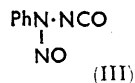
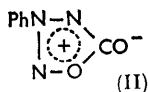
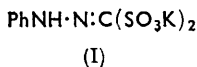


177. A New Route to Two Meso-ionic Ring Systems.

By W. V. FARRAR.

Two meso-ionic compounds are synthesised from diazonium salts and potassium diazomethanedisulphonate.

THE curious compound potassium diazomethanedisulphonate, $N_2C(SO_3K)_2$, has attracted very little attention since its discovery in 1895.¹ It is prepared by the action of potassium nitrite on potassium hydrogen aminomethanedisulphonate; this in turn is made from potassium hydrogen sulphite and potassium cyanide. The diazo-compound is a stable yellow crystalline substance which undergoes a variety of reactions, one of the most interesting being with benzenediazonium salts. Nitrogen is evolved and potassium hydrazonomethanedisulphonate (I) is formed.²



This substance reacts² with nitrous acid to give a sulphur-free, steam-volatile compound which was not identified. Repetition of this experiment has confirmed the isolation of this compound (m. p. 85°), and shown it to have the empirical formula $C_7H_5N_3O_2$; its formulation as 3-phenyloxatriazolone (II) then follows logically from its method of preparation. It appears to be identical with a compound of the same m. p. and empirical formula prepared by Quilico³ (see also ref. 4) by the spontaneous decomposition of benzenediazotrinotromethane in a solvent. Quilico described his compound as "nitroso carbonyl

¹ von Pechmann and Manck, *Ber.*, 1895, **28**, 2374.

² von Pechmann, *Ber.*, 1896, **29**, 2161.

³ Quilico, *Gazzetta*, 1932, **62**, 912.

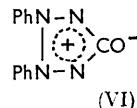
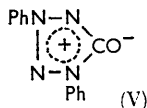
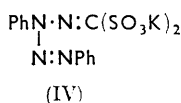
⁴ Ponzio, *Gazzetta*, 1915, **45**, II, 12.

phenylhydrazine" (III), but a structure very similar to (II) was put forward by Ponzio⁵ soon afterwards. These authors describe several reactions of this ring system.

The scope of this synthesis has not been explored, but no difficulty was encountered in making the *p*-chlorophenyl and 2,4-dichlorophenyl analogues.

It was found by von Pechmann² that the salt (I) on treatment with more benzenediazonium salt gave a compound (IV) which he called "diazobenzolphenylhydrazonomethan disulfonsäures Kalium." This salt, which could also be prepared directly from potassium diazomethanedisulphonate (or its bisulphite addition product), by coupling with two molecules of diazonium salt, is rather unstable. Acids decompose it to (I) and diazonium salt, but in neutral or alkaline solution a sulphur-free compound is precipitated, the m. p. of which was given as 187°.

Repetition of this experiment gave moderate yields of a compound, m. p. 157°, whose empirical formula was C₁₃H₁₀N₄O. The structure (V) again follows from the method of preparation; the only alternative (VI) is a known compound⁶ of quite different m. p. and chemical properties.



The diphenyltetrazolone (V) appears to be identical with a compound (m. p. 156°) of the same empirical formula, obtained by Busch and Schmidt,⁷ who ascribed a bridged-ring structure; and also with Backer's "bisphenylazomethanal"⁸; he obtained it as a by-product in the reaction of benzenediazonium salts with bisethylsulphonylmethane, a reaction closely related to the one described here. The ultraviolet spectrum is very similar to that recorded by Backer.

EXPERIMENTAL

3-Phenyl-1,2,3,4-oxatriazolone (II).—Potassium phenylhydrazonomethanedisulphonate (I) was prepared by von Pechmann's method.² The salt (I) (12 g.), dissolved in water (100 c.c.) containing sodium nitrite (3 g.), was added with stirring to 2*N*-hydrochloric acid (250 c.c.) at 20–30° during 1 hr. After being stirred for a further 2 hr., and warmed if necessary to complete the reaction, the coloured solid (3–4 g.) was crystallised from aqueous methanol, giving steam-volatile needles, m. p. 85°, whose chemical properties corresponded to those reported by Quilico³ and Ponzio^{4,5} (Found: C, 51.6; H, 3.6; N, 25.5. Calc. for C₇H₅N₃O₂: C, 51.5; H, 3.1; N, 25.75%).

The *p*-chlorophenyl analogue, m. p. 137°, was made by a similar method; Quilico³ gives m. p. 133° (Found: C, 42.7; H, 1.8. C₇H₄ClN₃O₂ requires C, 42.5; H, 2.0%); ν (in Nujol) 1785 cm.⁻¹ (C=O); λ_{max} . (0.001% in ethanol) 275 m μ (ϵ 13,500) and 218 m μ (ϵ 9900).

The 2,4-dichlorophenyl analogue had m. p. 100° (from ethanol) (Found: C, 36.0; H, 1.3. C₇H₃Cl₂N₃O₂ requires C, 36.2; H, 1.3%).

1,3-Diphenyltetrazolone (V).—Following the directions of von Pechmann² a solution of the salt (IV) was made from aniline (21 g.) without isolation. At pH 8–10 a coloured solid (5–10 g.) was precipitated during the night, or more quickly on warming to 50°. Recrystallisation from ethanol gave colourless platelets, m. p. 157° (Found: C, 65.3; H, 4.1; N, 23.6. Calc. for C₁₃H₁₀N₄O: C, 65.5; H, 4.2; N, 23.5%); ν (Nujol) 1695 cm.⁻¹ (C=O); λ_{max} . (0.001% in ethanol) 325 m μ (ϵ 13,200), 261 m μ (9400), and 225 m μ (14,300); this spectrum is very similar to that recorded by Backer⁸ (solvent and concentration not specified).

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⁵ Ponzio, *Gazzetta*, 1933, **63**, 471.

⁶ Bamberger, Padova, and Ormerod, *Annalen*, 1926, **446**, 264.

⁷ Busch and Schmidt, *Ber.*, 1929, **62**, 1449.

⁸ Backer, *Rec. Trav. chim.*, 1951, **70**, 733.