

Photoreduction of Benzophenone by Amines. Photochemical Oxidative Deamination¹

Sir:

We wish to report that ultraviolet irradiation of benzophenone in primary and secondary amines containing the grouping >CHNH- leads to high yields of benzpinacol and aldimine or ketimine. Since the imines may be hydrolyzed to aldehydes or ketones, this provides an efficient oxidative deamination of primary amines and an effective degradative procedure for secondary amines.

Irradiation of degassed 0.3 *M* benzophenone in isobutylamine for 2.3 hr., followed immediately by distillation under vacuum at low temperature, leads to a residue, benzpinacol, 85% yield, m.p. and m.m.p. 186–188°, and, in the distillate, to *N*-isobutylideneisobutylamine [(CH₃)₂CHCH=NCH₂CH(CH₃)₂, I] 90% yield based upon the ketone, as assayed by comparison in the infrared and by vapor phase chromatography with an authentic sample.^{2a,b} Treatment of the distillate with 2,4-dinitrophenylhydrazine reagent leads to the 2,4-dinitrophenylhydrazone of isobutyraldehyde, m.p. 182–184°, identical with that prepared from an authentic sample of I and that from isobutyraldehyde.

The synthetic usefulness is seen in reactions in inert solvent without excess amine. Irradiation of 0.60 *M* benzophenone and 0.33 *M* isobutylamine in benzene leads to ca. 95% conversion of the amine to the imine I. Irradiation of 0.80 *M* benzophenone and 0.80 *M* 2-butylamine in benzene for 24 hr. leads to 91% isolation of benzpinacol and to ca. 95% conversion to *N*-2-butylidene-2-butylamine (CH₃CH₂C(CH₃)=NCH(CH₃)CH₂CH₃, II), assayed by comparison in the infrared and by vapor phase chromatography with an authentic sample prepared by the method of Norton, *et al.*,³ and characterized by its infrared spectrum,^{2b} chromatographic identity, and conversion to the 2,4-dinitrophenylhydrazone of 2-butanone, m.p. 109–111°.

Irradiation of 1.0 *M* benzophenone and 0.50 *M* diisopropylamine in benzene for 35 hr. leads to 92% recovery of benzpinacol and ca. 95% yield *N*-isopropylideneisopropylamine [(CH₃)₂C=NCH(CH₃)₂, III], assayed by comparison with an authentic sample,³ and characterized from its infrared spectrum^{2b} and by conversion to the 2,4-dinitrophenylhydrazone of acetone. The imines I and II apparently arise from reaction of the initially formed aldimine, RCH=NH, and ketimine, RR'C=NH, with a second molecule of the primary amine; the imine III is formed directly from the secondary amine by photooxidation.

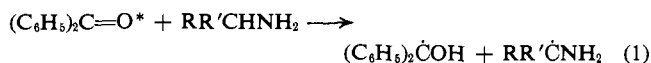
The effect of structure on the rate of the photoreactions was examined in 0.2 *M* solutions of benzophenone in the amine or other reducing material as solvent. Solutions were degassed and irradiated under argon in

Thunberg tubes, samples being analyzed periodically for remaining benzophenone by absorption at 336 μ or at 6.02 μ . Reduction of benzophenone was followed to 60–90% reaction and showed approximate zero-order kinetics. The rates, relative to photoreduction in 2-propanol, are summarized in Table I. The relative rates of photoreduction of benzophenone by some aliphatic hydrocarbons under the same conditions are also included for comparison.

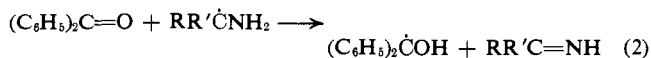
Table I. Relative Rates of Photoreduction of 0.2 *M* Benzophenone

Reducing solvent	Relative rate ($\pm 10\%$)
2-Propanol	1.00
2-Butylamine	1.06
Cyclohexylamine	0.87
<i>n</i> -Butylamine	0.80
<i>n</i> -Hexylamine	0.80
Isobutylamine	0.80
<i>t</i> -Butylamine	0.13
Di- <i>n</i> -propylamine	0.37
Di- <i>n</i> -butylamine	0.42
Diisopropylamine	0.29
Triethylamine	0.15
2,2,4-Trimethylpentane	0.27
<i>n</i> -Hexane	0.20
Cyclohexane	0.19

The primary amines which contain the group RR'-CHNH₂ show rates quite comparable to that of the structurally related alcohol, 2-propanol, and may react with the high limiting quantum yield of 2 which has been reported for the reaction in the alcohol.⁴ The primary amines (RCH₂NH₂) show somewhat lower relative rate, 0.8, possibly reflecting the stronger α -C-H bond. In the alcohol the α -C-H bond is weaker than the O-H bond and abstraction of hydrogen by oxygen of the triplet⁵ ketone is from the α -C. In the amine the C-H and N-H bond dissociation energies may be similar⁶; in view of the abstraction of α -H from ethers,⁷ it seems likely that attack by the triplet ketone occurs at the α -C-H of the amines also (eq. 1).



The high efficiency of these amines in this reaction indicates that a second hydrogen transfer occurs, leading to an imine (eq. 2), corresponding to the reaction in the alcohol system which leads to the ketone.⁸



The secondary amines are 0.3–0.4 as reactive as the standard, despite the presence of ample α -H. Perhaps

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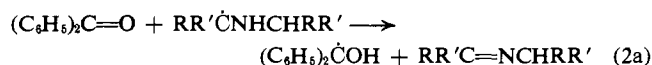
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(1) We are pleased to acknowledge generous support of this work by the National Science Foundation (GP 1833).

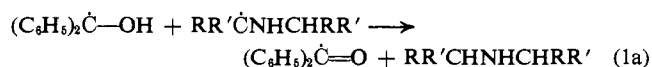
(2) (a) K. N. Campbell, A. H. Sommers, and B. K. Campbell, *J. Am. Chem. Soc.*, **66**, 82 (1944); M. A. Berg, *Bull. soc. chim.* [3] **7**, 547 (1892); (b) F. H. Suydam, *Anal. Chem.*, **35**, 193 (1963).

(3) D. G. Norton, V. E. Haury, F. C. Davis, L. J. Mitchell, and S. A. Ballard, *J. Org. Chem.*, **19**, 1054 (1954).

steric factors diminish the rate of the second step (eq. 2a).



The reverse of reaction of type 1, thermodynamically favorable but frequently not observed for kinetic reasons,⁹ may then intervene and reduce the observed rate of photoreduction (eq. 1a). Evidence for such reversibility has been seen in photoreduction of benzophenone in optically active methyl 2-octyl ether.⁷



The tertiary amine reacts quite slowly, comparable to the hydrocarbons; half of the rate, as compared with *n*-butylamine or with the secondary amine, may be lost because of absence of the reaction related to eq. 2, and the remainder again possibly because of reversibility.⁷ The low reactivity of *t*-butylamine may indicate that α -C-H is necessary for high reactivity, while the low reactivity of the tertiary amine indicates that presence of α -C-H is clearly not sufficient. The 5:1 relative reactivity of 2-propanol and cyclohexane in our work is similar to that observed in competitive experiments.¹⁰

It remains possible that the abstractions of hydrogen occur in the reverse order, triplet ketone abstracting hydrogen from nitrogen and the radical transferring α -H from carbon to ground-state ketone. Experiments with suitably deuterated amines and with optically active amines will give information about this and about the reversibility. Experiments with suitable diamines may lead readily to heterocyclic compounds.

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Stable Carbonium Ions. XIII.¹

Generation of Stable Alkyl, Arylalkyl, and Cycloalkyl Carbonium Ions from Alcohols in Fluorosulfonic Acid and Antimony Pentafluoride

Sir:

Attempts to generate simple alkyl, arylalkyl, and cycloalkyl carbonium ions in sulfuric acid or oleum solution generally result in the formation of complex mixtures in which the stable carbonium ions present are of the methylated cyclopentenyl cation type (stabilized allylic cations²).

Sulfuric acid and oleum as solvents have the serious disadvantage that they are quite viscous and possess relatively high freezing points. This generally results in the need to carry out the investigations at or above +10°. At these temperatures the rate of secondary reactions leading to the cyclized allylic type ions is so high that no simple alkyl (cycloalkyl) carbonium ions

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(2) For a summary, see N. C. Deno, *Progr. Phys. Org. Chem.*, **2**, (1964).

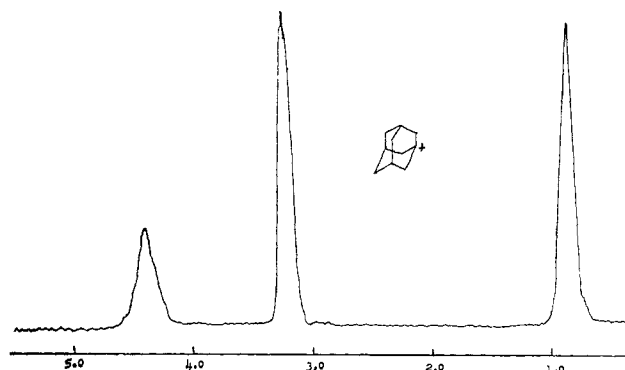


Figure 1.

corresponding to the alcoholic precursors are observable.

One of us was previously able to report that stable alkyl (cycloalkyl) carbonium ions are formed from halide (fluoride, chloride) precursors in neat antimony pentafluoride or mixed SbF_5-SO_2 , SO_2F_2 , SO_2F_2 , or SO_2ClF solvent systems.³

It was of substantial interest to try to extend the scope of forming stable carbonium ions by using alcohols as precursors. In many instances the alcohols as precursors are much more readily available, and their conversion to the corresponding halides without isomerization can represent serious problems.

We would like now to report our observations concerning the generation of stable carbonium ions from alcohols under conditions where no rearrangements (a characteristic of sulfuric acid and oleum systems) take place.

Fluorosulfonic acid is one of the strongest pure acids that has yet been studied.⁴ H_0 for the neat acid is about -12.6 (compared with -11 for 100% sulfuric acid and -10 for anhydrous hydrogen fluoride). At the same time fluorosulfonic acid has a low freezing point (-87.3°) and can be readily purified. As to be expected very few coacids are capable of enhancing the acidity of fluorosulfonic acid. Gillespie and his co-workers, however, observed that antimony pentafluoride acts as acid in fluorosulfonic acid solution by enhancing ionization according to $SbF_5 + 2FSO_3H = H_2SO_3F^+ + SbF_5(SO_3F)^-$. Solutions of SbF_5 in fluorosulfonic acid are considered the most acidic media that have yet been studied.

When alcohols like *t*-butyl alcohol, *t*-amyl alcohol, methylethylphenylcarbinol, diphenylethylcarbinol, 2-*exo*-norborneol, and 1-adamantanol were dissolved in fluorosulfonic acid-antimony pentafluoride solutions diluted with sulfur dioxide (in order to achieve better mixing of the less viscous solutions and to avoid the possibility of local overheating) at temperatures ranging around -60°, stable, slightly colored solutions are formed. The p.m.r. spectra of these solutions (Figures 1-5) show the corresponding carbonium ions with generally good resolution.

We have also found that solutions of the alcohols in SbF_5-SO_2 show formation of the corresponding carbonium ions, indicating ionization in the strong Lewis

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(4) R. J. Gillespie in "Friedel-Crafts and Related Reactions," Vol. 1, G. A. Olah, Ed., Interscience Publishers, Inc., New York, N. Y., 1963.