Formation of *spiro*[1*H*-Indene-1,2′(3′*H*)-1,3,4-thiadiazoles] in the Cycloaddition of 2-Dialkylaminoindenes to Dehydrodithizone; *X*-Ray Crystal Structure of 3′-Phenyl-5′-phenylazo-2-pyrrolidino-*spiro*[1*H*-indene-1,2′(3′*H*)-1,3,4-thiadiazole]

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Summary Addition of 2-pyrrolidinoindene to dehydrodithizone proceeds with loss of hydrogen to give a novel type of product, 3′-phenyl-5′-phenylazo-2-pyrrolidino-*spiro*[1*H*-indene-1,2′(3′*H*)-1,3,4-thiadiazole], whose constitution was determined by single crystal *X*-ray structure analysis; the formation of this and analogous compounds from 2-piperidino- and 2-morpholino-indene is thought to occur *via* the acyclic valency tautomer of dehydrodithizone.

CYCLOADDITION reactions of dehydrodithizone (I) and related mesoionic compounds, such as pyrazolium-4-oxides[1] and -4-amidates[2] and the corresponding dithiolium,[3] isoxazolium,[2] and isothiazolium[2] betaines, have not been studied extensively. Rajagopalan and Penev[4] obtained 1,3-cycloadducts (II) from dehydrodithizone and electron-poor acetylenes and reported that enamines behaved analogously, yielding compounds of type (III). In contrast, addition of ynamines gives phenylazopyrazoles with extrusion of sulphur.[5] We have now observed yet another kind of product in the reaction of dehydrodithizone with enamines derived from indan-2-one.

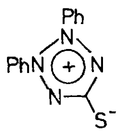
Treatment of dehydrodithizone with 2-pyrrolidino-, 2-piperidino-, or 2-morpholino-indene (IV a—c) in chloroform at room temperature over 24—48 h gave red crystalline products† of m.p. 166—167°, 138—140°, and 170—171°, respectively, in *ca.* 40% yield, whose i.r. and electronic spectra were closely similar. Their n.m.r. spectra contained only signals due to the amine unit, 14 aromatic protons, and one uncoupled olefinic proton; hence the compounds were monodehydro-adducts and formulae of type (III) were ruled out. An *X*-ray structure determination of the pyrrolidino-derivative showed that it was the *spiro*-compound (Va) (see Figure); the other products, because of their similarity to the former, are formulated as (Vb) and (Vc).

A number of mechanisms can be envisaged for the formation of compounds (V); they differ in detail but all involve the acyclic valency isomer (VI) of dehydrodithizone, which was invoked to rationalise the reaction with ynamines.[5] One possibility is attack by the isomer on the enamines to give the dipolar compounds (VII) which then undergo concerted ring-closure and [1,2]-hydride shift to (VIII). Dehydrogenation finally yields the more highly conjugated products.

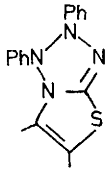
Crystal data: Compound (Va), $C_{26}H_{23}N_5S$; $M = 437\cdot6$; monoclinic, $a = 8\cdot152(5)$, $b = 20\cdot711(12)$, $c = 13\cdot739(8)$ Å, $\beta = 100\cdot42(4)°$, space group $P2_1/c$ (C^5_{2h}, No. 14), $D_c = 1\cdot27$ g cm^{-3}, $Z = 4$, $\mu(\text{Cu-}K_\alpha) = 14\cdot0$ cm^{-1}.

X-Ray intensity data were collected on a Hilger-Watts Y290 automated four-circle diffractometer using Ni-filtered Cu radiation. The structure analysis was based on 1256 independent reflections with $I \geqslant 3\sigma(I)$ and recorded over the range $0° \leqslant 2\theta \leqslant 100°$. The intensity data were corrected for Lorentz and polarisation effects but no correction was made for absorption.

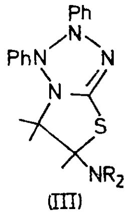
The structure was determined with difficulty using the conventional heavy-atom procedure and has been refined



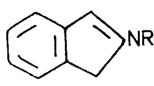
(I)



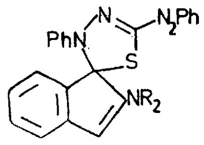
(II)



(III)

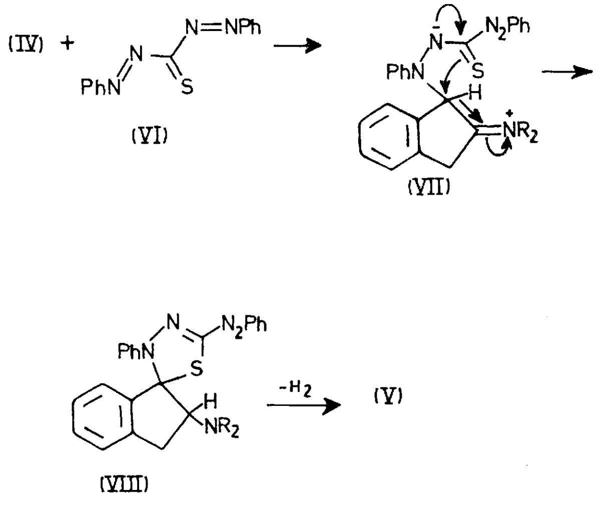


(IV)



(V)

a; NR_2 = pyrrolidino
b; NR_2 = piperidino
c; NR_2 = morpholino



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† Satisfactory analytical data were obtained for all new compounds.

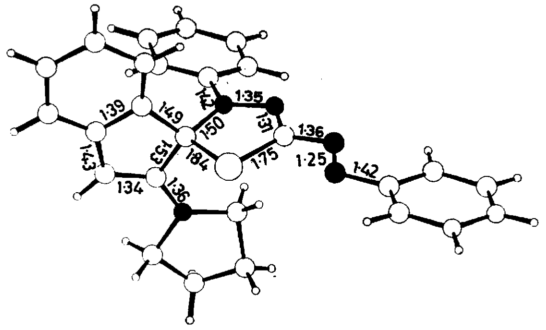

FIGURE. Structure of 3′-phenyl-5′-phenylazo-2-pyrrolidino-*spiro*[1*H*-indene-1,2′(3′*H*)-1,3,4-thiadiazole] showing the more important bond lengths; all estimated standard deviations are less than 0·02 Å. The nitrogen atoms are shaded.

using a partial full-matrix technique to give a *R* value of 0·091 with all non-hydrogen atoms treated anisotropically.

The Figure shows one molecule of the *spiro*-compoind together with the more important bond lengths. The thiadiazole ring is planar within experimental error. The nitrogen atoms of the phenylazo unit lie within 0·05 Å of this plane and are orientated so that the nitrogen atom not directly attached to the thiadiazole ring is only 2·79 Å distant from the sulphur atom. The indene unit is almost planar, the maximum deviation being 0·06 Å for the *spiro*-carbon atom, and the dihedral angle between the least-squares planes defined by the atoms of the thiadiazole ring and the indene unit is 90·5°.

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