# Approaches to the Synthesis of Compounds containing Fused Mesoionic Rings

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[1,2,3]Oxadiazolo[4,3-c][1,2,4]benzotriazinium-3-olate has been prepared by diazotization of 3-(2-aminophenyl)-1,2,3-oxadiazolium-5-olate [3-(2-aminophenyl)sydnone]. The tricyclic compound has been converted by hydrolysis. thermolysis. and reduction with sodium borohydride into 1,2,4-benzotriazine-3-carboxylic acid. It underwent alkylation with Meerwein's reagent but did not react with 1,3-dipolarophiles even under forcing conditions. Unsuccessful attempts were made to prepare azidoaryl derivatives of mesoionic triazoles. thiazoles, and tetrazoles. 3-(2-Azidocarbonylphenyl)-1,2,3-oxadiazolium-5-olate is converted photochemically into a mesoionic [1,2,3]oxadiazolo[3,4-a]quinoxaline derivative and 3-(2-carbamoylphenyl)-1,2,3-oxadiazolium-5-olate. The pyrolysis of mesoionic tetrazoles is described and aspects of the chemistry of 1,3-diphenyltetrazolium-5-thiolate are briefly discussed. A novel carbonylation reaction of 2.3-diphenyltetrazolium-5-thiolate (dehydrodithizone) is reported, as are complexes of this compound formed by treatment with dipotassium tetrachloropalladate.

A VARIETY of monocyclic mesoionic compounds are known,[1] but derivatives containing fused mesoionic rings are less common, especially those with the second ring aromatic or heteroaromatic. We report attempts to synthesise such compounds by three approaches: (a) via nitrene or nitrene-like intermediates; (b) by thermal and photochemical reactions; and (c) via transition metal intermediates.

(a) via *Nitrenes.*—A number of heterocycles have been synthesised by intramolecular reactions of nitrenoaryl heteroaromatic systems.[2] In principle, application of this type of reaction to mesoionic systems can lead to a variety of tricyclic compounds [see (1) ⟶ (2) and/or
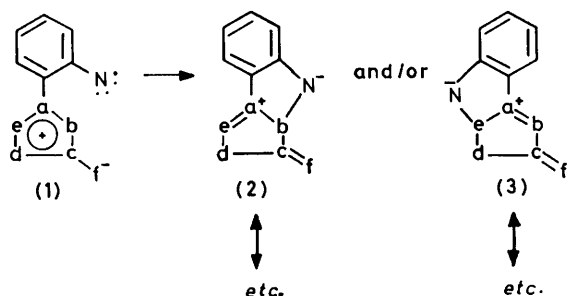
(3)]; such processes might also be valuable mechanistic probes of the relative nucleophilic character of atoms or groups on the mesoionic ring (*cf.* ref. 2d). We required nitro-compounds [3] and azides [4] as conventional nitrene precursors and attempted the synthesis of such derivatives in the sydnone, triazole, thiazole, and tetrazole series.

Sydnones. With the intention of preparing 3-(2-azidophenyl)-1,2,3-oxadiazolium-5-olate [3-(2-azidophenyl)sydnone] (4a), we diazotized the amino-derivative (4b) [5] at 0 °C and treated the product with sodium azide. A compound $C_8H_4N_4O_2$ was formed in 81% yield apparently in the initial diazotization process. The mesoionic [1,2,3]oxadiazolo[4,3-c][1,2,4]benzotriazine structure † (5) was evident from spectroscopic data: for example the characteristic [6] n.m.r. absorption of the sydnone ring 4-proton was absent, and the mass spectrum indicated fragmentation modes typical [7] of sydnones, *viz.* ions at m/e values corresponding to $M^{+•} - NO$ and $M^{+•} - (NO + CO)$. Compound (5) is thus formed by attack of the diazonium group at the sydnone 4-position, a site known to be susceptible to electrophilic substitution.[6]

Structure (5) was also evident from the results of chemical degradation by aqueous sodium hydroxide at room temperature, which gave 1,2 4-benzotriazine-3-carboxylic acid (6) in 83% yield after acidic work-up. Evidently the reactivity of the oxadiazole ring in the fused derivative (5) parallels the behaviour of 3-arylsydnones from which alkaline hydrolysis regenerates the precursor *N*-nitroso-*N*-arylglycines;[8] presumably in this case the carboxylic acid (6) arises from a transient dihydro-intermediate containing an *N*-nitroso-function. The same carboxylic acid (6) was isolated in 64% yield from acidic hydrolysis of the benzotriazine derivative (5) by hot 2M-hydrochloric acid. Possibly in this re-action a similar ring-opening mechanism operates in which nucleophilic attack at the carbonyl group is facilitated by protonation of the sydnone ring. In this

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† Compounds (4b) and (5) have been investigated X-ray crystallographically (T. J. King, P. N. Preston, and K. Turnbull, unpublished results).

[1] (a) W. Baker and W. D. Ollis, *Quart. Rev.,* 1957, **15**; (b) M. Ohta and H. Kato in ' Nonbenzenoid Aromatics,' ed. J. P. Snyder, Academic Press, New York, 1969, ch. 4; (c) W. D. Ollis and C. A. Ramsden, *Adv. Heterocyclic Chem.,* 1976, **19**, 3.

[2] See *e.g.* (a) J. C. Kauer and R. A. Carboni, *J. Amer. Chem. Soc.,* 1967, **89**, 2633; (b) A. W. Murray and K. Vaughan, *Chem. Comm.,* 1967, 1282; (c) Y. Y. Hung and B. M. Lynch, *J. Hetero-cyclic Chem.,* 1965, **2**, 218; (d) I. M. McRobbie, O. Meth-Cohn, and H. Suschitzky, *Tetrahedron Letters,* 1976, 925.

[3] *Cf.* J. I. G. Cadogan, *Quart. Rev.,* 1968, **22**, 222; *Synthesis,* 1969, 11.

[4] *Cf.* R. A. Abramovitch and E. P. Kyba, in ' The Chemistry of the Azido Group,' ed. S. Patai, Interscience, New York, 1971, ch. 5.

[5] R. A. Coburn and J. P. O'Donnell, *J. Org. Chem.,* 1972, **37**, 1707.

[6] *Cf.* F. H. C. Stewart, *Chem. Rev.,* 1964, **64**, 129.

[7] J. H. Bowie, R. A. Eade, and J. C. Earl, *Austral. J. Chem.,* 1968, **21**, 1665; R. S. Goudie, M. H. Palmer, and P. N. Preston, *Org. Mass. Spectrometry,* 1969, **2**, 953; W. D. Ollis and C. A. Ramsden, *J.C.S. Perkin I,* 1974, 645.

[8] W. Baker, W. D. Ollis, and V. D. Poole, *J. Chem. Soc.,* 1949, 307.

context the reaction is different from that of 3-phenyl-sydnone which is converted into phenylhydrazine, formaldehyde, and carbon dioxide by acidic hydrolysis.[9]

No detailed study of the thermolysis of sydnones has

R
(4)a; N₃
   b; NH₂
   c; CON₃
   d; CO·NH·NH₂
   e; NCO
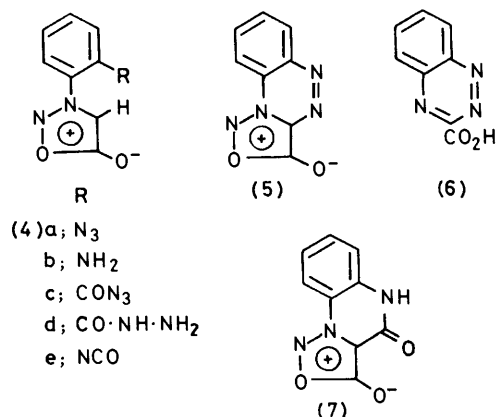
been carried out, although the odour of isocyanides was noted during pyrolysis of certain derivatives.[10] When compound (5) was pyrolysed in admixture with sand at 140 °C, the carboxylic acid (6) was again formed in 77% yield, possibly by valence isomerisation to a nitroso-keten and subsequent hydrolysis by adventitious water.

The carboxylic acid (6) was also formed, in 52% yield, together with (1,2,4-benzotriazin-3-yl)methanol (41%) and methyl 1,2,4-benzotriazine-3-carboxylate (6%) when the sydnone (5) was treated with an excess of sodium borohydride in methanol; when an equimolar quantity of sodium borohydride was used only the carboxylic acid (6) (78%) and its methyl ester (20%) were formed. 3-Phenylsydnone was stable to this reductant in a control reaction.

An attempt to ascertain the site of alkylation of compound (5) was partially successful: a red compound was formed in 70% yield when (5) was treated [11] with tri-ethyloxonium tetrafluoroborate, but this product rapidly reverted to starting material when efforts were made to purify it chromatographically. From i.r. evidence we tentatively conclude that alkylation occurs in conventional [11] fashion at the sydnone exocyclic oxygen atom (absence of sydnone C–O stretching band at 1 780 cm⁻¹ and presence of C–O stretching absorption at 1 030—1 110 cm⁻¹).

Compound (5) does not appear to be valuable for the synthesis of heterocycles via 1,3-dipolar cycloadditions:[6] no reaction occurred when it was treated with dimethyl but-2-ynedioate, diethyl azodiformate, or 4-phenyl-1,2,4-

triazoline-2,5-dione under forcing conditions, and a complex inseparable product was formed when it reacted with phenyl isocyanate.[12]

As an extension of the nitrene study * we investigated the photolysis of 3-(2-azidocarbonylphenyl)sydnone (4c). The normal [13] arenecarbonyl chloride route could not be used for its synthesis (see Experimental section), but it was obtained by the alternative hydrazide route.[14] A solution of the arenecarbonyl azide (4c) decomposed photolytically to give a mixture of the known [5] mesoionic oxadiazoloquinoxaline derivative (7) (15%) and 3-(2-carbamoylphenyl)sydnone (20%). The azide (4c) thus behaves normally [4] and the intermediate photo-Curtius product (4e) is transformed into the quinoxaline deriv-ative (7). Compound (7) was also obtained by pyrolysis of the azide (4c) in benzene.

Triazoles, thiazoles, and tetrazoles. The desired nitro-arene (8) was obtained as one of three compounds, (8)—(10), when 1-(2-nitrophenyl)-4-phenylthiosemicarbazide
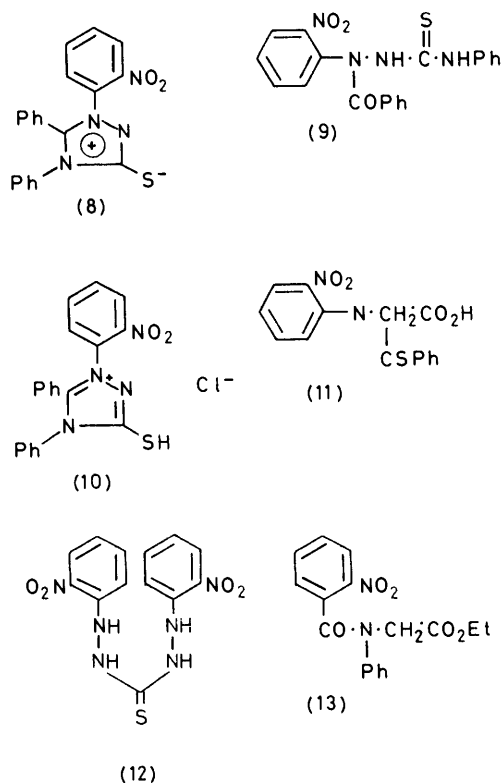
was treated with benzoyl chloride in acetonitrile;[15] the triazolium salt (10) could be converted into the mesoionic triazole (8) by hot pyridine.[15] Unfortunately this nitro-

* Alternative approaches to sydnone nitrenes based on reactions of 3-(2-nitrophenyl)sydnone and 4-nitro-3-phenylsydnone with triethyl phosphite in cumene were unsuccessful: complex inseparable mixtures resulted.

[9] J. C. Earl, *Rec. Trav. chim.*, 1956, **75**, 1080.
[10] J. C. Earl, *Chem. and Ind.*, 1953, 746.
[11] *Cf.* K. T. Potts, E. Houghton, and S. Husain, *Chem. Comm.*, 1970, 1025.

[12] *Cf.* H. Kato, S. Sato, and M. Ohta, *Tetrahedron Letters*, 1967, 4261.
[13] M. E. C. Biffin, J. Miller, and D. B. Paul in ' The Chemistry of the Azido Group,' ed. S. Patai, Interscience, New York, 1971, ch. 2.
[14] W. Lwowski in ' The Chemistry of the Azido Group,' ed. S. Patai, Interscience, New York, 1971, ch. 9.
[15] K. T. Potts, S. K. Roy, and D. P. Jones, *J. Org. Chem.*, 1967, **32**, 2245.

compound (8) could not be reduced to the amine, and furthermore attempted deoxygenation with triethyl phosphite led to a complex product from which only a low yield (ca. 17%) of an uncharacterised compound ($C_{13}H_{10}N_4, 0.5H_2O$) was isolated.

Related studies on mesoionic thiazoles and tetrazoles were disappointing: conventional [16,17] cyclization procedures on intermediates (11) and (12) were unsuccessful, and an intermediate amide (13) could not be converted into the thioamide.

(b) *Thermal and Photolytic Reactions.*—A number of heterocycles including the fused mesoionic compounds (14) and (15) [18a,b] have been prepared by photochemical oxidative cyclization, and it was decided to attempt this type of reaction with the mesoionic tetrazoles (16). Disappointingly, solutions of both compounds (16a and b) were stable over long periods to u.v. irradiation. It was

(14)   (15)

(16)   (17)   (18)

a; X = S
b; X = O
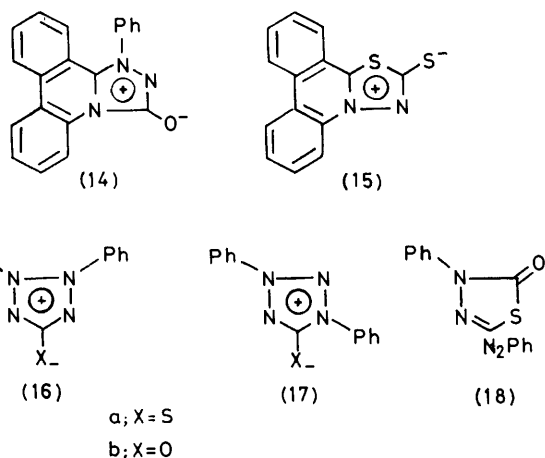
therefore decided to pyrolyse them in the solid phase at 150 °C or in xylene solution under reflux. In both cases formal 1,2-shift of a phenyl group occurred to give the isomeric mesoionic tetrazoles (17a) [19] and (17b), [20] respectively.

Like dehydrodithizone (16a), [21] the isomer (17a) forms an *S*-methyltetrazolium iodide with methyl iodide but

formed a complex inseparable product when treated with dimethyl but-2-ynedioate; [22] it did not react with pentacarbonyliron (*cf.* the dehydrodithizone ——► thiadiazolone conversion described below). The electronic absorption spectrum of dehydrodithizone (16a) exhibits a pronounced influence of solvents on the position of $\lambda_{max.}$ (*e.g.* 480 nm in EtOAc and 380 nm in H_2O). [23] A similar, though less marked solvent-induced hypsochromic shift is evident in the spectrum of the isomer (17a) (*e.g.* 406 nm in EtOAc and 377 nm in MeOH) which might imply [20a] that the isomer (17a) is considerably less polar in the ground state than dehydrodithizone.

The mechanism of the rearrangements (16) ——► (17) have not been studied but such reactions may prove valuable for the synthesis of a variety of heterocycles, including new mesoionic compounds.

(c) *Transition Metal Intermediates.*—A number of transition metal complexes have been prepared [24] by *ortho*-metallation procedures with substrates containing the aryl–X–N moiety. In some cases such compounds (*e.g.* azobenzene [25] and Schiff's base [26] complexes) can be transformed into heterocycles by carbonylation; in the case of azobenzene a subsequent reaction converts [27] the product 2-phenylindazolone into 3-phenylquinazoline-2,4-dione. An attempt was thus made [28] to extend such processes to mesoionic compounds with the hope of obtaining fused derivatives or six-membered ring mesoionic compounds, hitherto difficult to obtain.

No reaction occurred when 3-phenylsydnone, a mesoionic triazole (8; H for NO_2), or the mesoionic tetrazoles (16b) and (17a) were heated with pentacarbonyliron in tetrahydrofuran; 3-(2-nitrophenyl)sydnone underwent reduction [29] to the amino-derivative (4b). In marked contrast, dehydrodithizone was converted into the thiadiazolinone derivative (18) in 80% yield. A sequential process involving reductive ring-opening to dithizone appeared possible [29] but in a separate control experiment it was found * that the latter is converted into the thiadiazolinone (18) in only 20% yield, together with four other compounds.†

With the intention of isolating intermediate complexes in this type of process (16a) ——► (18) we used three other catalysts: $[C_5H_5Fe(CO)_2]_2$, $RhHCO(PPh_3)_3$, and $Co_2(CO)_8$ all gave rise to complex products containing ca.

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* Preparative experiments indicated that our earlier [28] qualitative t.l.c. analyses were unsatisfactory.

† It has been suggested that the thiadiazolinone (19) is formed by a mechanism involving an intermediate dehydrodithizone valence tautomer (see ref. 1c, p. 118, and G. V. Boyd, T. Norris, and P. F. Lindley, *J.C.S. Perkin I*, 1976, 1673).

[16] M. Ohta and C. Shin, *Bull. Chem. Soc. Japan*, 1965, **38**, 704.

[17] E. Bamberger, R. Padova, and E. Ormerod, *Annalen*, 1926, **446**, 260.

[18] (a) H. Kato, T. Shiba, E. Kitajima, T. Koyosawa, F. Yamada, and T. Nishiyama, *J.C.S. Perkin I*, 1976, 863; (b) R. M. Moriarty, J. M. Kliegman, and R. B. Desai, *Chem. Comm.*, 1967, 1255.

[19] Preliminary report, P. N. Preston, K. K. Tiwari, K. Turnbull, and T. J. King, *J.C.S. Chem. Comm.*, 1976, 343; see also R. N. Hanley, W. D. Ollis, and C. A. Ramsden, *ibid.*, 1976, 307.

[20] (a) P. B. Talukdar, S. K. Sengupta, A. K. Datta, and A. Chakravorty, *Indian J. Chem.*, 1973, **11**, 611; (b) W. V. Farrer, *J. Chem. Soc.*, 1964, 906; (c) M. Busch and W. Schmidt, *Ber.*, 1929, **62**, 1449.

[21] J. W. Ogilvie and A. H. Corwin, *J. Amer. Chem. Soc.*, 1961, **83**, 5023.

[22] *Cf.* P. Rajagopalan and P. Ponev, *Chem. Comm.*, 1971, 490.

[23] A. M. Kiwan and H. M. N. H. Irving, *J. Chem. Soc.* (B), 1971, 898.

[24] *Cf.* G. W. Parshall, *Accounts Chem. Res.*, 1970, **3**, 139.

[25] H. Takahashi and J. Tsuji, *J. Organometallic Chem.*, 1967, **10**, 511.

[26] J. M. Thompson and R. Heck, *J. Org. Chem.*, 1975, **40**, 2667.

[27] 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).

[28] Preliminary communication, P. N. Preston, N. J. Robinson, K. Turnbull, and T. J. King, *J.C.S. Chem. Comm.*, 1974, 998.

[29] *Cf.* the reducing properties of iron carbonyls with αβ-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).

15%, a trace amount, and none of compound (18) respectively.

In an alternative approach [26] to *ortho*-metallated complexes, dehydrodithizone (16a) was treated with dipotassium tetrachloropalladate. An insoluble complex of approximate composition (dehydrodithizone)PdCl₂ was obtained, but this material was not converted into carbonyl-containing compounds when heated under carbon monoxide pressure as a dispersion in ethanol.[25]

The complex is possibly a chlorine-bridged polymer: it reacts rapidly with *ca.* 1 mol. equiv. of triphenyl-phosphine at room temperature to give a complex of approximate composition (dehydrodithizone)Pd(Ph₃P)-Cl₂, the structure of which is under investigation.

EXPERIMENTAL

[1,2,3]*Oxadiazolo*[4,3-c][1,2,4]*benzotriazinium-3-olate* (5).— 3-(2-Aminophenyl)sydnone [5] (2.5 g, 13.3 mmol) was suspended in water (6 ml) and concentrated hydrochloric acid (3 ml). The suspension was cooled to 0 °C and treated dropwise with sodium nitrite (1 g) in water (3.5 ml). After 1 h the resultant yellow solid was washed with water and dried. Recrystallisation from acetone–light petroleum (b.p. 40—60 °C) (1 : 1) gave small *plates* (2.0 g, 81%), m.p. 174—176° (decomp.), $\nu_{max.}$ 1 840, 1 780, 1 253, and 770 cm⁻¹; $\tau[(CD_3)_2SO]$ 1.67 (m, ArH); $\lambda_{max.}$ (EtOH) 238 (ε 16 900), 268sh, and 392 (ε 3 774); *m/e* 188.0341 (*M⁺·*, 33%; $C_8H_4N_4O_2$ requires 188.0334), 158 (100%, *M⁺·* − NO), and 130 (15%, *M⁺·* − NO − CO) (Found: C, 50.85; H, 2.3; N, 29.9. $C_8H_4N_4O_2$ requires C, 51.05; H, 2.1; N, 29.8%).

Reactions of the Fused Sydnone (5).—The sydnone (5) was converted into 1,2,4-benzotriazine-3-carboxylic acid [30] under the following conditions: (*a*) 2M-sodium hydroxide at room temperature for 1 h; (*b*) 2M-hydrochloric acid under reflux for 6 h; (*c*) thermolysis in acid-washed sand (B.D.H.) at 140 °C for 2 h; (*d*) with an equimolar quantity of sodium borohydride in methanol at room temperature. Yields of the acid (6) were 83, 77, 77, and 78%, respectively and the material had m.p. 215—216° (decomp.) (lit.,[30] decomp. before melting); $\lambda_{max.}$ (EtOH) 305, 237, and 210 nm; *m/e* 175.0378 (*M⁺·*; calc. for $C_8H_5N_3O_2$: 175.0382). Heating to the m.p. gave a sublimate of 1,2,4-benzotriazine, m.p. 73—74° (lit.,[30] 74°), *m/e* 131 (*M⁺·*).

When a 5 molar excess of borohydride was used in (*d*) the acid (6) was produced (52%) together with (1,2,4-benzo-triazin-3-yl)methanol (41%) and methyl 1,2,4-benzotri-azine-3-carboxylate (6%). The products were separated chromatographically (silica gel; ethyl acetate–petroleum (1 : 6)].

Alkylation. The sydnone (5) (300 mg, 18 mmol) in dry dichloromethane (80 ml) was treated with triethyloxonium tetrafluoroborate (350 mg 19 mmol) under nitrogen. The solution darkened immediately and a red oil separated. This oil was washed with dry diethyl ether; it slowly crystallised to give a red solid (300 mg), m.p. 160° (decomp.); $\nu_{max.}$ 1 800, 1 600, 1 580, 1 110—1 030, and 790 cm⁻¹; $\lambda_{max.}$ (EtOH) 365, 312, 237, and 212 nm. This material decomposed to starting material and other, unidentified compounds on attempted chromatographic purification (thin-layer and column).

With 1,3-*dipolarophiles.* Starting material (90%) was recovered from reactions of compound (5) with (i) dimethyl but-2-ynedioate in *p*-xylene under reflux for 12 h or in nitrobenzene under reflux; (ii) 4-phenyl-1,2,4-triazoline-2,5-dione in ethyl acetate under reflux for 12 h; and (iii) diethyl azodiformate in ethyl acetate under reflux for 12 h.

Attempted Preparation of 3-(2-*Chlorocarbonylphenyl)syd-none.*—3-(2-Carboxyphenyl)sydnone [31] could not be con-verted into the acid chloride under the following conditions: (*a*) in chloroform solution with thionyl chloride under reflux for 6 h; (*b*) with thionyl chloride (neat) under reflux for 3 h; and (*c*) with a mixture [32] of thionyl chloride and triethylamine. In reaction (*a*) the carboxylic acid was recovered (90%) and in (*b*) indazolin-3-one (20%), m.p. 254° (lit.,[33] 254°), was formed.

N-(2-*Methoxycarbonylphenyl)*-N-*nitrosoglycine.*— Sodium nitrite (3.45 g, 50 mmol) was added over 30 min to *N*-(2-methoxycarbonylphenyl)glycine [34] in concentrated sulphuric acid (150 ml) at 0 °C. After a further 2 h the mixture was poured onto ice to precipitate the red-brown product (4.9 g, 41%), m.p. 76—79°; $\nu_{max.}$ (KBr) 3 100—2 500, 1 710, 760, and 695 cm⁻¹; $\tau[(CD_3)_2SO]$ 1.08 (s, CO₂H), 2.13 (4 H, m), 5.32 (s, CH₂), and 6.2 (s, CO₂Me); *m/e* 238 (*M⁺·*), 230, and 186. This was used without further purification.

3-(2-*Methoxycarbonylphenyl)sydnone.*—The foregoing nitroso-derivative (4.76 g, 20 mmol), methylene chloride (25 ml) and trifluoroacetic anhydride (5.0 g, 23.8 mmol) were stirred together for 1 h at 5 °C. Evaporation under reduced pressure to *ca.* 5 ml followed by trituration with dry ether gave an off-white crystalline *compound* (3.3 g, 75%), m.p. 104—106° (from ethanol); $\nu_{max.}$ (KBr) 3 130, 3 040, 2 935, 1 720, 775, and 690 cm⁻¹; $\tau[(CD_3)_2SO]$ 1.8 (4 H, m), 2.17 (s, sydnone 4 H), and 6.07 (s, CO₂Me); *m/e* 220 (*M⁺·*), 180, and 162; $\lambda_{max.}$ (EtOH) 228 and 298 nm (Found: C, 54.25; H, 3.75; N, 12.95. $C_{10}H_8N_2O_4$ requires C, 54.55; H, 3.65; N, 12.75%).

3-(2-*Carbazoylphenyl)sydnone* (4d).—3-(2-Methoxycar-bonylphenyl)sydnone (2.20 g, 10 mmol) and hydrazine hydrate (1.0 g, 20 mmol) were warmed in methanol (25 ml) for 45 min. Evaporation under reduced pressure and trituration with methanol gave *needles* (from 1 : 1 EtOH–Me₂CO), m.p. 177—179°; $\nu_{max.}$ (KBr) 3 300, 3 130, 3 034, 1 740, 1 650, 934, and 730 cm⁻¹; $\tau[(CD_3)_2SO]$ 2.15 (4 H, m), 2.51 (s, sydnone 4 H), and 4.5 (s, NH·NH₂); *m/e* 220 (*M⁺·*), 190, and 162; $\lambda_{max.}$ (EtOH) 226 and 301 nm (Found: C, 49.3; H, 3.6; N, 25.4. $C_9H_8N_4O_3$ requires C, 49.1; H, 3.65; N, 25.45%).

3-(2-*Azidocarbonylphenyl)sydnone* (4c).—Sodium nitrite (0.57 g, 8.2 mmol) was added to 3-(2-carbazoylphenyl)-sydnone (1.8 g, 8.2 mmol) in M-hydrochloric acid (35 ml) and water (108 ml) over 30 min at 0 °C. After a further 30 min the precipitate was washed with water and dried *in vacuo* to give *compound* (4c), m.p. 93—95° (from 1 : 1 chloroform–petroleum); $\nu_{max.}$ (KBr) 3 120, 2 160, 2 120, 1 725, 1 676, 990, and 730 cm⁻¹; τ (CDCl₃) 2.1 (4 H, m) and 3.35 (s, sydnone 4-H); *m/e* 231 (*M⁺·*), 203, 173, and 145 (Found C, 46.5; H, 2.05; N, 30.2. $C_9H_5N_5O_3$ requires C, 46.75; H, 2.15; N, 30.3%).

Decomposition of the Azide (4c).—(a) *Thermal.* Compound (4c) (0.1 g, 0.43 mmol) was heated for 2 h under reflux in

[30] R. Fusco and S. Rossi, *Gazzetta*, 1956, **86**, 484.
[31] R. A. Eade and J. C. Earl, *J. Chem. Soc.*, 1948, 2307.
[32] S. Kukolja, S. R. Lammert, M. R. Gleissner, and A. I. Ellis, *J. Amer. Chem. Soc.*, 1975, **97**, 3192.

[33] R. Janssen, *Adv. Mol. Spectroscopy*, 1959, **2**, 820.
[34] ' Dictionary of Organic Compounds,' Eyre and Spottiswoode, vol. 4, p. 2689.

benzene (10 ml) under nitrogen. The precipitate was washed with ether and dried *in vacuo* to give 4,5-dihydro-4-oxo[1,2,3]oxadiazolo[3,4-*a*]quinoxalinium-3-olate (7) (0.02 g, 23%), m.p. 312° (lit.,[5] 308°), spectroscopically (i.r. and mass) identical with an authentic[5] sample.

(b) *Photochemical.* Dioxan was deoxygenated by passing nitrogen through it for 30 min. Photolysis was carried out with a medium-pressure mercury quartz insertion lamp. Compound (4c) (1.0 g, 4.5 mmol) was irradiated in dioxan for 1.5 h. The solution was filtered to remove an uncharacterised buff-coloured solid (0.07 g) and then evaporated under reduced pressure. The residual oil was chromatographed (silica gel; ethyl acetate–petroleum, 1 : 10) to give 3-(2-carbonylphenyl)sydnone (see below) and the quinoxaline (7) (0.16 g, 15%).

3-(2-*Carbamoylphenyl*)*sydnone*.— 3-(2-Methoxycarbonylphenyl)sydnone (0.5 g, 2.3 mmol) was heated with ammonia-saturated methanol (40 ml) for 2 h at 45 °C in a sealed tube. The solution was evaporated and the residue was triturated with methanol to give the *product* (0.3 g, 64%), m.p. 209—211° (from acetone); $\nu_{max.}$ (KBr) 3 340, 3 190, 3 097, 1 735, 1 670, 850, and 783 cm^{-1}; τ [(CD$_3$)$_2$SO] 2.15 (4 H, m) and 2.57 (s, sydnone 4-H); $\lambda_{max.}$ (EtOH) 229 and 303 nm (Found: C, 52.9; H, 3.5; N, 20.25. C$_9$H$_7$N$_3$O$_3$ requires C, 52.7; H, 3.4; N, 20.5%).

2-(2-*Nitrophenyl*)-3,4-*diphenyl*-s-*triazolium*-5-*thiolate* (8). —This was prepared by a modification of the method of Potts *et al.*[15] Benzoyl chloride (5.2 g, 37 mmol) was added dropwise to 1-(2-nitrophenyl)-4-phenylthiosemicarbazide (10 g, 35 mmol) in acetonitrile (400 ml) at 3 °C. After 4 days the solvent was evaporated off and the residue was extracted with ether (Soxhlet) to give yellow 1-*benzoyl*-1-(2-*nitrophenyl*)-4-*phenylthiosemicarbazide* (9) (8.0 g, 59%), m.p. 143—144° (from methanol) (Found: C, 61.1; H, 4.2; N, 14.1; S, 8.0. C$_{20}$H$_{16}$N$_4$O$_3$S requires C, 61.2; H, 4.1; N, 14.3; S, 8.15%). Soxhlet extraction was continued with methanol to afford yellow 5-*mercapto*-2-(2-*nitrophenyl*)-3,4-*diphenyl*-s-*triazolium chloride* (10) (2.5 g, 18%), m.p. 260—262° (Found: C, 58.85; H, 3.85; N, 13.9; S, 8.45. C$_{20}$H$_{15}$ClN$_4$O$_2$S requires C, 58.55; H, 3.65; N, 13.65; S, 7.8%). The residue after methanol extraction was the *mesoionic triazole* (8), m.p. 305—307° (Found: C, 64.05; H, 3.8; N, 14.85; S, 8.35. C$_{20}$H$_{14}$N$_4$O$_2$S requires C, 64.15; H, 3.75; N, 14.95; S, 8.55%). Compound (8) could not be reduced to an amino-derivative by Fe–AcOH, Fe(CO)$_5$, or Na$_2$S$_2$O$_4$.

N-(2-*Nitrophenyl*)-N-*thiobenzoylglycine* (11).—This was prepared by standard procedures from *N*-(2-nitrophenyl)-glycine ethyl ester[35] by benzoylation[36] (PhCOCl) followed by treatment with phosphorus pentasulphide[36] and then alkaline hydrolysis. The yellow *product* had m.p. 133—136° (from ethanol) (Found: C, 56.7; H, 3.75; N, 8.95. C$_{15}$H$_{12}$N$_2$O$_4$S requires C, 56.95; H, 3.8; N, 8.85%). This could not be cyclized to a mesoionic thiazole under standard[16] conditions.

1,5-*Bis*-(2-*nitrophenyl*)*thiocarbonohydrazide* (12).—This material, m.p. 182—184°, was prepared by analogy with a literature procedure[37] from 2-nitrophenylhydrazine and an excess of carbon disulphide in tetrahydrofuran–diethyl ether (4 : 1).

Pyrolysis of Mesoionic Tetrazoles (16).—These were

carried out either with dispersions in acid-washed sand (B.D.H.) or in xylene under nitrogen.

(a) *Dehydrodithizone* (16a). The tetrazole (16a)[21] (3.0 g, 12 mmol) in sand (150 g) was heated for 5 h at 150 °C. The mixture was extracted with methanol (Soxhlet) to give an oil which on trituration with toluene gave dehydrodithizone (1.2 g, 40%). The remainder was chromatographed (silica gel; ethyl acetate–petroleum, 1 : 6) to give yellow 1,3-*diphenyltetrazolium*-5-*thiolate* (17a) (0.29 g, 16%), m.p. 156—157°; $\nu_{max.}$ (KBr) 3 020, 1 590, 1 488, 1 368, 1 172, 757, 769, 697, and 678 cm^{-1}; τ (CDCl$_3$) 1.51—2.59 (m) (Found: C, 61.3; H, 3.9; N, 21.7. C$_{13}$H$_{10}$N$_4$S requires C, 61.4; H, 3.95; N, 22.05%). This product (17a) was also obtained (7%) by a similar work-up procedure from pyrolysis of dehydrodithizone (1.0 g, 4 mmol) in *o*-xylene (100 ml).

(b) 2,3-*Diphenyltetrazolium*-5-*olate* (16b).[20a]—The tetrazole (2.0 g, 8.4 mmol) was heated in sand (100 g) for 6 h at 150 °C. A methanol-soluble portion (Soxhlet) of the product was chromatographed as above to yield starting material (0.4 g) and 1,3-diphenyltetrazolium-5-olate (0.72 g, 45%), identical (i.r. and mass spectra) with an authentic sample prepared by a literature[20a] method.

Reaction of Dehydrodithizone (16a) *with Pentacarbonyliron.* —Dehydrodithizone (0.50 g, 1.9 mmol) and pentacarbonyliron (0.89 g, 5 mmol) were heated in dry tetrahydrofuran under nitrogen for 3 h. Evaporation under reduced pressure followed by extraction (Soxhlet) of the residue with chloroform gave yellow 4-phenyl-2-phenylazo-Δ^2-1,3,4-thiazolin-5-one (18) (0.45 g, 80%), m.p. 140° (lit.,[38] 139°), spectroscopically (i.r. and mass) identical with an authentic sample prepared by a literature[38] procedure.

Reaction of 3-(2-*Nitrophenyl*)*sydnone with Pentacarbonyl-iron.*—3-(2-Nitrophenyl)sydnone (0.8 g, 3.9 mmol) and pentacarbonyliron were heated under reflux for 3 h in dry tetrahydrofuran under dry nitrogen. The solution was evaporated under reduced pressure and the residue (1.6 g) was extracted with ethyl acetate (Soxhlet). The extracted material was 3-(2-aminophenyl)sydnone, m.p. 136—137° (lit.,[5] 136°).

Reaction of Dehydrodithizone (16a) *with Dipotassium Tetrachloropalladate.*—Dipotassium tetrachloropalladate (3.4 g, 10.4 mmol) in water (40 ml) was added to a warm solution of dehydrodithizone (2.54 g, 10 mmol) in ethanol-water (2 : 1; 150 ml). After 1 h the orange precipitate was washed with water, then ether, and was dried *in vacuo* to give a product (3.7 g, 85%), m.p. 245° (decomp.), $\nu_{max.}$ (KBr) 3 050, 1 489, 1 465, 1 340, 996, 765, and 687 cm^{-1} (Found: C, 35.6; H, 2.3; Cl, 15.6; N, 12.9; Pd, 25.35; S, 6.9. Calc. for C$_{13}$H$_{10}$Cl$_2$N$_4$PdS: C, 36.2; H, 2.3; Cl, 16.45; N, 13.0; Pd, 24.6; S, 7.4%). This complex (2.15 g) in methylene chloride (50 ml) was treated with triphenylphosphine (1.31 g, 5 mmol) at room temperature and the mixture was kept at 0 °C for 18 h. The microcrystalline orange precipitate (2.13 g, 64%) had m.p. 221—224° (Found: C, 52.75; H, 3.65; Cl, 11.05; N, 7.8; P, 4.6; S, 5.15. Calc. for C$_{31}$H$_{23}$Cl$_2$N$_4$PPdS: C, 53.7; H, 3.6; Cl, 10.25; N, 8.1; P, 4.45; S, 4.6%).

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