due, weighing 12.4 g. was in two phases, one of which was undoubtedly mineral oil. The second phase was separated from the mineral oil by dissolving it in a small amount of methanol in which the mineral oil was not very soluble.[9] The crude product was distilled *in vacuo*. The initial distillate contained 2-aminopyridine. The desired product boiled at 73–74° at 0.004 mm. n_D^{25} 1.5323, yield 1.95 g., 13%.

Anal. Calcd. for $C_9H_{15}N_3O$: C, 59.64; H, 8.34; N, 23.19. Found: C, 59.92; H, 8.16; N, 22.88.

2-[2-N-Methyl-N-methoxyaminoethyl)(p-methoxybenzyl)-amino]pyridine (IV). A 41% emulsion of sodium hydride (4.25 g., 0.073 mole) in mineral oil was suspended in 30 ml. purified dioxane. To this mixture 11.5 g. III (0.063 mole) in 30 ml. purified dioxane was added. This mixture was heated with stirring. At 75° a vigorous reaction took place with a temperature rise and foaming. When the reaction ceased, the preparation was cooled to 30°. A solution of 13.4 g. *p*-methoxybenzyl bromide[4] (0.067 mole, b.p. 80.5–81.5° at 1 mm.) in 20 ml. dry dioxane was added at such a rate that the temperature of reaction did not exceed 50°. The reaction product was stirred for a short time after the addition was complete and then the product was diluted with 100 ml. of ether, and the mixture which formed was filtered. The filtrate was extracted with 2.5*N* HCl in four portions of 25 ml. each. The extracts were combined, washed with ether, and then made alkaline with 2.5*N* NaOH.The alkaline solution was extracted thrice with 100 ml. ether. The ether extracts were combined, washed with water, dried and concentrated under reduced pressure. The residue, after the removal of solvent *in vacuo* weighed 18.1 g. (95%) n_D^{25} 1.5688.

Anal. Calcd. for $C_{17}H_{23}N_3O_2$: C, 67.74; H, 7.69; N, 13.95. Found: C, 67.59; H, 7.76; N, 13.79.

The ultraviolet spectrum was identical with that of pyrilamine with maxima at 311 mμ, ϵ 4,540; 285 mμ, ϵ 2,890; 278 mμ, ϵ 2,740; 251 mμ, ϵ 19,280; 227 mμ, ϵ 12,400.

The infrared spectrum was very similar to that of pyrilamine except for an intensification of absorption in 9.6μ region and the absence of a band at 3.6μ. This band was also absent in the infrared spectrum of 2-[(2-*N*-methyl-*N*-methoxyaminoethyl)amino]pyridine (III).

A portion of the above analyzed residue was distilled, b.p. 150–152° (20 mm.), n_D^{25} 1.5683.

Anal. Calcd. for $C_{17}H_{23}N_3O_2$: C, 67.74; H, 7.69. Found: C, 67.81; H, 7.45.

Investigations of the purity of the 2-[(2-N-methyl-N-methoxyaminoethyl)(p-methoxybenzyl)amino]pyridine (IV). (1) *Distribution:* Distilled IV (31.6 mg.) was added to 10 ml. of isooctane and 10 ml. of 90% methanol. After shaking the mixture for a few minutes, 1 cc. of each phase was removed and diluted to 50 ml. with spectrographically pure methanol. The ultraviolet spectra of the two phases were identical. The absorbance of the isooctane sample at 311 mμ was 0.332 and the absorbance of the methanol sample at 311 mμ was 0.729. The distribution ratio was 0.46.

(2) *Paper strip analysis.* Distilled IV (185 μg.) was chromatographed on paper in an isooctane–90% methanol solvent system. When the paper was viewed in ultraviolet light through a phosphor screen, one spot was visible which had an R_f value of 0.75. Assay by ultraviolet spectrum showed that 95% of the original material was in this spot.

A similar experiment using a ligroin-Carbitol solvent system also failed to produce any separation.

Salts of 2-[(2-N-methyl-N-methoxyaminoethyl)(p-methoxybenzyl)amino]pyridine (IV). *Hydrochloride.* Gaseous HCl produced an amorphous white solid when bubbled into a solution of IV in dry ether. The solid was very hygroscopic. Chloride analysis of 17.3% indicated that the hydrochloride was largely the dihydrochloride mixed with some monohydrochloride. *Hydrobromide.* Gaseous HBr precipitated an amorphous white hydroscopic solid when bubbled into a solution of IV in ether.

Picric acid, maleic acid, sulfuric acid, nitric acid, and perchloric acid gave oily salts with IV which did not crystallize or solidify.

Chloroplatinates. Two chloroplatinates of IV were obtained, depending on whether IV was added to a solution of chloroplatinic acid or the reverse. (1) Compound IV (102 mg., 0.00034 mole) was dissolved in ethanol. To this solution was slowly added 4.25 ml. of a 0.04 molar solution of chloroplatinic acid (0.17 mole) in ethanol. The precipitate which formed was recrystallized by adding water dropwise to the hot alcoholic suspension of the salt until a solution occurred. Cooling precipitated 105 mg. of a chloroplatinate of IV; m.p. 146–148° with decomposition.

Anal. Calcd. for $(C_{17}H_{23}N_3O_2)_2H_2PtCl_6$: C, 40.32; H, 4.78; Cl, 21.01; Pt, 19.28. Found: C, 40.14; H, 4.85; Cl, 20.92; Pt, 20.11; 20.17.

(2) A solution of IV (85 mg., 0.00028 mole) in ethanol was added to 9.0 ml. of 0.04 molar H_2PtCl_6 (0.00036 mole) in ethanol. The precipitate which formed was recrystallized from hot ethanol containing a very small amount of water. The salt which was obtained had no definite melting point but slowly sintered above 140°.

Anal. Calcd. for $C_{17}H_{23}N_3O_2.H_2PtCl_6$: C, 28.70; H, 3.54; Cl, 29.91; Pt, 27.44. Found: C, 28.95; H, 3.40; Cl, 29.76; Pt, 26.91, 27.31.

Chloroaurate. A solution of IV (86 mg., 0.00029 mole) in ethanol was added to 6.0 ml. of 0.05*M* $HAuCl_4$ (0.0003 mole). The solution which was obtained yielded a precipitate when diluted with 200 ml. ether. It was recrystallized from butanol; yield, 106 mg., m.p. 100–101°.

Anal. Calcd. for $C_{17}H_{23}N_3O_2.HAuCl_4$: C, 31.83; H, 3.77; Cl, 22.11; Au, 30.75. Found: C, 31.94; H, 3.72; Cl, 21.84; Au, 30.93, 31.06.

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(9) In later preparations the separation was effected more easily by extracting the combined ether solutions with dilute hydrochloric acid, adding NaOH solution to the acid fraction and then reextracting the base with ether.

Note on the Structure of Certain Nitrobenzene Addition Compounds

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Several addition compounds of nitrobenzene with inorganic halides have previously been recorded. The compound $C_6H_5NO_2{\cdot}TiCl_4$ was reported by Pushin and coworkers,[1] who studied the nitrobenzene–titanium tetrachloride system cryoscopically. The addition compound $C_6H_5NO_2{\cdot}AlCl_3$ is well known[2]; an adduct of nitrobenzene with antimony pentachloride, $2C_6H_5NO_2{\cdot}SbCl_5$, has also been re-

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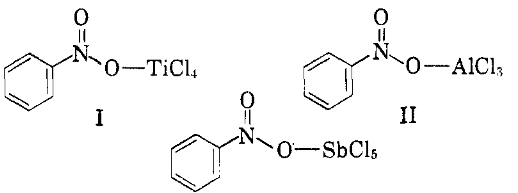
(1) N. A. Pushin, L. Nikolic, A. Radojcin, and T. Voroponova, *Ann.*, **551**, 259 (1942).

(2) B. Menschutkin, *Chem. Zentr.*, **I**, 1240 (1910).

ported.[3] No evidence concerning the structure of these compounds is as yet available.

The infrared spectrum of the compound $C_6H_5NO_2 \cdot TiCl_4$ was obtained as a Nujol mull and recorded on a Perkin-Elmer Model 21 Infrared Spectrophotometer. The infrared spectrum of nitrobenzene is characterized by two strong bands at 1575 and 1340 cm.$^{-1}$, arising from the unsymmetrical and symmetrical N=O stretching modes of vibration.[4] The spectrum of the addition compound has but one band attributable to the nitro group, a moderately strong band at 1330 cm.$^{-1}$ No absorption was noted in the 1500–1600 cm.$^{-1}$ range, excepting the customary benzene bands. The observation of but one mode of N=O stretching can be interpreted only in terms of a single N=O structural group in the molecule. The reaction of nitrobenzene with titanium tetrachloride must, therefore, involve coordination of one of the oxygens of the nitro group to titanium. The proposed structure (I) should have a single N=O stretching frequency.



I II III

The spectrum of $C_6H_5NO_2 \cdot AlCl_3$ is quite similar, only one N=O band occurring, at 1340 cm.$^{-1}$, as would be expected for structure (II).

Addition of antimony pentachloride to nitrobenzene yielded a solid compound of the composition $C_6H_5NO_2 \cdot SbCl_5$. The compound $C_6H_5NO_2 \cdot SbCl_5$, reported by Maki and Yokote,[3] was not obtained. The infrared spectrum of this compound, obtained as a mull in halocarbon oil, is quite similar to those of the titanium and aluminum compounds, the single N=O band noted at 1335 cm.$^{-1}$ Structure III is therefore proposed.

This series of compounds is, therefore, a typical donor-acceptor system, an oxygen of the nitro group functioning as an electron pair donor.

Future studies of addition compounds of organic ligands through the medium of infrared spectrophotometry are planned.

EXPERIMENTAL

Nitrobenzene–titanium tetrachloride. Nitrobenzene, purified by repeated distillation, was added to dry titanium tetrachloride in a Dry Box. Yellow crystals were collected, m.p. 80–81°, reported 75°.[1]

Anal. Calcd. for $C_6H_5NO_2 \cdot TiCl_4$: Cl, 45.3; Found: 44.6.

Nitrobenzene–aluminum chloride. Prepared as above, yellow-green crystals, m.p. 90°, reported 90°.[2]

Nitrobenzene–antimony pentachloride. Conductometric titration of antimony pentachloride with nitrobenzene, using anhydrous chlorobenzene as the solvent, yielded a sharp break at an equimolar ratio. Combination of the factors in a Dry Box yielded yellow crystals, m.p. 111–112°; Maki and Yokote report that their compound melted 107–108°.

Anal. Calcd. for $C_6H_5NO_2 \cdot SbCl_5$: Cl, 41.99; Sb, 28.84. Found: Cl, 41.40, 41.90; Sb, 28.62.

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[3] T. Maki and M. Yokote, *J. Soc. Chem. Ind. Japan*, **39**, 441 (1936).

[4] L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, Methuen and Co., London, 1954, 250–254.

$AlCl_3$-Catalyzed Condensation of Phenanthrene with Maleic Anhydride[1]

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In a search for new derivatives of phenanthrene, the Friedel-Crafts reactions of phenanthrene were investigated. That with maleic anhydride was found to be unusual in that it gave a cyclopentenophenanthrene derivative.

Baddeley *et al.*[2] described a two-stage reaction of naphthalene and maleic anhydride in which aluminum chloride was the catalyst. The initial step in the reaction was the Friedel-Crafts acylation; and the second step, an acid-catalyzed attack on the double bond of maleic anhydride to effect ring closure. The reaction product was a ketocyclopentenonaphthalene carboxylic acid, the ring closure having taken place at the 1- and 2-positions of the naphthalene molecule.

In the closely related work of Alder and Wolff,[3] naphthalene was condensed with maleic anhydride in two steps to give a tricyclic product, traces of iodine instead of aluminum chloride being used in the initial step. This resulted in a reversal of the order of the condensations: The reaction with the double bond of maleic anhydride, not the acylation, took place first. The final product differed from that of Baddeley in that the maleic anhydride moiety entered the naphthalene nucleus at a different place, so that a ketoperinaphthane carboxylic acid was produced. In addition, Baddeley and Williamson[4] demonstrated that 5-octahydrophenanthrene reacts with maleic anhydride and aluminum chloride to give a 9,10-cyclopenteno derivative. All these reactions consisted of the substitution of a 1-keto-3-carboxytrimethylene group into an aromatic nucleus.

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[1] This investigation was conducted by the Coal Chemicals Fellowship of Mellon Institute, a Multiple Fellowship sustained by the United States Steel Corp., Pittsburgh, Pa.

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[3] K. Alder and O. Wolff, *Ann.*, **576**, 182–214 (1952).

[4] G. Baddeley and R. Williamson, *J. Chem. Soc.*, 2120 (1953).