

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 Difluoramino with Carbonium Ions

Sir:


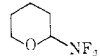
The previously reported chemistry of difluoramino has emphasized the acidic character of the N-H bond. Thus, the reactions of difluoramino with various amines¹ and imines² have been described. Chemistry occurring at the nitrogen atom itself is much rarer, due presumably to the effect of the attached fluorine atoms on the availability of the unshared pair of nitrogen. Aside from the reports that difluoramino does form weak adducts with boron trifluoride³ and with boron trichloride,⁴ there is no indication in the literature that difluoramino has any synthetically useful nucleophilic properties.

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 difluoramino 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 complex⁸ 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 de-

Table I. Difluoramino Compounds from Alkylation of Difluoramino

Alkylating agent	Reaction conditions	Product ^f	¹⁹ F nmr, ϕ
(C ₆ H ₅) ₃ CBr	SO ₂ , -25°	(C ₆ H ₅) ₃ CNF ₂ ^{a, b}	-32.4 (s)
(C ₆ H ₅) ₂ CHOH	Amberlyst 15, ^c SO ₂	(C ₆ H ₅) ₂ CHNF ₂	-48.6 (d, $J = 27$ cps)
C ₆ H ₅ CCl ₃	CF ₃ CO ₂ H	C ₆ H ₅ CCl ₂ NF ₂	-43.5 (s)
(CH ₃) ₂ C=CH ₂	96% H ₂ SO ₄ or BF ₃ -H ₃ PO ₄	(CH ₃) ₃ CNF ₂ ^a	-27.1 (s)
(CH ₃) ₂ C=CHCH ₃	96% H ₂ SO ₄ or BF ₃ -H ₃ PO ₄	C ₂ H ₅ C(CH ₃) ₂ NF ₂ ^a	-25.1 (s)
CH(OCH ₃) ₃	Neat, 25°	CH(OCH ₃) ₂ NF ₂ ^c	-23 (d, $J = 28$ cps)
CH ₃ C(OCH ₃) ₃	Neat, 25°	CH ₃ C(OCH ₃) ₂ NF 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 difluoramino 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 N₂F₄.⁵

The position of the fluorine resonance was typical of

(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.

compose by the rearrangement process reported recently.^{9,10}

The ether derivatives reacted without added catalyst, and it is assumed that they react with difluoramino 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 thermal⁵ and photochemical¹¹ reactions of tetrafluorohydrazine.

(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. Zavgorodni, 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, triphenylmethylidifluoramino decomposes to difluoramino: W. H. Graham and C. O. Parker, *J. Org. Chem.*, **28**, 850 (1963).

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

Previous warnings concerning the explosive nature of difluoramino itself and of organic difluoramino derivatives should be heeded.

(12) This research was conducted under Army Ordnance Contract DA-01-021 ORD-5135.

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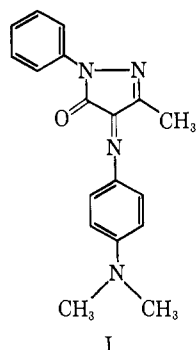
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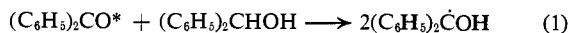
Photoreduction of a Pyrazolone Azomethine Dye by Benzophenone Ketyl Radicals. Dependence on Light Intensity

Sir:

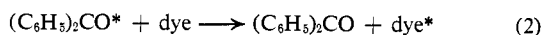
We have been investigating the reaction in degassed benzene solution of benzophenone ketyl radicals with the pyrazolone azomethine dye I. We generate our



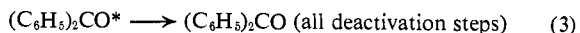
ketyl radicals by reaction of photoexcited benzophenone with benzhydrol, a reaction (1) which has been investigated in other laboratories.¹⁻³ An obvious complica-



tion in such a system could be reaction 2, whereby



energy is transferred from the benzophenone triplet ($(\text{C}_6\text{H}_5)_2\text{CO}^*$) to dye I. Assuming the latter reaction to be diffusion controlled and using the rate constants of Bell and Linschitz for reactions 1 and 3, we calculated



that no more than 4-5% of the benzophenone triplets should react by path 2 in a system in which $[(\text{C}_6\text{H}_5)_2\text{CHOH}] = 0.5 M$ and $[\text{dye}] = 10^{-5} M$. These are the concentrations which we have used in most of our experiments. In all cases the benzophenone concentration was 0.02 M.

Irradiations were performed with a Hanovia utility ultraviolet quartz lamp No. 30600. This is a medium pressure, mercury arc lamp rated at 100 w. The 3660-A emission was isolated by passing the light through a $1/8$ -in. thickness of plate glass and a Corning No. 7-37 filter. At a benzophenone concentration of 0.02 M, virtually all radiation at 3660 A is absorbed by the benzophenone. Samples were prepared by degassing

(1) W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1961).

(2) J. A. Bell and H. Linschitz, *ibid.*, **85**, 528 (1963).

(3) C. Walling and M. J. Gibian, *ibid.*, **87**, 3361 (1965).

3-ml aliquots in 18×156 mm Pyrex glass culture tubes and sealing them. Actinometry was performed in identical tubes, but the degassing step was omitted. Potassium ferrioxalate actinometry⁴ was used throughout.

The reaction of benzophenone ketyl radicals with dye I results in bleaching of the dye; the disappearance of dye is readily followed by spectrophotometry in the visible region. Approximately 85% of the dye loss results in the formation of a leuco dye which is quantitatively oxidized to starting dye upon admission of air to the tubes. In air-saturated benzene, the oxidation of the leuco dye follows first-order kinetics with $k = 1.3 \times 10^{-2} \text{ sec}^{-1}$.

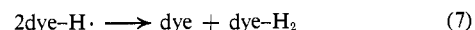
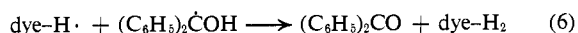
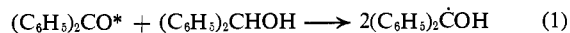
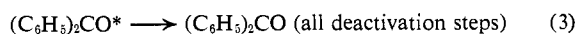
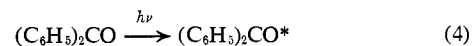
With regard to the reaction between benzophenone ketyl radicals and dye, the following facts are pertinent. (1) The rate of dye loss is precisely first order in light intensity over a 100-fold range (Table I). A log-log plot of the data in Table I gives a line with unit slope.

Table I. Rate of Dye Loss as a Function of Light Intensity

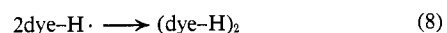
$10^8 \times \text{rate,}$ $M \text{ sec}^{-1}$	$10^8 \times I,$ $\text{einstein l.}^{-1} \text{ sec}^{-1}$
0.419	0.542
4.23	5.28
40.2	52.0

The data fit the expression, $\text{rate} = 0.78I$, or equivalently $\phi = 0.78$. Under our conditions, then, quenching of benzophenone triplets by benzophenone ketyl radicals does not occur.⁵ (2) The reaction is zero order in dye. This was determined by a fivefold variation in dye concentration, the two rates being within 3% of each other. It was thought that an increase in dye concentration beyond $5 \times 10^{-5} M$ could lead to complications from the incursion of reaction 2.

These data may be accommodated by the following mechanism.



Chain transfer of dye-H· with benzhydrol to yield leuco dye and a ketyl radical is precluded by the first-order dependence on light intensity (and/or the zero-order dependence on dye), as is also termination by combination of two ketyl radicals to yield benzpinacol. These steps predict half-order or mixed half- and first-order dependence on light intensity. The fact that the quantum yield for dye loss is <1 indicates that termination by reaction 8 to form a leuco dimer is unimportant. The proposed mechanism predicts a



quantum yield of dye loss equal to half the quantum yield of ketyl radical formation. The latter, by using

(4) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc. (London)*, **A235**, 518 (1956)

(5) N. C. Yang and S. Murov, *J. Am. Chem. Soc.*, **88**, 2852 (1966).