Tetrafluorohydrazine as Radical Scavenger in the Photoreduction of Benzophenone

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The irradiation of benzophenone dissolved in a hydrocarbon in the presence of tetrafluorohydrazine was found to yield equimolar amounts of difluoraminodiphenylmethanol and the respective difluoramino-substituted hydrocarbon. The hydrocarbons investigated include cyclohexane, 3-methylpentane, toluene, and cumene. The rates of tetrafluorohydrazine consumption were measured.

The mechanism of the photoreduction of benzophenone in solution has been investigated in many laboratories since the pioneering experiments of Ciamician and Silber.[1] There is much supporting evidence that the first excited triplet state of benzophenone is the dehydrogenating species in these systems. The formation of the products isolated was explained by combination and disproportionation reactions of the monoradicals formed in the dehydrogenation step.[2] More recently this mechanism has been modified by postulation of intermediate adducts[3-5] or charge transfer complexes[6] to accommodate conflicting experimental evidence.

Evidence for the existence of the postulated monoradicals by trapping experiments has not been reported to our knowledge. The commonly used scavengers for radicals, such as diphenyl picrylhydrazyl or galvinoxyl, cannot be used because they absorb strongly in the wavelength region utilized for the photoreduction of aromatic ketones.

Superficially, the formation of benzpinacol itself could be considered as such a trapping experiment. However, the initial formation of 1,2-diphenyl-1,2-bis(*p*-chlorophenyl)-1,2-ethanediol during irradiation of *p*-chlorobenzophenone and benzhydrol[7] and the initial formation of unlabeled benzpinacol during the photolysis of benzophenone and benzhydrol (labeled with ^{14}C)[7] in benzene solution indicated that the isolated products do not arise simply by combination reactions of the postulated initial monoradical. Also, the formation of terebic acid during photolysis of benzophenone in isopropyl alcohol in the presence of maleic anhydride[8] has been considered as proof for a trapping reaction of the postulated dimethyl hydroxymethyl radicals. However, no 2,2-diphenylparaconic acid, which should form from the postulated diphenyl hydroxymethyl radicals in an analogous fashion, could be isolated in these experiments.[9] The latter reaction has been shown to occur when diphenyl hydroxymethyl radicals are thermally generated in the presence of maleic anhydride.[9] More recently, *tert*-nitrosobutane has been employed as a radical scavenger. The reported results, however, are inconclusive. Whereas Leaver and Ramsay[10] reported the trapping of dimethyl hydroxymethyl radicals by *tert*-nitrosobutane during the photoreduction of benzophenone in isopropyl alcohol, Perkins and Ward[11] reported the formation of *tert*-butyl nitroxide in the reaction of *tert*-butyl peroxyoxalate and isopropyl alcohol in the presence of *tert*-nitrosobutane. They attribute the formation of *tert*-butyl nitroxide to a hydrogen transfer reaction from the dimethyl hydroxymethyl radical to *tert*-nitrosobutane. Leaver and Ramsay also observed the *tert*-butyl nitroxide; however, they postulate its formation to arise from a hydrogen transfer from the diphenyl hydroxymethyl radical.

It is concluded that trapping experiments in radical reactions are significant evidence for the proposed mechanism only if all postulated radicals are trapped simultaneously and quantitatively.

Tetrafluorohydrazine was expected to be an effective radical scavenger in photochemical dehydrogenation reactions because of its reported properties and reactions. It has been shown to be in equilibrium with difluoroamino radicals at ambient temperature[12] and to react with monoradicals produced by either

$$F_2NNF_2 \rightleftharpoons 2\cdot NF_2$$

thermal or photochemical[13] decomposition. Undesirable side reactions were not expected, since no ionic addition reactions of tetrafluorohydrazine have been reported and the difluoroamino radicals have been found to abstract hydrogen only at elevated temperatures.[14]

It has been reported in a previous publication[15] that α-difluoramino ethers were formed by irradiation of an ether solution of benzophenone in the presence of tetrafluorohydrazine. This reaction was extended to solutions of benzophenone in hydrocarbons and a detailed investigation of all reaction products was performed.

Results

Difluoraminoalkanes.—Benzophenone dissolved in hydrocarbons was irradiated with a high-pressure mercury lamp while purging with tetrafluorohydrazine from a reservoir. Figure 1 represents a typical plot of gas consumption *vs.* time. The rate of tetrafluorohydrazine uptake slowed down during irradiation

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and stopped after an amount of gas approximately equimolar to the starting benzophenone was consumed. During irradiation the solution turned yellow; however, this color was not connected with the decrease in tetrafluorohydrazine consumption. The addition of more benzophenone to the yellow reaction solution again started the photoreaction with tetrafluorohydrazine at the same rate as at the beginning of the experiment.

In Table I, the tetrafluorohydrazine consumption rates for the hydrocarbons investigated are listed.

TABLE I

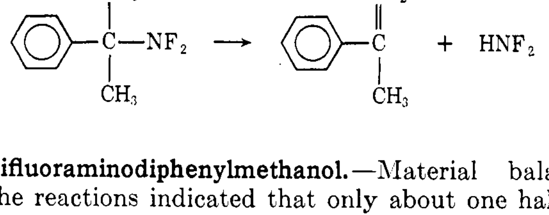
CONSUMPTION OF TETRAFLUOROHYDRAZINE AND RELATIVE QUANTUM YIELDS

Substrate	Consumption, ml/min	Rel ϕ
Cumene	3.58	1.02
Cyclohexane	3.5	1
3-Methylpentane	2.38	0.68
Diethyl ether (15)	3.09	0.88
Dioxane (15)	2.25	0.64
Tetrahydrofuran (15)	1.67	0.48
Diisopropyl ether (15)	0.80	0.23

These values were taken from the initial straight line of plots as in Figure 1.

The hydrocarbon solvents and volatile reaction products were distilled together after irradiation. Vapor phase chromatographic analysis of the distillates indicated one photoproduct in the experiments with toluene and cyclohexane and one major and several minor products in the experiments with 3-methylpentane. The sum of the minor products, however, was less than 5% of the main product. No efforts were undertaken to elucidate the structures of these minor products. The other photoproducts were identified as α-difluoroaminotoluene, difluoroaminocyclohexane, and 3-difluoroamino-3-methylpentane, respectively.

Two products were observed in the distillates of the cumene experiments; infrared analysis indicated the presence of difluoroamino groups (absorption at 885 cm^{-1}). During attempted separation and purification of the two products by distillation, one of them disappeared accompanied by a corresponding increase in the concentration of the other product. The latter showed no absorption at 885 cm^{-1} and was identified as α-methylstyrene, indicating that the product which disappeared was indeed the expected α-difluoraminocumene which lost difluoramine during attempted distillation.



Difluoraminodiphenylmethanol.—Material balance of the reactions indicated that only about one half of the consumed tetrafluorohydrazine could be accounted for in the isolated difluoraminoalkanes. The reaction with cyclohexane was selected for a careful investigation of the distillation residue.

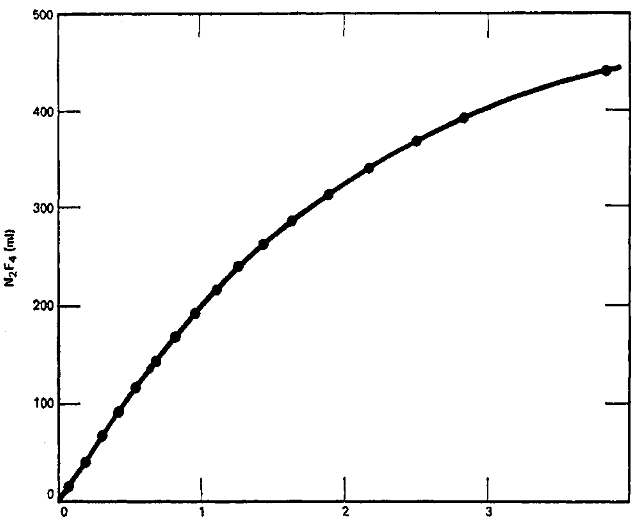
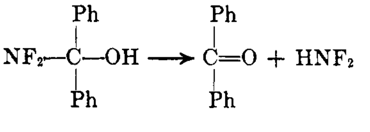


Figure 1.—Photolysis of 4 g of benzophenone in 400 ml of cyclohexane in the presence of tetrafluorohydrazine.

The benzophenone–cyclohexane solution was photolyzed with tetrafluorohydrazine, purging until the gas consumption had ceased; 0.9 mol of tetrafluorohydrazine was consumed for every 1 mol of starting benzophenone. Then the solvent and the volatile reaction product were removed under vacuum at room temperature.

The viscous distillation residue exhibited hydroxyl, difluoramino, and phenyl absorption in the infrared, but only a trace of a carbonyl band could be observed. After hydrolysis of the residue with aqueous acetic acid, over 96% of the original benzophenone could be isolated. Elemental iodine was liberated when the hydrolysis was carried out in the presence of potassium iodide; titration of the iodine gave values of 1.8 molecules of iodine liberated for each molecule of starting benzophenone.

All available data are consistent with the structure of difluoraminodiphenylmethanol for the residue. Compounds containing a difluoramino and a hydroxyl group at the same carbon are known[16] to be easily hydrolyzed to the parent carbonyl compound and difluoramine. Difluoramine itself reacts quantitatively with potassium iodide in acidic solution.[17]



$$NF_2-\underset{Ph}{\overset{Ph}{C}}-OH \longrightarrow \underset{Ph}{\overset{Ph}{C}}=O + HNF_2$$

$$HNF_2 + 4HI \longrightarrow 2I_2 + NH_4F + HF$$

Discussion

Mechanism.—The isolation of equimolar amounts of difluoraminocyclohexane and difluoraminodiphenylmethanol constitutes the first example in which both monoradicals, postulated as intermediates in the photo-

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[16] (a) J. P. Freeman, W. H. Graham, and C. O. Parker, *J. Amer. Chem. Soc.*, **90**, 121 (1968); (b) S. F. Reed, Jr., *J. Org. Chem.*, **32**, 2894 (1967).

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reduction of benzophenone (steps 1 and 2 below), were trapped simultaneously and quantitatively.

$$Ph_2CO \xrightarrow{h\nu} {}^1Ph_2CO \longrightarrow {}^3Ph_2CO \qquad (1)$$

$${}^3Ph_2CO + RH \longrightarrow Ph_2\dot{C}OH + R\cdot \qquad (2)$$

$$Ph_2\dot{C}OH + \cdot NF_2 \longrightarrow Ph_2C(OH)NF_2 \qquad (3)$$

$$R\cdot + \cdot NF_2 \longrightarrow RNF_2 \qquad (4)$$

$$Ph_2\dot{C}OH + F_2NNF_2 \longrightarrow Ph_2C(OH)NF_2 + \cdot NF_2 \qquad (5)$$

$$R\cdot + F_2NNF_2 \longrightarrow RNF_2 + \cdot NF_2 \qquad (6)$$

The reported experiments do not yield conclusive evidence that the monoradicals originating according to reaction 2 form the difluoramino compounds exclusively *via* reactions 3 and 4. Another attractive possibility is their formation through reaction of the monoradicals with undissociated tetrafluorohydrazine according to 5 and 6. The low bond energy of the N–N bond in the tetrafluorohydrazine of 19.9 kcal[18] makes reactions 5 and 6 exothermic by about 50 kcal. Considerations with respect to the concentration of the different radicals in the solution during photolysis further support the possibility of reactions 5 and 6.

High efficiency of the trapping reactions 3–6 was demonstrated by the fact that neither benzpinacol nor mixed radical combination products could be isolated in the experiments carried out in the presence of tetrafluorohydrazine. Benzpinacol would have precipitated during photolysis in the experiments with cyclohexane and 3-methylpentane, since it is practically insoluble in the hydrocarbons.

In the system benzophenone–cyclohexane, 96.3% benzophenone was recovered of the hydrolysis of the distillation residue. Since the theoretical mixed combination product would not yield benzophenone under the reaction conditions, cage combination reactions did occur to less than 4% if at all.

Relative Quantum Yield for Hydrogen Abstraction by Triplet Benzophenone.—The observed rates of tetrafluorohydrazine consumption in the different hydrocarbons should be directly proportional to the quantum yield for hydrogen abstraction by triplet benzophenone providing that the quenching of the excited states of benzophenone by tetrafluorohydrazine is negligible. Whether or not this assumption is correct will be investigated in future experiments. Preliminary data do not indicate a significant quenching. The measured consumption rates of tetrafluorohydrazine are presented in Table I together with values from previous experiments with ethers.[15] The differences in relative quantum yields can be rationalized by a combination of electronic and steric effects.

Selectivity of Triplet Benzophenone.—In the experiments with 3-methylpentane more than 95% of the reaction product resulted from the attack of the triplet benzophenone on the tertiary hydrogen, indicating high selectivity of the excited benzophenone. Similar results were reported in experiments with ethers, where only products could be isolated which resulted from hydrogen abstraction adjacent to the ether oxygen. In Table II relative reactivities per hydrogen are tabulated together with results reported by Walling and Gibian.[19] The values from the experiments with triplet benzophenone are in fair agreement. They show the same high selectivity for the hydrocarbons.

TABLE II

RELATIVE REACTIVITIES PER H ATOM

Substrate	This paper	Ref 19
Cyclohexane	1	1
Cumene	12.2	19.8
3-Methylpentane	8.2	
2,3-Dimethylbutane		6.0
Diethyl ether	2.6	
Dioxane	1.0	
Tetrahydrofuran	1.4	
Diisopropyl ether	1.4	

Conclusion

The results reported in this paper have supported our original postulation[15] that tetrafluorohydrazine can be used as a valuable "reagent" in the investigation of the mechanisms of photochemical reactions and pinpoint the site of attack of excited states.

Experimental Section

General.—Infrared and ultraviolet spectra were obtained with Beckman IR-8 and Bausch & Lomb 505 spectrometers, respectively. The nmr spectra were obtained with a Varian DP 60 spectrometer using deuteriochloroform as the solvent and tetramethylsilane as an internal standard. Reaction mixtures and distillation fractions were monitored on a Perkin-Elmer 154 gas chromatograph and the preparative gas chromatograph work was performed on a Beckman Megachrom equipped with standard Beckman 6 ft × 0.75 in., 20% Paraplex G-25 on 42–60 Chromosorb W columns. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Materials.—Tetrafluorohydrazine (Air Products, 99% pure) was used as received. Toluene (Matheson Coleman and Bell, spectroquality), benzophenone (Fisher, reagent grade), isopropyl alcohol (Fisher, spectrograde), cumene (Baker, Baker grade), and 3-methylpentane (Aldrich, research grade) were used without further purification.

Apparatus and Procedure.—All irradiations were performed in the following manner. Solutions consisting of 4.0 g of benzophenone in 400 ml of the appropriate hydrocarbon solvent were placed in a photoreactor which was equipped with a fritted gas inlet tube at the bottom and gas outlet tube at the top. A jacketed, water-cooled, 100-W Hanovia high-pressure mercury lamp (Type SOL, 608-36A) was immersed in the reactor utilizing a Pyrex 7740 filter to protect the difluoramino radicals and the expected products from the light. Tetrafluorohydrazine was pumped through the solution with a Cole-Parmer Masterflex tubing pump during irradiation and recycled to a reservoir to measure gas consumption. The solutions were thoroughly purged with purified nitrogen both prior to introduction of tetrafluorohydrazine and after completion of irradiation *to avoid potentially hazardous mixtures of organic compounds, tetrafluorohydrazine, and oxygen.* None of the reported photochemical reactions occurred in the absence of ultraviolet light.

The difluoramino compounds and unreacted solvents were separated from the reaction mixture by distillation under vacuum followed by preparative glpc to give the pure difluoramino compounds.

Photolysis of Toluene Solution.—Tetrafluorohydrazine was bubbled through a solution of benzophenone in toluene and irradiated at ambient temperature for 3 hr, yielding only one photoproduct that could be detected by glpc analysis. The unreacted toluene was removed by vacuum distillation (80 mm, 50°). The remaining residue was vacuum distilled at 1 mm and 50° to collect the photoproduct and some toluene. The distillate, containing photoproduct and toluene, was separated by preparative glpc to give the analytically pure sample of α-difluoramino-

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[18] J. A. Kerr, *Chem. Rev.*, **66**, 496 (1966).

[19] C. Walling and M. J. Gibian, *J. Amer. Chem. Soc.*, **87**, 3361 (1965).

toluene: ir (neat) 805, 890, and 925 cm^{-1} (-NF_2); nmr ($CDCl_3$) δ 4.58 (t, 2, J = 29 Hz, -CH_2NF_2) and 7.37 ppm (s, 5, C_6H_5-).

Anal. Calcd for $C_7H_7F_2N$: C, 58.74; H, 4.93; F, 26.54; N, 9.78. Found: C, 58.92; H, 5.19; F, 26.58; N, 9.59.

Photolysis of Cumene Solution.—The above photolysis procedure was repeated substituting cumene for toluene. Two photoproducts were detected by glpc analysis. The unreacted cumene was removed by vacuum distillation (15 mm, 50°) and the remaining residue was distilled at 1 mm and 50°. After the distillate was purified by preparative glpc only one of the original photoproducts could be detected. The photoproduct that decomposed showed difluoramino absorption at 885 cm^{-1} and the remaining photoproduct was passed through the preparative glpc to give an analytical sample of α-methylstyrene.

Anal. Calcd for C_9H_{10}: C, 91.46; H, 8.54. Found: C, 91.38; H, 8.51.

Photolysis of 3-Methylpentane Solution.—The photolysis procedure was repeated using 3-methylpentane as the solvent with an irradiation time of 4 hr. One major and several minor (total <5%) photoproducts were detected by glpc analysis. The major photoproduct was isolated by a similar distillation procedure (450 mm, 50°, then 1 mm, 50°) and purified by preparative glpc to give an analytical sample of 3-methyl-3-difluoraminopentane: ir (neat) 850 and 945 cm^{-1} (-NF_2); nmr ($CDCl_3$) δ 0.92 [t, 6, J = 7 Hz, $(CH_3CH_2)_2CCH_3$-], 1.17 [t, 3, J = 2 Hz, $(CH_3CH_2)_2CCH_3$-], and 1.67 ppm [m, 4, $(CH_3CH_2)_2CCH_3$-].

Anal. Calcd for $C_6H_{13}F_2N$: C, 52.54; H, 9.55; F, 27.70; N, 10.21. Found: C, 52.71; H, 9.61; F, 27.64; N, 10.04.

Photolysis of Cyclohexane Solution.—The photolysis procedure was repeated using cyclohexane as the solvent with an irradiation time of 325 min. Only one major and one minor volatile photoproduct were detected by glpc analysis. The photoproducts were concentrated by distillation. Because of the potentially hazardous nature of the products, only a small fraction of the concentrate was passed through the preparation glpc to give an analytical sample of difluoraminocyclohexane for the major product: ir (neat) 840, 910, and 960 cm^{-1} (NF_2); nmr ($CDCl_3$) δ 1.63 (m, 10, $C_6H_{10}NF_2$-) and 3.32 ppm (t, 1, J = 26 Hz).

Anal. Calcd for $C_6H_{11}F_2N$: C, 53.32; H, 8.20; F, 28.19; N, 10.27. Found: C, 53.50; H, 8.20; F, 28.19; N, 10.27.

A sample of the minor product was also isolated; however, the amount was too small for full characterization. This compound did not contain difluoramino groups, since no nitrogen was found by microchemical methods.

In a second experiment (uptake of tetrafluorohydrazine 440 ml, 0.0196 mol) the sequence of distillation was changed to elucidate the composition of the reaction residue. Both photoproduct and unreacted cyclohexane were vacuum distilled (1 mm, 25°) leaving undecomposed residue and trace amounts of cyclohexane and cyclohexane photoproduct. Infrared analysis of the pot residue showed peaks at 3500 (OH) and 885, 855 cm^{-1} (NF_2).

Hydrolysis of the residue was accomplished by adding aqueous acetic acid and excess potassium iodide, liberating iodine. The aqueous solution was extracted with methylene chloride and the resulting aqueous solution was diluted to 2 l. Twenty milliliters of standard arsenous acid (0.099 mol) was needed to titrate a 100-ml aliquot of the stock iodine solution using starch indicator. The total liberated iodine was calculated as 0.0398 mol which corresponds to 0.0199 mol of difluoraminodiphenylmethanol. The methylene chloride extract was evaporated under vacuum (1 mm) leaving 3.85 g (96% recovery) of benzophenone, which was identified by matching the infrared spectrum and melting point with those of an authentic sample.

Proper caution should be taken during distillation of potentially hazardous difluoramino compounds.

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Registry No.—Tetrafluorohydrazine, 10036-47-2; benzophenone, 119-61-9; toluene, 108-88-3; α-difluoroaminotoluene, 23162-99-4; cumene, 98-82-8; α-methylstyrene, 98-83-9; 3-methylpentane, 96-14-0; 3-methyl-3-difluoraminopentane, 40715-62-6; cyclohexane, 110-82-7; difluoroaminocyclohexane, 14182-78-6.

The Pyrolysis of Alkyl Sulfide Tosylhydrazone Salts. A Search for R_2S-4 Participation in Carbene Reactions. The Pyrolysis of Sodium Toluenesulfinate

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Sodium salts of alkyl sulfide tosylhydrazones **6**, **7**, and **8** have been pyrolyzed at several temperatures to see if sulfur-carbene interaction would lead to intramolecular sulfur ylide formation of the R_2S-4 type. Analysis of the results shows no evidence for sulfur ylide formation but rather α-insertion products typical of singlet carbene reactions producing olefins **9** and **10** and **13** and **15**, respectively. Sodium toluenesulfinate was pyrolyzed at 250 and 320° to establish products resulting from its thermal decomposition at these temperatures.

Recently, evidence for R_2S-4[1] participation in the photolytic reactions of keto sulfides **1**[2] and α-dione sulfides **2**[3] has been reported. Evidence for similar interaction in solvolytic **3**,[4,5] carbonium ion **4**,[6] and radical **5**[7] reactions has also been proposed. We wish to report here our initial search for R_2S-4 participation in sulfur-carbenoid species.[8]

While no exact proximity requirements for sulfur neighboring-group participation have emerged for the different R_2S-4 type transition states, careful solvolysis studies by Ireland[4] and later by Paquette[5] using caged alkyl thiatosylates have shown that sulfur can interact in ground-state reactions by stabilizing a developed reactive species, in these cases carbonium ions. Further, in those systems where conformational mobility is limited and stereochemical requirements are ideal, R_2S-4 effects can accelerate[5,7] the rate of formation of reactive species.

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[1] The symbolism R_2S-n is used here to denote the size of a bicyclic ring (n members) ultimately realizable if cyclization were to occur as a result of neighboring group participation. (See ref 5 for other examples of this useful nomenclature.)

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[7] A. Ohno and Y. Ohnishi, *Tetrahedron Lett.*, 339 (1972).

[8] For a review on carbene chemistry, see W. Kirmse, "Carbene Chemistry," 2nd ed, Academic Press, New York, N. Y., 1971, and references cited therein.