hygroscopic) which was used immediately. Table IV summarizes physical data of various examples of VI. Hydrochloric acid salts were prepared as described above.

For 3-dimethylamino-2-methylimidazo[1,2-*a*]pyridine monohydrate (free base, m.p. 60–63°) the ultraviolet spectrum showed λ_{max}^{EtOH} 228 mμ (ε 27,700), 234 (27,700), 284 (3961), and 306 (3500); potentiometric titration with aqueous hydrochloric acid indicated a pK_a (pH at half-neutralization) of 7.35 and a neutralization equivalent of 204 (calcd. 207).

2-(3,3,3-Trichloro-2-hydroxy-1-propyl)imidazo[1,2-*a*]pyridine Hydrochloride (IX).—The free base V was prepared as described above for the preparation of VI. To 4.4 g. (0.033 mole) of V was added 25 ml. of chloral and the dark red solution was heated on a steam bath for 24 hr. Cooling caused solidification of the reaction, due mainly to the presence of a trimer of chloral. Reheating the reaction produced a suspension which was filtered while hot and the solids were washed with a little ether. A tan solid, m.p. 249.5–252.5° dec., 4.79 g. (51%), resulted. Recrystallization from ethanol–ether gave a white solid, m.p. 240.5–241.5° dec.

Anal. Calcd. for $C_{10}H_9Cl_3N_2O \cdot HCl$: C, 38.00; H, 3.19; N, 8.87. Found: C, 37.85; H, 3.31; N, 8.52.

β-(Imidazo[1,2-*a*]pyrid-2-yl)acrylic Acid Hydrochloride (X).—To 1.6 g. (0.005 mole) of IX in 3 ml. of ethanol at reflux, was slowly added a solution of 1.0 g. (0.025 mole) of sodium hydroxide in 2 ml. of water. After vigorous reaction subsided, the mixture was refluxed for 20 min. Cooling, filtration, and evaporation yielded a red-yellow residue which was redissolved in 25 ml. of ethanol and acidified with excess ethanolic hydrochloric acid. Cooling, filtration, and evaporation of the filtrate produced a light pink solid, 0.56 g. (51%), m.p. 245.5–247.5° dec. An analytical sample was crystallized from ethanol–ether: m.p. 252.5–254.5° dec.; λ_{max}^{EtOH} 248 mμ (ε 17,200), 256 (20,800), 300 (6700), and 324 (8050).

Anal. Calcd. for $C_{10}H_8N_2O_2 \cdot HCl$: C, 53.46; H, 4.04; N, 12.47. Found: C, 53.80; H, 4.35; N, 12.85.

Catalytic Reduction of 3-Dimethylaminomethylimidazo[1,2-*a*]-pyridine.—After saturating a suspension of 0.75 g. of 10% palladium on charcoal in 10 ml. of ethanol with hydrogen at atmospheric pressure, a solution of 0.7 g. (0.005 mole) of 3-dimethylaminomethylimidazo[1,2-*a*]pyridine in 30 ml. of ethanol and 0.88 ml. of 6 *N* hydrochloric acid was added. Stirring at room temperature overnight allowed absorption of 268 cc. (100%, 2 equiv.) of hydrogen. No further hydrogen was absorbed. Filtration and concentration followed by addition of ether produced 0.59 g. (60%) of a white solid in two crops, probably **dimethylaminomethyl-5,6,7,8-tetrahydroimidazo[1,2-*a*]pyridine dihydrochloride**, m.p. 233–240°. Recrystallization from ethanol–ether gave m.p. 251.5–253.5°.

Anal. Calcd. for $C_{10}H_{17}N_3 \cdot 2HCl$: C, 47.62; H, 7.59; N, 16.66. Found: C, 47.40; H, 7.35; N, 16.84.

An ultraviolet spectrum in ethanol exhibited no maxima but absorption decreased steadily from 220 to approximately 350 mμ.

Attempts to Displace Dimethylamine from IV or VI. A.—Combining 4.0 g. (0.023 mole) of 3-dimethylaminomethylimidazo[1,2-*a*]pyridine (IV, R_1 and R_2 = methyl), 6.09 (0.122 mole) of sodium cyanide, 50 ml. of ethanol, and 14 ml. of water produced a pale yellow suspension which was refluxed for 3 days. Cooling produced a solid shown to be sodium cyanide. Evaporation of the filtrate to dryness produced a residue which was triturated with acetone. Evaporation of the acetone yielded 3.3 g. (83% recovery) of starting material, m.p. 74.5–79.5°, m.m.p. 76–80°. The infrared spectrum was identical with that of IV (R_1 and R_2 = methyl).

B.—In dimethyl sulfoxide solvent with excess sodium cyanide at 175° for 7.5 hr., IV (R_1 and R_2 = methyl) was essentially unaffected (paper chromatogram evidence).

C.—Attempted reaction of VI (R_1 and R_2 = methyl) with sodium cyanide in ethanol–water produced no dimethylamine during 57 hr. of reflux. Evaporation to dryness and acetone trituration followed by evaporation of the acetone yielded 68% of recovered starting material, m.p. 62.5–65.5°; mixture melting point with authentic VI (R_1 and R_2 = CH_3, m.p. 60–63°) was 61.5–64.5°.

Attempts to Displace Trimethylamine from VII. A.—Treatment of 0.64 g. (0.002 mole) of VII with 0.5 g. of sodium cyanide, 10 ml. of ethanol, and 10 ml. of water produced no significant gas evolution after attaining reflux temperature. The pale yellow solution was refluxed for 70 hr. with no change in appearance. After evaporation, paper chromatographic evidence showed significant amounts of starting material together with a few trace impurities.

B.—An attempt to displace trimethylamine from VII using sodium diethyl acetamidomalonate in refluxing toluene produced no significant gas evolution during 24 hr. of refluxing. Paper chromatographic analysis showed unchanged VII as a major spot.

Acknowledgment.—The author is grateful to Mr. Nelson Treadway and Mr. Ronald Seidell for assistance in the synthetic work. Discussions of the n.m.r. data with Dr. I. M. Goldman and Dr. K. Murai of these laboratories were most helpful.

4,6-Dinitrobenzofuroxan. I. Covalent Hydration[1]

WILLIAM P. NORRIS AND JAMES OSMUNDSEN

Chemistry Division, Research Department, U. S. Naval Ordnance Test Station, China Lake, California

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4,6-Dinitrobenzofuroxan (I) reacts with bases, including water, to give classical Meisenheimer addition compounds (IIIa) characteristic of polynitroaromatics. The behavior of I is unusual because of the formation of an addition compound with the very weak base water. The acid resulting from the adduction of water is sufficiently strong to liberate carbon dioxide from bicarbonate. The structure of IIIa is established from analytical data, ultraviolet, infrared, and n.m.r. spectroscopic data and deuterium and O^{18} exchange experiments.

Since 4,6-dinitrobenzofuroxan (I) was first prepared its acidic character in aqueous solution has intrigued investigators.[2–6] It has no obviously acidic functional group, except that it is a strong π acid, forming complexes with many aromatic hydrocarbons,[7] yet it readily displaces carbon dioxide from bicarbonates to give stable salts. Treatment of the salts with mineral acids regenerates I. π acids of comparable or greater strength, such as 1,3,5-trinitrobenzene, 5,6-dinitrobenzofuroxan, and benzotrifuroxan, do not displace carbon dioxide from bicarbonate solutions under the same conditions.

4,6-Dinitrobenzofuroxan titrates as a strong monobasic acid in 50% ethanol showing a pH of 7.0 at the

(1) Presented before the Division of Organic Chemistry, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964; Abstracts, p. 81S.

(2) P. Drost, *Ann.*, **307**, 49 (1899); **313**, 299 (1900).

(3) T. Zincke and P. Schwartz, *ibid.*, **307**, 32 (1899).

(4) A. G. Green and F. M. Rowe, *J. Chem. Soc.*, **103**, 2023 (1913).

(5) C. L. Jackson and R. B. Earle, *Am. Chem. J.*, **29**, 89 (1903).

(6) R. J. Gaughran, J. P. Picard, and J. V. R. Kaufman, *J. Am. Chem. Soc.*, **76**, 2233 (1954).

(7) A. S. Bailey and J. R. Case, *Tetrahedron*, **3**, 113 (1958).

equivalent point. A saturated solution of I in 50% ethanol has an indicated pH of 3. In water solution I has virtually the same ultraviolet-visible spectrum as its potassium salt (Table I). The addition of excess sodium hydroxide solution to an aqueous solution of I increases the absorption due to the anion only slightly and does not increase the absorption over that of the potassium salt. This means that not only is I present mainly as the anion in dilute solution but also that the potassium salt is not hydrolyzed appreciably in dilute solution. The spectra of I in chloroform and in 10^{-3} *M* hydrochloric acid are similar and distinctly different from that of the anion.

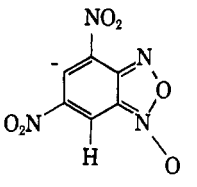
TABLE I

ULTRAVIOLET AND VISIBLE SPECTRA OF I[a]

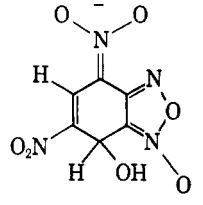
Compd., 5×10^{-5} *M*	Solvent	λ_{max}, mμ (ϵ_{max})		
I	$CHCl_3$	420 (7,600)	272 (12,800)	258 (12,300)
I	H_2O (10^{-3} *M* HCl)	416 (7,600)	278 (10,600)	259 (10,000)
I	H_2O	463 (21,200)	302 (7,000)	263 (10,100)
I	H_2O (10^{-3} *M* NaOH)	463 (25,200)	302 (8,000)	263 (11,200)
K salt	H_2O	463 (25,500)	302 (8,060)	263 (11,200)

[a] Spectra were obtained on a Model 11 Cary spectrophotometer.

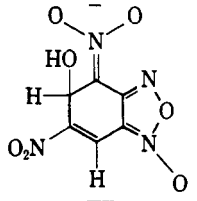
The nature of the anion has never been carefully examined. Drost,[2] on the basis of a limited amount of analytical data, suggested that a ring proton ionizes in aqueous solution to give an anion of the composition, $C_6HN_4O_6^-$. Gaughran, *et al.*,[6] reached a similar conclusion and proposed II for the structure of the anion. Jackson and Earle[5] disagreed with Drost and preferred



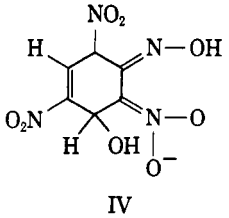
II



IIIa



IIIb



IV

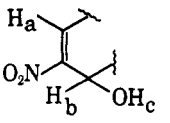
instead a metal hydroxide addition complex with I to give an anion such as IIIa or IIIb which is similar to the addition complex formed by metal hydroxides and 1,3,5-trinitrobenzene, but did no experimental work on the problem.

Structure IV, which could be formed by opening the furoxan ring with water or hydroxide ion, is also considered here despite the lack of precedent for this type of reaction because it gives a highly stabilized anion which is required to explain the acidic reaction of I in water. Also, 2,4,6-trinitrophenylhydroxylamine is known[8] and apparently does eliminate water under certain conditions to give I.[9] It will be noted that the empirical formula for II differs from that of III and IV by one molecule of water only.

Our elemental analyses for the potassium and the rubidium salts are in excellent agreement with the formulas for III and IV. To check on the possibility that the salts are merely very stable hydrates of II, the potassium salt was prepared in deuterium oxide. This salt exhibits an O–D infrared absorption band at 3.92 μ and heating at 100° for 24 hr. under vacuum fails to diminish the intensity of the band. Acidification of the deuterated salt with deuterium sulfate gives back I containing no deuterium as judged by its infrared spectrum.[10] This eliminates II since deuterium–hydrogen exchange would have occurred had II been the structure of the anion.

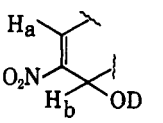
Structure IV contains an oxygen that derives from the water solvent. Conversion of the salt back to I could result in the incorporation of some of the water oxygen into the furoxan ring and into the adjacent nitro group. When the salt was prepared in O^{18}-enriched water and then converted back to I, no excess O^{18} could be found. The sensitivity of the method is such that exchange to the extent of 3% for a single oxygen can be detected. Hence, if IV is involved at all, the water oxygen entering upon anion formation departs when I re-forms.

Proton magnetic resonance offers the best evidence for deciding on the structure of the anion. The spectrum of a saturated solution of the potassium salt in dimethyl sulfoxide at 25° gives τ 1.07, 3.80 (doublet), and 3.45 (doublet) with J = 7 c.p.s. for the latter two. When the potassium salt that has been prepared in deuterium oxide is used, peaks at τ 1.07 and 3.80 are obtained. These results are consistent with the structure segments V and VI and together with the O^{18} experiments eliminate IV. The use of the deuterated salts permits assignment of τ values for all the protons.



V

H_a, τ 1.07
H_b, τ 3.80 (J = 7 c.p.s.)
H_c, τ 3.45 (J = 7 c.p.s.)



VI

H_a, τ 1.07
H_b, τ 3.80 ($J \sim 1$ c.p.s.)

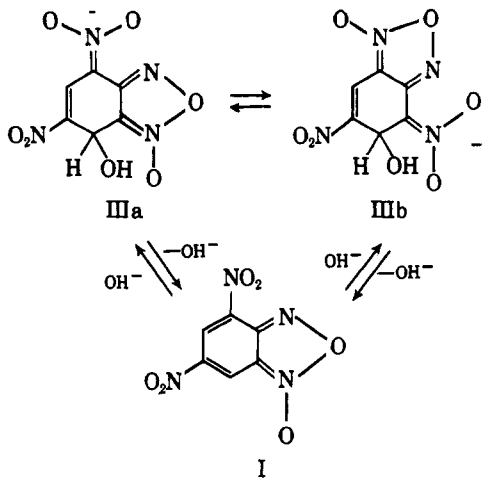
Structures IIIa and IIIb then are both consistent with the n.m.r. results and it is not possible to discriminate between the two on this basis. Actually, both may exist, particularly in solution. Interconversion between IIIa and IIIb is possible by two different paths. One path is by reversible hydroxylation at the 5- and the 7-positions and the other path involves a rearrangement in which a new nitro group appears *meta* to the 4-nitro group and the 4-nitro group is incorporated in a new furoxan ring. Boulton and Katritzky[11] found that 5-methyl-4-nitrobenzofuroxan rearranges in this manner, when heated, to 7-methyl-4-nitrobenzofuroxan. What the effect of a

(8) W. Borsche, *Ber.*, **56**, 1939 (1923).

(9) R. Nietzki and R. Dietschy, *ibid.*, **34**, 55 (1901); F. K. Beilstein, "Handbuch der organischen chemie," Vol. 7, 4th Ed., 1925, p. 608.

(10) This might be expected since 1,3,5-trinitrobenzene does not undergo hydrogen–deuterium exchange in basic deuterium oxide [J. A. A. Ketelaar, A. Bier, and H. T. Vlaar, *Rec. trav. chim.*, **73**, 37 (1954); R. E. Miller and W. F. K. Wynn-Jones, *J. Chem. Soc.*, 2375 (1959)].

(11) A. J. Boulton and A. R. Katritzky, *Proc. Chem. Soc.*, 257 (1962).



IIIa IIIb

I

negative charge in the molecule would be on the rate of such a rearrangement is not known. The n.m.r. spectrum indicates only one substance in dimethyl sulfoxide solution. If a second substance is present, its n.m.r. spectrum is identical with the other, it is present in too small an amount to detect, or the two are exchanging at a rapid rate.

Consideration of resonance forms that can be written indicates that IIIa should be slightly more stable than IIIb and hence at equilibrium IIIa should predominate. The correct structure for the anion formed by the reaction of 4,6-dinitrobenzofuroxan with water or an aqueous base then is considered to be IIIa and its various resonance forms.

Experimental

Preparation of the Potassium Salt of I.—One gram (4.4 mmoles) of 4,6-dinitrobenzofuroxan was added to an aqueous solution of 2.0 g. (20 mmoles) of potassium bicarbonate in 15 ml. of water. The mixture was stirred for 4 hr. at 25°.[12] The fine golden platelets were filtered off, washed with 10 ml. of cold water, then with acetone, and dried to give 1.05 g. (85% yield), m.p. 210° (explodes). (Caution!! These salts, in the dry state, are extremely sensitive to friction and impact and explode with great force.)

Anal. Calcd. for $C_6H_3KN_4O_7$: C, 25.53; H, 1.07; K, 13.85; N, 19.85. Found: C, 25.40, 25.35; H, 1.01, 0.95; K, 13.78, 13.87; N, 19.67, 19.59.[13]

The deuterated salt was prepared by the same procedure using 99.5% deuterium oxide instead of water.

Anal. Calcd. for $C_6H_2DKN_4O_7$: N, 19.78. Found: N, 20.14.

The rubidium salt was prepared by the same procedure, except rubidium carbonate was used instead of potassium bicarbonate, to give fine orange-red needles, 1.25 g. (87% yield). The salt may be recrystallized by dissolving in water and cooling to give beautiful deep red needles.

Anal. Calcd. for $C_6H_3N_4O_7Rb$: C, 21.93; H, 0.92; N, 17.05; Rb, 26.01. Found: C, 22.09, 22.03; H, 0.86, 1.01; N, 17.20, 17.21; Rb, 25.88, 25.98.[13]

Attempted Oxygen Exchange with I.—The potassium salt of I was prepared by combining 0.35 g. (1.5 mmoles) of 4,6-dinitrobenzofuroxan with 0.154 g. (1.5 mmoles) of potassium bicarbonate and 4 ml. of water, containing 7.75% excess O^{18}, in a small bottle with a screw cap. The bottle was placed on a shaker for 1 hr. The salt of I was separated by filtration, washed with 1 ml. of the O^{18}-enriched water, and dried under vacuum at 50° for 24 hr. The salt was then suspended in 5 ml. of dry ethylene dichloride and treated with dry hydrogen chloride. The potassium chloride was filtered off, and the filtrate was concentrated to 2 ml. 4,6-Dinitrobenzofuroxan, 0.18 g., crystallized from solution. Its melting point and infrared spectrum were identical with those of the initial 4,6-dinitrobenzofuroxan. The oxygen in the molecule was analyzed for excess O^{18} by first converting it to carbon monoxide and then analyzing the carbon monoxide on a Consolidated mass spectrometer, Model 21-103. Carbon monoxide was produced by pyrolyzing a sample of the above prepared 4,6-dinitrobenzofuroxan and passing the gases through a tube packed with platinum on carbon at 950°.[14] The exit gases, using helium as the carrier, were trapped on charcoal at liquid nitrogen temperature. The trap was warmed to room temperature and the carbon monoxide was separated from the nitrogen by gas chromatography. Four samples were run and none showed enrichment in O^{18} within experimental error. Check runs using O^{18}-labeled dicyclohexylurea proved the reliability of the system. If one oxygen of I had exchanged fully with O^{18} in the water then there would have been an excess of 1.27% O^{18} in the carbon monoxide. By using a sample size that gives a reading of 5000 divisions on the mass spectrometer for mass 28 (CO^{16}) then the normal abundance of 0.2% CO^{18} would give 10 divisions of mass 30 and the 1.27% excess O^{18} would register an additional 64 divisions at mass 30. The accuracy of the method is such that 2 divisions excess of mass 30 would be significant which means that 2/64 or 3% exchange could be detected. Hence less than 3% exchange occurred.

Preparation of Dicyclohexylurea-O^{18}.—Crude dicyclohexylcarbodiimide was dissolved in cyclohexane and filtered, and the cyclohexane was evaporated under vacuum. The purified dicyclohexylcarbodiimide was dissolved in 3 ml. of dry tetrahydrofuran and to this was added 0.27 g. of water which contained approximately 1.4% excess O^{18}. The system was refluxed for 30 min. The crystalline solid was filtered off and recrystallized from chloroform to give dicyclohexylurea, m.p. 228–229°. The analysis (see Table II) shows 1.2% excess O^{18} in the sample. No independent analysis on the O^{18} content was obtained.[15]

TABLE II

MASS SPECTROMETER DATA ON CO FROM I AND DICYCLOHEXYLUREA

	—Divisions, mass spectrometer reading—		
Sample	Mass 28	Mass 30 (calcd. normal abundance)	Excess mass 30
I[a]	4428	8.9	+0.1
I[a]	6935	13.9	−0.7
I[a]	4516[b]	9.0[b]	−0.3[b]
	4971[c]	9.9[c]	+0.2[c]
I[a]	4677[b]	9.4[b]	−0.5[b]
	4208[c]	8.4[c]	+0.5[c]
I	6598	13.2	+0.9
I	4736	9.5	0.0
Dicyclohexylurea-O^{18}	6114	12.2	71.8
Dicyclohexylurea-O^{18}	6129	12.3	71.9

[a] Received O^{18}-enriched water treatment. [b] Front part of v.p.c. peak. [c] Back part of v.p.c. peak.

(12) Heating the reaction mixture as in Drost's procedure[2] causes it to turn dark and lowers the yield of the salt.

(13) Analyses were performed by Alfred Bernhardt, Mülheim, Germany.

(14) D. B. Denney and M. A. Greenbaum, *J. Am. Chem. Soc.*, **79**, 979 (1957).

(15) The gas chromatography and mass spectrometry were performed by J. H. Johnson of this laboratory.