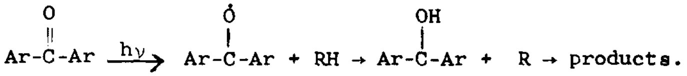
Tetrahedron Letters No.8, pp. 813-817, 1966. Pergamon Press Ltd.
Printed in Great Britain.

PHOTOCHEMICAL REACTIONS IN THE PRESENCE OF TETRAFLUOROHYDRAZINE THE SYNTHESIS OF α-DIFLUOROAMINO ETHERS

M. J. Cziesla, K. F. Mueller, and Orlando Jones
U. S. Naval Propellant Plant, Indian Head, Md.

(Received 2 December 1965)

During the last several years photoreduction of aromatic ketones has been intensively investigated in many laboratories. The excited ketone is believed to abstract hydrogen from the substrate and the observed products are explained by combination and/or disproportionation of the intermediate monoradicals:



$$\mathrm{Ar}-\overset{\overset{O}{\|}}{C}-\mathrm{Ar} \xrightarrow{h\nu} \mathrm{Ar}-\overset{\overset{\dot{O}}{|}}{C}-\mathrm{Ar} + RH \rightarrow \mathrm{Ar}-\overset{\overset{OH}{|}}{C}-\mathrm{Ar} + R \rightarrow \text{products.}$$

In most investigations the main interest has centered around the ketonic component and its transformations. As far as the hydrogen donor and its changes are concerned, much less is known. This is mainly due to experimental difficulties. The commonly used radical scavengers, such as diphenylpicrylhydrazyl, absorb light under the reaction conditions. Oxygen leads to formation of alkylperoxy radicals (1) which can abstract hydrogen, thereby complicating the system. Therefore, the site of the primary attack by the excited ketones is unknown in many cases.

Difluoroamino radicals present in equilibrium with tetrafluorohydrazine (2,3) at ambient temperatures

$$N_2F_4 \rightleftharpoons 2\ \cdot NF_2$$

were anticipated to be effective radical scavengers in photochemical dehydrogenation systems, since they have been found to combine with alkyl radicals, generated by thermal decomposition of azoisobutyronitrile, azoisobutane, and hexaphenylethane, to yield the corresponding alkyl difluoroamines (4).

The benzophenone/ether system in Pyrex glass equipment was selected for the first investigations, since Pyrex glass absorbs all light with wave lengths shorter than 2800 Å. Under these conditions only the benzophenone is activated; the difluoroamino radicals (λ max. 2600 Å) as well as the expected reaction products are protected from the light and accordingly, the formation of side products is minimized.

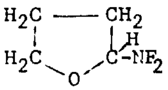
Solutions of benzophenone in aliphatic ethers were placed in a photoreactor which was equipped with a gas inlet tube at the bottom ending in a glass frit, and a gas outlet at the top. Immersed into the reactor was a water-cooled Hanovia high pressure mercury vapor lamp (type 608-36A). After thoroughly flushing the system with purified nitrogen, tetrafluorohydrazine was passed through the solution under irradiation.* The uptake of tetrafluorohydrazine was measured by recycling to a reservoir. At the end of the irradiation, the system was again flushed with nitrogen prior to opening to the atmosphere.

The products were isolated by distillation and characterized by elemental analysis, infrared and nuclear magnetic resonance spectroscopy.

*No tetrafluorohydrazine was consumed without irradiation.

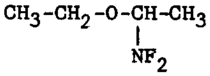
Only α-substituted difluoroamino ethers could be isolated; β-substituted products would have been detected if formed in amounts larger than 1% with respect to the α-substituted products.

α-Difluoroaminotetrahydrofuran showed N-F absorption in the infrared (940 cm^{-1} and 860 cm^{-1}). The proton NMR spectrum gave the following data: for the methyne group a triple-triplet centered at 5.31τ (J_{HF} = 21 cps, J_{HH} = 4 cps) due to coupling with fluorine and methylene; for the methylene adjacent to oxygen a triplet centered at 6.24τ (J = 6 cps) due to coupling with methylene; for the remaining two methylene groups a multiplet centered at 8.05τ. The area ratio was 1:2:4 as required for the structure:



Anal. calcd. for $C_4H_7F_2NO$: C, 39.03; H, 5.73; F, 30.88; N, 11.39.
Found: C, 39.47; H, 5.40; F, 30.26; N, 11.36.

In a similar reaction with diethyl ether as substrate α-difluoroamino diethyl ether was obtained. The compound showed N-F absorption in the infrared (945 cm^{-1}, 860 cm^{-1}). The proton NMR spectrum of this compound is rather complex. For the methyne group it has a triple-quartet centered at 5.62τ (J_{HF} = 18 cps, J_{HH} = 6 cps) due to coupling with fluorine and methyl. The absorptions of the methylene and methyl groups show multiplets at 6.04 to 6.75τ, and 8.55 to 9.05τ, respectively. The area ratio of methyl to methylene and methyne is 2:1, which is only consistent with the structure:



$$CH_3\text{-}CH_2\text{-}O\text{-}\underset{\displaystyle NF_2}{\underset{|}{CH}}\text{-}CH_3$$

Other aliphatic ethers reacted similarly. Detailed information will be reported in a future publication.

The rate of tetrafluorohydrazine consumption for different ethers is listed in Table I. The data refer to 0.055 molar solutions of benzophenone in the respective ethers.

TABLE I

Rate of N_2F_4 Consumption

Ether	ml/min	Rel. react./α-H
Diethylether	3.09	2.74
Dioxane	2.25	1.00
Tetrahydrofuran	1.67	1.48
Diisopropylether	0.80	1.42

At the present time, investigations are being undertaken to establish the cause for the different rates in consumption of tetrafluorohydrazine together with the determination of the quantum yields.

Benzophenone and its excited states do not react with tetrafluorohydrazine under the employed conditions. No consumption of tetrafluorohydrazine was observed during irradiation of benzophenone solutions in benzene; benzophenone was recovered unchanged.

The isolation of α-difluoroamino ethers has encouraged the authors to further investigate photochemical dehydrogenation reactions in the presence of tetrafluorohydrazine. Substrates, other than ethers such as alkanes and alkenes, will be investigated together with variation of the dehydrogenating component.

It is hoped that tetrafluorohydrazine will become a valuable reagent to trap the first monoradicals, generated in photochemical reactions.

References:

1. G. O. Schenk, H. D. Becker, K. H. Schulte-Elte, and C. H. Krauch, Chem. Ber., 96, 509 (1963)
2. C. B. Colburn and A. Kennedy, J. Amer. Chem. Soc., 80, 5004 (1958)
3. F. A. Johnson and C. B. Colburn, J. Amer. Chem. Soc., 83, 3043 (1961)
4. R. C. Petry and J. P. Freeman, J. Amer. Chem. Soc., 83, 3912 (1961)

Acknowledgment:

The authors are pleased to acknowledge support of this work by the Foundational Research Program of the U. S. Bureau of Naval Weapons; additional funding was obtained under Task Assignment: RMMP-22-004/286-1/F009-06-01.