[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

REARRANGEMENT OF N-TRIPHENYLMETHYL-O-BENZYLHYDROXYLAMINE BY MEANS OF POTASSIUM AMIDE OR BORON TRIFLUORIDE

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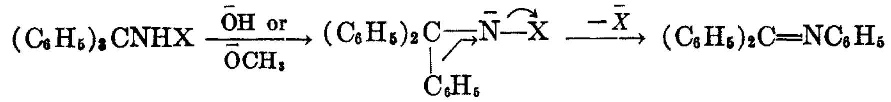
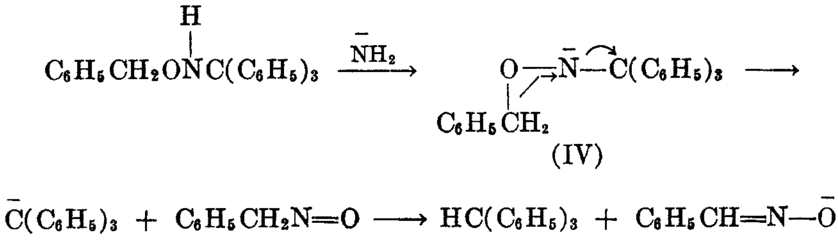
The Stieglitz rearrangement of triphenylmethylamine derivatives (I) to form benzophenone anil (III), involving α-elimination of HX and the shift of a phenyl group from carbon to nitrogen, has been effected by acidic reagents where X is alkoxy or hydroxy (1) and by basic reagents where X is halogen (2). With hydroxyl or methoxyl ion, anion (II) is presumably formed as an intermediate, thus



$$(C_6H_5)_3CNHX \xrightarrow[\bar{O}CH_3]{\bar{O}H\text{ or}} (C_6H_5)_2\underset{\underset{C_6H_5}{|}}{C}-\bar{N}-X \xrightarrow{-\bar{X}} (C_6H_5)_2C{=}NC_6H_5$$

(I) (II) (III)

In the present investigation a study has been made of the decomposition of N-triphenylmethyl-O-benzylhydroxylamine (I, X = benzyloxy) in the presence of the amide ion, which should be a sufficiently strong base to produce a relatively high concentration of anion (II). However, aniline and benzophenone, the characteristic products of the Stieglitz rearrangement and subsequent hydrolysis, have been obtained in very low yields (generally less than 3%). With excess potassium amide in liquid ammonia and ether, the dark red color characteristic of the triphenylmethide ion soon develops, and from the reaction mixture there was obtained mainly triphenylmethane (60–65%) and benzaldoxime (25–37%). The latter was evidently not produced from benzaldehyde and hydroxylamine (or benzyloxyamine), which might conceivably have been formed in the reaction mixture, since blank experiments with these compounds, potassium amide, and triphenylmethane yielded no appreciable amount of the oxime under the conditions employed. Apparently the intermediate anion (IV) releases mainly the triphenylmethide ion concurrently with the shift of the benzyl group from oxygen to nitrogen to form α-nitrosotoluene, which is ionized to give the anion of benzaldoxime, thus



$$C_6H_5CH_2O\overset{\overset{H}{|}}{N}C(C_6H_5)_3 \xrightarrow{\bar{N}H_2} \underset{\underset{C_6H_5CH_2}{|}}{O}-\bar{N}-C(C_6H_5)_3 \longrightarrow$$

(IV)

$$\bar{C}(C_6H_5)_3 + C_6H_5CH_2N{=}O \longrightarrow HC(C_6H_5)_3 + C_6H_5CH{=}N{-}\bar{O}$$

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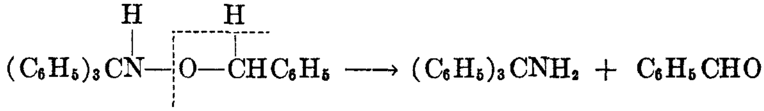
This reaction appears to be the first example of α-elimination of HX and rearrangement of a compound of the type RONHX; in the present case, X is the triphenylmethyl group.

In addition to triphenylmethane, benzaldoxime, and the small amounts of aniline and benzophenone, there have been obtained from the reaction mixture of the benzyloxy derivative and potassium amide some triphenylmethylamine ($<4\%$), triphenylcarbinol, and benzoic acid (trace). As Guthmann and Stieglitz (1) have pointed out, the benzyloxy derivative might decompose to form triphenylmethylamine or triphenylcarbinol, thus

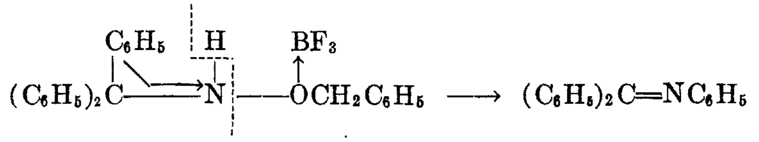


$$(C_6H_5)_3C\overset{H}{N}{-}O{-}\overset{H}{C}HC_6H_5 \longrightarrow (C_6H_5)_3CNH_2 + C_6H_5CHO$$

$$(C_6H_5)_3CNHOCH_2C_6H_5 \xrightarrow[H_2O]{HCl} (C_6H_5)_3COH + H_2NOCH_2C_6H_5$$

The first of these reactions could presumably be effected by potassium amide, but the second probably involved unreacted benzyloxy derivative and the hydrochloric acid used in the hydrolysis of benzophenone anil. The by-products, benzaldehyde and benzyloxyamine, have not been isolated; at least below 160°, the extent of the first of these reactions appears to be very small.

Guthmann and Stieglitz (1) realized the Stieglitz rearrangement of N-triphenylmethyl-O-benzylhydroxylamine (I, X = benzyloxy) in 40% yield with phosphorus pentoxide at 160°. We have effected this rearrangement at 60° (or less) with boron trifluoride, although the yield has been somewhat lower (29%). In contrast to basic reagents which remove the proton, these acidic reagents probably attack the benzyloxy group to form a coordination complex, for example, (V),[2] which undergoes the rearrangement, thus



$$(C_6H_5)_2\overset{C_6H_5}{C}{-}\overset{H}{N}{-}\overset{BF_3 \uparrow}{O}CH_2C_6H_5 \longrightarrow (C_6H_5)_2C{=}NC_6H_5$$

(V) (III)

It is significant that no benzaldoxime and not more than a trace of triphenylmethane, the products of the new rearrangement, could be isolated from the boron trifluoride reaction mixture. Since the triphenylmethyl carbon has no free pair of electrons, the acidic reagent, boron trifluoride, could not coordinate with it.

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[2] It is recognized that boron trifluoride may coordinate at the nitrogen to a greater extent than at the oxygen; however, on the basis of modern theory, only the coordination at the oxygen should facilitate the Stieglitz rearrangement, which presumably involves the removal of the benzyloxy group with its bond pair of electrons. The yield (29%) of rearrangement product may be explained on the basis that either the coordination at the oxygen occurs to the extent of at least 29% or that this coordination takes place to a smaller extent but is in somewhat mobile equilibrium with that at the nitrogen.

EXPERIMENTAL

N-triphenylmethyl-O-benzylhydroxylamine. This substance (m.p. 118–119°) was prepared from triphenylmethyl chloride and O-benzylhydroxylamine as described by Guthmann and Stieglitz (1).

Reaction with potassium amide. The reaction of N-triphenylmethyl-O-benzylhydroxylamine with potassium amide has been carried out several times. Typical experiments are described below.

To a stirred solution of 0.028 mole of potassium amide in 125 ml. of liquid ammonia was added during five minutes a solution of 3.65 g. (0.01 mole) of N-triphenylmethyl-O-benzylhydroxylamine in 125 ml. of absolute ether. The mixture became dark red within five minutes. After three hours the ammonia was driven off, more ether being added to maintain constant volume, and the ether suspension refluxed for an hour or two. Wet ether and water were carefully added (the red color disappearing) and the mixture shaken. The aqueous (alkaline) phase, with which was combined a 5% sodium hydroxide extract of the ether phase, was saturated with carbon dioxide, and the oily *syn*-benzaldoxime[3] (0.3 g., 25%), obtained after extraction with ether and evaporation of the solvent, was identified by conversion (3) to the *syn*-benzaldoxime benzoate (m.p. and mixed m.p. 101–102°). The ether phase, after three extractions with 3% hydrochloric acid (neutralization with aqueous ammonia yielding traces of triphenylmethylamine and of an unidentified oil), was distilled from the steam-bath, and the residue refluxed for ninety minutes with 10% hydrochloric acid. The mixture was diluted with water and shaken with ether. The aqueous acid phase was treated with bromine water, yielding a trace of tribromoaniline. The ether phase was divided into two equal portions and evaporated. The residue from one portion was refluxed in aqueous alcohol with hydroxylamine hydrochloride and sodium hydroxide, yielding a trace of benzophenone oxime (triphenylmethane mixed with triphenylcarbinol was mainly obtained). The residue from the other portion was dissolved in purified ligroin (b.p. 54–64°) and the solution extracted several times with cold concentrated sulfuric acid (the last extract was only slightly colored). After washing with water, the ligroin solution was dried and evaporated, yielding 0.9 g. of white solid, m.p. 81–87°. On dissolving in hot ethanol (0.1 g. of material m.p. 170–190° remained undissolved) and subsequent dilution with water, there was obtained 0.8 g. (65%) of triphenylmethane (m.p. and mixed m.p. 91–92°).

When N-triphenylmethyl-O-benzylhydroxylamine and potassium amide were allowed to react for 35 hours in liquid ammonia and ether (partly at room temperature), there were obtained yields of 37% of benzaldoxime, 61% of pure triphenylmethane, and 3% each of benzophenone oxime, tribromoaniline, and triphenylmethylamine.

When N-triphenylmethyl-O-benzylhydroxylamine (0.01 mole) and potassium amide (0.0115 mole) were refluxed in benzene for about two hours, there were obtained a 41% yield of crude benzaldoxime and a 57% yield of crude triphenylmethane, identified[4] by carbonation of its potassium salt to form triphenylacetic acid (m.p. and mixed m.p. 262–263° uncor.).

Reaction with boron trifluoride. Boron trifluoride was passed over the surface of a stirred suspension of 3.65 g. (0.01 mole) of N-triphenylmethyl-O-benzylhydroxylamine in 75 ml. of ligroin (b.p. 74–90°) for thirty minutes at room temperature and then for ninety minutes longer as the temperature was gradually raised to 60°. The cooled mixture was stirred with 25 g. of sodium acetate in 80 ml. of water, the caked material on the sides of the flask being broken up. After being made alkaline with sodium hydroxide solution, the mixture

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[3] It is possible that this product was contaminated with the *anti*-isomer, since a mixture of the two isomers is produced on oxidation of benzyloxyamine to *bis*-nitrosotoluene and treatment with sodium ethoxide; [Behrend and Konig, *Ann.*, **263**, 214, 348 (1891)]. If formed, the *anti*-benzaldoxime would probably have been partly decomposed by the potassium amide to benzonitrile or benzamidine [see Vermillion and Hauser, *J. Org. Chem.*, **6**, 507 (1941)], small amounts of which may have been overlooked.

[4] We are indebted to Dr. Erwin Baumgarten for this identification.

was shaken vigorously and filtered. The solid was dissolved in ether and the solution extracted with sodium hydroxide. The combined aqueous alkaline solution was saturated with carbon dioxide, but no benzaldoxime could be isolated. The combined ligroin and ether solution was evaporated and the residue heated with 10% hydrochloric acid, diluted, and shaken with ether. The aqueous acid phase, on treatment with aqueous bromine, gave 0.962 g. (29%) of tribromoaniline (m.p. and mixed m.p. 119–120°). The ether phase, on evaporation, yielded benzophenone, which was converted to its oxime (27%, m.p. and mixed m.p. 143–144°). A search for triphenylmethane yielded only a trace of what might have been this substance, melting at 87–90°.

SUMMARY

1. In the presence of potassium amide, N-triphenylmethyl-O-benzylhydroxylamine undergoes the Stieglitz rearrangement (to benzophenone anil) to only a small extent; instead, the main reaction involves elimination of triphenylmethane accompanied by rearrangement of the benzyl group from oxygen to nitrogen to form benzaldoxime.

2. The Stieglitz rearrangement is realized in the presence of boron trifluoride.

3. Mechanisms are considered.

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REFERENCES

(1) See GUTHMANN AND STIEGLITZ, *J. Org. Chem.*, **1**, 31 (1936).

(2) STIEGLITZ AND VOSBURGH, *Ber.*, **46**, 2151 (1913).

(3) VERMILLION AND HAUSER, *J. Am. Chem. Soc.*, **62**, 2939 (1940).