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ON THE REACTION OF DIPHENYLDIAZOMETHANE WITH CO AND CN BONDS

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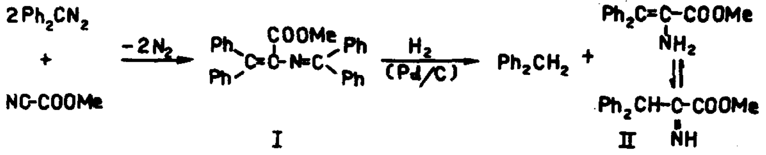
Diphenyldiazomethane (DDM) has been shown, chiefly through the work of Schönberg and co-workers,[1-4] to react with o-quinones and with activated CO double bonds, yielding benzodioxoles resp. epoxides. Little is known about the reaction between DDM and CN triple bonds.

It has now been found that DDM reacts, in the absence of solvent, with some CN bonds, for example with methyl cyanoformate and with trichloroacetonitrile.

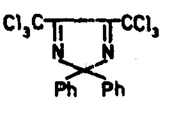
In the former case a mixture of solid products was obtained, and further elaboration allowed to isolate, besides some tetraphenylethylene and benzophenone azine, a yellow compound $C_{29}H_{23}NO_2$, m. p. 130-131°. Its infrared spectrum showed an α,β-unsaturated ester C=O band (1718 cm^{-1}) but no C≡N. Catalytic hydrogenolysis afforded with very good yields diphenylmethane along with a product, m. p. 137-138°, whose analysis and spectrum are consistent with structure II. From these data structure I is suggested for the yellow addition compound. Its formation may eventually occur by an initial attack of the nucleophilic terminal nitrogen atom of DDM on the carbon atom of the nitrile group, similarlyto the mechanism proposed by Schönberg and Junghans[3] for the addition of DDM to ketones. Initial attack of diphenylcarbene seems



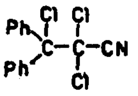
$$2Ph_2CN_2 + NC\text{-}COOMe \xrightarrow{-2N_2} Ph_2C{=}C(COOMe){-}N{=}CPh_2 \xrightarrow[(Pd/C)]{H_2} Ph_2CH_2 + Ph_2C{=}C(NH_2){-}COOMe \rightleftharpoons Ph_2CH{-}C({=}NH){-}COOMe$$

less likely, since the reaction has been carried out in the dark at 10° or less. Studies on the mechanism of the reaction are in progress.

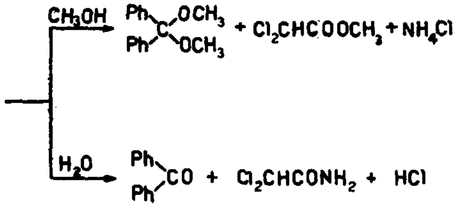
The course of the addition between DDM and trichloroacetonitrile at O-3° is entirely different. From the reaction mixture two principal products could be isolated: (i) a colourless compound, m.p. 168-169°, whose analysis, infrared band (no nitrile band) and alkaline degradation suggested a cyclic structure III, generated by the cycloaddition of a second molecule of the nitrile to the initially formed dipolar intermediate; (ii) a yellow compound, m.p. 39-41°, very unstable, for which structure IV could be assigned on the basis of hydrolysis and alcoholysis reactions:



III



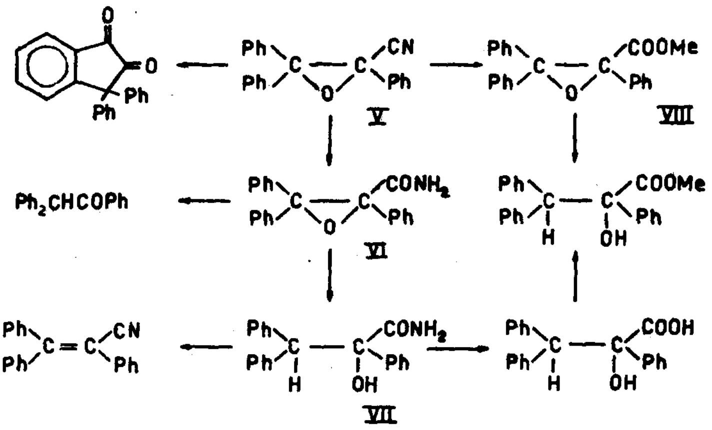
IV



Having ascertained the possibility of the CN triple bond to react with DDM, it appeared interesting to prove the reactivity of the latter towards acyl cyanides RCOCN. Benzonitrile oxide, another 1,3-dipole, is known to react with the CN bond of pyruvonitrile;[5,6] the CO double bond reacts only in a second step.[6]

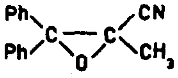
In our hands a mixture of DDM and benzoyl cyanide gave with 90-94 % yield the epoxide V, m.p. 140-141°. Its structure follows from infrared ($\nu_{CN} = 2232\ cm^{-1}$; no carbonyl band) and chemical evidence; some pertinent reactions are summarized below.

Treatment of V with H_2SO_4 led to the known diphenylindandione through epoxide ring cleavage, pinacol rearrangement and following cyclization under the influence of the strong acid. The apoxide ring of V is remarkably stable: treatment with methan. KOH led to the amide VI, m.p. 216-217°, which on catalytic hydrogenation gave the open-chain hydroxy-amide VII, m.p. 216-217°. Heating VI at 110° with conc. HCl afforded the known diphenylacetophenone, whereas dehydration

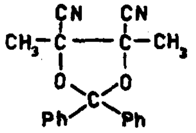


of VII with P_2O_5 yielded 2, 3, 3-triphenylacrylonitrile, identical in every respect with authentic material. Epoxide V on treatment with KCN/MeOH, followed by acidification with H_2SO_4 4 N, furnished the epoxy-ester VIII, m. p. 110-111°, whose structure was demonstrated by catalytic hydrogenation on Pd/C to methyl 2, 3, 3-triphenyllactate, identical with an authentic sample obtained from the free acid by treatment with CH_2N_2. The free acid was also prepared from the amide VII on reaction with isoAmONO.

From the reaction mixture of DDM with an excess of pyruvonitrile two different products were isolated after chromatographic separation: (i) a compound, m p. 79-80°, obtained in 55 % yield, for which the IR spectrum (ν_{CN} = 2247 cm^{-1}; no carbonyl band) and an independent synthesis from benzophenone and 2-chloropropio-



IX



X

nitrile demonstrated a structure IX; (ii) a by-product $C_{19}H_{16}N_2O_2$, m.p. 127° (16 % yield), having possibly the structure X.

Experimental details and further work in the same field will be published elsewhere.

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