

SHORT
COMMUNICATIONS

Condensation of Aniline and *o*-Hydroxyaniline with 1,2-Dibromoethane

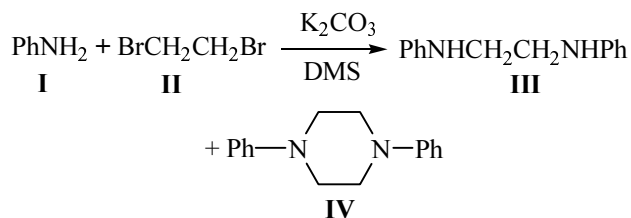
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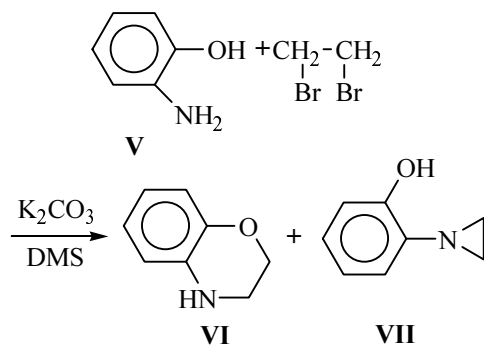
The alkylation of aniline with 3-chloro-2-chloromethyl-1-propene is known to furnish *N*-(2-chloromethylpropen-1-yl)aniline and cyclic tertiary amines [1].

We demonstrated that in the presence of excess K_2CO_3 in DMSO aniline **I** condensation with 1,2-dibromoethane **II** afforded products of linear (1,2-dianilinoethane **III**) and cyclic (*N,N*-diphenyl-1,4-diazine **IV**) structure.



Apparently first aniline undergoes *N*-alkylation with 1,2-dibromoethane in 2:1 ratio yielding reaction product **III** that further enters in the condensation with another 1,2-dibromoethane molecule to form compound **IV**.

The alkylation of *o*-hydroxyaniline **V** by dibromoethane **II** under the same conditions occurs as *N,O*- and *N,N*-dialkylation affording a products mixture: benzo-1,4-oxazine **VI** and 2-hydroxyphenylaziridine **VII**. We failed



to separate these compounds, and their structure and molar ratio (7:3) were estimated from the ^1H NMR spectrum.

The composition and structure of compounds **III**, **IV**, **VI**, and **VII** were proved by elemental analyses, IR and ^1H NMR spectra

1,2-Dianilinoethane (III). To a mixture of 12.1 g (0.13 mol) of aniline and 37.6 g (0.25 mol) of potassium carbonate in DMSO was added dropwise 25 g (0.13 mol) of 1,2-dibromoethane. Then the reaction mixture was stirred for 5 h at 20°C. The following 1.5 h the mixture was stirred at 50°C, then 7–8 h at 70–80°C. On cooling the mixture was treated with ethyl ether. The residue formed on evaporating the ether was recrystallized from 2-propanol. We obtained 16 g (20%) of reaction product **III** of coffee color, mp 63–65°C. ^1H NMR spectrum, δ , ppm: 3.25 s (4H, 2CH₂), 3.75 s (2H, 2NH), 7.2 m (10H, 2C₆H₅). Found, %: C 88.9; H 8.7; N 14.9. C₁₄H₁₆N₂. Calculated, %: C 87.7; H 8.3; N 14.5.

***N,N*-Diphenyl-1,4-diazine (IV).** The initial mixture prepared as above for preparation of compound **III** was stirred for 1.5 h at 50°C, then for 10–12 h at 110–120°C. On cooling the reaction mixture was treated with ethyl ether. The residue formed on evaporating the ether was recrystallized from 2-propanol. We obtained 20 g (21%) of reaction product **IV**, mp 159–160°C. ^1H NMR spectrum, δ , ppm: 3.26 s (8H, 4CH₂), 7.2 m (10H, 2C₆H₅). Found, %: C 79.1; H 8.1; N 12.4. C₁₆H₁₈N₂. Calculated, %: C 80.6; H 7.6; N 11.8.

***o*-Hydroxyaniline V condensation with dibromoethane II.** To a mixture of 100 ml of DMSO, 15 g (0.13 mol) of *o*-hydroxyaniline **V**, and 37.6 g (0.25 mol) of potassium carbonate was added dropwise at stirring 24.4 g (13 mol) of dibromoethane **II**. The reaction mixture temperature was raised to 80°C while stirring for 8 h,

the mixture was treated with water and then with ethyl ether. The extract was dried with CaCl_2 . On distilling off the ether a mixture of compounds **VI** and **VII** was obtained. In the ^1H NMR spectrum of the reaction mixture appear signals of compound **VI**, δ , ppm: 3.9 t [2H, OCH_2 , 3J (HH) 7.5 Hz], 3.25 m [2H, NCH_2 , 3J (HH) 7.5 Hz], and compound **VII**: 1.9 d.d [4H, of aziridine ring, J (HH) 2.5 Hz]. The phenyl protons of

both compounds are observed as a signal at 6.6 ppm [8H, Ar-H in compounds **VI**, **VII**].

^1H NMR spectra were recorded on spectrometer Varian T-60, solvent CCl_4 , internal reference HMDS.

REFERENCES

1. Lukin, S.S., Levashova, V.I., Bunin-Krivorukova, L.I., and Zlotskii, S.S., *Zh. Org. Khim.*, 1989, vol. 25, p. 2453.