

The Reaction of Isatin with an Excess of Ethylamine

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It has been reported (1) that the reaction of isatin with an equimolar quantity of ethylamine gave the expected imine **1**, while reaction of isatin with an excess of ethylamine provided a relatively unstable compound, $C_{14}H_{21}N_3O$, to which Haslinger (1) assigned structure **2**.

We have confirmed that the reaction of isatin in an excess of ethylamine gives rise to a compound, $C_{14}H_{21}N_3O$. We should, however, like to propose **3** as a more reasonable structure for this compound. Compound **3** is also obtained when the imine **1** or the analogous propyl imine is allowed to stand overnight in ethylamine. When the reaction of isatin or of **1** with an excess of ethylamine is carried out in ethanol a purple gum, from which no crystalline products have been obtained, is isolated.

Although no molecular ion is detected in the high resolution mass spectrum of **3** there is a weak $(m + H)^+$ with the correct composition ($m/e = 248$, $C_{14}H_{22}N_3O$) and the chemical ionization mass spectrum shows a very intense peak at $m/e = 248$. The very intense $C_4H_{10}N$ fragment ion peak ($m/e = 72$) together with the moderately strong peak at $m/e = 177$ corresponding to the loss of C_4H_8N from the apparent molecular ion strongly suggests the presence of a nitrogen attached to two ethyl groups. The $m/e = 177$ ion is probably the protonated molecule ion of **4** which would be expected to be readily generated from **3**. An $m/e = 353$ ion in the chemical ionization mass

spectrum of **3** is probably the protonated dimer of **4**. The ir spectrum of **3** is also consistent with the structure assigned, (2).

Further confirmation of the structure **3** was obtained by treatment of **3** with hydrochloric acid to give **4** which was isolated as its hydrochloride. Compound **4** was also obtained from catalytic hydrogenation of **1**. A comparison of the mass spectra of **3** and **4** indicates that except for the peaks at m/e 72 (99%) and 71 (18%) which are present in **3**, all of the major peaks are identical ($m/e = 177, 148, 147, 134, 133$ (100%), 132, 120, 119, 106, 104, 77).

EXPERIMENTAL

Reaction of Isatin with an Excess of Ethylamine.

Ethylamine (18.0 g.) was added to 5.88 g. of isatin and the mixture was allowed to stand in an open flask overnight at room temperature. Filtration and recrystallization from ethyl acetate gave 1.76 g. of **3**, m.p. 125-126°; ir (potassium bromide): 3300, 3200, 3100, 3000, 2800, 1725, 1635 cm^{-1} . Mass spectrum: 248 (0.14%), 202 (3%), 177 (26%), 175 (8%), 174 (8%), 159 (11%), 149 (12%), 148 (56%), 147 (25%), 134 (9%), 133 (C_8H_7NO) (100%), 133 ($C_8H_9N_2$) (45%), 132 (83%), 130 (7%), 120 (11%), 119 (63%), 118 (11%), 106 (46%), 104 (15%), 92 (8%), 77 (15%), 72 (99%), 71 (18%), 70 (14%), (2).

Anal. Calcd. for $C_{14}H_{21}N_3O$: C, 67.98; H, 8.55; N, 16.99. Found: C, 68.14; H, 8.41; N, 16.73.

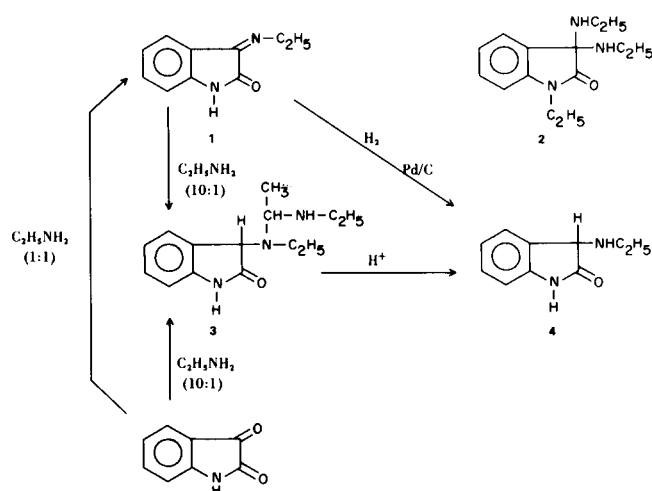
When this reaction was carried out in absolute or 95% ethanol a thick purple gum was obtained. No crystalline products were isolated from this gum.

Reaction of Isatin Imines with an Excess of Ethylamine.

A mixture of 1.74 g. of **1** and 4.5 g. of ethylamine was allowed to stand overnight in an open flask at room temperature. Addition of ethyl acetate and filtration gave 1.11 g. of **3** identical with that obtained from isatin. In a similar manner, the propyl analogue of **1** also gave **3**.

Acid Hydrolysis of **3**.

A solution of 2.47 g. of **3** in 10 ml. of concentrated hydrochloric acid and 60 ml. of ethanol was stirred at room temperature for 30 minutes. The solvent was removed *in vacuo* and the residue treated with acetone to give 1.87 g. of the hydrochloride of **4**, m.p. 199-202° from ethanol-water; ir (potassium bromide): 3200, 2900, 2700, 2520, 2350, 1720, 1620 cm^{-1} ; nmr (DMSO- d_6): 11.2 (1), 10.4 (2), 8.0 (1), 7.2 (3), 5.0 (1), 3.2 (2), 1.2 δ (3); mass spectrum: 177 (41%), 148 (60%), 147 (33%), 134 (10%), 133 (100%), 132 (49%), 120 (9%), 119 (56%), 106 (21%), 104 (9%),



77 (11%).

Anal. Calcd. for $C_{10}H_{13}ClN_2O$: C, 56.47; H, 6.16; N, 13.17; Cl, 16.67. Found: C, 56.44; H, 6.12; N, 13.14; Cl, 16.47.

Catalytic Hydrogenation of **1**.

A slurry of 1.74 g. of **1**, 0.25 g. of 10% Pd/C, and 30 ml. of ethyl acetate was shaken under hydrogen. The reaction mixture was filtered and the solvent removed *in vacuo*. Addition of ether to the residue yielded 0.60 g. of **4**. This product was dissolved in ethyl acetate and hydrogen chloride bubbled in to give the hydrochloride of **4** identical in all respects to that described above.

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REFERENCES

(1) C. Haslinger, *Ber.*, **40**, 3598 (1907); *ibid.*, **41**, 1444 (1908).

(2) Compound **3** underwent decomposition or was insoluble in all useful nmr solvents.