CHEMISTRY LETTERS, pp.569-570, 1974. Published by the Chemical Society of Japan

THE REACTION OF BIS(NITROMETHYL)PREHNITENE WITH AQUEOUS AMMONIA

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When bis(nitromethyl)prehnitene (1) was treated with 28% aqueous ammonia at 100°C in a sealed tube, N-hydroxytetramethylphthalimide (6"), 2-cyano-3,4,5,6-tetramethylbenzoic acid (9"), tetramethylphthalimide (10") and 2-hydroxy-3-hydroxyimino-4,5,6,7-tetramethylphthalimidine (5") were formed as ammonium salts.

It seems that 5" is initially formed, and then rapidly hydrolyzed to produce 6", which is finally converted to 10" via 9".

The acid hydrolysis of a salt of a primary or secondary nitroalkane affords an aldehyde or a ketone, respectively, and nitrous oxide (Nef reaction).[1,2] Closely related to the Nef reaction is the hydrolysis of free primary nitroalkanes with concentrated mineral acid to the corresponding carboxylic acids and hydroxylamine salts.[3] And, it is considered that the above reactions of nitroalkanes require an initial acid-catalyzed isomerization to nitronic acid.[4]

On the other hand, no reports of the alkaline hydrolysis of a salt of a nitroalkane or free nitroalkane have been found.

In the present letter, the reaction of bis(nitromethyl)prehnitene (1), which has two adjacent nitromethyl groups, with aqueous ammonia was studied.

1 (0.1 g) was treated with 28% aqueous ammonia (15 ml) at 100°C in a sealed tube. The resulting pale yellow solution was cooled to room temperature, and treated with a large excess of silver nitrate solution (50 g / 20 ml) under cooling. The precipitate was collected by filtration, dried, and refluxed with methyl iodide in benzene. An insoluble material was filtered off, and the filtrate was evaporated to dryness under reduced pressure. From the residue, N-methyltetramethylphthalimide (10'), N-methoxytetramethylphthalimide (6'), methyl 2-cyano-3,4,5,6-tetramethylbenzoate (9') and small amounts of unknowns were isolated by column chromatography on alumina. But neither tetramethylphthalate nor tetramethylphthalamidate was detected. 10', mp 180-181°C, and 9', mp 75-76°C, were identified by comparison with IR and NMR spectra of authentic samples.[5] The structure of 6', mp 203-204°C, was deduced from its elemental analysis and spectral data; Found: C, 67.15; H, 6.32; N, 6.18 %; mol wt(Rast),236. Calcd for $C_{13}H_{15}N\,O_3$: C, 66.93; H, 6.48; N, 6.01 %; mol wt, 233. IR(KBr, cm^{-1}): 1760, 1719(C=O), 1254, 1146, 1102, 998,and 905(C-N, C-O or N-O). NMR($CDCl_3$, δ ppm from TMS): 2.24(s, Ar-CH_3, 6H), 2.56(s, Ar-CH_3, 6H) and 4.00(s, O-CH_3, 3H).

Further, from the reaction mixture in a early stage (Expt. No. 1), trace of 2-methoxy-3-methoxyimino-4,5,6,7-tetramethylphthalimidine (5'), mp 156-158°C, was isolated in a similar manner; Found: C, 64.61; H, 7.06; N, 10.73 %. Calcd for $C_{14}H_{18}N_2O_3$: C, 64.10; H, 6.92; N, 10.68 %. IR(KBr, cm^{-1}): 1725(C=O), 1637 (C=N), 1265, 1146, 1121, 1037, 994, and 932(C-N, C-O or N-O). NMR($CDCl_3$, δ ppm from TMS): 2.15(d, Ar-CH_3, 6H), 2.50(d, Ar-CH_3, 6H) and 4.04(d, O-CH_3, 6H).

As shown in Table 1, 6' was initially obtained as a major product. But, on continued warming, 6' decreased, whereas 10' increased.

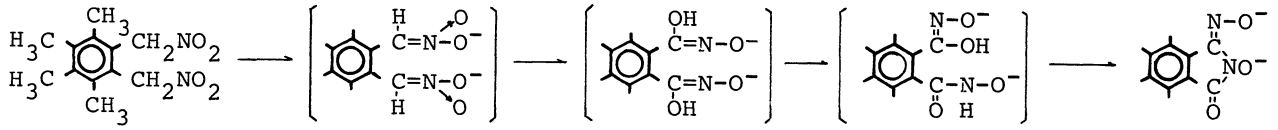
From above results, a plausible reaction path is shown in the following scheme. There is no evidence pertaining to the mechanism of conversion of nitronate to hydroxamate. But, it seems reasonable to assume that nitronate (2) formed by the reaction of 1 with aqueous ammonia is converted to hydroxamate (3 or 4). Ammonium tetramethylphthalamidate is easily converted to ammonium tetramethylphthalimide even at room temperature, probably since the steric repulsion of the four methyl groups on the benzene ring facilitates the cyclization between the amide group and the carboxyl group.[5] Similarly, 4 would be easily converted to the cyclized product (5), which is hydrolyzed to produce ammonium salt of N-hydroxytetramethylphthalimide (6). Also, it is certain that 2-cyano-3,4,5,6-tetramethylbenzoate (9) is rapidly converted to ammonium tetramethylphthalimide (10).[5]

Further work is under way to determine the mechanism of this reaction.

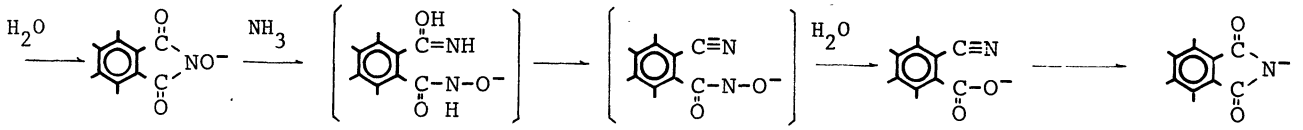
Table 1 Experimental results

Expt.No.	Conditions		Products(mol%)*			
	Temp.(°C)	Time(hr)	6'	9'	10'	Unknowns
1	100	0.5	50	12	20	-
2	100	2	27	12	36	6
3	100	7	10	4	44	20

* The yields were determined by g.l.c.(Silicone DC550 / Celite 545 1 m, 215°C, N_2 40 ml / min)



1 2 3 4 5



6 7 8 9 10

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The reaction of tetramethylphthalic anhydride with aqueous ammonia was studied.

(Received April 4, 1974)