Reaction of Dehydrodithizone with Pentacarbonyliron. An Unusual Transformation Involving Carbonyl Insertion

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Summary Dehydrodithizone reacts with pentacarbonyliron to give a 1,3,4-thiadiazole derivative the structure of which was elucidated by *X*-ray crystallography.

In 1956, Murahashi and Horiie[1] reported that 2-phenylindazolone (**1**) was converted into the quinazoline derivative (**2**) by the action of carbon monoxide in the presence of either pentacarbonyliron or octacarbonyldicobalt. The scope of such reactions in heterocyclic chemistry has not been assessed although recently the enneacarbonyldi-iron-induced conversion of an oxazine into an oxazepin has been described.[3]

We wished to determine whether this type of ring expansion [*cf.* (**1**) → (**2**)] could be used for the interconversion of mesoionic ring systems and accordingly we allowed dehydrodithizone (**3**) to react with pentacarbonyliron under reflux for 3 h in dry tetrahydrofuran. The major product, m.p. 140° (54% yield), had analytical and spectroscopic properties in accord with a product of carbonyl insertion with concomitant ring expansion [*e.g.* (**4**) or isomers therof] *viz.* $C_{14}H_{10}N_4OS$: M^+ 282·0577 (calc. 282·0576); ν_{max} 1690 cm^{-1} (doublet); no NH str.; λ_{max} (EtOH) 372 nm (ϵ_{max} 12,490); n.m.r.: aromatic multiplets centred on τ 1·97 and 2·68. However, an *X*-ray crystallographic determination indicated that the product was in fact a 1,3,4-thiadiazole derivative (**5**).[4]

Crystals of the compound were triclinic, $P\bar{1}$, with a = 15·443 (5), b = 7·475 (2), c = 6·303 (2) Å, α = 106·34 (2)°, β = 102·13 (2)°, γ = 101·06 (2)°, U = 657·7 Å^3, Z = 2, D_c = 1·435, D_m = 1·421 g cm^{-3}.

The intensities of 2168 reflections with $\theta \leqslant 25°$ were measured on a Hilger-Watts four circle diffractometer using graphite-monochromatised Mo-K_α radiation. The structure was solved using MULTAN and refined using 1905 'observed' (net count $> 3\sigma$) reflections. In the final stages of the refinement using the block-diagonal method the hydrogen atoms, which had been located from a difference map, were allowed to refine isotropically and the other atoms were refined anisotropically. The final conventional R was 5·5%, and bond lengths and angles were all close to expected values.

The mechanism of formation of the product (**5**) is unclear. A sequential process,[5] (**3**) → (**6**) → (**5**), appears unlikely since dithizone (**6**) is not converted† into the thiadiazole (**5**) under the conditions used for the transformation (**3**) → (**5**); an alternative intermediate is the mesoionic compound (**4**) or six-membered ring isomers thereof.

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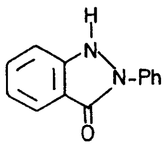
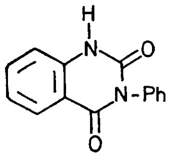


(1)



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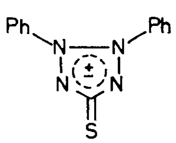
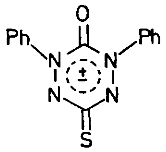
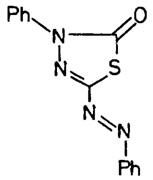


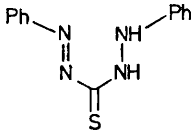
(3)



(4)



(5)



(6)

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† In a separate experiment dithizone was allowed to react with $[Fe(CO)_5]$ in THF under reflux for 3 h. Four as yet unidentified compounds were formed, none of which was (5) [t.l.c. examination].

[1] S. Murahashi and S. Horiie, *J. Amer. Chem. Soc.*, 1956, **78**, 4416; *Bull. Chem. Soc. Japan*, 1960, **33**, 88. See also W. W. Pritchard, U.S.P. 2,769,003; (*Chem. Abs.*, 1957, **51**, 7412).

[2] *Cf.* C. W. Bird, *Chem. Rev.*, 1962, **62**, 283; A. Rosenthal and I. Wender in 'Organic Syntheses *via* Metal Carbonyls,' eds. I.Wender and P. Pino, Interscience, New York, 1968, pp. 405—466; M. Ryang and S. Tsutsumi, *Synthesis*, 1971, 55.

[3] Y. Becker, A. Eisenstadt, and Y. Shvo, *Tetrahedron*, 1974, **30**, 839.

[4] M. Freund and F. Kuh, *Ber.*, 1890, **23**, 2821; H. M. N. H. Irving and D. C. Rupainwar, *Analyt. Chim. Acta*, 1969, **48**, 187.

[5] The intermediacy of (**6**) appeared possible in view of the known reducing properties of iron carbonyls; *cf.* their behaviour with $\alpha\beta$-unsaturated carbonyl compounds [R. Noyori, I. Umeda, and T. Ishigami, *J. Org. Chem.*, 1972, **37**, 1542] and nitroarenes [J. M. Landesberg, L. Katz, and C. Obsen, *J. Org. Chem.*, 1972, **37**, 930].