Studies on *v*-Triazoles. Part III. On the Nitration of 9-Oxo-1*H*,9*H*-benzopyrano[2,3-*d*]-*v*-triazole

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The nitration of 9-oxo-1*H*,9*H*-benzopyrano[2,3-*d*]-*v*-triazole (**1**) leads not to the expected benzenoid substitution product **2** but to initial attack on the triazole moiety resulting in fission to 3-diazo-2-nitrimino-2*H*-[1]benzopyran-4-yl oxide (**3**). Mild hydrolysis of **3** results in cleavage of the nitrimine to give 3-diazo-2-oxo-2*H*-[1]benzopyran-4-yl oxide (**4**). Further nitration of **3** under more forcing conditions leads to the 6-nitro derivative of **3** which also undergoes facile hydrolysis to a diazocoumarin.

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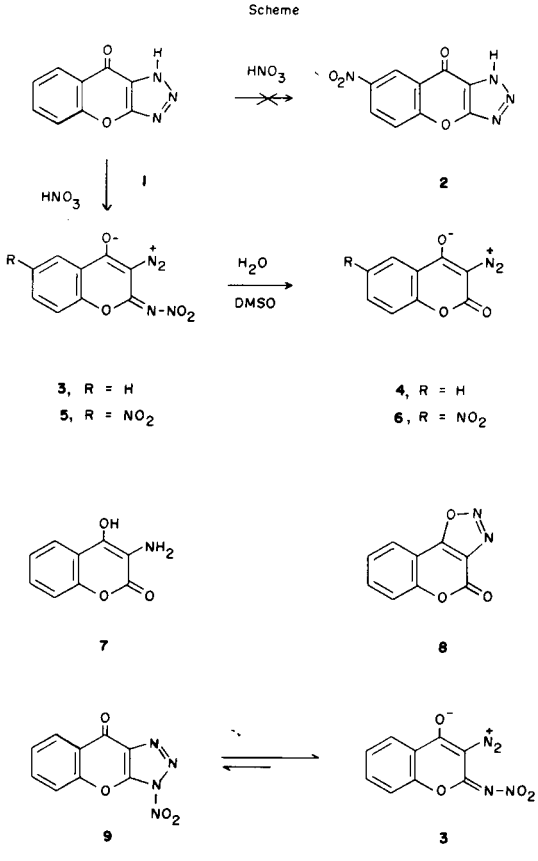
In a previous publication (1) we reported the synthesis of a novel class of heterocycles, the 9-oxo-1*H*,9*H*-benzopyrano[2,3-*b*]-*v*-triazoles, which were of interest as potential antiasthmatic agents. As part of this programme we were interested in the derivatization of the parent compound (**1**) and our findings on the nitration of this compound are the subject of this report.

By analogy with xanthone (2) the nitration of **1** (see Scheme) might be expected to yield the 7-nitro derivative **2** but the only material isolable from this reaction, under the mildest conditions for reaction to take place, was a yellow crystalline compound of mp 143° which was clearly not a simple aromatic nitro compound. The product, formed in 55% yield, showed a strong diazo absorbance at 2170 cm^{-1} in its ir spectrum although the elemental analysis and mass spectrum (M^+ 232.0232 mu) were consistent with the formula $C_9H_4N_4O_4$. Both of these results suggested the insertion of a single nitro group. The ^1H nmr spectrum, however, was complex but addition of the lanthanide shift reagent Eu($[^2H_9]$fod)$_3$ and spin decoupling experiments clearly identified four aromatic protons thus precluding insertion of the nitro group into the benzenoid nucleus. Moreover, mild hydrolysis of this derivative gave 74% of a second compound of mp 155.5-156° which also showed a diazo peak at 2170 cm^{-1} in its ir spectrum. The elemental analysis and mass spectrum (M^+ 188.0215) of this compound were consistent with the formula $C_9H_4N_2O_4$ and it was assigned the diazocoumarin structure **4** on the basis of its spectral properties. Indeed, it was identical spectroscopically and by mixed melting point with the compound formed on diazotization of 3-amino-4-hydroxycoumarin (**7**) (3,4) although this product had been incorrectly assigned the cyclic structure **8** by Huebner and Link (3).

On the basis of this assignment the initial nitro product was formulated as the diazonitrimine **3**, which is believed to result from initial attack of nitric acid at the N-3 atom of **1**. The initially formed product **9** undergoing ring cleavage of the Dimroth type to give **3**.

The reversible ring opening of vicinal triazoles

Scheme



substituted on nitrogen by electron withdrawing groups, as for example the 1-cyano and 1-arenesulphonyl derivatives, is well-known (5) and it is not surprising therefore that a nitro group would effect a similar cleavage even more favourably. The reversibility of this ring opening has not been demonstrated.

The subsequent hydrolytic reaction in dimethylsulphoxide is readily rationalised in view of the notoriously hygroscopic nature of this solvent and other hydrolytic reactions in dimethylsulphoxide have been described (6).

Using stronger nitric acid (d, 1.5) further nitration of the intermediate **3** can be effected such that the 6-nitro derivative **5** is formed in 78% yield. This compound

hydrolyses so readily in 'wet' dimethylsulphoxide that the ^{1}H nmr spectrum shows extensive cleavage and is a composite with the diazocoumarin **6** and nitramine. It can be preparatively hydrolysed to 6-nitrodiazocoumarin (**6**) in 82% yield in a similar manner to compound **4**.

These reactions are of interest in view of the ease with which the triazole moiety is cleaved. It is noteworthy that nitration of benzotriazole under forcing conditions results in an aryl substituted derivative (7), although an apparently stable cyclic *N*-nitro compound has been reported using acetyl nitrate (8).

EXPERIMENTAL

Melting points were determined using a Buchi melting point apparatus and are recorded uncorrected. The ir spectra were determined with a Perkin-Elmer 197 spectophotometer as dispersions in nujol. The pmr spectra were obtained with a Varian EM 390 90 MHz spectrometer as solutions in either deuteriochloroform or DMSO-d_6 and are measured in ppm (δ) with respect to TMS. Mass spectra were obtained on a VG-7770F spectrometer. The uv spectra were measured using a Perkin-Elmer 554 spectrophotometer.

3-Diazo-2-nitrimino-2*H*-[1]benzopyran-4-yl Oxide (**3**).

Finely powdered benzopyranotriazole (**1**, 0.250 g, 1.34 mmoles) was added portionwise with stirring to a cold (0°) mixture of concentrated nitric acid (3.0 ml, d, 1.41) and fuming nitric acid (1.5 ml, d, 1.52) and the solution was stirred at ice-bath temperature for 1 hour. Dilution with water (20 ml) resulted in the precipitation of a crystalline solid which was filtered off, washed well with water and dried *in vacuo* to give 0.17 g (55%) of **3** of mp 142°. Recrystallisation from ethyl acetate-light petroleum bp 40-60° gave material of mp 143°; ir: ν max 2170, 1658, 1610 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 7.32 (2H, complex m), 7.70 (1H, d.t, J = 2 Hz, 8Hz), 8.07 (1H, dd, J = 2 Hz, 8Hz); ms: M$^+$ 232.0232 ($C_9H_4N_4O_4$).

Anal. Calcd. for $C_9H_4N_4O_4$: C, 46.56; H, 1.74; N, 24.13. Found: C, 47.11; H, 1.75; N, 24.08 (9).

3-Diazo-2-oxo-2*H*-[1]benzopyran-4-yl Oxide (**4**).

A solution of the nitrimine (**3**, 0.100 g, 0.43 mmole) in dimethylsulphoxide (5 ml) was stirred at 35-40° for 2.5 hours and the yellow solution was then diluted with water (20 ml). The precipitated crystalline solid was filtered off, washed with water and dried *in vacuo* to give 0.060 g (74%) of **4** of mp (methanol) 155.5-156°; ir: ν max 2170, 1720, 1708, 1645, 1615 cm^{-1}; ^{1}H nmr (DMSO-d_6): δ 7.40 (2H, complex m), 7.85 (2H, complex m); uv (methanol): λ max 225 (19,600), 265 (10,900), 278 (11,200) nm; ms: M$^+$ 188.0215 ($C_9H_4N_2O_3$).

Anal. Calcd. for $C_9H_4N_2O_3$: C, 57.45; H, 2.14; N, 14.89. Found: C, 57.20; H, 2.42; N, 14.99.

An authentic sample of **4** prepared by diazotization of 3-amino-4-hydroxycoumarin (**7**) (3,4) had mp 156° and mixed mp 156°. The ir and ^{1}H nmr spectra were identical with that prepared above.

3-Diazo-2-nitrimino-6-nitro-2H-[1]benzopyran-4-yl Oxide (**5**).

Finely powdered (**1**, 0.250 g, 1.34 mmoles) was added portionwise with stirring to fuming nitric acid (3 ml, d, 1.52) at 0° and the resulting solution was maintained at this temperature for 90 minutes. Dilution of the yellow solution with water (20 ml) afforded a yellow crystalline precipitate which was separated, washed with water and dried *in vacuo* to give 0.29 g (78%) of **5** of mp 195° dec. Recrystallization from ethyl acetate did not improve the melting point; ir: ν max 2190, 1670, 1635, 1600, 1575 cm^{-1}; ms: M$^+$ 277.0072 ($C_9H_3N_5O_6$). The ^{1}H nmr spectrum in DMSO-d_6 showed evidence of extensive hydrolysis to the diazocoumarin **6** and nitramine but had signals at δ 7.78 (1H, d, J = 10 Hz), 8.55 (1H, dd, J *ca* 2Hz, 10 Hz), 8.60 (1H, d, J *ca* 2Hz) consistent with the assigned structure.

Anal. Calcd. for $C_9H_3N_5O_6$: C, 39.00; H, 1.09; N, 25.27. Found: C, 39.09; H, 0.93; N, 25.25.

3-Diazo-6-nitro-2-oxo-2*H*-[1]benzopyran-4-yl Oxide (**6**).

A solution of the nitrimine (**5**, 0.28 g, 1 mmole) in dimethylsulphoxide (10 ml) was stirred at 35-40° for 2 hours and then diluted with water (40 ml). The yellow fibrous crystals which separated were filtered off, washed with water and dried *in vacuo* to give 0.19 g (82%) of **6** of mp 209-210° dec. Recrystallisation from methanol afforded material of mp 213-214° dec; ir: ν max 2180, 1735, 1720, 1655, 1620, cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 7.47 (1H, d, J = 9.3 Hz), 8.52 (1H, dd, J = 2.5 Hz, 9.3 Hz), 8.92 (1H, d, J = 2.5 Hz); ms: M$^+$ 233.0085 ($C_9H_3N_3O_5$).

Anal. Calcd. for $C_9H_3N_3O_5$: C, 46.36; H, 1.29; N, 18.02. Found: C, 46.42; H, 1.28; N, 18.03.

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(9) A more satisfactory analysis for carbon could not be obtained because of the unstable nature of **3**.