251. *2-Diazoindane-1,3-dione from a Novel Cyclisation Reaction of 2-Cyano-ω-diazo-acetophenone.*

By G. Holt and D. K. Wall.

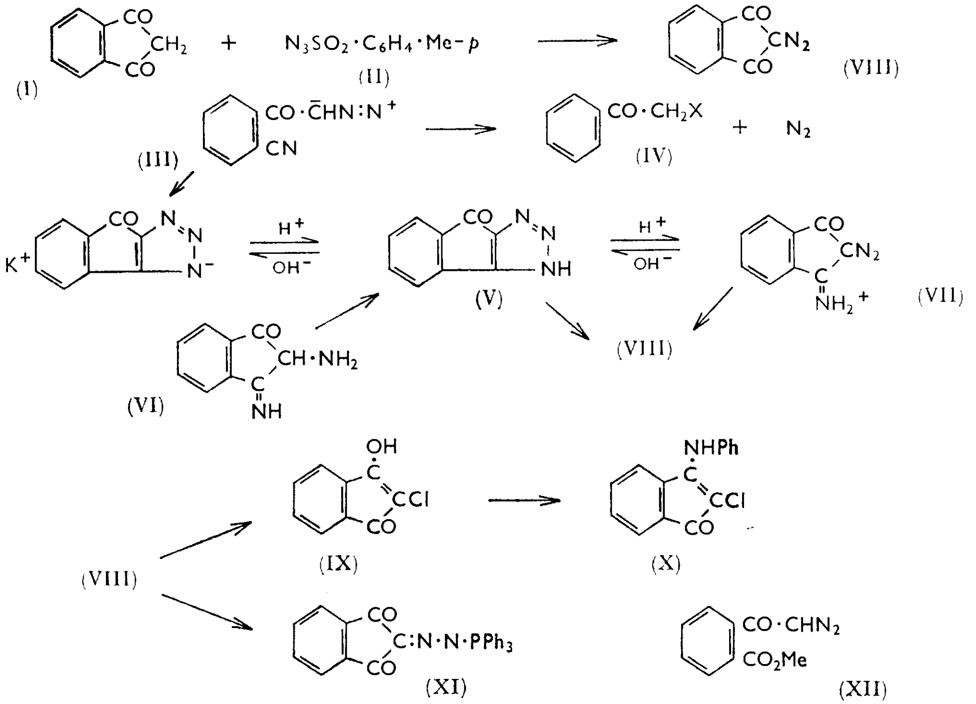
8-Oxoindeno[1,2-*d*]triazole, resulting from the base-induced cyclisation of 2-cyano-ω-diazoacetophenone, on warming with dilute acid provides 2-diazoindane-1,3-dione and ammonia.

The very recent preparation of 2-diazoindane-1,3-dione[1] (VIII) from indane-1,3-dione (I), toluene-*p*-sulphonazide (II), and potassium ethoxide or, less satisfactorily, from ninhydrin and *p*-substituted benzenesulphonhydrazides, prompts us to report our own independent synthesis of this diazo-ketone from 2-cyano-ω-diazoacetophenone (III). The

---

[1] M. Regitz and G. Heck, *Chem. Ber.*, 1964, **97**, 1482.

latter was obtained in excellent yield by the interaction of 2-cyanobenzoyl chloride and diazomethane, and was characterised by elemental analysis, infrared spectrum [ν (Nujol) 2220m (CN), 2125s cm.$^{-1}$ (diazo)] and by the formation of the chloro-ketone (IV; X = Cl) and toluene-*p*-sulphonate [2] (IV; X = $OSO_2{\cdot}C_6H_4{\cdot}Me$-*p*) when it was treated with hydrochloric acid and toluene-*p*-sulphonic acids, respectively.



The 2-cyano-diazo-ketone dissolved, without evolution of nitrogen, when it was agitated with 1 molecular proportion of cold N/4-potassium hydroxide. Cautious addition of dilute acid to the orange solution provided a yellow solid (m. p. 171—172°) to which, on the basis of elemental analysis, infrared spectrum [ν (Nujol) 1708s (CO), 3165s cm.$^{-1}$ (NH), absence of CN and diazo-bands], and equivalent and molecular weights, we have ascribed the triazole structure (V). Further confirmation was obtained by synthesising the triazole from 2-amino-1-iminoindane-3-one (VI) and nitrous acid.

Attempts to effect the Wolff rearrangement of 2-cyano-ω-diazoacetophenone by silver benzoate in triethylamine [3] were unsuccessful. No nitrogen was evolved but there resulted a near-quantitative yield of the silver salt of the triazole (V). This triazole, when treated with hydrogen chloride in either ether or acetonitrile, provided a hydrochloride, presumably the imine hydrochloride (VII), since its infrared spectrum showed typical diazo-absorption. The addition of alkali to an aqueous solution of the hydrochloride reprecipitated the triazole which dissolved when excess of alkali was added. The imine hydrochloride, when warmed with water, yielded ammonia and 2-diazoindane-1,3-dione (VIII). This diazo-diketone (m. p. 147°) was obtained more simply by boiling the triazole with dilute aqueous acid (V ⟶ VIII). This reaction is the reverse of triazole formation from an acyclic α-diazo-ββ'-dicarbonyl compound and ammonia [4] or a primary amine.[5] The ready opening of the

---

[2] A. L. Crowther and G. Holt, *J.*, 1963, 2818.

[3] M. S. Newman and P. F. Beal, *J. Amer. Chem. Soc.*, 1950, **72**, 5163.

[4] L. Wolff, *Annalen*, 1902, **325**, 129.

[5] L. Wolff and R. Krüche, *Annalen*, 1912, **394**, 48.

triazole ring is doubtless a consequence of mesomeric stabilisation of the immonium ion (VII). Like Regitz and Heck's[1] compound (m. p. 149°), our product (m. p. 147°) showed characteristic diazo-absorption at 2128s cm.$^{-1}$. The compound m. p. 149°, however, is quoted as having carbonyl absorption at 1727 cm.$^{-1}$ whilst our product showed strong broad absorption between 1625 and 1740 cm.$^{-1}$ (max. at 1681 cm.$^{-1}$). We further characterised our product by converting it into the corresponding chloro-ketone (IX) which, although it could not be obtained in a pure condition, was converted by aniline into the known anilino-derivative (X).[6] With triphenylphosphine, by the general procedure of Bestmann *et al.*,[7] 2-diazoindane-1,3-dione gave an excellent yield of the corresponding phosphazine (XI).

Since, under the influence of base, ω-diazo-2-methoxycarbonylacetophenone (XII) fails to provide 2-diazoindane-1,3-dione, the cyclisation of the cyano-diazo-ketone (III) is to be regarded as a 1,3-dipolar addition (compare the reactions of diazo-alkanes with cyanogen, the cyanogen halides, and methyl cyanoformate[8]) rather than a Dieckmann-type reaction.

EXPERIMENTAL

8-*Oxoindeno*[1,2-d]*triazole*.—(1) To a stirred solution of diazomethane (5·65 g.) in ether (460 ml.) was added, during 1 hr., a solution of 2-cyanobenzoyl chloride[9] (8·9 g.) in ether (210 ml.). After completion of the addition, stirring was continued for a further hour, after which time 90% of the theoretical volume of nitrogen had been evolved. The excess of diazomethane was removed by distillation under reduced pressure, the mixture was cooled to −70°, and the crude 2-*cyano-ω-diazoacetophenone* [7·4 g.; 81%; m. p. 139—141° (decomp.)] was separated. Recrystallisation from methanol gave yellow needles, m. p. 143·5—144·5° (decomp.) (Found: C, 63·4; H, 3·0; N, 24·3. $C_9H_5N_3O$ requires C, 63·2; H, 2·9; N, 24·6%). With hydrogen chloride in dry ether and with toluene-*p*-sulphonic acid monohydrate,[2] this diazo-ketone gave, respectively, *ω-chloro-*2-*cyanoacetophenone*, m. p. 115—117° [white plates from methanol–light petroleum (b. p. 60—80°)] (Found: C, 60·5; H, 3·5; Cl, 19·2; N, 7·2. C_9H_6ClNO requires C, 60·2; H, 3·4; Cl, 19·7; N, 7·8%) [ν 2217m (CN), 1695s (CO), 721 cm.$^{-1}$ (CCl)], and 2-*cyano-ω-(toluene-*p*-sulphonyloxy)acetophenone*, m. p. 100—101·5° (aqueous alcohol) (Found: C, 61·1; H, 4·1; N, 4·4. $C_{16}H_{13}NO_4S$ requires C, 61·0; H, 4·2; N, 4·4%) [ν 2217m (CN), 1704s (CO), 1353s, and 1176s cm.$^{-1}$ (OSO_2)].

2-Cyano-ω-diazoacetophenone (2·0 g.) was agitated with 0·25N-potassium hydroxide (32 ml.) at room temperature (18—24°). No nitrogen was evolved, but a clear orange solution was obtained within 3—4 min. The addition of N-hydrochloric acid gave a yellow precipitate of 8-*oxoindeno*[1,2-d]*triazole* [1·68 g.; 84%; m. p. 171—172° (decomp.)] [Found: C, 63·2; H, 3·1; N, 24·5%; Equiv. 172; *M* (vapour-phase osmometer in methanol), 177. $C_9H_5NO_3$ requires C, 63·2; H, 2·9; N, 24·6%; equiv., 171; *M*, 171]. Attempted recrystallisation of the triazole apparently led to its partial decomposition.

(2) 2-Amino-1-iminoindan-3-one hydriodide[10] (0·48 g.) in water (15 ml.) was made just alkaline with 2N-sodium hydroxide, and the free base was extracted with ether. The ether layer was extracted with dilute hydrochloric acid (25 ml.) and, to the acid solution of the base hydrochloride cooled at 0°, was added, dropwise, 5% sodium nitrite solution to a starch–iodide end-point. Cautious addition of N-sodium carbonate gave a yellow solid (0·063 g.), m. p. 160—165° (decomp.), which was purified by chromatography on alumina, using ethanol as eluent; a product resulted that did not depress the m. p. [171—172° (decomp.)] of 8-oxoindeno[1,2-*d*]-triazole.

(3) *Attempted Wolff Rearrangement of* 2-*Cynao-ω-diazoacetophenone*.—When 10% silver benzoate in triethylamine[3] solution was added to the diazo-ketone (2·0 g.) in methanol (150 ml.)

---

[6] T. Zincke, *Ber.*, 1887, **20**, 1265.

[7] H. J. Bestmann, H. Buckschewski, and H. Leube, *Chem. Ber.*, 1959, **92**, 1345.

[8] R. Huisgen, *Angew. Chem. Internat. Edn*, 1963, **2**, 565.

[9] R. Scholl and W. Neuberger, *Monatsh.*, 1912, **33**, 517.

[10] G. Vanags and E. Vanaga, *Latvijas PSR Zinatnu Akad., Vestis*, 1954, 137 (*Chem. Abs.*, 1955, **49**, 15833b).

no nitrogen was evolved, but a yellow precipitate formed. Precipitation was complete when 1 mol. of silver benzoate had been added. The washed and dried solid proved to be the *silver salt* of 8-oxoindeno(1,2-*d*)triazole (3·1 g.; 95%) (Found: C, 38·6; H, 1·4; N, 15·3. $C_9H_4AgN_3O$ requires C, 38·9; H, 1·4; N, 15·1%). On warming with dilute hydrochloric acid, the latter yielded silver chloride and 2-diazoindane-1,3-dione (86%; m. p. and mixed m. p. 147°).

Reactions of 8-*Oxoindeno*[1,2-d]*triazole.*—2-*Diazoindane*-1,3-*dione.* When dry, saturated, ethereal hydrogen chloride was added to a saturated solution of the triazole in the same solvent, there was quantitatively precipitated what is presumably 2-diazo-1-iminoindane-3-one hydrochloride, since its solution in water gave a positive test for chloride ion and cautious addition of alkali reprecipitated the triazole [m. p. and mixed m. p. 171—172° (decomp.)]. The infrared spectrum of the hydrochloride showed characteristic diazo-absorption (doublet at 2151s and 2165s cm.$^{-1}$) and CO str. (at 1724s cm.$^{-1}$). Warming an aqueous solution of the hydrochloride, almost instantaneously gave a precipitate of 2-diazoindane-1,3-dione (m. p. 147°). The solution from which the latter had been separated gave a positive test for ammonia. The diazo-diketone was most conveniently prepared by warming 8-oxoindeno[1,2-*d*]triazole (1·53 g.) with 2N-hydrochloric acid (42 ml.) on a steam-bath. The resulting yellow solution almost immediately gave a precipitate of the diazo-diketone (1·36 g.; 88%; m. p. 146·5—147°). Crystallisation from hot water gave cream rhombic prisms, m. p. 147° (Found: C, 62·4; H, 2·3; N, 16·7. Calc. for $C_9H_4N_2O_2$: C, 62·8; H, 2·3; N, 16·3%).

Boiling the diazo-ketone with excess of concentrated hydrochloric acid gave crude 2-chloro-1-hydroxyindene-3-one (65%), the m. p. of which (109—113°) could not be raised by recrystallisation (Zincke gives m. p. 114°).[6] The chloroketone, with aniline in glacial acetic acid,[6] gave the crude anilino-derivative (78%; m. p. 195—197°) which, after chromatography on alumina and crystallisation from benzene, provided red needles, m. p. 202—203·5° (Found: C, 70·7; H, 4·2; Cl, 14·2; N, 5·3. Calc. for $C_{15}H_{10}ClNO$: C, 70·5; H, 3·9; Cl, 13·9; N, 5·5%) (Zincke gives 1-anilino-2-chloroindene-3-one, m. p. 203—204°).[6] By the procedure of Bestmann *et al.*,[7] 2-diazoindane-1,3-dione and triphenylphosphine gave (1,3-*dioxo*-2-*indanylidenehydrazono*)*triphenylphosphorane* as red prisms (76%), m. p. 105—106° (from methanol) (Found: C, 74·6; H, 4·8; N, 6·8. $C_{27}H_{19}N_2O_2P$ requires C, 74·7; H, 4·4; N, 6·5%).

The diazo-compound coupled with resorcinol under the conditions described by Severin,[11] to give a product which was presumably 2-(2,4-*dihydroxyphenylazo*)-1-*hydroxyindene*-3-*one*, as purple-brown micro-prisms from benzene–acetone, chars above 250°. (Found: C, 63·5; ·H, 3·8; N, 10·2. $C_{15}H_{10}N_2O_4$ requires C, 63·8; H, 3·6; N, 9·9%).

All infrared spectra were determined in Nujol mulls.

Micro-analyses were carried out by Mr. B. Manohin.

MANCHESTER COLLEGE OF SCIENCE AND TECHNOLOGY,
MANCHESTER 1.

[*Received, August* 5*th*, 1964.]

---

[11] T. Severin, *Angew. Chem.*, 1958, **70**, 745; *Chem. Ber.*, 1959, **92**, 1517.