Tetrahedron Vol 24, pp 6145 to 6148 Pergamon Press 1968 Printed in Great Britain

SOME AMINODINITRO DERIVATIVES OF BENZOFURAZAN AND BENZOFURAZANOXIDE

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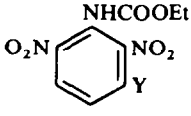
(*Received in the UK* 29 *April* 1968; *accepted for publication* 16 *May* 1968)

Abstract—7-ethoxycarbonamido-4,6-dinitrobenzofurazanoxide was observed to undergo rearrangement under the nitrating conditions employed for its formation into 5-ethoxycarbonamido-4,6-dinitrobenzofurazanoxide. Hydrolysis of this urethan gave the amino compound which was also prepared by other methods. A related benzofurazan derivative, 4-amino-5,7-dinitrobenzofurazan was prepared by two different routes.

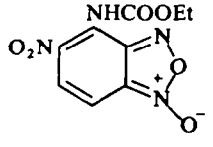
A. *Derivatives of benzofurazanoxide*

THERMAL treatment of 3-azido-2,6-dinitro-1-ethoxycarbonamidobenzene (I) and of 3-azido-4,6-dinitro-1-ethoxycarbonamidobenzene (II), prepared from sodium azide and the corresponding 3-bromo compounds (III and IV) or the 3-nitro compound (V), yielded the corresponding benzofurazanoxides (VI and VII) respectively.



I: Y = N_3
III: Y = Br

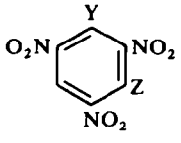
II: Y = N_3
IV: Y = Br
V: Y = NO_2



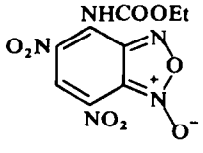
VI

VII

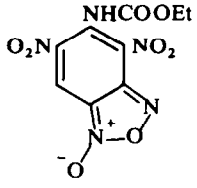
Likewise, 3-azido-2,4,6-trinitro-1-ethoxycarbonamidobenzene (VIII) gave rise to a benzofurazan oxide for which there were two possible structures (IX or X)



VIII: Y = NHCOOEt, Z = N_3
XI: Y = NH_2, Z = N_3
XII: Y = NH_2, Z = NH_2
XVI: Y = NHCOOEt, Z = Br
XVII: Y = NH_2, Z = Br



IX



X

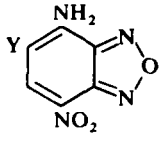
An investigation of the NMR spectrum of this compound dissolved in acetone and comparison with the spectra of VI and VII as model compounds, was carried out in these Laboratories.[1] For VI the chemical shifts of the Et group protons were CH_3 = 8·58 τ and CH_2 = 5·56 τ; those of the ring protons were 1·27 τ and 1·99 τ. For VII, CH_3 = 8·69 τ, CH_2 = 5·73 τ and ring protons 1·40 τ and 1·75 τ. The observed chemical shift of the ring proton in the unknown IX or X was 1·1 τ. From these results Williams and Hutchison deduced that the appropriate structure was X and not IX.

Compounds identical to X (in respect of m.p., mixed m.p., IR spectra and TLC) were also obtained by nitration of either VI or of VII. This indicates that compound IX, formed initially by nitration of VI, underwent rearrangement under the conditions of reaction into X. Such inter conversions of 4-nitrobenzofurazanoxides have been reported by Katritzky *et al.*,[2-4] e.g. the rearrangement of 4-nitro-5-methylbenzofurazan oxide into 4-nitro-7-methyl benzofurazan oxide.[3]

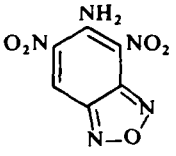
Of the above urethans, only X was successfully hydrolysed. The resultant amino compound was identical to the aminodinitrobenzofurazan oxide obtained either from nitrated 5-chlorobenzofurazan oxide by reaction with alcoholic ammonia or from 3-azido-2,4,6-trinitroaniline (XI) subjected to thermal treatment. It has not been established that the molecule retains its structure on hydrolysis i.e. that it corresponds to the hydrolysis product of X rather than that of IX.

B. *Derivatives of benzofurazan*

Thermal decomposition of 1,3-diamino-2,4,6-trinitrobenzene (XII) yielded an aminodinitrobenzofurazan for which two structures were possible (XIII or XIV).



XIII: Y = NO_2
XV: Y = H



XIV

An identical compound (in respect of IR spectrum and TLC) was obtained by nitration of 4-amino-7-nitrobenzofurazan (XV); the appropriate structure is therefore XIII rather than XIV.

EXPERIMENTAL

Starting materials. Compounds III, IV, XVI and XVII were obtained from 3-bromoaniline by the methods of De Monchy.[5] Compound V was obtained by nitration of 3-nitro-1-ethoxycarbonamidobenzene in a similar manner. Compound XII was obtained quantitatively from XVII by reaction with hot alcoholic ammonia.

Azides. Unless otherwise stated the azides were prepared by the technique described by Gaughran *et al.*[6] for the synthesis of 1,3-dinitro-4,6-diazidobenzene.

3-*Azido*-2,6-*dinitro*-1-*ethoxycarbonamidobenzene* (I) was obtained from III (0·8 g). Solvent quantities were increased threefold because of the low solubility of III and the reaction was allowed to proceed for 24 hr. The azide was obtained as a yellow ppt (0·6 g) ν_{max} 3360 (NH) 2160 cm^{-1} (N_3).

3-*Azido*-4,6-*dinitro*-1-*ethoxycarbonamidobenzene* (II) was obtained from IV (0·5 g). The azide separated as a pink ppt (0·3 g) ν_{max} 3340 (NH) 2110 (N_3) 1740 cm^{-1} (C=O).

Alternatively, this azide was obtained from V by the technique described by Boulton *et al.*[4] for the preparation of 3-azido-2-nitroacetanilide.

3-Azido-2,4,6-trinitro-1-ethoxycarbonamidobenzene (VIII) was obtaned from XVI (0·20 g). The azide separated as a yellow ppt (0·18 g) on addition of a small amount of water; ν_{max} 3245 (NH), 2160 (N_3) 1715 cm^{-1} (C=O).

3-Azido-2,4,6-trinitroaniline (XI) was obtained from XVII (0·4 g) as a yellow ppt (0·3 g); ν_{max} 3445, 3340 (NH_2) 2160 cm^{-1} (N_3).

It was also obtained from 2,3,4,6-tetranitroaniline (1·0 g) in acetone (10 ml) by reaction with sodium azide (1·0 g) in ethanol/acetone/water (2:2:1, 10 ml). The azide separated when the mixture was cooled to −10°; a further quantity separated on addition of water (5 ml), yield 0·70 g. Extended reaction times e.g. 24 hr without cooling were avoided because under such conditions crystals of a sodium derivative of 3-hydroxy-2,4,6 trinitroaniline separated.

Benzofurazanoxide derivatives

4-Ethoxycarbonamido-5-nitrobenzofurazan oxide (VI) was obtained from I (0·5 g) heated under reflux of xylene (5 ml) for 1 hr. Evolution of N_2 commenced at 110° and the benzofurazan oxide separated as orange crystals from the cooled soln; further quantities were obtained on addition of pet. ether (60–80°). The product (0·3 g) was recrystallized from MeOH m.p. 165·5–166·5° uncorrected. (Found: C, 40·1; H, 3·0; N, 21·0. $C_9H_8N_4O_6$ requires: C, 40·3; H, 3·05; N, 20·9%); ν_{max} 3330 (NH) 1730 (C=O) 1630, 1580 (benzofurazanoxide) 1360 cm^{-1} (NO_2).

5-Nitro-6-ethoxycarbonamidobenzofurazan oxide (VII) was obtained from II (0·2 g) heated under reflux of toluene (3 ml) for 1 hr. Evolution of N_2 commenced at 80°. The benzofurazanoxide (0·13 g) separated as dark red crystals and was recrystallized from CCl_4 m.p. 118·5–119·5° uncorrected. (Found: C, 39·8; H, 2·9; N, 20·8; $C_9H_8N_4O_6$ requires: C, 40·3; H, 3·05; N, 20·9%); ν_{max} 3360 (NH), 1750 (C=O) 1625, 1605, 1555 (benzofurazanoxide) 1330 cm^{-1} (NO_2).

5-Ethoxycarbonamido-4,6-dinitrobenzofurazan oxide (X) was obtained from VIII (0·17 g) heated under reflux of toluene (3 ml) for 1 hr. Evolution of N_2 commenced at 90°. The benzofurazan oxide was precipitated as an orange solid (0·14 g) by addition of pet. ether (60–80°) to the cooled soln; it was recrystallized from CCl_4, m.p. 152–153° uncorrected. (Found: C, 34·5; H, 2·6; N, 22·1. $C_9H_7N_5O_8$ requires: C, 34·5; H, 2·25; N, 22·4%); ν_{max} 3265 (NH) 1740 (C=O) 1630 1600 cm^{-1} (benzofurazanoxide).

The same compound was also obtained by nitration of either VI or VII as follows: The oxide VI or VII (0·50 g) was dissolved in cold fuming HNO_3 (5 ml) and after 10 min the soln was poured onto ice to precipitate X (0·46 g), which was washed with water and purified as above.

Aminodinitrobenzofurazanoxide (Either 4-amino-5,7-dinitro- or 5-amino-4,6-dinitro-) was obtained from XI (0·6 g) heated under reflux of toluene for 1 hr. The benzofurazan oxide separated from the hot soln as orange crystals (0·45 g): it melted with decomposition at 266° but darkened at a lower temperature. (Found: C, 30·0; H, 1·5; N, 28·7. $C_6H_3N_5O_6$ requires: C, 29·9; H, 1·25; N, 29·1%); ν_{max} 3395, 3290 (NH_2) 1630, 1620, 1590 (benzofurazanoxide) 1510, 1360 cm^{-1} (NO_2).

The same compound was also obtained by hydrolysis of X as follows: The urethan X (0·13 g) was dissolved in conc H_2SO_4 (3 ml) and water added dropwise until the soln was on the point of precipitation. The mixture was then heated under reflux (15 min), diluted with water, cooled and the precipitated amine (0·07 g) filtered off.

Benzofurazan derivatives

4-Amino-5,7-dinitrobenzofurazan (XIII). (a) *Nitration of 4-amino-7-nitrobenzofurazan* (XV). Compound XV (0·22 g), prepared by the method of Katritzky *et al.*[4] was added slowly with stirring to ice-cold fuming HNO_3 (3 ml). When dissolved the soln was immediately poured into crushed ice (4 g) and the resultant mixture extracted with ether (3 × 75 ml). The combined extracts were washed with cold water (10 ml), dried over Na_2SO_4 and solvent-stripped in a rotary film evaporator to give the product as a red-brown solid. A pure specimen (0·066 g) was obtained by dissolution in MeOH followed by chromatography through alumina using MeOH as eluent.

On heating, decomposition commenced at about 215° and liquefaction occured at about 245°. The mol wt (mass spectrometry) was 225 ($C_6H_3N_5O_5$ has mol wt of 225). (Found: C, 31·8; H, 1·4; N, 31·4. $C_6H_3N_5O_5$ requires: C, 32·0; H, 1·34; N, 31·1%); ν_{max} 3405, 3305 (NH_2) 1650, 1625 cm^{-1} (benzofurazan).

(b) *Thermal dehydration of 1,3-diamino-2,4,6-trinitrobenzene* (XII). 1,3-diamino-2,4,6-trinitrobenzene (1·0 g) in tetradecane (100 ml) was heated under reflux (≃253°) for 15 min. The mixture was cooled, diluted with pet. ether (60–80°, 300 ml) and the ppt filtered off and washed with pet. ether. It was heated under reflux of acetone (50 ml), cooled and filtered. The filtrate was evaporated and heated under reflux of MeOH

(20 ml) cooled and filtered. The filtrate was then passed through an alumina column and eluted with MeOH; the first eluent contained starting material (XII) but this was followed by a bright yellow band containing XIII (0·02 g), identical by TlC and IR to that prepared by method (a) above.

Acknowleŭgement—The author is grateful to Dr. A. J. Owen for helpful discussion and to Mr. D. F. Debenham, Mr. W. H. G. Wright and Mrs. P. Fuller for some experimental assistance.

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