

Nitroso-ethylbenzenes.

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Derivatives of ethylbenzene are of great interest as the materials for investigating the electronic nature of alkyl radicals. But unhappily only little is known of these compounds in contrast with substituted methylbenzenes, probably because of the fact that pure ethylbenzene has not hitherto been an easily accessible compound.

The present author has now prepared *o*- and *p*- nitroso-ethylbenzenes with a view to compare their properties with those of nitroso-toluenes.⁽¹⁾ Among these compounds, however, *o*- nitroso-ethylbenzene is already obtained by R. E. Lutz and M. R. Lytton,⁽²⁾ who described it briefly as a substance melting at 61°, and being difficult to bring in the state of analytical purity.

The present author has synthesized nitroso-ethylbenzenes by the reduction of the corresponding nitro-compounds, obtained by the nitration of ethylbenzene.

(1) Y. Tsuzuki, T. Uemura and N. Hirasawa, *J. Chem. Soc. Japan*, **61** (1940), 1063; *Ber.*, **74** (1941), 616.

(2) *J. Org. Chem.*, **2** (1937), 68.

Nitration of Ethylbenzene.⁽³⁾ The mixture of 83 g. fuming nitric acid ($d=1.45$) and 81 g. concentrated sulphuric acid ($d=1.84$) was added drop by drop to 100 g. ethylbenzene (boiling point 133° , $n_D^{20}=1.49540$, $d_4^{20}=0.86644$, obtained by fractionating technical ethylbenzene) for several hours at 0°C ⁽⁴⁾ with mechanical stirring. Oil was separated from the layer of the acid, washed with water and distilled under reduced pressure with a Tichwinski fractionating column. The thrice repeated fractional distillation gave 30 g. pure *o*-nitro-ethylbenzene (boiling point $86-88^\circ$ (5 mm.), $n_D^{20}=1.53483$, $d_4^{20}=1.1139$) and 15 g. pure *p*-nitro-ethylbenzene (boiling point $101-102^\circ$ (5 mm.), $n_D^{20}=1.54585$, $d_4^{20}=1.1192$).

***o*- and *p*-Nitroso-ethylbenzenes.** The reduction of the nitro-ethylbenzenes into the corresponding nitroso-compounds was carried out in a similar way as described in the previous paper.⁽¹⁾ 7.5 g. nitro-compound were dissolved in 30 c.c. boiling ethyl alcohol, and 10 c.c. hot 2 *n*-ammonium chloride were added. To this solution 10 g. zinc dust were added in small portions in 10 minutes with vigorous shaking. After 5 minutes the residue was filtered off and a dilute ice-cold solution of 27 g. $\text{FeCl}_3+6\text{H}_2\text{O}$ was poured to the solution. The reaction product was subjected to steam distillation immediately, whereby the nitroso-compound was isolated and purified. Yield 2 g. (30% of the theory).

o-Nitroso-ethylbenzene: colourless bright needles (from ethyl alcohol) melting at 61.5° . Found: N, 10.04. Calculated for $\text{C}_8\text{H}_9\text{NO}$: N, 10.37%. *p*-Nitroso-ethylbenzene: volatile green oil; it becomes very sticky at -30°C , but does not solidify even at -80°C ; it decomposes slowly on standing, and rapidly at 120°C . Found: N, 10.27. Calculated for $\text{C}_8\text{H}_9\text{NO}$: N, 10.37%.

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(3) Cf. Beilstein and Kuhlberg, *Ann.*, **156** (1870), 206; Schultz and Flachsländer, *J. prak. Chem.*, [2] **66** (1902), 153; Cline and Reid, *J. Am. Chem. Soc.*, **49** (1927), 3150; Schreiner, *J. prak. Chem.*, [2] **81** (1910), 557; H. Kondo and S. Uyeo, *Ber.*, **70** (1937), 1091.

(4) Higher temperature was avoided, because it is expected that rising temperature increases the yield of the ortho isomer—the main product of the reaction—and decreases that of the para isomer, and also favours meta substitution. Cf. the work of Holleman and his co-workers on the nitration of toluene (Holleman and van den Arend, *Rec. trav. chim.*, **28** (1909), 408; Holleman, Vermeulen, and de Muoy, *Rec. trav. chim.*, **33** (1914), 1; further Holleman, *Chem. Rev.*, **1** (1925), 187; Rease, *Chem. Rev.*, **14** (1934), 55.