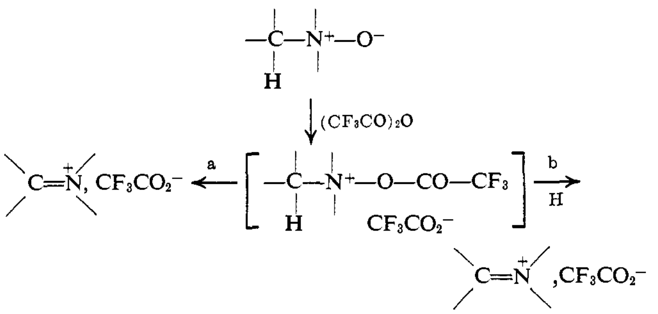
class of compounds.[1] Mild treatment of N-oxides with methylene chloride solutions of trifluoroacetic anhydride leads to immonium trifluoroacetates by one of two reaction paths.



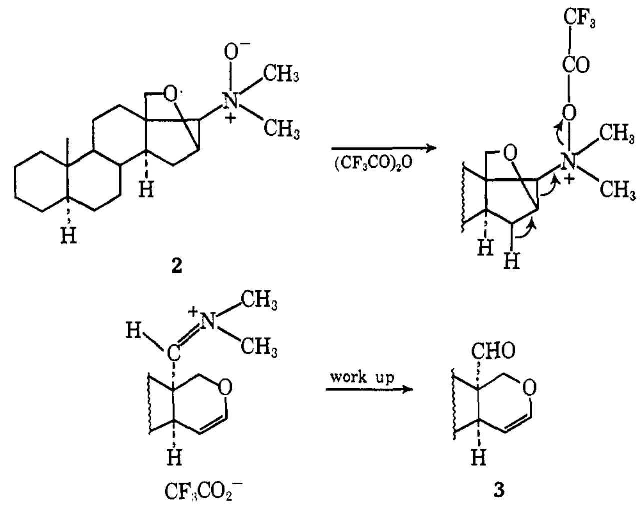
In this manner, trimethylamine oxide is transformed into N,N-dimethylformaldimmonium trifluoroacetate (**1**) (path a above) in methylene chloride solution.[2,3] Its highly characteristic proton magnetic resonance spectrum reveals a six-proton quintuplet at 3.87 ppm (methyl groups) and a two-proton pseudoseptuplet 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 $\rightarrow$ α-dimethyaminomethyl-5α-cholestan-3-one (yield 95%; mp 106°); 3α,5-cyclo-5α-androstan-6-one $\rightarrow$ 7-dimethylaminomethyl-3α,5-cyclo-5α-androstan-6-one (yield 94%; mp 102°); $3\beta,20\alpha$-diacetoxy-5α-pregnan-6-one $\rightarrow$ 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).

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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).

Table I. Bond Distances and Angles

Atoms	Distance,[a] Å	Atoms	Angle,[b] deg	Atoms[b]	Angle,[b] deg
Cu–O(1)	2.065	O(1)–Cu–O(1′)	88.5	P–N(1)–C(1)	118.0
P–O(1)	1.477	O(1′)–Cu–O(1″)	90.4	P–N(1)–C(2)	124.1
P–O(2)	1.602	O(1)–Cu–O(1″)	90.7	C(1)–N(1)–C(2)	114.3
P–N(1)	1.616	Cu–O(1)–P	137.2	P–N(2)–C(3)	122.4
P–N(2)	1.612	P–O(2)–P	135.0	P–N(2)–C(4)	120.9
N(1)–C(1)	1.479	O(1)–P–O(2)	111.1	C(3)–N(2)–C(4)	114.8
N(1)–C(2)	1.431	O(1)–P–N(1)	118.5		
N(2)–C(3)	1.474	O(1)–P–N(2)	110.7		
N(2)–C(4)	1.459	O(2)–P–N(1)	100.5		
		O(2)–P–N(2)	109.0		
		N(1)–P–N(2)	106.3		

[a] Esd is ±0.001–0.005 Å. [b] Esd is ±0.15–0.25°.

the colorless crystals are M = 1121.2, trigonal with a = 12.855 ± 0.001 Å, c = 18.260 ± 0.003 Å; V = 2613 Å^3 (λ = 1.54051 Å for the cell determination); D_c = 1.425 g/cm^3 for two formula units per unit cell, D_m = 1.421 g/cm^3 (flotation method); centrosymmetric with space group P$\bar{3}$c1 ($D_{3d}{}^4$, no. 165); μ = 7.85 cm^{-1} for Mo Kα radiation. A four-circle diffractometer, the 2θ scan technique, a NaI scintillation detector using pulse-height discrimination, and Mo

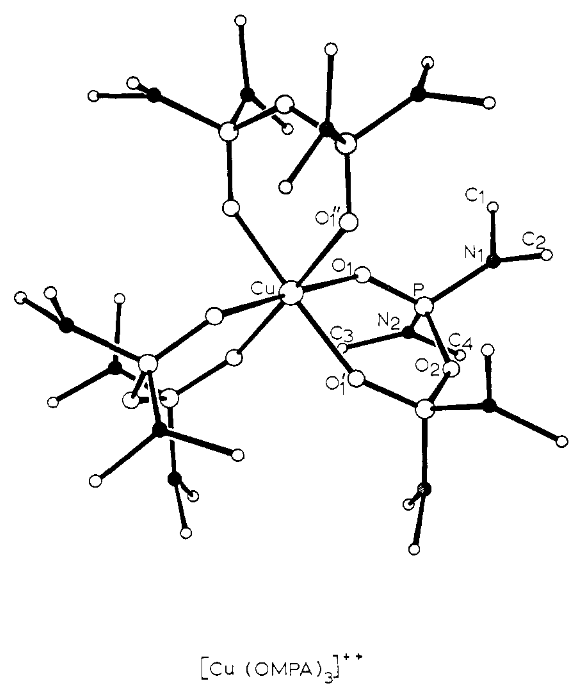

Figure 1. Chelate ring geometry in $Cu(OMPA)_3{}^{2+}$. The a axis is directed from Cu to O(2) and the molecule is viewed approximately along the c axis.

Kα radiation with Nb incident beam filter (for reflections with $2\theta > 10°$) were used to collect intensity data for 2200 reflections out to sin θ/λ = 0.66 Å^{-1}. The conventional R factor is 4.9% based on 1993 observed reflections.

The Wyckoff positions a and f are occupied by Cu(II) and O(2), respectively, and d is occupied by chlorine and one oxygen atom of the perchlorate anion. A projection of the cation is shown in Figure 1, and bond distances and angles are listed in Table I. The complete structure will be discussed in detail in a later paper.

The structure determinations of the corresponding OMPA complexes of Mg(II) and Co(II) were completed previously.[6] The Cu(II) complex is isomorphous with the Mg(II) and Co(II) complexes, and all bond distances for the latter two complexes are within 0.01 Å of the values listed in Table I except for the Co–O(1) bond distance which is 2.085 Å. The chelate rings in all three compounds are planar within 0.05 Å and the O(1)–M–O(1′) angles are 86.2, 87.9, and 88.4° for the Mg(II),[6] Co(II),[6] and Cu(II) complexes, respectively. Thus, the Cu(II) complex has the *smallest* distortion from a perfect octahedron.

X-Ray data for $Cu(OMPA)_3(ClO_4)_2$ indicate that the average structure at room temperature is trigonal. This is an apparent contradiction to the Jahn–Teller theorem. However, the standard X-ray analysis does not eliminate the possibility (1) that the complex is oscillating among three equivalent nontrigonal distortions or (2) that each molecular is trapped in one of three such distortions on a random basis. In this analysis both possibilities 1 and 2 would result in higher temperature factors. However, the temperature factors of the oxygen atoms bonded to Cu(II) are quite normal and essentially the same within experimental error as those for the corresponding Mg(II) and Co(II) complexes.[7]

An independent and possibly more sensitive method of studying the immediate environment of Cu(II) is epr spectroscopy. Spectra of polycrystalline $Cu(OMPA)_3$-$(ClO_4)_2$ at 300°K indicate an isotropic g value of 2.25. This eliminates possibility 2 above since an anisotropic g value would be expected if molecules are trapped in the lattice on a random basis. The possibility that small dynamic Jahn–Teller distortions are present cannot be eliminated. However, these distortions are evidently considerably less than the normal root-mean-square vibration amplitudes.[7]

We are obtaining epr spectra for single crystals of $Cu(OMPA)_3(ClO_4)_2$ at several different temperatures and orientations. These epr results will be compared with those reported for other tris-chelate complexes of Cu(II)[8] in an attempt to determine the importance of Jahn–Teller distortions in trigonal systems.

Acknowledgment. The computing facilities at the Common Research Computer Facility, Houston, Texas, were made available under USPHS Grant No. Fr00254.

(6) M. D. Joesten and P. G. Lenhert, to be submitted for publication.
(7) In $Cu(OMPA)_3(ClO_4)_2$ the root-mean-square vibration amplitudes for the anisotropic thermal motion are 0.26, 0.25, and 0.22 Å for the oxygen atom and 0.22, 0.19, and 0.21 Å for Cu(II).
(8) G. F. Kokoszka, C. W. Reimann, H. C. Allen, Jr., and G. Gordon, *Inorg. Chem.*, **6**, 1657 (1967).

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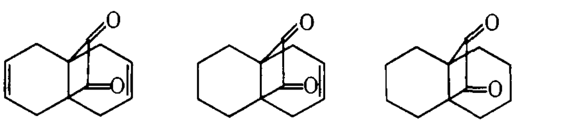
1,2-Cyclobutanediones. II. Spectral Characteristics of [4.4.2]Propella-3,8-diene-11,12-dione and Its Di- and Tetrahydro Derivatives

Sir:

The title compounds, prepared *via* acyloin condensation[1] followed by dimethyl sulfoxide–acetic anhydride oxidation,[2] exhibit rather remarkable spectral properties, particularly in the visible region (Figure 1).[3]

The diene **1**, pink in the crystalline state and in solution, possesses a complex spectrum with its longest wavelength absorption at λ_{max} 537.5 mμ (ϵ 71.7). This spectrum remains unchanged in ethanol, in mixtures of



1 2 3

ethanol–cyclohexane, and in the presence of benzene, acetic acid, or triethylamine. No deviation from Beers' law is observed in any of these solutions. Compound **3**, the tetrahydro derivative of **1**, is yellow and gives yellow solutions with λ_{max} 461 mμ (ϵ 73). In contrast, the dihydro derivative **2** is pink in the solid state but gives orange solutions. It shows two absorption maxima at λ_{max} 460–464 (ϵ 38.8) and 532–535 mμ (32.0) and the spectrum appears to be almost that of a simple mixture of **1** and **3**.

The infrared spectra[4] of **1**–**3** lead to a similar conclusion. Compound **1** shows two carbonyl absorptions with equal intensities at 1794 and 1759 cm^{-1}. In **3** the carbonyl spectrum is somewhat more complex, with a doublet at 1812 (strong) and 1772 cm^{-1} (very strong) and a shoulder with strong absorption at 1785 cm^{-1}. The position and shape of the very broad intense band peaking at 1772 cm^{-1} in **2** again approximate an algebraic addition of the spectra of **1** and **3**. Shifts to lower frequency in **1** relative to **3**, similar to but somewhat less than those observed in α,β-unsaturated ketones, suggest an interspatial interaction between a double bond in the six-membered ring and the dione system. The electronic spectra and molecular models of **1** and **3** make it possible to speculate upon both the origin and strength of this interaction.

Diketones **1** and **2** have the highest λ_{max} of all reported diketones[5–9] except for the completely con-

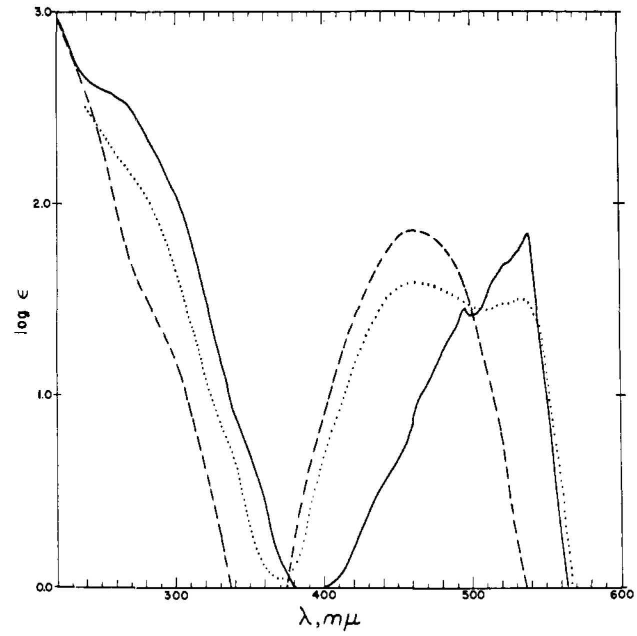
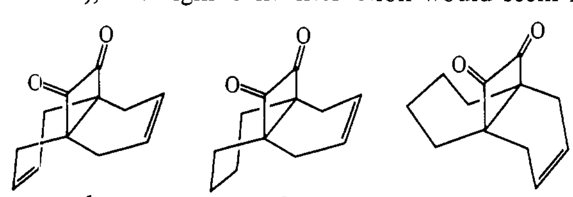


Figure 1. Ultraviolet spectra in cyclohexane solutions: ——, **1**; ····, **2**; ----, **3**.

jugated perchlorodimethylene-1,2-cyclobutanedione which absorbs at 550–560 mμ (ϵ 400).[10] Cyclobutenediones absorb at somewhat higher energies, with the diphenyl[11] and benzo[12] derivatives and 3,4-bis(diphenylmethylene)cyclobutanedione[13] reported to have maxima at 410 (ϵ 163), 427 (276), and 376 mμ (7300), respectively.

We suggest that the shift toward longer wavelength of absorption in **1** results from the enhanced possibility for resonance stabilization of the excited state involving interaction between a double bond and the dione system. This interaction must be at a maximum when the respective π orbitals can interact end to end as in **1a** and **2a**. In conformation **2b** these orbitals are parallel but farther apart (molecular models suggest 3.0–3.5 Å), and significant interaction would seem less



1a 2a 2b

likely.[14] The double maxima of **2** would result then from Franck–Condon controlled excitation of **2a** (peak

(1) (a) J. J. Bloomfield and J. R. S. Irelan, *J. Org. Chem.*, **31**, 2017 (1966); (b) J. J. Bloomfield, *Tetrahedron Letters*, 587 (1968).

(2) (a) J. D. Albright and L. Goldman, *J. Am. Chem. Soc.*, **87**, 4214 (1965); **89**, 2416 (1967); (b) M. Van Dyke and N. D. Pritchard, *J. Org. Chem.*, **32**, 3204 (1967).

(3) The data presented in the text and the spectra recorded in Figure 1 are for cyclohexane solutions. Spectra were taken on a Bausch and Lomb Spectronic 505.

(4) Recorded on a Beckman IR-8 instrument in carbon tetrachloride solution.

(5) Previous investigators have described the spectra[6–8] and discussed the excited-state geometries[9] of a variety of cyclic and linear diketones.

(6) N. J. Leonard and P. M. Mader, *J. Am. Chem. Soc.*, **72**, 5388 (1950).

(7) K. Alder, H. K. Schafer, H. Esser, H. Krieger, and R. Reubke, *Ann.*, **593**, 23 (1955).

(8) H. Birnbaum, R. C. Cookson, and N. Lewin, *J. Chem. Soc.*, 1224 (1961).

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(11) A. T. Blomquist and E. A. LaLancette, *J. Am. Chem. Soc.*, **83**, 1387 (1961).

(12) M. P. Cava, D. R. Napier, and R. J. Pohl, *ibid.*, **85**, 2076 (1963).

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(14) Additional data suggesting the staggered conformation is presented in a paper which concerns the radical anions related to these diketones: J. M. Fritsch and J. J. Bloomfield, *Spectry. Letters*, in press.