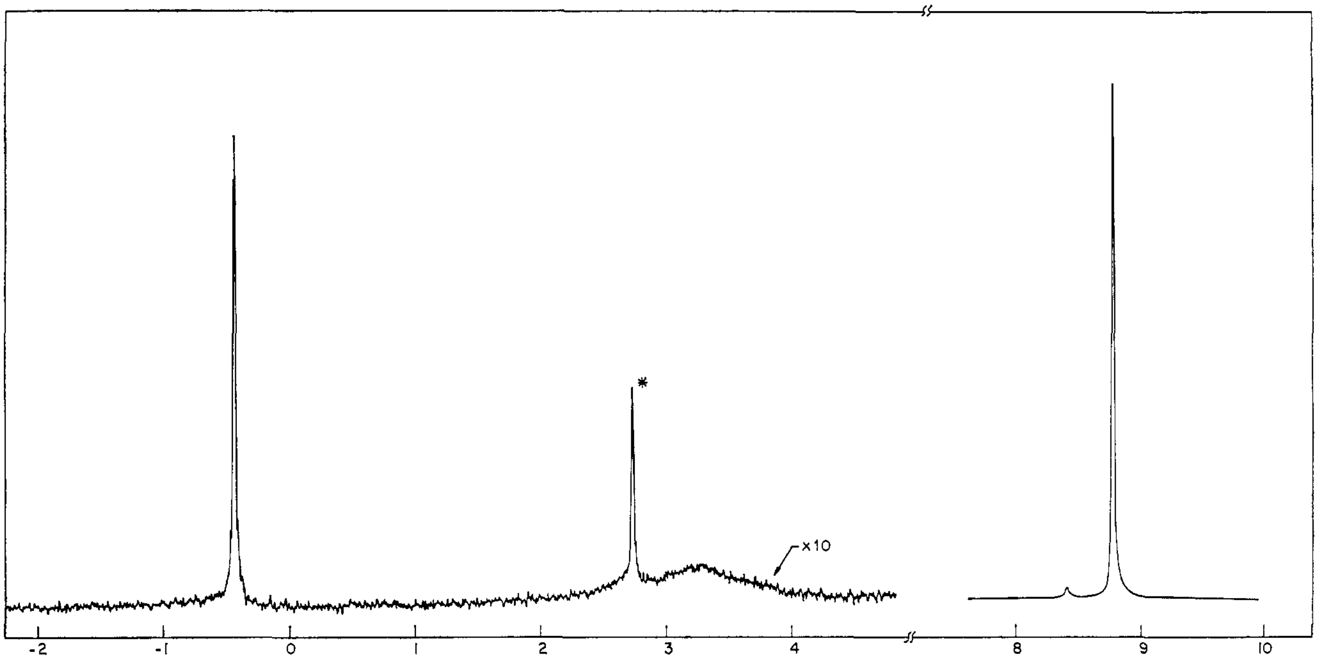


Figure 2. The proton nmr spectrum of dichlorobis(trimethylacetamide)platinum(II) in $CDCl_3$. The peak marked with an asterisk is due to a solvent impurity.

The proton nmr spectrum of II, Figure 2, exhibits sharp absorptions at τ −0.44 and 8.77 and a broad band at *ca.* τ 3.25, with relative intensities of 1:9:1. The nmr spectrum of $(CH_3)_3CCONH_2$ itself in $CDCl_3$ contains a broad band at *ca.* τ 4.16 and a sharp band at τ 8.78, with relative intensities 2:9, as expected for the normal amide structure. Thus the comparison of the nmr spectra shows that the two protons are bonded to the nitrogen in the free amide, but that in the amide complex II there is only one proton on the nitrogen, the other presumably being on the oxygen. This last conclusion follows from the fact that the nmr of protons on amides almost invariably appear in the region τ 3–4 as very broad lines due to relaxation effects of the nitrogen quadrupole moment, whereas the low-field absorption in II (τ −0.44) is sharp and is found far outside the τ range quoted above. The hydroxyl proton of the iminol structure would be expected to exhibit a low-field shift, such as is observed in the isoelectronic pivalic acid (τ −2.08)[7] and protonated amides.[8] In addition, solution of I in an acetone–D_2O mixture resulted in the deuteration of both the nitrogen and oxygen, as judged from the disappearance of the τ −0.44 and 3.25 bands following this treatment. The only interpretation compatible with all of the above facts is that the amide groups in II are in the $-C(=NH)-OH$ iminol form. Since the C=N distance would be much shorter than the C–O distance, and it is the shorter of these that is bonded to the platinum in I (Figure 1), it appears that the iminol ligands bond through nitrogen rather than oxygen. Moreover, since the proton nmr of the needles I is simply the sum of those of the components separated by chromatography, there was no interconversion of compounds on the silica gel column.

The infrared spectrum of II is also consistent with the proposed iminol structure. Crystalline trimethylacetamide shows strong bands at 1655 and 1627 cm^{-1}, which can be assigned as the amide I [ν(C=O)] and amide II [$\delta(NH_2)$] bands, respectively.[9] In the complex, however, there is only one absorption in this region, at 1639 cm^{-1}. For an iminol complex, only one band is expected in this region, a C=N stretching motion, and this we assign to the 1639-cm^{-1} band. Moreover, the amide itself, having two N–H bonds, exhibits two N–H stretching vibrations at 3180 and 3370 cm^{-1},[9] whereas the complex II has only one, at 3280 cm^{-1}, consistent again with the proposed iminol structure. The O–H stretching vibration of II in CCl_4 solutions can be located only with some difficulty (3020 cm^{-1}), for it is nearly coincident with the C–H stretching vibrations. However, on deuteration, the band shifts to 2280 cm^{-1}, where it is clearly visible.

Work is now in progress on the elucidation of the molecular and electronic structure of the amorphous blue material IV and the second yellow fraction III. Preliminary work shows that III has only one of its two amide groups in the iminol form, while IV does not contain the iminol configuration at all.

Acknowledgment. It is a pleasure to acknowledge the assistance of J. J. Ryan with the operation of the nmr spectrometer, and discussions with Frank A. Bovey.

---

(7) F. A. Bovey, "NMR Data Tables for Organic Compounds," Interscience Publishers, New York, N. Y., 1967, p 105.

(8) R. J. Gillespie and T. Birchall, *Can. J. Chem.*, **41**, 148 (1963).

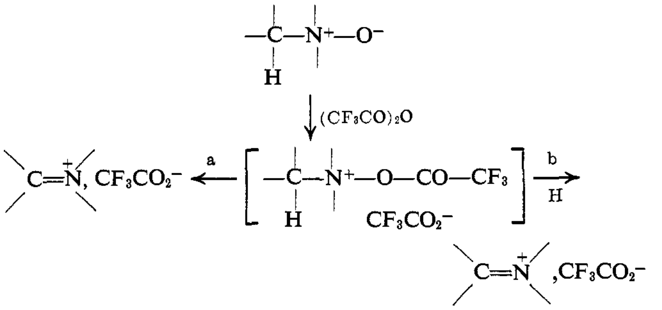
(9) L. J. Bellamy "The Infrared Spectra of Complex Molecules," Methuen & Co. Ltd., London, 1958.

D. B. Brown, M. B. Robin, R. D. Burbank
Bell Telephone Laboratories, Inc.
Murray Hill, New Jersey
Received July 3, 1968

Facile N–O Bond Cleavages of Amine Oxides

Sir:

We wish to report a facile method of preparation of immonium salts, including the simplest member of this class of compounds.[1] Mild treatment of N-oxides with methylene chloride solutions of trifluoroacetic anhydride leads to immonium trifluoroacetates by one of two reaction paths.



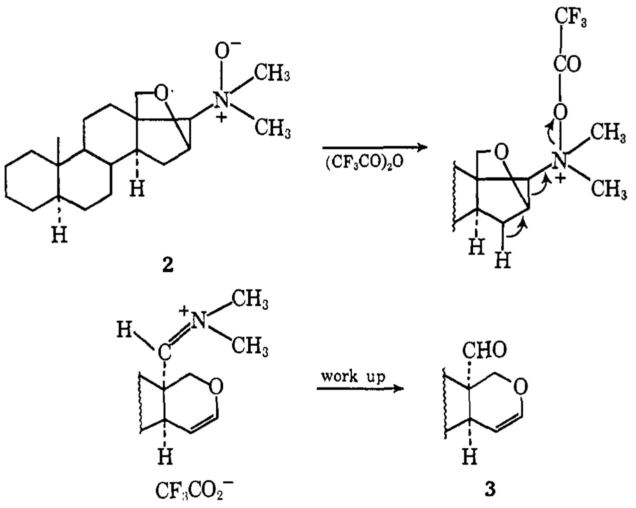
In this manner, trimethylamine oxide is transformed into N,N-dimethylformaldimmonium trifluoroacetate (**1**) (path a above) in methylene chloride solution.[2,3] Its highly characteristic proton magnetic resonance spectrum reveals a six-proton quintuplet at 3.87 ppm (methyl groups) and a two-proton pseudoseptuplet at 7.95 ppm (methylene group). Decoupling causes the latter to collapse into a singlet, while the former becomes a triplet, presumably due to heteronuclear coupling between the methyl groups and ^{14}N.[4]

$$H_2C{=}\overset{+}{N}(CH_3)_2,CF_3CO_2^-$$

1

Since salt **1** has long been considered the intermediate in Mannich reactions utilizing formaldehyde and dimethylamine,[5] its solution was exposed to different carbonyl derivatives and shown to give products more easily and in higher yields than those obtained, *e.g.*, in classical Mannich reactions: 5α-cholestan-3-one → α-dimethyaminomethyl-5α-cholestan-3-one (yield 95%; mp 106°); 3α,5-cyclo-5α-androstan-6-one → 7-dimethylaminomethyl-3α,5-cyclo-5α-androstan-6-one (yield 94%; mp 102°); 3β,20α-diacetoxy-5α-pregnan-6-one → 3β,20-diacetoxy-7-dimethylaminomethyl-5α-pregnan-6-one (yield 94%; mp 215°). Thus, a solution of **1** represents an excellent Mannich reagent.[6]

Some reactions of N-oxides with trifluoroacetic anhydride follow path b (see above). Such new fragmentation is exemplified by the conversion of **2** into the aldehyde **3**:



M^+ 288; $C_{19}H_{28}O_2$; $\nu_{KBr}^{cm^{-1}}$ 3062, 1648 (double bond), 1725 (carbonyl), 2710 (CHO); obtained in 50% yield. The pmr spectrum displays an aldehydic proton (s, 9.38 ppm), a doublet at 6.25 ppm (H_{16}), a triplet at 4.88 ppm (H_{15}), and an AB system centered at 4.10 ppm (17a-CH_2).

The possible applications of these N-O bond cleavages of amine oxides are under current investigation.

Acknowledgment. We are grateful to Dr. A. D. Cross (Syntex Research Laboratories, Palo Alto, Calif.) for the generous gift of some material and to Professors M.-M. Janot and J. Le Men for encouragement.

---

[1] For the first comments on the important modification of the Polonovski reaction, see A. Cave, C. Kan-Fan, P. Potier, and J. Le Men, *Tetrahedron*, **23**, 4681 (1967), and A. Cave and R. Michelot, *C. R. Acad. Sci., Paris, Ser. C*, **265**, 669 (1967).

[2] For a partial description of this salt, obtained by decomposition of bis(dimethylamino)methane, see (a) H. Böhme and E. Köhler, *Sitzber. Ges. Befoerder. Ges. Naturw. Marburg*, **83**, 535 (1961); *cf. Chem. Abstr.*, **59**, 11416*c* (1963); (b) H. Böhme, H. J. Bohn, E. Köhler, and J. Roehr, *Ann.*, **664**, 130 (1963); (c) J. De Luis, Ph.D. Thesis, The Pennsylvania State University, 1964; (d) A. F. McDonagh and H. E. Smith, *J. Org. Chem.*, **33**, 8 (1968).

[3] The following represents the exact method of preparation and utilization of this reagent. Trifluoroacetic anhydride, 0.14 ml (1 mmol), is added dropwise to a solution of 75 mg (1 mmol) of freshly sublimed trimethylamine oxide in 5 ml of methylene chloride cooled to 0°. The mixture is left at room temperature for 1 hr and then evaporated to dryness at 100° (14 mm). To the residual oil (crystalline at −5°) there is added a methylene chloride solution of 1 mmol of ketone. After the solution has been kept at 40° for 2–8 days, the resultant Mannich base is isolated in the usual manner.

[4] A complete pmr analysis of immonium salts will be reported elsewhere.

[5] B. Reichert, "Die Mannich Reaktion," Springer-Verlag, Berlin, Göttingen, Heidelberg, 1959; H. Hellmann and G. Opitz, "α-Amino Alkylierung," Verlag Chemie GMBH, Weinheim/Bergstr., 1960.

[6] CNRS, French Patent, Application 136.761 (1968).

[7] To whom all inquiries must be sent.

Alain Ahond, Adrien Cavé, Christiane Kan-Fan
Henri-Philippe Husson, Jacques de Rostolan, Pierre Potier[7]
Institut de Chimie des Substances Naturelles du C.N.R.S.
Gif sur Yvette, France

Received June 21, 1968

Structure of Tris(octamethylpyrophosphoramide)copper(II) Perchlorate

Sir:

We herewith report the structure of $Cu\{[([CH_3]_2N)_2P(O)]_2O\}_3(ClO_4)_2$. This compound crystallizes in the trigonal space group, $P\bar{3}c1$, which requires all Cu–O bond distances to be equal (2.065 Å). The site symmetry of Cu(II) is D_3 and should be unstable according to the Jahn–Teller theorem.[1] The only previous tris-chelate complex of Cu(II) for which structure data are available is tris(ethylenediamine)copper(II) sulfate.[2,3] The site symmetry of Cu(II) in this complex is also D_3. These tris-chelate structures are of special interest since they along with $K_2Pb[Cu(NO_2)_6]$[4] are the only known Cu(II) structures which do not show tetragonal distortion.

We reported previously the preparation and characterization of the colorless Cu(II) complex of octamethylpyrophosphoramide (OMPA).[5] Crystal data for

---

[1] H. A. Jahn and E. Teller, *Proc. Roy. Soc.* (London), **A161**, 220 (1937); H. A. Jahn, *ibid.*, **A164**, 117 (1938).

[2] M. Cola, G. Giuseppeti, and F. Mazzi, *Atti Acad. Sci. Torino*, **96**, 381 (1962).

[3] E. C. Lingafelter has redetermined this structure and confirmed the $P\bar{3}1c$ space group and geometry of the cation: private communication.

[4] N. W. Isaacs, C. H. L. Kennard, and D. A. Wheeler, *Chem. Commun.*, 587 (1967).

[5] M. D. Joesten and J. F. Forbes, *J. Am. Chem. Soc.*, **88**, 5465 (1966).