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THE BROMINATION OF TRIETHYLAMINE

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Summary: The products of bromination of triethylamine have been reinvestigated and shown to be N,N-diethyl di- and tribromoacetamides. The rotational barrier for the dibromoamide was measured, $E_a = 40$ kJ mol^{-1} and found to be considerably lower than that of N,N-diethylacetamide.

That bromine reacts with tertiary aliphatic amines appears to be little known and hardly investigated. Norris in 1889 reported that triethylamine reacted with bromine to give a dark red oil which was not characterised,[1] and that other tertiary amines behaved similarly. We now report the structures of these products.

A solution of anhydrous triethylamine (19.2g, 0.336 mol) in dichloromethane (100 ml) was cooled in ice and stirred. Bromine (43g, 0.27 mol) in dichloromethane (100 ml) was added dropwise over 1 hour. Initially, the bromine was instantly decolourised although, as the addition proceeded, the solution became progressively more yellow. A test with starch-iodide showed that no oxidising species was present in the solution until about 75% of the bromine had been added, corresponding to an uptake of 1 mol bromine by about 1.7 mol amine. The dark red solution was allowed to stand for 1 hour then washed with water and dried ($CaCl_2$). The aqueous washings contained triethylammonium bromide. The solvent was removed from the organic layer leaving a dark red oil, presumably that reported by Norris. A portion was distilled using a short path distillation bulb when a clear red oil was obtained, b.p. 120^o/0.05 mm. Distillation on a larger scale was unsuccessful as extensive decomposition set in. The mass spectrum of the red oil showed a quartet of parent ion isotopic peaks at m/e = 349, 351, 353 and 355 indicating a formula $C_6H_{10}NOBr_3$. The presence of a carbonyl group ($\bar{\nu} = 1680$ cm^{-1}) and the ^{1}H-NMR spectrum showing absorption due only to ethyl groups ($\delta = 1.25$, (triplet), 3.5 (quartet)) confirmed the structure as N,N-diethyl tribromoacetamide, $CBr_3CO.N(C_2H_5)_2$, I. This compound has not previously been reported and so was independently synthesised from tribromoacetyl chloride and excess diethylamine. After workup as detailed above, a red oil was obtained having the same spectroscopic properties as I.

Bromination of triethylamine as above but with a 3 to 4 molar excess of amine gave a yellow liquid product which was separated by flash liquid chromatography on silica (eluent ether-cyclohexane, 1:1) into two fractions, one being I. The other crystallised on pumping, m.p. 80°. The infrared, mass, and NMR spectra of this compound were consistent with the structure being N,N-diethyl dibromoacetamide, $CHBr_2CON(C_2H_5)_2$, II, which was confirmed by synthesis of an authentic specimen, lit. m.p. 81°.[2] No monobromo acetamide nor diethyl acetamide were detected. Though these are likely precursors they must be brominated rapidly.

The ^1H NMR spectrum of II (δ = 5.9 (singlet), α-CH; 3.3 (doublet quartet), $-CH_2$ and 1.3 (doublet triplet), $-CH_3$) showed clear non-equivalence of the ethyl groups at 30°. Spectra were run over the range 30-72° and the temperature at which coalescence occurred established as 50° ± 0.5. Measurement of the line-widths allowed an estimate to be made of the rotational rates in this temperature range , which led to an activation energy for rotation of 40 ± 5 kJ mol^{-1}. This is considerably less than that for rotation in N,N-diethylacetamide (74 kJ mol^{-1})[3] presumably on account of the electron-withdrawing bromines which reduce the C-N bond order.

It seems, therefore, that bromination of triethylamine is initiated by oxidation at an α-carbon followed by rapid bromination of the β-carbon, presumably by a base-catalysed sequence of steps since diethylacetamide itself is not rapidly brominated in neutral dichloromethane solution.

The oxygen in the product must originate from water and, since careful drying of the reagents did not affect the outcome of the reaction, we conclude that some hydrolytic step occurred in the workup.

References.

1. J.F.Norris, Amer.Chem.J., 20, 51 (1889).
2. A.B.Sen and K.C.Joshi, J.Ind.Chem.Soc., 25, 483 (1948).
3. T.H.Siddall, W.E.Stewart, and F.D.Knight, J.Phys.Chem., 74, 3580 (1970).

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