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CELÂL TÜZÜN

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Reaction of N-Methylaniline And N-Ethylaniline With β-Chloroethanol

CELÂL TÜZÜN*

Department of General Chemistry, Faculty of Science, University of Ankara, Ankara, Turkey

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The reaction between N-methylaniline and N-ethylaniline with β-chloroethanol in 1:2, 1:1 and 2:1 mole ratios at 60°C and 90°C for 72 hrs, was studied. In the 60°C reactions, all mole ratios gave the moderate yield of N-methyl/or ethyl-N-β-hydroxyethylaniline, about 50 %, while in 90°C reactions, 1:2 and 2:1 mole ratios gave low yield but 1:1 mole ratio gave the highest yield, 90 %.

INTRODUCTION

Reaction between N-methylaniline and aniline with β-chloroethanol have been widely investigated. Otto [1] heated aniline and β-chlorethanol and obtained N-β-hydroxyethylaniline. Rindfuzs and Harnac [2] heated the same compounds in the presence of sodium carbonate, Dashen and Brewster [3] refluxed the same compounds in an aqueous medium, Yamamoto and Ikegami [4] heated at 90–100°C for 4–6 hours, all of these authors obtained the same compound, N-β-hydroxyethylaniline, in different yields. Laun [5] heated N-methylaniline and β-chloroethanol in a sealed tube, Wilson [6] heated the same compounds at 100°C for 35 hours, Teplov, Godovikow and Kabachnic [7] heated together the same compounds and all obtained N-methyl-N-β-hydroxyethylaniline. On the other hand, very little work has been done on the reaction between N-ethylaniline and β-chloroethanol. Laun [5] heated N-ethylaniline and β-chloroethanol in a sealed tube and obtained N-ethyl-N-β-hydroxyethylaniline which has

* Mailing address: Umumi Kimya, Fen Fakültesi, Ankara, Turkey.

been sythesized by different ways: Gabel [8] heated aniline in a stream of ethylene oxide, Bent et al. [9] heated the same compounds in a sealed tube. Horyna, Virac and Petranek [10] heated the above compounds in the presence of N, N-diethylaniline. Tüzün [11] treated the magnesium salt of N-ethylaniline with ethylene oxide in etheral solution at room temperature, all obtained N-ethyl-N-β-hydroxyethylaniline in different yields.

In the present work, the reaction between N-methylaniline and N-ethylaniline with β-chloroethanol was investigated in various mole ratios (1:2, 1:1 and 2:1) and at two different temperatures, 60°C and 90°C. The reaction period was 72 hours. At the end of the reactions, the mixtures were cooled down, treated with a sufficienta omunt of 10 % sodium hydroxide and extracted with benzene. The benzene extracts were dried, the solvent removed *in vacuo*, and the remaining materials fractionally distilled under diminished pressure. The results are shown in Table I and Table II.

Table I.

Reaction between N-methylaniline and β-chloroethanol (72 hrs)

Temperature →	60°C	90°C
Mole ratio of N-Methylaniline: β-chloroethanol	Per cent of (C)	Per cent of (C)
1:2	52	9.7
1:1	57	92
2:1	56	46

(C), N-methyl-N-β-hydroxyethylaniline

Table II.

Reaction between N-ethylaniline and β-chloroethanol (72 hrs)

Temperature →	60°C	90°C
Mole ratio of N-Ethylaniline: β-Chloroethanol	Per cent of (D)	Per cent of (D)
1:2	48	8.1
1:1	45	88
2:1	47	42

(D), N-Ethyl-N-β-hydroxyethylaniline

DISCUSSION

According to above results, the yield at 60°C is virtually independent from the mole ratios of N-alkylaniline and β-chloroethanol. This is a moderate yield, about 50 per cent. Probably the the reason for this, is that excess of N-alkylaniline or β-chloroethanol is inactive against the reaction product, N-alkyl-N-β-hydroxyethylaniline, at 60°C, and an equilibrum is reached.

On the other hand, at 90°C, in 1:1 mole ratio gave the maximume yield, but 1:2 or 2:1 mole ratios gave the lower yields. Probably, excess of the material, either N-alkylaniline or β-chloroethanol reacts on the product, at the higher temperature, 90°, and lowers the yield. In the case of excess of β-chloroethanola considerable amount of water soluble material is formed, in the case of excess of N-alkylaniline a viscous and high boiling material (probably high molecular compounds) is formed and effected a lower yield.

EXPERIMENTAL SECTION

In a constant temperature glycerol bath, whose temperature kept constant at 60 ± 1°C, were placed 6 glass-stoppered 100 ml bottles, in which the following composition of mixtures were introduced:

Bottle No.	N-Alkylanilines*	β-Chloroethanol	Mole ratio
1	5.36 g (50 mmoles) of (A)	16.1 g (100 mmoles)	1:2
2	10.7 g (100 mmles) of (A)	16.1 g (100 mmoles)	1:1
3	10.7 g (100 mmoles) of (A)	8.05 g (50 mmoles)	2:1
4	6.06 g (50 mmoles) of (B)	16.1 g (100 mmoles)	1:2
5	12.1 g (100 mmoles) of (B)	16.1 g (100 mmoles)	1:1
6	12.1 g (100 mmoles) of (B)	8.05 g (50 mmoles)	2:1

* (A), N-Methylaniline; (B), N-Ethylaniline.

The bottles were heated for 72 hrs., then cooled down to room temperature. 25 ml of 5N NaOH was added in each of No. 1., 2., 4. and 5. bottle and 12.5 ml of 5N NaOH in each No. 3. and 6. bottle and shaken well. Each mixture was transferred into

a separatory funnel, extracted twice with 25 ml of benzene. Benzene extracts were combined, dried over anhydrous potassium carbonate, the solvent removed by distillation and residue fractionally distilled under diminished pressure. N-Methyl-Neβ-hyroxyethylaniline, (C), was collected at 116–118°C (2 mm Hg) [11], N-ethyl-N-β-hydroxyethylaniline,(D), at 120–122°C(2 mm Hg) [11]

The same operations were repeated for 90 ± 1°C also. The following result are obtained:

For 60°C reaction:*

1. 3.9 g (26 mmoles) of (C), yield: 52 %,
2. 8.6 g (57 mmoles) of (C), yield: 57 %,
3. 8.5 g (56 mmoles) of (C), yield: 56 %
4. 4.0 g (24 mmoles) of (D), yield: 49 %,
5. 7.5 g (45 mmoles) of (D), yield: 45 %,
6. 7.8 g (47 mmoles) of (D), yield: 47 %→

For 90°C reaction:*

1. 0.73 g (4.8 mmoles) of (C), 9.7 %,
2. 13.9 g (92 mmoles) of (C), yield: 92 %,
3. 7.1 g (46 mmoles) of (C), yield: 46 %,
4. 0.68 g (5.1 mmoles) of (D), yield: 8.1 %,
5. 14.6 g (88 mmoles) of (D), yield: 88 %,
6. 7.0 g (42 mmoles) of (D), yield: 42 %.

* The yields based on the alkylanilines.

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ÖZET

Bu çalışmada, N-metil anilin ve N-etil anilinin, β-klor etanolle 1:2, 1:1 ve 2:1 mol oranlarındaki karışımları 60°C ve 90°C sıcaklıklarda 72 saat süre ile reaksiyona sokulmuştur. 60°C de orta bir verimle (yaklaşık olarak % 50) N-metil-N-β-hidroksietil ani'in veya N-etil-N-β-hidroksietil anilin elde edilmiştir. 90°C de ise, 1:2 ve 2:1 mol oranlarında düşük verimler elde edildiği halde, 1:1 mol oranında % 90 gibi yüksek bir verim elde edilmiştir.

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