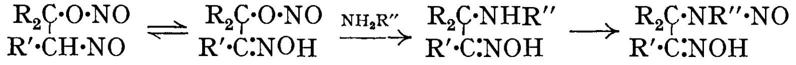
77. *The Action of Alkaline Reagents on Some Nitroso-α-arylamino-ketones and their Oximes.*

By J. Campbell Earl and Stanley J. Hazlewood.

The " nitrolamines " formed by the interaction of nitrosochlorides, nitrosites or nitrosates of ethylenic compounds with primary amines are themselves secondary amines and as such yield nitrosoamines when treated with nitrous acid (Wallach, *Annalen*, 1887, **241**, 290). Working with nitro-anilides and -toluidides derived from trimethylethylene nitrosate,



$$\begin{array}{l} R_2C\cdot O\cdot NO \\ R'\cdot CH\cdot NO \end{array} \rightleftharpoons \begin{array}{l} R_2C\cdot O\cdot NO \\ R'\cdot C{:}NOH \end{array} \xrightarrow{NH_2R''} \begin{array}{l} R_2C\cdot NHR'' \\ R'\cdot C{:}NOH \end{array} \longrightarrow \begin{array}{l} R_2C\cdot NR''\cdot NO \\ R'\cdot C{:}NOH \end{array}$$

Wallach noted that the nitroso-derivatives dissolved in sodium hydroxide solution and that, when the alkaline solutions were boiled, nitrogen was evolved and red tarry products formed. This reaction has now been further examined for derivatives not only of trimethylethylene but also of methyl-Δ^1-*cyclo*hexene, α-terpineol, and α-pinene. All such nitroso-α-anilino-ketoximes, when treated with an alkaline solution of β-naphthol, give rise to benzeneazo-β-naphthol, slowly in the cold and more quickly on warming, especially in aqueous-alcoholic solution.

By hydrolysing the nitrolamines with dilute mineral acid, the corresponding α-anilino-ketones are produced (Wallach, *loc. cit.*). These α-anilino-ketones readily yield nitrosoamines, which do not, however, react with alkaline β-naphthol solution. This behaviour is in contrast with that of certain nitroso-β-anilino-ketones (Jones and Kenner, J., 1933, 363), which, when subjected to the action of alkali in the presence of β-naphthol, give benzeneazo-β-naphthol. It appears from these results that the tendency of phenylnitrosoamines, $R\cdot N(NO)\cdot C_6H_5$, to fission by the action of alkali is strongly influenced by the nature of the group R. The presence of a keto-group in the appropriate position in the group R inhibits the tendency to breakdown, but the inhibition is overcome by oximation of the keto-group.

From trimethylethylenenitrosonitrolanilide, a secondary product of fission has been obtained. This is a well-crystallised, relatively stable *substance*, has the molecular composition $C_{16}H_{24}O_3N_4$, contains a nitroso-group, and is produced apparently by the condensation of one molecule of the nitrosonitrolanilide with one molecule of its hypothetical primary fission product, $OH\cdot CMe_2\cdot CMe{:}NOH$:

$$C_{11}H_{15}O_2N_3 + C_5H_{11}O_2N \longrightarrow C_{16}H_{24}O_3N_4 + H_2O.$$

Further examination of this product and its homologues, obtained by substituting *o*- and *p*-toluidine for aniline, together with an investigation of other structural types giving rise to similarly decomposable nitrosoamines, is in progress.

Experimental.

Preparation of α-Anilino-ketoximes.—The preparation of trimethylethylenenitrolanilide is typical. The method of Earl and Kenner (J., 1927, 1269) was first used, but a method similar to that employed by the same workers for the preparation of pinenenitrolanilide is simpler and equally satisfactory as regards yield.

A solution of trimethylethylenenitrosochloride (10 g.), aniline (8 g.), and crystallised sodium acetate (20 g.) in methylated spirit (100 ml.) was refluxed on a water-bath for 10 minutes and poured into an excess of ice-water. The product, after solidifying, was dissolved in glacial acetic acid, and the diluted solution filtered into concentrated aqueous ammonia cooled in ice; trimethylethylenenitrolanilide (13·5 g.) was obtained, m. p. 143° after recrystallisation from aqueous alcohol.

The following were similarly prepared: trimethylethylenenitrol-*p*-toluidide, m. p. 115°; trimethylethylenenitrol-*o*-toluidide, m. p. 109°; *methyl*-Δ^1-cyclo*hexenenitrolanilide*, m. p. 139° (Found: N, 12·85. $C_{13}H_{18}ON_2$ requires N, 12·9%); and α-terpineolnitrolanilide, m. p. 149°.

Preparation of Nitroso-α-anilino-ketoximes.—The case of trimethylethylene is again typical. A solution of the nitrolanilide of trimethylethylene (6 g.) in excess of dilute hydrochloric acid was cooled with ice and slowly treated with aqueous sodium nitrite until no further precipitate was formed. The pale yellow, flocculent nitrosoamine (6 g.) was filtered off almost immediately; after solution in chloroform and precipitation with light petroleum (b. p. 60—80°) it formed colourless needles, m. p. 127·5°.

The following also were prepared: *nitrosonitrolanilide* of methyl-Δ^1-*cyclo*hexene, m. p. 148·5° (Found: N, 17·1. $C_{13}H_{17}O_2N_3$ requires N, 17·0%); *nitrosonitrolanilide* of α-terpineol, m. p. 144·5° (Found: N, 13·9. $C_{16}H_{23}O_3N_3$ requires N, 13·8%); *nitrosonitrolanilide* of α-pinene, m. p. 100·5° (Found: N, 14·7. $C_{16}H_{21}O_2N_3$ requires N, 14·6%); nitrosonitrol-*p*-toluidide of trimethylethylene, m. p. 155·5°; and *nitrosonitrol*-o-*toluidide* of trimethylethylene, m. p. 148° (Found: N, 18·0. $C_{12}H_{17}O_2N_3$ requires N, 17·9%). All these substances gave a definite Liebermann nitroso-reaction.

Preparation of α-Anilino-ketones.—Wallach's method (*Annalen*, 1887, **241**, 299) was used and the ketoanilide of trimethylethylene, m. p. 63°, the *ketoanilide* of methyl-Δ^1-*cyclo*hexene, m. p. 91—92° (Found: N, 6·8. $C_{13}H_{17}ON$ requires N, 6·9%), and the keto-*p*-toluidide of trimethylethylene, m. p. 98°, were prepared.

Preparation of Nitroso-α-anilino-ketones.—The method was similar to that used for the nitroso-α-anilino-ketoximes. The products, if oils, were extracted from aqueous suspension with ether, dried (anhydrous sodium carbonate), and distilled under reduced pressure. The yields were good. The *nitrosoketoanilide* of trimethylethylene, b. p. 157°/2 mm. (Found: N, 13·75. $C_{11}H_{14}O_2N_2$ requires N, 13·6%), the *nitrosoketo*-p-*toluidide* of trimethylethylene, b. p. 145°/0·8 mm. (Found: N, 12·6. $C_{12}H_{16}O_2N_2$ requires N, 12·7%) and the *nitrosoketoanilide* of methyl-Δ^1-*cyclo*hexene, m. p. 102° (Found: N, 11·9. $C_{13}H_{16}O_2N_2$ requires N, 12·0%), were prepared. All these substances gave a definite Liebermann nitroso-reaction.

Action of Alkaline β-Naphthol on α-Anilino-ketoximes and α-Anilino-ketones.—A solution of β-naphthol (0·5 g.) in 5% aqueous or alcoholic sodium hydroxide (20 ml.) was divided into two parts, to one was added the nitrosonitrolanilide of methyl*cyclo*hexene (0·1235 g.), to the other the corresponding nitrosoketoanilide (0·1160 g.), and each solution was made up to 30 ml. After 1½ hours, the first solution was brilliant red and the second faintly yellow. They were then warmed for 5 minutes at 70°; benzeneazo-β-naphthol separated from the first (aqueous) solution and no colour suggestive of an azo-dye was visible in the second. A similar comparison was made with the two types of derivatives from trimethylethylenenitrol-*p*-toluidide and trimethylethylenenitrolanilide, dyes separating from the solutions containing the ketoximes and no colour being produced in the solutions containing the ketones.

Attempted isolation of the second product of decomposition. Benzeneazo-β-naphthol having been identified, m. p. and mixed m. p. 128°, the other part of the disrupted molecule was sought. Fractional precipitation of the dye from the alcoholic reaction solution by the addition of water, followed by fractional crystallisation of the later fractions from light petroleum, yielded a colourless material. A less tedious procedure was to substitute the disodium or dipotassium salt of β-naphthol-3 : 6-disulphonic acid for β-naphthol; the soluble dye formed could then be removed from the product sought by washing with warm water or with dilute alkali. The nitrosonitrolanilide of trimethylethylene (17·3 g.), suspended in water (500 ml.) and methylated spirit (150 ml.) and treated with sodium naphtholdisulphonate (30 g.) and 20% sodium hydroxide solution (20 ml.) for 24 hours, gave, after dilution with ice-water to 1 l., 7·8 g. of product, m. p. 130—131° after recrystallisation from light petroleum (Found: C, 60·0; H, 7·7; N, 17·2; *M*, cryoscopic in benzene, 397. $C_{16}H_{24}O_3N_4$ requires C, 60·0; H, 7·5; N, 17·5%; *M*, 320).

The same *substance* is formed together with much tar by the action of alkali alone. It gives a definite Liebermann reaction, indicating the presence of a nitroso-group. It is apparently unaffected by 20% sodium hydroxide solution, with or without the addition of naphthol, but is unstable in the presence of warm mineral or strong organic acids, decomposing with evolution of gas into neutral and basic products which have not yet been identified.

The authors' thanks are due to Miss E. Goulston for the performance of some of the microanalyses.

THE UNIVERSITY, SYDNEY, N.S.W.

[*Received, November 2nd,* **1936.**]