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Extrusion of Sulphur in the Cycloaddition of Ynamines to Dehydrodithizone

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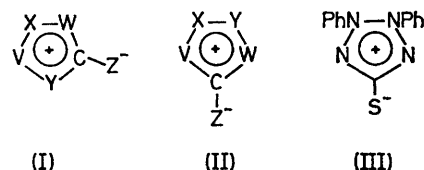(Department of Chemistry, Chelsea College, London SW3 6LX)

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Summary Addition of 1-diethylaminoprop-1-yne to dehydrodithizone yields 3-phenylazo-5-diethylamino-4-methyl-1-phenylpyrazole, whose structure has been established by single crystal X-ray structure analysis; the formation of this compound and that of an analogous product from 1-dimethylamino-2-phenylacetylene is thought to involve the hitherto unknown acyclic valency tautomer of dehydrodithizone.
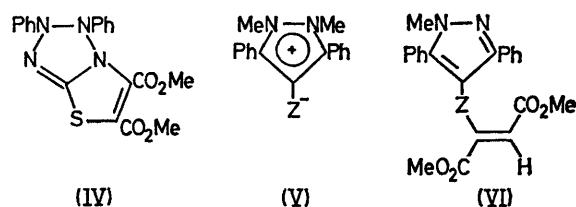
Cycloaddition reactions of mesoionic compounds of type (I) *e.g.* sydnones (I; X = NR, Y = Z = O, V = N, W = CR)[1] and oxazolium 5-oxides (I; X = NR, Y = Z = O, V = W = CR)[2] have been extensively investigated but little is known about the behaviour of systems of type (II) towards dipolarophiles. Dehydrodithizone (III) affords[3] the cycloadduct (IV) with dimethyl acetylenedicarboxylate and analogous products are reported[3] to be formed with enamines. The pyrazolium oxide (Va) and imidate (Vb), on the other hand, yield the demethylated pyrazole derivatives (VIa) and (VIb), respectively, when treated with the acetylenic ester.[4]

We have observed a third mode of addition in the reaction of dehydrodithizone with ynamines. 1-Diethylaminoprop-1-yne gave a mixture of two orange compounds in the ratio 7:1 (65%), which were separated by column and thick-layer chromatography. Mass spectroscopy indicated that each had the composition of a 1:1 adduct minus sulphur and their u.v. - visible, i.r., and n.m.r. (Me, NEt_2, and two N–Ph signals) spectra were almost identical. The major isomer, m.p. 103–104°,† was shown to have a phenylazo-substituent since on reduction with Sn–HCl, followed by basification, it gave aniline and another primary amine, $C_{14}H_{20}N_4$, charac-
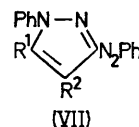

(I) (II) (III)

X, Y, Z = O, S, or NR

V, W = CR or N

(IV) (V) (VI)

a; Z = O

b; Z = N·O_2S·C_6H_4 Me-*p*

(VII)

a; R^1 = NEt_2, R^2 = Me

b; R^1 = Me, R^2 = NEt_2

c; R^1 = NMe_2, R^2 = Ph

d; R^1 = Ph, R^2 = NMe_2

† Satisfactory analytical and spectral data were obtained for all new compounds.

terised as its *p*-toluenesulphonyl derivative, m.p. 204—205°. We considered that the major reaction product was most likely a phenylazopyrazole (VIIa or b); an *X*-ray structure determination showed that it was (VIIa) (see Figure).

The minor product from the dehydrodithizone–diethylaminopropyne reaction, because of its similarity to compound (VIIa), is assigned the isomeric structure (VIIb) and an analogous orange product, m.p. 138—139° (83%), obtained from 1-dimethylamino-2-phenylacetylene, is formulated as either (VIIc) or, less probably, (VIId).
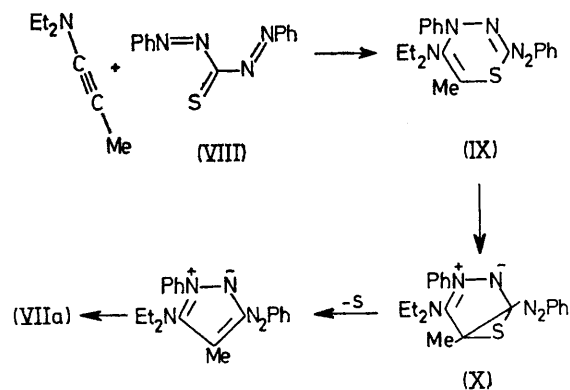
SCHEME

A possible mechanism for the formation of the pyrazole (VIIa) (see Scheme) involves the intermediacy of the unknown acyclic dehydrodithizone valency tautomer (VIII).[5] Its Diels–Alder adduct (IX) to the ynamine could undergo disrotatory cyclisation to the ylide (X), which forms the product by expulsion of sulphur. The process (IX) → (VIIa) is analogous to the formation of benzene derivatives from thiepins.[6]

Crystal data: 3-Phenylazo-5-diethylamino-4-methyl-1-phenylpyrazole (VIIa), $C_{20}H_{23}N_5$; $M = 333.4$; orange-brown monoclinic crystals; $a = 9.817(4)$, $b = 10.003(4)$, $c = 20.326(7)$ Å, $\beta = 113.11(1)°$; $Z = 4$, $D_c = 1.206$ g cm^{-3}; space group $P2_1/c$ (C_{2h}^5, No. 14); μ(Cu-K_α radiation) = 5.9 cm^{-1}.

The structure analysis was based on 1542 unique reflections, $I/\sigma(I) \geqslant 3.0$, recorded over the range $0° \leqslant 2\theta \leqslant 140°$ using a Hilger-Watts Y290 automated four-circle diffractometer and Ni-filtered copper radiation. The intensity data were corrected for Lorentz and polarisation effects but no correction was made for absorption.

The structure was solved by using a method based on the tangent formula[7] for the initial phases of 252 reflections with $|E| > 1.8$ and by Fourier methods thereafter. Full-matrix least-squares refinement with all non-hydrogen atoms treated anisotropically gave a final R value of 0.053.
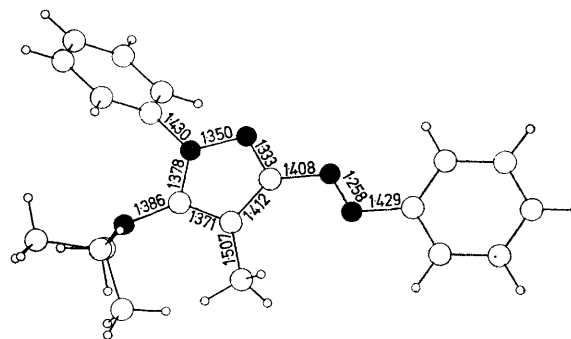

FIGURE. Structure of phenylazo-5-diethylamino-4-methyl-1-phenylpyrazole showing the more important bond lengths; all estimated standard deviations are less than 0.006 Å.

The Figure shows one molecule of the phenylazopyrazole viewed along the *c* axis, together with the more important bond lengths. The pyrazole ring is planar within experimental error. In the azobenzene moiety the nitrogen atom directly attached to the pyrazole ring lies in the plane of the ring whereas the second nitrogen atom is displaced out of this plane by 0.115 Å. The phenyl ring of the azobenzene group is inclined by an angle of 6.0° to the pyrazole ring. The corresponding angle for the remaining phenyl ring is 51.0°.

[1] R. Huisgen, H. Gotthardt, and R. Grashey, *Chem. Ber.*, 1968, **101**, 536.
[2] E. Brunn, E. Funke, H. Gotthardt, and R. Huisgen, *Chem. Ber.*, 1971, **104**, 1562, and earlier papers.
[3] P. Rajagopalan and P. Penev, *J.C.S. Chem. Comm.*, 1971, 490.
[4] G. V. Boyd and T. Norris, *J.C.S. Perkin I*, 1974, 1028.
[5] For the *X*-ray structure of dehydrodithizone, see Q. Fernando and Y. Kushi, *Chem. Comm.*, 1969, 1240, and for an attempt to prepare (VIII), J. W. Ogilvie and A. H. Corwin, *J. Amer. Chem. Soc.*, 1961, **83**, 5023.
[6] D. N. Reinhoudt and C. G. Kouwenhoven, *J.C.S. Chem. Comm.*, 1972, 1233.
[7] P. Main, M. M. Woolfson, and G. Germain, 1971, MULTAN, a Computer Program for the Automatic Solution of Crystal Structure.