

Figure 1. Part of the structure of  $\text{CsCl} \cdot \frac{1}{3} \text{H}_3\text{OHCl}_2$ . The  $c$  axis is vertical in the figure. The disorder of the oxygen positions is not shown, nor are the hydrogen positions. The shaded lines represent probable hydrogen bonds.

ment found in  $\text{H}_3\text{OCl}$ .<sup>6</sup> Yet in  $P6_3/m$  an atom at  $0, 0, z$  is related by symmetry to an atom at  $0, 0, \frac{1}{2} - z$ , and this leads to an O-O distance of 1.8 Å. Thus we believe that the strings of hydronium ions along the  $c$  axis are disordered in the sense that there is no common origin for these strings; in effect each oxygen position is a half-position since there is equal probability that a given oxygen will be above or below its chlorine plane. Precisely this type of disorder is found in  $\text{H}_3\text{OCl}$ .<sup>6</sup> The usual  $R$  and weighted  $R$  factors (for least-squares refinement on  $F_o$ ) that had been 0.126 and 0.150 before inclusion of the half-oxygen dropped to 0.093 and 0.103, respectively, after its inclusion. A final difference Fourier showed no features higher than  $3 \text{ e}/\text{Å}^3$  and provided some evidence for anisotropy in the cesium position. However, since the data were collected around only one axis (there being no choice in this case) and since the absorption correction is an approximate one, we felt that the anisotropic thermal parameters that could have been obtained would reflect systematic errors in our data rather than physical reality. Thus the calculations were terminated at the isotropic refinement.

Upon location of the half-oxygen positions, the composition of the material becomes  $\text{CsCl} \cdot \frac{2}{3} \text{HCl} \cdot \frac{1}{3} \text{H}_2\text{O}$ , where the hydrogen atoms have been added to balance charge. No direct evidence for the hydrogen atoms has been obtained from the present data. However, as we remarked above, the geometrical arrangement strongly suggests the presence of the hydronium ion. In fact, the geometry here is remarkably similar to that in  $\text{H}_3\text{OCl}$ .<sup>6</sup> The comparative values between the present study and that one are O-Cl distance:  $2.92 \pm 0.02$ ,  $2.95 \pm 0.01$  Å; Cl-O-Cl angle:  $110.1$ ,  $110.4^\circ$ . (The hydrogen atom positions were located, albeit inexactly, in  $\text{H}_3\text{OCl}$ .<sup>6</sup>) Thus the composition of our material at this point becomes  $\text{CsCl} \cdot \frac{1}{3} \text{H}_3\text{O}^+ \cdot \frac{1}{3} \text{H}^+$ .

(6) Y. K. Yoon and G. B. Carpenter, *Acta Cryst.*, **12**, 17 (1959).

$\frac{2}{3} \text{Cl}^-$  and there is the implication that the compound contains the bichloride ion,  $\text{HCl}_2^-$ . This is readily supported in more direct fashion by the Cl-Cl distances. All of these are 3.6 Å (the normal van der Waals distance) or greater with the exception of one Cl(2)-Cl(2) contact which is 3.14 Å, some 0.50 Å shorter than that reported in any compounds where there are only van der Waals interactions. Clearly, then, this is strong evidence for a chemical bond between the two chlorines and hence for the existence of the bichloride ion in this compound. Thus we believe that we have prepared the remarkable compound  $\text{CsCl} \cdot \frac{1}{3} \text{H}_3\text{O}^+ \cdot \text{HCl}_2^-$ . The Cl-Cl distance in the bichloride ion in this compound, the first such distance to be determined, is  $3.14 \pm 0.02$  Å. This distance is reasonable on the basis of the 0.5-Å shortening between  $\text{F} \cdots \text{F}$  (2.8 Å) and  $\text{F}-\text{F}$  in the bifluoride ion (2.26 Å).

Part of the structure is shown in Figure 1. Both strings of bichloride ions and of hydronium ions run parallel to the  $c$  axis. The Cs atom is nine-coordinated with the Cs-Cl distance ranging from 3.44 to 3.70 Å. The Cl(2)-Cl(2) distances alternate between 3.14 and 3.64 Å; all other Cl-Cl contacts exceed 4.07 Å. The Cl(1) atoms which enter into hydrogen bonds with the hydronium ion may be thought of as being arranged at the corners of octahedra which are contracted along their threefold axis. These octahedra share faces.

Infrared studies of our material have been largely inconclusive, owing to the rapid decomposition of the material in Nujol or perfluorocarbon mulls, although we have obtained some indications of band positions corresponding to those expected for the hydronium ion. Further studies are in progress.

A neutron-diffraction study is planned on this compound since it contains both the hydronium ion and the bichloride ion and since detailed geometries of both of these ions are of interest.

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## The Photochemical Reaction of Pummerer's Ketone<sup>1</sup>

Sir:

The photochemical reaction of 2-cyclohexenones in various organic solvents has been shown to result in the formation of several types of products<sup>2-5</sup> and has been explained in terms of triplet biradical intermediates by Zimmerman, *et al.*<sup>5</sup> We wish to report on a new type of the reaction of a 2-cyclohexenone, *i.e.*,

(1) Photo-induced Reactions. IV. Part III: T. Matsuura and K. Omura, *Bull. Chem. Soc. Japan*, in press.

(2) (a) A. Butenandt, L. Poschmann, G. Failer, U. Schiedt, and E. Bieckert, *Ann.*, **575**, 123 (1951); (b) P. D. Gardner and H. F. Hamil, *J. Am. Chem. Soc.*, **83**, 3531 (1961); (c) W. W. Kwie, B. A. Shoulder, and P. G. Gardner, *ibid.*, **84**, 2268 (1962).

(3) (a) O. L. Chapman, T. A. Rettig, A. A. Griswold, A. I. Dutton, and P. Fitton, *Tetrahedron Letters*, 2049 (1963); (b) O. L. Chapman, J. B. Sieja, and W. J. Welstead, Jr., *J. Am. Chem. Soc.*, **88**, 161 (1966).

(4) (a) H. Wehrli, R. Wagner, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **46**, 678 (1963); (b) B. Nann, D. Gravel, R. Schorta, H. Wehrli, K. Schaffner, and O. Jeger, *ibid.*, **46**, 2473 (1963).

(5) (a) H. E. Zimmerman and J. W. Wilson, *J. Am. Chem. Soc.*, **86**, 4036 (1964); (b) H. E. Zimmerman, R. C. Hahn, H. Morrison, and M. C. Wani, *ibid.*, **87**, 1138 (1965); (c) H. E. Zimmerman, R. C. Lewis, J. J. McCullogh, A. Padwa, S. Stanley, and M. Semmelhack, *ibid.*, **88**, 159 (1966), and references cited therein.

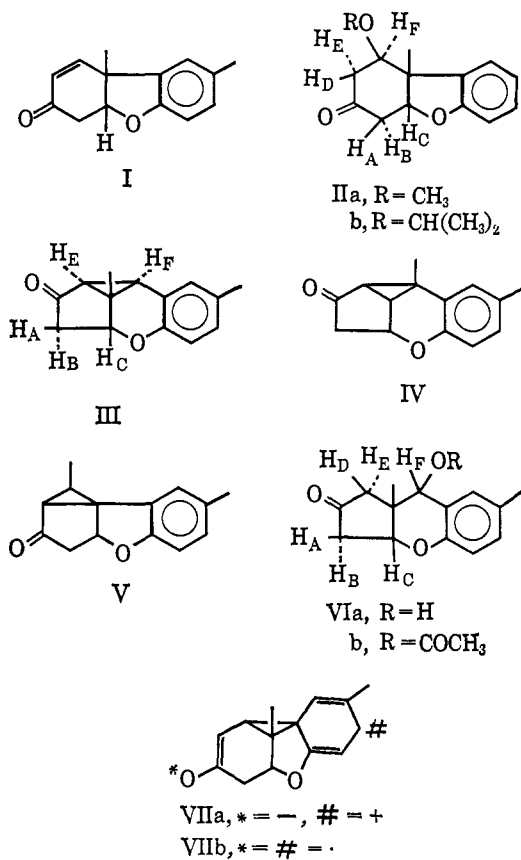
Table I. Nmr Data for Compounds IIa, IIb, III, and VIa<sup>a</sup>

	Chemical shifts, $\tau$						Coupling constants, cps							
	H <sub>A</sub>	H <sub>B</sub>	H <sub>C</sub>	H <sub>D</sub>	H <sub>E</sub>	H <sub>F</sub>	J <sub>AB</sub>	J <sub>AC</sub>	J <sub>BC</sub>	J <sub>DE</sub>	J <sub>DF</sub>	J <sub>EF</sub>	J <sub>CE</sub>	J <sub>CF</sub>
IIa <sup>b</sup>	7.17 q	7.41 q	5.53 t	7.40 q	8.04 q	6.49 q	17.0	3.5	3.5	17.5	12.0	3.5	...	...
IIb <sup>c</sup>	7.15 q	7.41 q	5.30 t	7.51 q	7.95 q	6.32 q	17.0	3.5	3.5	17.5	12.0	3.5	...	...
III	7.35 q	8.11 q	4.96 <sup>d</sup>	...	7.90 <sup>e</sup>	7.60 <sup>e</sup>	20.0	9.0	3.0	...	...	11.0	<1	1
VIa	7.37 q	7.85 q	5.39 t	8.03 s	...	5.63 s	19.5	3.5	3.5	...	...	...	...	...

<sup>a</sup> Peak multiplicities are represented by s (singlet), d (doublet), t (triplet), and q (quartet). All four compounds show a multiplet at  $\tau$  2.8–3.5 (three aromatic protons), a singlet at  $\tau$  7.71–7.73 (aromatic methyl protons), and a singlet at  $\tau$  8.40–8.78 (angular methyl protons). <sup>b</sup> IIa shows a singlet at  $\tau$  6.63 (methoxy protons). <sup>c</sup> IIb shows a septet at  $\tau$  6.34 and two doublets at  $\tau$  8.80 and 8.90 with  $J = 6$  cps (isopropoxyl protons). <sup>d</sup> Doublet of diffused quartet. <sup>e</sup> Diffused doublet.

a photochemical Michael-type addition of alcohols to form a 3-alkoxycyclohexanone.

Irradiation<sup>6</sup> of Pummerer's ketone (I)<sup>7</sup> in methanol solution (*ca.* 1%) yielded 79%<sup>6</sup> of a 1:1 methanol adduct, C<sub>15</sub>H<sub>18</sub>O<sub>3</sub>,<sup>8</sup> mp 106–107°. The infrared band



at 1726 cm<sup>-1</sup> (CHCl<sub>3</sub>) and the ultraviolet maximum at 229 m $\mu$  (log  $\epsilon$  4.17) of its semicarbazone indicate that the adduct is a saturated ketone. The structure of IIa of the adduct was suggested by the nmr spectrum<sup>9</sup> (Table I), which showed a signal of a methoxyl group and two ABX patterns (H<sub>A</sub>H<sub>B</sub>H<sub>C</sub> and H<sub>D</sub>H<sub>E</sub>H<sub>F</sub>). The coupling constants of the ABX systems revealed that the stereochemistry of the adduct is represented

(6) Irradiation was carried out with a 450-w high-pressure mercury vapor lamp (Ushio UM 450) surrounded by a Pyrex cooling jacket under bubbling nitrogen. All yields were calculated on the basis of the reacted I.

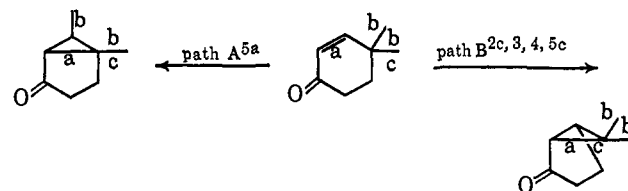
(7) The *cis* ring fusion in Pummerer's ketone (I) has been deduced by nmr analysis: *cf.* J. Shoji, *Chem. Pharm. Bull.*, 10, 483 (1962). One enantiomeric structure is given in all formulas.

(8) Satisfactory microanalyses and spectral data were obtained for all new compounds, in addition to those discussed in the communication. The results will be given in a full paper. All ultraviolet spectra were measured in ethanol.

(9) The nmr spectra were taken with a Varian A-60 spectrometer at the Faculty of Pharmaceutical Science of Kyoto University.

as IIa. Confirmation of the structure assignment was derived from the facts that IIa reverted to I by treatment with sodium methoxide followed by hydrolysis,<sup>10</sup> and that both I and IIa were converted to 2,4'-dimethyl-2',4-dihydroxybiphenyl<sup>11</sup> by mild treatment with hydrobromic acid and acetic acid (1:1).

Irradiation of I in isopropyl alcohol under the similar conditions yielded 37% of an adduct, C<sub>17</sub>H<sub>22</sub>O<sub>3</sub>, mp 109.5–110.5°, and 22% of a photoketone, mp 86.5–87.5°, isomeric to I. Spectral data of the adduct were quite similar to those of IIa and the structure IIb was given. The photoketone was also obtained by irradiation of I in *t*-butyl alcohol (43% yield), dioxane (31%), or benzene (72%). The photoketone shows an infrared band at 1734 cm<sup>-1</sup> and a maximum at 240 m $\mu$  (log  $\epsilon$  4.14) in the difference curve between the ultraviolet spectra of its semicarbazone and of the photoketone or of IIa. These values agree with those expected for a bicyclo[3.1.0]hexan-2-one structure.<sup>12,13</sup> Insofar as reported,<sup>2c-5</sup> the rearrangement of 2-cyclohexenones to bicyclo[3.1.0]hexan-2-ones involves, at least formally, a switching of bond a and one of bonds b and c at the C-4 position. This view suggests that the structure of the photoketone may be represented by formulas III, IV, or V. The structure V is elimi-



nated by the fact that the nmr signal of the aliphatic methyl group is not splitting. Structure IV cannot account for the small values of the coupling constants, J<sub>CE</sub> and J<sub>CF</sub> (Table I). Treatment of the photoketone with 3% hydrobromic acid in acetic acid at room temperature yielded 42% of VIa, a five-membered ketone ( $\nu_{\max}$  1752 cm<sup>-1</sup>), and 34% of VIIb which was also obtained by acetylation of VIa. The nmr spectrum (Table I) of VIa is consistent with the formula VIa. Thus we tentatively assigned structure III to the photoketone. The photoisomerization of I to III can be rationalized by the formation of an intermediate, either VIIa or VIIb, analogous to that proposed by Zimmerman and Wilson.<sup>5a</sup>

(10) By similar treatment I was recovered unchanged: V. Arkley, F. M. Dean, A. Robertson, and P. Sidisunthorn, *J. Chem. Soc.*, 2322 (1956).

(11) R. Pummerer, H. Puttfarthen, and P. Schopflocher, *Ber.*, 58, 1808 (1925).

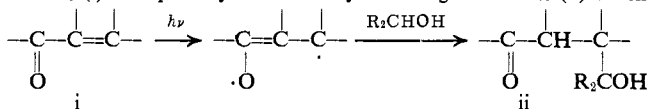
(12) H. O. House, S. G. Boots, and V. K. Jones, *J. Org. Chem.*, 30, 2519 (1965).

(13) R. H. Bastman and S. K. Freeman, *J. Am. Chem. Soc.*, 77, 6642 (1955).

The formation of the photoadducts, IIa and IIb, which involves a polar intermediate, does not appear to have any parallel in the photoreaction of  $\alpha,\beta$ -unsaturated ketones in alcoholic solvents.<sup>14</sup> Although the nature of this addition reaction has not been determined, we wish to mention three possible explanations. First, the addition can simply arise from alcohol opening up the phenonium ion VIIa which is formed from the  $n-\pi^*$  excited state of I.<sup>5a</sup> Second, it is possible that the  $\pi-\pi^*$  excited state, which is classically pictured as  $^+C=C=C-O^-$ ,<sup>15</sup> is involved in the reaction. Third, it is also reasonable to assume that an interaction between the  $\pi$  orbitals of the benzene and enone groups of I leads to a polar intermediate whose  $\beta$ -carbon atom of the carbonyl group is electron deficient. Inspection of a scale model demonstrates that the distance (ca. 4 Å) between the centers of both chromophores in I is enough close to interact each other. Such an interaction may be suggested by an unusual bathochromic shift<sup>16,16a</sup> of the ultraviolet maximum (302  $m\mu$  ( $\log \epsilon$  3.39)) of I compared to those of IIa (284  $m\mu$  ( $\log \epsilon$  3.58)) and of the dihydro derivative of I<sup>17</sup> (286  $m\mu$  ( $\log \epsilon$  3.58)).

The scope, limitations, and detailed mechanism are being studied in our laboratory.

(14) It has been reported that irradiation of some  $\alpha,\beta$ -unsaturated ketones (i) in a primary or secondary alcohol give adducts (ii) which



are formed by a radical process: M. Pfau, R. Dulou, and M. Vilkas, *Compt. Rend.*, **254**, 1817 (1962); I. A. Williams and P. Blandon, *Tetrahedron Letters*, 257 (1964).

(15) S. F. Mason, *Quart. Rev. (London)*, **15**, 287 (1961).

(16) This has analogy in the spectrum of flavothebaone (A. I. Scott, "Interpretation of the Ultraviolet Spectra of Natural Products," Pergamon Press, New York, N. Y., 1964, p 347). It should be noted that only normal benzenoid absorption and the usual unsaturated ketone absorption with a typical  $n-\pi^*$  band have been observed in the spectrum of 4a-methyl-4,4a,9,10-tetrahydro-2(3H)-phenanthrone, which on irradiation in methanol gives exclusively a photoisomer *via* path B.<sup>5c</sup> We are indebted to Dr. H. E. Zimmerman for his information of the spectra data.<sup>16a</sup>

(16a) NOTE ADDED IN PROOF. It should be also noted that in dilute acetic acid the above phenanthrone gives Michael-type addition products in low yields.<sup>3b</sup>

(17) D. H. R. Barton, A. M. Deflorin, and O. E. Edwards, *J. Chem. Soc.*, 530 (1956).

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## Trifluoramine Oxide

Sir:

We wish to report the synthesis and characterization of the unusual new compound trifluoramine oxide,  $F_3NO$ , first member of the hitherto unknown perfluorinated amine oxides.<sup>1</sup> The new compound, bp  $-85^\circ$ , mp  $-160^\circ$ , was identified by chemical analysis (Calcd: F, 65.5; N, 16.1. Found: F, 66.2; N, 16.0), molecular weight (Calcd: 87.0. Found, 86.8), and mass spectroscopy (principal fragments  $F_2NO^+$ ,  $FNO^+$ ,  $NO^+$ ,  $NF^+$ ). The  $F^{19}$  nmr spectrum (56.4 Mc/sec) of

(1) As this manuscript was being prepared for publication, we learned of the independent discovery of  $F_3NO$  by others: N. Bartlett and S. P. Beaton, *Chem. Commun.*, 167 (1966); N. Bartlett, S. P. Beaton, and N. K. Jha, *ibid.*, 168 (1966). These workers found  $F_3NO$  as a trace product in reactions of  $OsF_6$  and  $PtF_6$  with nitric oxide, but gave no details of its properties. We are grateful to Professor Bartlett for preprints of his work.

liquid  $F_3NO$  at  $-90^\circ$  consists of a sharply defined 1:1:1 triplet at  $\delta_{CCl_4F} -363 \pm 2$  ppm with  $J_{NF} = 136$  cps, indicating that the fluorine atoms are equivalent and bonded to nitrogen in the highly symmetrical environment expected of an amine oxide structure.

The nearly tetrahedral  $C_{3v}$  symmetry of  $F_3NO$  is further manifested in the infrared spectrum of the molecule, with fundamental bands ( $cm^{-1}$ ) and assignments as follows: 1687 (vs), N-O stretch; 743 (s), sym N-F stretch; 558 (vw), sym  $NF_3$  deformation; 887 (vvs), unsym N-F stretch; 528 (s), F-N-O deformation; 398 (w), unsym  $NF_3$  deformation. These represent the modes  $\nu_1$  through  $\nu_6$ , respectively, the first three being type A (with PQR branching) and the last three of type E, as required by the  $C_{3v}$  symmetry. Other bands observed were at 3345 (m), 2435 (w), 1772 (s), 1622 (w), 1410 (m), 1055 (m), 929 (w), and 801 (w)  $cm^{-1}$ . A complete normal coordinate analysis of the vibrational spectrum of  $F_3NO$  has been carried out and will be published elsewhere.<sup>2</sup>

Trifluoramine oxide can be prepared in 10-15% yields by the action of an electric discharge (5000 v, 30 ma) on equimolar  $NF_3-O_2$  mixtures at  $-196^\circ$ . The apparatus and techniques used were similar to those employed by others for the electric discharge syntheses of  $O_2F_2$  and  $O_3F_2$  from oxygen and fluorine.<sup>3</sup> The crude product was fractionated through traps at  $-140$ ,  $-160$ , and  $-196^\circ$ , the  $F_3NO$  collecting in the  $-160^\circ$  trap.

Trifluoramine oxide is a strong oxidizing agent toward many organic and inorganic materials but is resistant to hydrolysis even by strong aqueous bases. The latter property is useful in purification, since common impurities ( $SiF_4$ ,  $NO_2$ ,  $NOF$ ,  $NO_2F$ ) are easily removed by scrubbing with strong aqueous KOH solution without significant loss of  $F_3NO$ . Carefully purified  $F_3NO$  is stable in glass and most metals at  $25^\circ$  and can be recovered intact after heating to  $300^\circ$  in nickel or Monel vessels. The compound adds to some fluorinated olefins to form the corresponding  $RONF_2$  derivatives.

Trifluoramine oxide forms stable 1:1 complexes with  $AsF_5$  and  $SbF_5$ . These complexes are probably ionic (e.g.,  $F_2NO^+MF_6^-$ ) since the  $F^{19}$  nmr spectrum of each in HF solution shows a 4:5:4 triplet N-F resonance at  $\delta_{CCl_3F} -331 \pm 3$  ppm ( $J_{NF} = 250$  cps) along with the high-field resonance of the corresponding  $MF_6^-$  anions<sup>4</sup> ( $AsF_6^-$ , 60 ppm;  $SbF_6^-$ , +135 ppm) in HF solution. The area of the low-field N-F resonance is one-third that of the high-field  $MF_6^-$  resonances. Infrared spectra of thin films of the solid complexes show strong bands at 1857, 1162, and 905  $cm^{-1}$  (N=O, sym N-F, asym N-F stretches, respectively), along with the appropriate  $MF_6^-$  bands.

Photolysis of  $F_3NO$  at  $-196^\circ$  produces the relatively stable  $F_2NO\cdot$  radical, identified by its nine-line esr spectrum with  $a_N = 94.3$  gauss,  $a_F = 142.2$  gauss, and  $g = 2.009$ . A more complete account of the preparation and chemistry of  $F_3NO$  will be presented in a forthcoming series of publications.

**Acknowledgment.** This research was supported by the Advanced Research Projects Agency, Propellant

(2) J. R. Holmes, J. S. MacKenzie, and W. B. Fox, to be published.

(3) A. D. Kirshenbaum and A. V. Grosse, *J. Am. Chem. Soc.*, **81**, 1277 (1959).

(4) B. B. Stewart and C. A. Wamser, unpublished results.