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

$$\mathrm{I} + C_6H_5NH_2 \longrightarrow CH_3—C(NHCH_3) = N—C_6H_5$$
$$C_6H_5—CCl{=}N—C_6H_5 + SbCl_5 \longrightarrow$$
III

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

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

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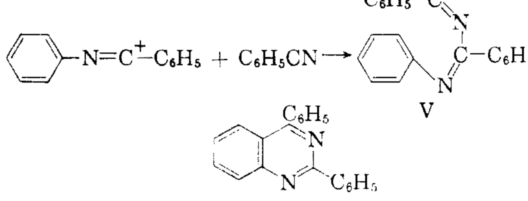
(1) Ethylidynemethylammonium chloroantimonate (V) and benzylidynephenylammonium chloroantimonate (V).

(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.

Our observations on the infrared spectrum of I support and refine the structure given for that material. The observed fundamental vibrational frequencies for the *N*-methylacetonitrilium ion were assigned[6] by analogy with those of the infrared and Raman spectra of the isoelectronic molecule dimethylacetylene[7,8] and are shown in Table I.

TABLE I

FUNDAMENTAL VIBRATIONAL FREQUENCIES AND ASSIGNMENTS FOR THE *N*-METHYLACETONITRILIUM ION

| Frequency (Cm.$^{-1}$) | Assignment | Description | Species |
|---|---|---|---|
| 2919 vs | $\nu_1$ | CH stretch | $A_1$ |
| 2416 vs | $\nu_2$ | $C\equiv N^+$ stretch | $A_1$ |
| 1343 vs | $\nu_3$ | $CH_3$ deform. | $A_1$ |
| 702 m | $\nu_4$ | C—C stretch | $A_1$ |
| (inactive) | $\nu_5$ | $CH_3$ torsion | $A_2$ |
| 2988 vs | $\nu_6$ | CH stretch | $A_1$ |
| 1383 m | $\nu_7$ | $CH_3$ deform. | $A_1$ |
| 1122 w | $\nu_8$ | $N^+$—C stretch | $A_1$ |
| 2988 vs | $\nu_9$ | CH stretch | E |
| 1421 m | $\nu_{10}$ | $CH_3$ deform. | E |
| 1090 s | $\nu_{11}$ | $CH_3$ rock | E |
| [~380] | $\nu_{12}$ | $C\equiv N^+$—C | E |
| 2955 s | $\nu_{13}$ | CH stretch | E |
| 1400 m | $\nu_{14}$ | $CH_3$ deform. | E |
| 1020 vs | $\nu_{15}$ | $CH_3$ rock | E |
| [~150] | $\nu_{16}$ | C—$C\equiv N^+$ bend | E |

[ ] Estimated from observed combination bands. vs = very strong, s = strong, m = medium, w = weak, vw = very weak.

Thirteen of the 15 expected infrared-active fundamentals were observed directly, and the two skeletal bending frequencies, which are beyond the range of the spectrometer, were estimated from observed combination bands. A comparison of the vibrational frequencies of dimethylacetylene and I shows only one significant difference; that is, in the —C≡C— stretching frequency of 2310 cm.$^{-1}$ in dimethylacetylene. which is to be compared with the —C≡N$^+$— stretching frequency of 2416 cm.$^{-1}$ in the *N*-methylacetonitrilium ion. This difference can be shown[6] to be due to an increase in the triple bond stretching force constant upon replacing ≡C— by ≡N$^+$—.

Although the close similarity of the spectrum of I with the combined infrared and Raman spectra of dimethylacetylene cannot be taken as proof that their structures are analogous, it does provide strong support for this assumption. Furthermore, the absence of any observed splitting of the E-species bands is consistant with a linear C—C≡N$^+$—C chain.

In the infrared spectrum of II the —C≡N$^+$— stretching frequency drops to approximately 2300 cm.$^{-1}$

## EXPERIMENTAL[9]

*Materials.* Acetonitrile (Eastman Spectro Grade) and methylene chloride were distilled from phosphorus pentoxide. Fisher Reagent antimony pentachloride was used without purification. *N*-Phenylbenzimidoyl chloride was prepared according to Wallach and Hoffman[10] and was distilled through a 2-ft. Podbielniak column, b.p. 151.5–152.5° (2 mm.), m.p. 40.5–42°.

*Infrared measurements.* Infrared spectra of the nitrilium salts I and II were observed from 400 cm.$^{-1}$ to 4000 cm.$^{-1}$ using potassium bromide, sodium chloride and calcium fluoride prisms. The sodium chloride region was investigated with a Perkin-Elmer model 137 "Infracord." A double-beam, ratio-recording infrared spectrometer of the type described by Hornig, Hyde, and Adcock[11] was used to cover the calcium fluoride and potassium bromide regions. The spectra were observed at room temperature from samples prepared in the form of Nujol and perfluorokerosene mulls pressed between sodium chloride plates.

*N-Methylacetonitrilium hexachloroantimonate* (I). Excess acetonitrile and 2.35 g. (0.00785 mole) of antimony pentachloride were placed in a Pyrex ampoule and the excess nitrile was evaporated at reduced pressure leaving the pale yellow crystalline complex. Methyl chloride was passed over Drierite and condensed in the ampoule at Dry Ice temperature to a volume of 3 ml.; the sealed ampoule was stored at room temperature with frequent shaking for 5 weeks during which time the powdery complex dissolved and large transparent prisms of the nitrilium salt were deposited. The latter were decanted and washed with 6 portions of methylene chloride giving 1.5 g., 49%, of the nitrilium salt, m.p. 178–181° dec.

*Anal.* Calcd. for $C_3H_6Cl_6NSb$: C, 9.22; H, 1.55; Cl, 54.47; N, 3.59. Found: C, 9.14; H, 1.80; Cl, 54.28,[12] 54.31,[12] 50.8,[13] N, 3.24.

*Reaction of N-methylacetonitrilium hexachloroantimonate with aniline.* Treatment of 1.88 g. (0.0048 mole) of the nitrilium salt with 0.45 g. (0.0048 mole) of aniline in 15 ml. of dry benzene at room temperature for 12 hr. gave a tarry mixture which was poured into 50 ml. of cold 3*N* sodium hydroxide; the aqueous phase and suspended solid were extracted thoroughly with benzene, and the combined dried (potassium carbonate) benzene solutions were evaporated to 0.51 g. of oil and crystals. The latter was chromatographed on 15 g. of Merck alumina, 280 ml. of benzene-hexane, 2:1, eluting 0.235 g., 33% of *N*-phenyl-*N'*-methylacetamidine, m.p. 70–71.5°, after an initial oily fraction weighing 0.88 g. The analytical sample was recrystallized four times from hexane (82% recovery) and sublimed at 0.1 mm. and 60°, m.p. 71-72.5° (reported[14] 72°).

*Anal.* Calcd. for $C_9H_{12}N_2$: C, 72.93; H, 8.16; N, 18.90. Found: C, 72.82; H, 8.11; N, 19.08.

*N-Phenylbenzonitrilium hexachloroantimonate*, (II). After the procedure of Meerwein *et al.*[3] antimony pentachloride and *N*-phenylbenzimidoyl chloride were mixed in methylene

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(6) For a normal coordinate treatment of the *N*-methylacetonitrilium ion see G. C. Turrell and J. E. Gordon, *J. Chem. Phys.*, in press.

(7) B. L. Crawford, Jr., *J. Chem. Phys.*, **7**, 555 (1939).

(8) I. M. Mills and H. W. Thompson, *Proc. Roy. Soc. (London)*, **226A**, 306 (1954).

(9) Unless otherwise stated, all manipulations were carried out in a dry box maintained with phosphorus pentoxide. Melting points are uncorrected; those above 150°, or for moisture sensitive compounds, were determined in evacuated capillaries. Microanalyses were performed by the Microchemical Laboratory, Massachusetts Institute of Technology, and the Mikroanalytisches Laboratorium im Max Planck Institüt für Kohlenforschung (Mülheim).

(10) O. Wallach and M. Hoffmann, *Ann.*, **184**, 79, (1877).

(11) D. F. Hornig, G. E. Hyde, and W. A. Adcock, *J. Optical Soc. Am.*, **40**, 497 (1950).

(12) By sodium peroxide fusion followed by chloride determination.[2]

(13) By the Carius method; the contaminated silver chloride obtained was dissolved in potassium iodide and determined by difference.

(14) P. Oxley and W. F. Short, *J. Chem. Soc.*, 1514 (1948).

chloride and the precipitate was washed with five portions of fresh solvent and dried on the vacuum line to give 95% of the nitrilium salt as a pale yellow powder, m.p. 230–233° to a scarlet melt (reported[3,2] 231–234°, 236–237°).

*Reaction of N-phenylbenzonitrilium hexachloroantimonate with aniline.* A solution of 0.58 g. (0.0062 mole) of aniline in 25 ml. of dry benzene was treated with 2.93 g. (0.0057 mole of II and the mixture was worked up as described for the reaction of I, giving 1.53 g. of yellow solid. Chromatography of a 0.63 g. aliquot on 13 g. of Merck alumina gave 0.38 g. of *N,N'*-diphenylbenzamidine, m.p. 145.7–147° (reported[14] 146.5–147°), eluted by 320 ml. of methylene chloride-hexane, 1:1. The yield is thus 59%. The analytical sample was crystallized three times from isopropanol (recovery, 89%) and sublimed at one micron and 135°.

*Anal.* Calcd. for $C_{19}H_{16}N_2$: C, 83.79; H, 5.92; N, 10.29. Found: C, 83.77; H, 5.95; N, 10.41.

The *picrate* was prepared in benzene, m.p. 218–219° (reported[14] 221°).

*Reaction of N-phenylbenzonitrilium hexachloroantimonate with phenol.* A mixture of 4.36 g. (0.00847 mole) of the nitrilium salt and 1.0 g. (0.0106 mole) of phenol in 25 ml. of dry benzene was kept overnight at room temperature, refluxed for 15 min. and finally treated with cold, aqueous alkali to *p*H 10. Working up as in the preceding section provided 2.18 g. of yellow solid. A 0.60-g. aliquot chromatographed on 18 g. of Merck alumina gave 0.325 g. of phenyl *N*-phenylbenzimidoate, m.p. 104–105°, eluted by 50 ml. of benzene-hexane, 3:1, yield, 51%. The analytical sample was crystallized twice from hexane and sublimed at one micron and 92°, m.p. 104.5–106° (reported[14] 104.5–105°).

*Anal.* Calcd. for $C_{19}H_{15}NO$: N, 5.13. Found: N, 5.14.

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## Nitrosation of Acylated 1,2-Diaminoethenes[1]

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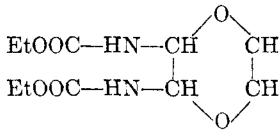
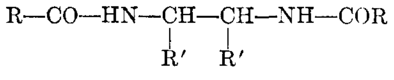
Acylated 1,2-diaminoethanes have been reported in the literature to react normally with nitrous acid to the expected bis-*N*-nitroso derivatives.[2] As reported in this paper the reaction of acylated 1,2-diaminoethenes takes an entirely different course.

Starting materials for this investigation were 1,2-di(benzoylamino)ethene[3] (I) and 1,2-di(carbethoxyamino)ethene (II). The latter compound could not be obtained *via* the Curtius degradation of fumaric acid as reported in the literature.[4] An isomer, probably the *cis*-II, however, was easily obtained by the Bamberger cleavage of imidazole with ethyl chloroformate and alkali. The identity of the *cis*-II was confirmed by catalytic hydrogenation to the known 1,2-di(carbethoxyamino)ethane. Both I and II reacted in alcoholic solution with ethyl or isoamyl nitrite in the presence of hydrochloric acid with immediate development of an intense blue-green color which soon disappeared whereupon colorless crystals deposited. These crystals turned out to be the corresponding 1,2-diethoxy-1,2-di(carbethoxyamino)ethanes (IIIa, resp. IIIb). Replacement of ethanol by isopropylalcohol in this reaction led from II to the corresponding isopropoxy compound IV while ethylene glycol yielded the dioxane derivative V. In an aqueous system the glycol VI was obtained from I with sodium nitrite and hydrochloric acid. Compounds IIIa and VI have previously been obtained from I *via* the dibromide VII.[3] In the case of IIIa we obtained apparently a stereoisomer, m.p. 240–241°, whereas Ruggli reports two isomers, m.p. 190–191°, and m.p. 219° *via* his route. The glycol VI was obtained as a mixture of two stereoisomers, m.p. 162–164°, and m.p. 180–182°, while Ruggli isolated in this case only the lower melting isomer. It is obvious the glycol and its ethers can occur both as meso- and racemic forms. When the nitrosation of II with isoamyl nitrite and alcoholic hydrogen chloride was carried out for a prolonged period, the originally formed crystals of IIIb went again into solution. A new compound could then be isolated which derived from IIIb by the loss of one molecule of alcohol. Presumably, ring closure to 1-carbethoxy-4,5-diethoxyimidazolidinone-2 (VIII) occurred.

R—CO—HN—CH═CH—NH—CO—R
I. R = $C_6H_5$, II. R = OEt

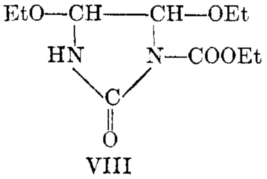


V



$$\mathrm{R{-}CO{-}HN{-}\underset{R'}{CH}{-}\underset{R'}{CH}{-}NH{-}COR}$$

IIIa. R = $C_6H_5$
R' = OEt
IIIb. R = OEt
R' = OEt
VI. R = $C_6H_5$
R' = OH
IV. R = OEt
R' = $OCH(CH_3)_2$
VII. R = $C_6H_5$
R' = Br



VIII

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[1] This article is based on work performed under Project 116 B of The Ohio State University Research Foundation sponsored by the Olin Mathieson Chemical Corp., New York, N. Y.

[2] H. Holter and H. Bretschneider, *Monatsh.*, **53/54**, 963 (1929); C. M. Samour and J. P. Mason, *J. Am. Chem. Soc.*, **76**, 441 (1954); T. Lieser and G. Beck, *Chem. Ber.*, **84**, 137 (1950); H. Lettre and U. Brose, *Naturwissenschaften*, **36**, 57 (1949).

[3] P. Ruggli, R. Ratti, and E. Henzi, *Helv. Chim. Acta*, **12**, 332 (1929).

[4] R. Radenhausen, *J. prakt. Chem.*, [2] **52**, 453 (1895).