

Aniline Alkylation with Di- and Tribromopropane

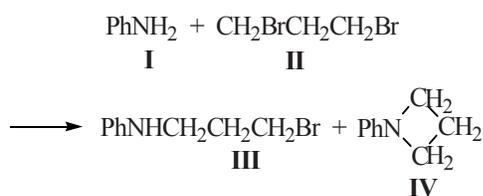
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Received May 20, 2008

DOI: 10.1134/S1070428009080247

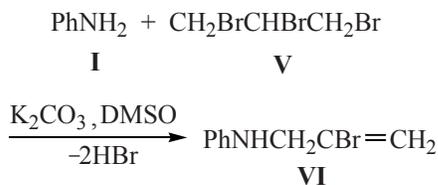
We formerly performed a condensation of aniline with 1,2-dibromoethane [1] that yielded compounds with a linear (1,2-dianilinoethane) and cyclic (N,N-diphenyl-1,4-diazine) structures. In extension of this study we investigated the aniline alkylation with di- and tribromopropane.



At excess K_2CO_3 in DMSO environment the condensation of aniline (I) with 1,3-dibromopropane (II) at heating (60–80°C) led to the formation of N-(3-bromopropyl)-aniline (III) and N-phenylazetidene (IV). At higher temperature the fraction of the cyclic product increased.

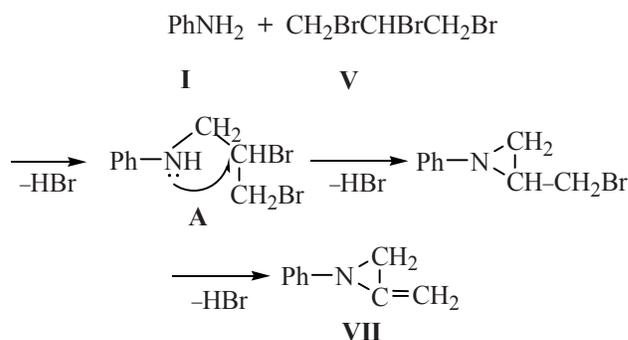
The structure of compounds III and IV was confirmed by ^1H NMR spectra.

Under similar conditions the aniline alkylation with 1,2,3-tribromopropane (V) also proceeded as N-alkylation and gave N-(2-bromoallyl)aniline (VI) and 2-methylene-1-phenylazirane (VII).



The formation of compound VI may be regarded as the N-alkylation of aniline with tribromopropane (V) with the simultaneous dehydrobromination.

2-Methylene-1-phenylazirane (VII) may form by two routes: either compound VI undergoes the intramolecular N-alkylation to give compound VII, or the product of the primary alkylation, 2,3-dibromopropylaniline A, suffers the intramolecular alkylation at the nitrogen atom forming an aziridine ring with subsequent dehydrobromination.



In the ^1H NMR spectrum of compound VII the resonance signals at δ , ppm, 7.5 m (5H), 5.1 m (2H), and 2.0 m (2H) should be assigned respectively to the protons of phenyl, vinyl, and methylene moieties.

Reaction of aniline with 1,3-dibromopropane. To a mixture of 0.13 mol of compound I and 0.25 mol of K_2CO_3 in 75 ml of DMSO was added dropwise within 1 h at stirring 0.13 mol of 1,3-dibromopropane at room temperature. While adding the reagent the mixture turned light-brown. Then the mixture was heated for 7 h at 60°C, cooled, diluted with water, and extracted with ether. The formed crystals of compound IV were filtered off. From the filtrate on removing the ether we obtained compound III as viscous fluid of dark-brown color.

N-(3-Bromopropyl)aniline (III). Yield 31 g (48%), bp 121°C (0.3 mm Hg), d_4^{20} 1.3432, n_D^{20} 1.4827. ^1H NMR

spectrum, δ , ppm: 1.25 m (2H, CCH₂C), 3.3 t (2H, CH₂Br), 3.9 m (2H, NCH₂), 4.2 br.s (1H, NH), 6.9 m (5H, C₆H₅). Found, %: C 50.41; H 5.87; Br 37.48; N 6.48. C₉H₁₂BrN. Calculated, %: C 50.46; H 5.40; Br 37.38; N 6.54.

N-Phenylazetidide (IV). Yield 22 g (49%), mp 212°C. ¹H NMR spectrum, δ , ppm: 1.2 m (2H, CH₂), 2.65 m (4H, 2CH₂), 7.1 m (5H, C₆H₅). Found, %: C 81.27; H 8.32; N 10.47. C₉H₁₁N. Calculated, %: C 81.20; H 8.27; N 10.52.

Reaction of aniline with 1,2,3-tribromopropane.

To a mixture of 0.13 mol of aniline and 0.25 mol of K₂CO₃ in DMSO was added dropwise 0.13 mol of 1,2,3-tribromopropane. The reaction mixture was stirred for 1.5 h at 20°C and 7–8 h at 110°C, it was cooled, diluted with water, and extracted with ether. The formed violet crystals of compound **VII** were filtered off, and compound **VI** was obtained from the ether extract.

N-(2-Bromoallyl)aniline (VI). Yield 7 g (26%), bp 110°C (0.5 mm Hg), d_4^{20} 1.4226. ¹H NMR spectrum, δ , ppm: 3.68 d (2H, NCH₂), 5.5 d (2H, =CH₂), 6.25–7.1 m (5H, C₆H₅). Found, %: C 50.6; H 4.7; Br 37.7; N 6.6. C₉H₁₀BrN. Calculated, %: C 50.9; H 4.7; Br 37.9; N 6.6.

2-Methylene-1-phenylazirane (VII). Violet crystals, recrystallized from 2-propanol. Yield 3.4 g (22%), mp 208°C. Found, %: C 82.7; H 7.0; N 10.4. C₉H₉N. Calculated, %: C 82.4; H 6.9; N 10.7.

¹H NMR spectra were registered on a spectrometer Varian T-60, solvent CCl₄, internal reference HMDS.

REFERENCES

1. Ismailov V.M., Mamedov I.A., and Yusubov N.N., *Zh. Org. Khim.*, 2004, vol. 40, p. 312.