## Rearrangement Resulting from Intramolecular Diazo Coupling and Cleavage

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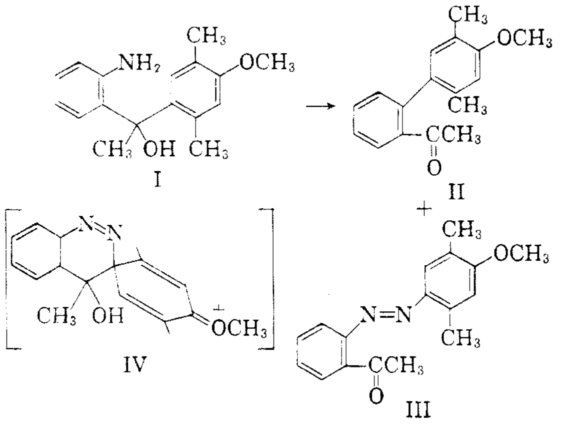
During an investigation of the 1,3-rearrangement which accompanies the deamination of certain *o*-aminophenylcarbinols[1] we prepared the amino alcohol I and treated it with nitrous acid. In addition to phenolic material and the expected rearrangement product II, an 18% yield of the azo ketone III was isolated. The structure of III was proved by comparison with the compound obtained from methylation of the coupling product of 2,5-dimethylphenol and diazotized *o*-aminoacetophenone.

This novel result may be rationalized in terms of cleavage of the intramolecular coupling product IV. The process may be similar to the cleavage reaction which occurs when various para substituted phenol or aniline derivatives are treated with diazonium salts[2] or halogen.[3,4] The cleavage of IV would be expected to lead to an azobenzene with the *syn* structure, but the aqueous acid present in the reaction mixture was apparently sufficient to cause isomerization to the more stable *anti* isomer.[5]



### EXPERIMENTAL

*1-o-Aminophenyl-1-(4-methoxy-2,5-dimethylphenyl)ethanol* (I). A solution of 8.0 g. (0.032 mole) of 2-amino-2′,5′-dimethyl-4′-methoxybenzophenone[6] in 100 ml. of benzene was added dropwise to a solution of methylmagnesium iodide, prepared from 11 g. (0.45 mole) of magnesium and 65 g. (0.46 mole) of methyl iodide in 300 ml. of ether. After 20 hr. at reflux the mixture was hydrolyzed with aqueous ammonium chloride, the organic layer was dried over calcium sulfate, and the solvent was evaporated. The residue crystallized from 70% petroleum ether–30% benzene. Recrystallization from the same solvents yielded 4.0 g. (47%) of colorless crystals, m.p. 121–122°.

*Anal.* Calcd. for $C_{17}H_{21}NO_2$: C, 75.28; H, 7.75; N, 5.16. Found: C, 75.24; H, 7.65; N, 5.22.

*Diazotization of the amino alcohol I.* The amino alcohol (5.4 g., 0.020 mole) was dissolved in a mixture of 200 ml. of water, 50 ml. of ethanol, and 4.0 g. of concentrated sulfuric acid. A solution of 2.5 g. (0.036 mole) of sodium nitrite in 20 ml. of water was added dropwise at 5°. Added standing for 1 hr. at 5° the solution was allowed to stand at room temperature until the evolution of nitrogen ceased. The precipitated oil was taken up in ether and the ether solution was extracted with dilute alkali to furnish 1.2 g. of acidic oily material, presumably a phenol. The neutral material was adsorbed on a column of ordinary alumina. Elution with 20–30% benzene in petroleum ether (30–60°) furnished 0.80 g. of a light oil ($\nu_{film}$ 1670 cm.$^{-1}$) which crystallized from 95% ethanol as a colorless solid (0.63 g., 13%), m.p. 77–78°. The ketone was assigned the structure *o*-(2,5-dimethyl-4-methoxyphenyl)acetophenone (II) on the basis of the spectrum, the formation of a carbonyl derivative, and the analogy to other examples of this rearrangement.[1,7]

*Anal.* Calcd. for $C_{17}H_{18}O_2$; C, 80.33; H, 7.08. Found: C, 80.55: H, 7.28.

The *2,4-dinitrophenylhydrazone* melted at 201.5–202.5°.

*Anal.* Calcd. for $C_{23}H_{22}N_4O_5$: C, 63.59; H, 5.07; N, 12.90. Found: C, 63.62; H, 5.11; N, 12.83.

Elution with 50% benzene–petroleum ether afforded a red oil which crystallized from 80% aqueous ethanol to yield 1.0 g. (18%) of orange-red needles, m.p. 92–93°, $\nu_{CHCl_3}$ 1680 cm.$^{-1}$ The compound was identical with the azo ketone III prepared as described in the following paragraphs.

*Anal.* Calcd. for $C_{17}H_{18}N_2O_2$: C, 72.34; H, 6.38; N, 9.93. Found: C, 72.18; H, 6.28; N, 9.97.

Repetition of the experiment in which the diazotization was carried out in aqueous dioxane and the period of standing at 5° was shortened to 15 min., led to essentially the same result (21% acidic material, 13% ketone II, 14% azo ketone III).

*o-Aminoacetophenone.* Thirty-five g. (0.21 mole) of *o*-nitroacetophenone[8] was suspended in a mixture of 200 ml. of water and 50 ml. of ethanol, and a solution of 100 g. of sodium dithionate in 100 ml. of water was added in three portions. After 1 hr. at 60° the reaction mixture was steam-distilled, and the yellow oil was distilled under reduced pressure to yield 15 g. (52%) of the amino ketone, b.p. 96–98°/4 mm. (reported,[9] 124°/10 mm.).

*2-Acetyl-2′,5′-dimethyl-4′-hydroxyazobenzene.* *o*-Aminoacetophenone (16 g., 0.12 mole) was diazotized in dilute aqueous acid and coupled with 15 g. (0.12 mole) of 2,5-dimethylphenol in the usual manner. After recrystallization from 95% ethanol there was obtained 20 g. (61%) of a red solid, m.p. 183–185°.

*Anal.* Calcd. for $C_{16}H_{16}N_2O_2$: C, 71.64; H, 5.97. Found: C, 71.57; H, 6.14.

*2-Acetyl-2′,5′-dimethyl-4′-methoxyazobenzene* (III). The azo phenol (20 g., 0.074 mole) was converted to its sodium salt with an equivalent of sodium ethoxide in ethanol, and the solution was treated with 20 g. (0.14 mole) of methyl iodide at reflux for 3 hr. After treatment of the crude product with alkali to remove unreacted phenol, the residue was crystallized from ethanol to yield 12 g. (60%) of orange-red

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(1) M. Stiles and A. J. Libbey, Jr., *J. Org. Chem.*, **22**, 1243 (1957); M. Stiles, A. J. Sisti, and A. J. Libbey, Jr., Abstracts of Papers, American Chemical Society, Miami, Fla., April 1957, p. 70-O.

(2) E. Ziegler and G. Snatzke, *Monatsh.*, **84**, 278 (1953).

(3) G. J. Esseler and L. Clarke, *J. Am. Chem. Soc.*, **36**, 308 (1914).

(4) E. P. Kohler and R. H. Patch, *J. Am. Chem. Soc.*, **38**, 1205 (1916).

(5) G. S. Hartley, *J. Chem. Soc.*, 633 (1938).

(6) W. C. Lothrop, *J. Am. Chem. Soc.*, **61**, 2115 (1939).

(7) M. Stiles and A. J. Sisti, unpublished results.

(8) C. R. Hauser and H. G. Walker, *J. Am. Chem. Soc.*, **68**, 1386 (1946).

(9) J. C. E. Simpson, C. M. Atkinson, K. Schofield, and O. Stephenson, *J. Chem. Soc.*, 646 (1945).

needles, m.p. 92–93°, undepressed by the compound obtained from the diazotization of amino alcohol I. The infrared spectra of the two samples were identical.

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## Observations on *N*-Methylacetonitrilium and *N*-Phenylbenzonitrilium Hexachloroantimonates[1]

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In recent years syntheses and some reactions of the *N*-substituted nitrilium salts, $R{-}C{\equiv}N^+{-}R'$, $X^-$ ($X^-$ = a complex anion of the type $BF_4^-$, $SbCl_6^-$, *etc.*), have been reported by Klages[2] and Meerwein[3] and their co-workers.

As a result of these investigations, the status of the unsubstituted nitrilium salts has been considerably clarified.[2] Further, a reliable knowledge of the structure and chemistry of the stable *N*-alkylnitrilium salts may be expected to improve our understanding of reactions which may involve nitrilium cations as reactive intermediates (*e.g.*, the Beckmann rearrangement of oximes and derivatives, various alkylations of nitriles,[4] and reactions of the imidoyl chlorides, $Ar{-}CCl{=}N{-}R$, and sulfonate esters, $Ar{-}C(OSO_2R'){=}NR$).

In this connection we wish to record the preparation of the simplest member of the alkylated series, *N*-methylacetonitrilium hexachloroantimonate (I), its spectroscopic characterization, and a comparison with the previously known *N*-phenylbenzonitrilium hexachloroantimonate (II), together with some new chemical observations on these materials.

Treatment of the acetonitrile–antimony pentachloride complex with excess methyl chloride produced 49% of I in five weeks at room temperature.

$$CH_3{-}C{\equiv}N \rightarrow SbCl_5 + CH_3Cl \longrightarrow [CH_3{-}C{\equiv}N^+{-}CH_3 \longleftrightarrow CH_3{-}C^+{=}N{-}CH_3] + SbCl_6^-$$

I

$$I + C_6H_5NH_2 \longrightarrow CH_3{-}C(NHCH_3) = N{-}C_6H_5$$

$$\underset{\text{III}}{C_6H_5{-}CCl{=}N{-}C_6H_5} + SbCl_5 \longrightarrow$$

$$[C_6H_5{-}C{\equiv}N^+{-}C_6H_5 \longleftrightarrow C_6H_5{-}C^+{=}N{-}C_6H_5] + SbCl_6^-$$

II

$$\begin{array}{l} II \xrightarrow{C_6H_5NH_2} C_6H_5{-}C(NHC_6H_5){=}N{-}C_6H_5 \\ \big\downarrow C_6H_5OH \\ C_6H_5{-}C(OC_6H_5){=}N{-}C_6H_5 \end{array}$$

The nitrilium salt was characterized chemically by conversion to the known *N*-methyl-*N*′-phenylacetamidine on treatment with aniline. *N*-Phenylbenzonitrilium hexachloroantimonate (II), was prepared according to Meerwein[3] by the action of antimony pentachloride on *N*-phenylbenzimidoyl chloride (III). Compound II also reacted with aniline to give *N*,*N*′-diphenylbenzamidine as well as with phenol which produced phenyl *N*-phenylbenzimidate.

The reaction producing I from acetonitrile–antimony pentachloride and methyl chloride fails when conducted in the presence of excess acetonitrile, in which case the mixture blackens in a few days and a tarry product results. In addition, partial destruction of the pure nitrilium salt (I), was observed when attempts were made to cast films for infrared measurements from acetonitrile solution. In each case the product was distinguished by intense infrared absorption in the 1650 cm.$^{-1}$ region, and various weaker bands at lower frequencies. These observations suggest polymerization involving intermediates such as

$$CH_3{-}N{=}C(CH_3){-}N{=}C^+{-}CH_3$$

IV

which is considered to arise by electrophilic attack on the nitrogen of the nitrile by the unsaturated carbon of the nitrilium cation.[5]

*N*-Alkylnitrilium salts have also been prepared[3] by direct alkylation of the nitrile with trialkyl oxonium salts or with decomposing aryldiazonium ions. Those prepared by Meerwein, including (II), were characterized by hydrolysis to *N*-alkylamides.[3] These facts taken with the above conversions to amidines and imidoesters amply confirm the main structural features of the indicated formulas. Furthermore, measurement of the electrical conductivity of *N*-methylbenzonitrilium hexachloroantimonate in liquid sulfur dioxide[2] clearly established the material as a strong electrolyte.

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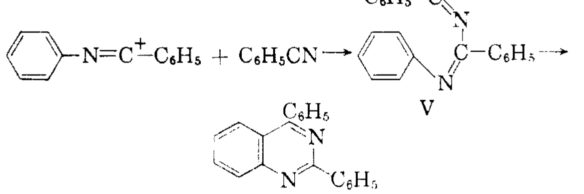
[1] Ethylidynemethylammonium chloroantimonate (V) and benzylidynephenylammonium chloroantimonate (V).

[2] F. Klages and W. Grill, *Ann.*, **594**, 21 (1955).

[3] H. Meerwein, P. Laasch, R. Mersch, and J. Spille, *Ber.*, **89**, 209 (1956); H. Meerwein, P. Laasch, R. Mersch, and J. Nentwig. *Ber.*, **89**, 224 (1956).

[4] E. E. Magat, U. S. Patent 2,628,216; *Chem. Abstr.*, **47**, 5129 (1953); *J. Am. Chem. Soc.*, **73**, 1028 (1951); and references cited by Meerwein.[3]

[5] The quinazoline synthesis reported by Meerwein[3] appears analogous, *e.g.*,



V

Indeed, when the *N*-aryl group is substituted in both *ortho* positions, the adducts analogous to V were isolated as stable salts. In this case there is no evidence for incorporation of more than one nitrile molecule.