. e) 326-327 (4.27), 387 mμ (3.99).). This observation suggest structure (I) for compound A and this was confirmed by reduction of compound A with sodium hydrosulfite in alkaline medium to anthranilic acid and o-aminophenol in good yield.

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* Before recrystallization, the IR spectrum was quite different from that of purified crystals, especially in C=O region (1707 cm^{-1}, nujol mull). The difference is due to dimorphism.

Investigation of molecular model shows that the boat form (Ia)* is only the possible conformation for compound A, which was supported by spectral data ($\nu^{Chl.}_{max}$ 1755 (nonconjugated ester), 1600, 1477, 1442 cm^{-1}; λ^{EtOH}_{max} (log. e) 243.5 (3.80), $287^{inf.}$ (3.39), 400 mμ (2.85)).

From the analytical data (Molecular weight determination: Rast's method, 299; mass spectrometry, M^+ m/e 300.0903. Elementary analysis; C 75.73%, H 4.26%, N 9.19%), compound B has a molecular formula $C_{19}H_{12}N_2O_2$ (Calc.; C 75.99%, H 4.03%, N 9.33%) which corresponds to the one composed of two molecules of dehydrobenzene and one molecule of benzenediazonium o-carboxylate. Spectral data showed this compound contained one N-H and one ester group.** Alkaline hydrolysis of compound B gave an amorphous acid,*** whose ultraviolet spectrum was very close to that of carbazole-1-carboxylic acid. Furthermore reduction of compound B with lithium aluminium hydride in dry THF furnished to give 1-hydroxymethylcarbazole, mp. 129°, which was identical in every respect to the authentic sample (hitherto unknown compound, elementary analysis, Found; C 79.27%, H 5.74%, N 7.09%. Calc.; C 79.16%, H 5.62%, N 7.10%. $\nu^{Chl.}_{max}$ 3600, 3475, 1625, 1605 cm^{-1}. λ^{EtOH}_{max} (log. e) 236 (4.64), 245.5 (4.44), 259 (4.33), 293 (4.23), 324 (3.61), 336 mμ (3.57).), prepared from carbazole-1-carboxylic acid.*4

The N-N bonding of the starting material being retained, the only conceivable structure for compound B by combining a partial structure (II) with a phenylene residue would be formulated as (III). Spectral data*5 are consistent with this structure.

Mechanism of the formation of this compound is not yet clear but we suggest this might be formed by the reaction of compound A with dehydrobenzene as shown below.*5

The mode of formation of compound A and B is quite interesting because, in our knowledge, this is the first example of 1,6-dipolar addition of dehydrobenzene,*7 and of cycloaddition reaction of benzenediazonium o-carboxylate.

We are greatly indebted to Professor S. Masamune of the University of Alberta for taking mass spectrum of compound B, to Dr. S. Senoh of the Institue of Food Chemistry for taking nmr spectra, and to Professor T. Sakan of our University for discussion of the results.

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* The similar conformation was suggested for compound (IV) (2).

** IR spectrum shows strong N-H and C=O absorptions (3315, 1734 cm^{-1}, nujol mull). In nmr spectrum, one proton signal at δ6.57 ppm. (N-H) disappeared after treatment with deuterium oxide.

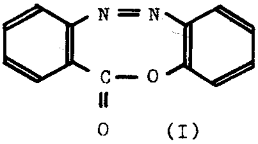
*** This acid was not obtained in pure form.

*4 Quite recently we could isolate o-aminophenol from the reaction mixture in small amount.

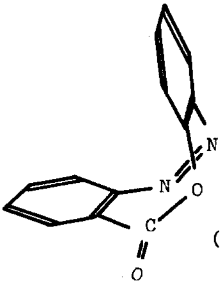
*5 Mass spectrum of compound B will be discussed in the full paper.

*6 It is well known that dehydrobenzene is feasible to be attacked by a lone pair on amines or alcohols.

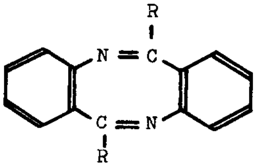
*7 1,2- and 1,4-Cycloaddition (3,4) and 1,3-dipolar addition reactions (5) are familiar to dehydrobenzene. A 1,5-dipolar addition reaction also had been found (6).



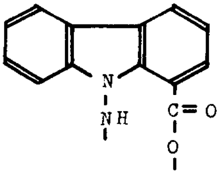
(I)



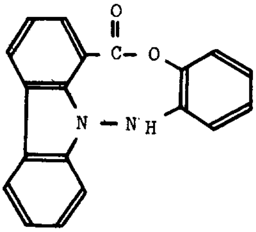
(Ia)



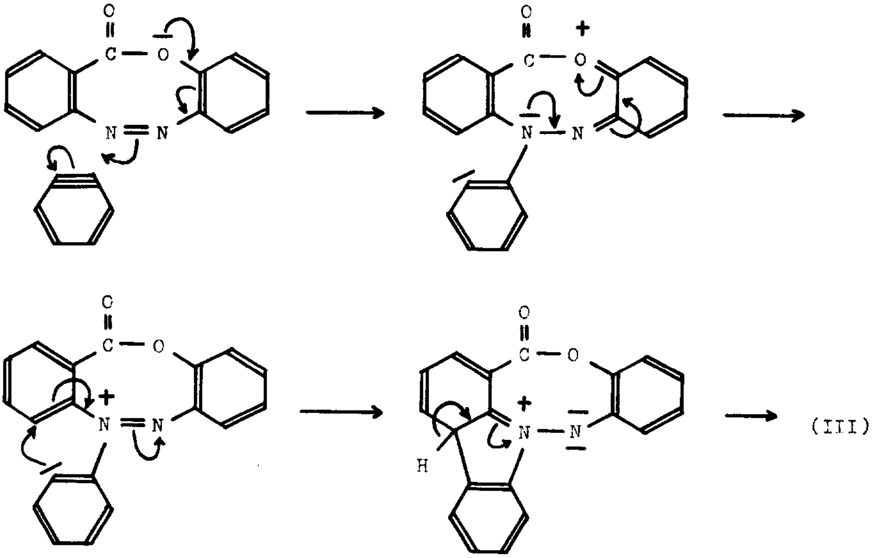
(IV)



(II)



(III)



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