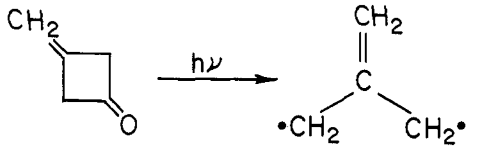
Trimethylenemethane from Photolysis of 3-Methylenecyclobutanone

Sir:

Trimethylenemethane (I) may be smoothly generated by the photolysis of 3-methylenecyclobutanone (II).



II I

The recently presented[1] hypothesis that trimethylenemethane (I) is a detectable intermediate in the photolysis of 4-methylene-Δ^1-pyrazoline[1,2] is now strongly supported by the experiments described herein. Direct irradiation of a dilute (5 μl in 1 ml) solution of 3-methylenecyclobutanone (II) in perfluorodimethylcyclobutane or perfluoromethylcyclohexane[3] at $-196°$ for 20 min with light of wavelength 270–310 mμ yielded, upon examination by electron spin resonance spectroscopy,[4] the identical triplet spectrum previously obtained by irradiation of the pyrazoline.[1] The spectrum obtained from the ketone is considerably stronger and better resolved than any previously obtained by prolonged irradiation of the pyrazoline. In addition, the monoradical impurity is here very weak, roughly one-third as intense as the triplet spectrum, and does not obscure the shape of the $\Delta m = 1$ lines. Further, the strong spectrum from the ketone has allowed the observation of the $\Delta m = 2$ transition[4b] at 1590 gauss. The $\Delta m = 2$ transition is approximately 40 times less intense than the $\Delta m = 1$ transitions and, as a consequence, could not be detected in the pyrazoline spectrum.

The comparative ease with which the 3-methylenecyclobutanone is transformed to trimethylenemethane may result from greater efficiency of intersystem crossing in the ketone as compared to the azo compound.[5]

The starting 3-methylenecyclobutanone (II) was obtained by oxidation of the corresponding 3-methylenecyclobutanol[6] using dicyclohexylcarbodiimide in dimethyl sulfoxide[7] with trifluoroacetic acid–quinaldine as catalyst. The 3-methylenecyclobutanone (II) is labile and elusive as a result of its rapid isomerization to the conjugated isomer, 3-methylcyclobutenone, under the influence of either mild acid[8] or mild base. For this reason, the oxidation was run at 15° under high vacuum (0.01 mm) in order that the desired unconjugated ketone be removed from the reaction mixture as rapidly as it was formed. A 20% yield of crude ketone was obtained. Purification was effected by bulb-to-bulb distillation followed by preparative vapor phase chromatography on Carbowax. In this manner, the 3-methylenecyclobutanone (II) was separated from approximately 5% of 3-methylcyclobutenone and approximately 5% of the trifluoroacetate of the starting alcohol.

Figure 1. Epr spectrum of trimethylenemethane from photolysis of 3-methylenecyclobutanone in perfluoromethylcyclohexane. The peak positions were measured at a klystron frequency of 9149.7 Mc.

The 3-methylenecyclobutanone[9] (II) showed in its nmr (CCl_4): a two-proton vinyl methylene quintet (J = 2.5 cps) at τ 4.78 and a four-proton aliphatic triplet (J = 2.5 cps) at τ 6.42; infrared (CCl_4): carbonyl at 5.52 μ, double bond at 5.94 and 11.2 μ; ultraviolet:[10] $\lambda_{max}^{cyclohexane}$ 215 mμ (ϵ 1550) 266 (12), 275 (19), 293 (22), 308 (15), and 320 (8); and mass spectrum: exact mass of molecular ion found, 82.0415; calcd for C_5H_6O, 82.0419. The pure conjugated ketone, 3-methylcyclobutenone, showed in its nmr (CCl_4): a three-proton methyl (slightly split) at τ 7.7, a two-proton methylene (broadened) at τ 6.9, and a one-proton vinyl (slightly split) at 3.83; infrared (CCl_4): carbonyl at 5.65 μ and double bond at 6.29 μ; ultraviolet: $\lambda_{max}^{cyclohexane}$ 219 mμ (ϵ 6300) and 310 (24); and mass spectrum: exact mass of molecular ion found, 82.0413; calcd for C_5H_6O, 82.0419. The trifluoroacetate of the starting alcohol was identified by its spectral properties and by direct comparison with an authentic sample.

Photochemical cleavage leading to trimethylenemethane is apparently a general reaction. It seems reasonable to suppose that other precursors to trimethylenemethane will be found, and that, in addition

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[1] P. Dowd, *J. Am. Chem. Soc.*, **88**, 2587 (1966).

[2] R. J. Crawford and D. M. Cameron, *ibid.*, **88**, 2589 (1966), have also synthesized and utilized this pyrazoline in a thermal route to trimethylenemethane.

[3] E. Wasserman, L. Barash, A. M. Trozzolo, and R. W. Murray, *ibid.*, **86**, 2304 (1964).

[4] (a) C. A. Hutchison, Jr., and B. W. Mangum, *J. Chem. Phys.*, **29**, 952 (1958); **34**, 908 (1961); (b) J. H. van der Waals and M. S. de Groot, *Mol. Phys.*, **2**, 333 (1959); **3**, 190 (1960); (c) W. A. Yager, E. Wasserman, and R. M. R. Cramer, *J. Chem. Phys.*, **37**, 1148 (1962).

[5] *Cf.* S. D. Andrews and A. C. Day, *Chem. Commun.*, 667 (1966).

[6] E. F. Kiefer and J. D. Roberts, *J. Am. Chem. Soc.*, **84**, 784 (1962).

[7] K. E. Pfitzner and J. G. Moffatt, *ibid.*, **87**, 5661, 5670 (1965).

[8] F. F. Caserio and J. D. Roberts, *ibid.*, **80**, 5837 (1958).

[9] This ketone is 99% pure. It does contain 1% of the conjugated ketone, 3-methylcyclobutenone, which is apparently formed by slow isomerization in the course of gas chromatography. A control photolysis of the conjugated ketone gave a strong monoradical signal in the epr, but no trace of any triplet spectrum could be detected.

[10] The 3-methylenecyclobutanone was originally sought[8] because it was anticipated that it might show a 1,3 π interaction between the ketone and the double bond. Indeed, it seems reasonable to suppose that the band at 215 mμ is a $\pi \rightarrow \pi^*$ charge-transfer band which arises as a result of puckering of the cyclobutane ring and consequent overlap of the π orbitals of the ketone and the double bond. Excellent analogy is provided by the work of S. Winstein, L. de Vries, and R. Orloski, *J. Am. Chem. Soc.*, **83**, 2020 (1961), who have reported a similar interaction between ketone and double bond situated at the bows of a boat cyclohexane ring. A theoretical basis for such interactions is provided by the work of H. Labhart and G. Wagniere, *Helv. Chim. Acta*, **42**, 2219 (1959). The normal intensity of the $n \rightarrow \pi^*$ band in the present case is also in accord with theory and experience. For further discussion of this type of interaction see J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," Methuen & Co., London, 1963, p 167.

to its theoretical and mechanistic importance, this molecule may become a synthetically useful reactive intermediate in organic chemistry.

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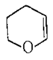
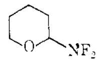
The Alkylation of Difluoramine with Carbonium Ions

Sir:

The previously reported chemistry of difluoramine has emphasized the acidic character of the N–H bond. Thus, the reactions of difluoramine with various amines[1] and imines[2] have been described. Chemistry occurring at the nitrogen atom itself is much rarer, due presumably to the effect of the attached fluorine atoms on the availability of the unshared pair of nitrogen. Aside from the reports that difluoramine does form weak adducts with boron trifluoride[3] and with boron trichloride,[4] there is no indication in the literature that difluoramine has any synthetically useful nucleophilic properties.

Table I. Difluoramino Compounds from Alkylation of Difluoramine

Alkylating agent	Reaction conditions	Product[f]	^{19}F nmr, ϕ
$(C_6H_5)_3CBr$	SO_2, $-25°$	$(C_6H_5)_3CNF_2$[a,b]	-32.4 (s)
$(C_6H_5)_2CHOH$	Amberlyst 15,[e] SO_2	$(C_6H_5)_2CHNF_2$	-48.6 (d, $J = 27$ cps)
$C_6H_5CCl_3$	CF_3CO_2H	$C_6H_5CCl_2NF_2$	-43.5 (s)
$(CH_3)_2C{=}CH_2$	96% H_2SO_4 or BF_3–H_3PO_4	$(CH_3)_3CNF_2$[a]	-27.1 (s)
$(CH_3)_2C{=}CHCH_3$	96% H_2SO_4 or BF_3–H_3PO_4	$C_2H_5C(CH_3)_2NF_2$[a]	-25.1 (s)
$CH(OCH_3)_3$	Neat, 25°	$CH(OCH_3)_2NF_2$[c]	-23 (d, $J = 28$ cps)
$CH_3C(OCH_3)_3$	Neat, 25°	$CH_3C(OCH_3)_2NF_2$[c]	-18.7 (s)
	Neat, 25°		-28.1 (m)[d]

[a] These compounds were identical with those previously reported.[5] [b] Reference 9. [c] These compounds were relatively unstable and hydrolyzed in moist air. [d] This resonance was a broad structureless band believed to be the central portion of an ABX multiplet. [e] Trade mark of the Rohm and Haas Co. A strong acid ion-exchange resin. [f] Yields ranged from 50 to 60% for the olefin reactions to quantitative for the ethers. These yields are sensitive to time and temperature.

It has now been found that difluoramine can be alkylated by carbonium ions generated under a variety of conditions. Some indications of the scope of reaction conditions and of the compounds that have been prepared by this method are listed in Table I.

The new compounds have been characterized by elemental analyses, infrared spectra, and, most convincingly, by their unique nuclear magnetic resonance spectra. Three of the compounds could also be prepared independently by previously described free-radical coupling reactions involving N_2F_4.[5]

The position of the fluorine resonance was typical of that found for other compounds containing the difluoramino group,[6] with increased shielding occurring in the oxygenated derivatives. The splitting of the resonance signal was also consistent with the structures assigned. For example, the pyran adduct exhibits an ABX type spectrum due to the dissimilarity of the two fluorines arising from the attachment of the difluoramino group to an asymmetric carbon.[7]

These reactions were all carried out on a vacuum line. Solvents were used for the solid derivatives. The reaction was conducted by condensing in difluoramine and stirring the mixture at room temperature under 200–500-mm pressure, or, as in the case when sulfur dioxide was used as a solvent, at $-25°$. The products were isolated by distilling the solvent.

With the olefins, concentrated sulfuric acid or, still better, the boron trifluoride–phosphoric acid complex[8] was used as a reaction medium to generate the carbonium ion. The difluoramino compound, which proved to be largely insoluble in the acid, separated as an oil as the reaction proceeded and was removed by distillation. It is important that the difluoramino compound be removed from the acid as soon as reaction is complete as it will gradually decompose by the rearrangement process reported recently.[9,10]

The ether derivatives reacted without added catalyst, and it is assumed that they react with difluoramine to produce the requisite oxycarbonium ion. These products were isolated by distillation and purified by gas chromatography.

The discovery of this reaction extends the scope of synthetic routes to organic difluoramines and complements those based on thermal[5] and photochemical[11] reactions of tetrafluorohydrazine.

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(1) C. L. Bumgardner, K. J. Martin,, and J. P. Freeman, *J. Am. Chem. Soc.*, **85**, 97 (1963); C. L. Bumgardner and J. P. Freeman, *ibid.*, **86**, 2237 (1964).

(2) W. H. Graham, *ibid.*, **88**, 4677 (1966).

(3) A. D. Craig, *Inorg. Chem.*, **3**, 1628 (1964).

(4) R. C. Petry, *J. Am. Chem. Soc.*, **82**, 2400 (1960).

(5) R. C. Petry and J. P. Freeman, *ibid.*, **83**, 3912 (1961).

(6) J. P. Freeman, Advances in Chemistry Series, No. 36, American Chemical Society, Washington, D. C., 1962, p 128.

(7) For a detailed discussion of this phenomenon, see F. A. Johnson, C. Haney, and T. E. Stevens, *J. Org. Chem.*, in press.

(8) A. N. Topchiev, S. V. Zavgorodnü, and Ya. M. Pauskhin, "Boron Fluoride and Its Compounds as Catalysts in Organic Chemistry," Pergamon Press Ltd., London, England, 1959.

(9) K. Baum and H. M. Nelson, *J. Am. Chem. Soc.*, **88**, 4459 (1966).

(10) In concentrated sulfuric acid, triphenylmethyldifluoramine decomposes to difluoramine: W. H. Graham and C. O. Parker, *J. Org. Chem.*, **28**, 850 (1963).

(11) C. L. Bumgardner, *Tetrahedron Letters*, 3683 (1964).