

Photochemistry of Benzophenone Hydrazone

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Benzophenone hydrazone was photolyzed at 2537 and 3000 Å in the presence and absence of air. The reaction is very inefficient with a quantum yield for the disappearance of starting material <0.01. Diphenylmethane is the major photoproduct with benzophenone, benzophenone imine, and benzophenone azine being formed in minor amounts. Triplet sensitization studies indicate that reaction occurs from the singlet state. Mechanisms for the formation of all photoproducts are discussed. Evidence for photooxidation as the principal process in air-exposed photolyses is presented.

Although the photochemistry of carbonyl compounds has been extensively investigated, it is only recently that much attention has been given to the photochemistry of compounds containing the C-N double bond.¹⁻⁴ One such account has reported that irradiation under nitrogen of benzophenone hydrazone in methanol through a vycor filter using a 450-W Hanovia high-pressure mercury lamp resulted in substantial conversion to diphenylmethane (25%) and benzophenone (33%) after 2 hr of irradiation.⁵ Since our experience with this compound has been quite different, both in regard to reaction efficiency and product ratios, we wish to report the results of an extensive investigation of the photochemistry of this molecule under various reaction conditions.

Results and Discussion

Reaction Conditions.—Samples consisting of 0.2 mmol of hydrazone in 10 ml of solvent were irradiated in quartz tubes at 2537 Å and in Pyrex at 3000 Å. The light source was a Rayonet chamber reactor equipped with a "merry-go-round." All solvents were thoroughly dried before use. Samples were degassed to less than 10⁻⁴ mm in four to five freeze-thaw cycles. After standing for 5 days, unirradiated samples showed no reaction. All product identities were confirmed by independent synthesis and comparison of spectral data with collected samples.

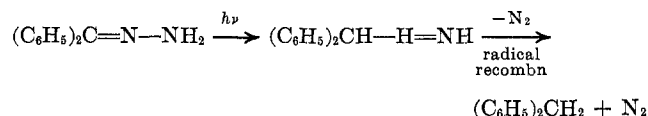
Products.—The products of the degassed photolysis of benzophenone hydrazone at 2537 Å in methanol, *n*-hexane, and benzene are listed in Table I. Percentage compositions were obtained by vpc analysis using *sym*-tetraphenylethane as an internal standard. Photolyses at 3000 Å resulted in the same products in the same relative proportions; however, owing to the lower source intensity the reaction was much slower at this wavelength.⁶ With the concentration of hydrazone used, essentially all incident light was absorbed at both wavelengths. Attempts to determine the quantum yield for the disappearance of hydrazone using potassium ferrioxalate actinometry at 2537 Å

were unsuccessful, owing to the inefficiency of the reaction. During the time required for 5% of the hydrazone to disappear, essentially all of the ferrioxalate reacted. The quantum yield of reaction is therefore considerably less than 0.01.

The results of Table I indicate that the major photoproduct is diphenylmethane. The remaining products, benzophenone, benzophenone imine, and benzophenone azine all photolyze at 2537 Å; none, however, yields diphenylmethane as a photoproduct.⁷ In order to determine the excited state of the hydrazone responsible for this product, a sensitized reaction using triphenylene as triplet sensitizer was run at 3500 Å. Benzophenone hydrazone is transparent at this wavelength.

Samples of 10:1 triphenylene:benzophenone hydrazone (0.05 *M*:0.005 *M*) in benzene were degassed and allowed to stand 24 hr prior to irradiation to rule out dark reactions. Aliquots were taken every 2 hr, and, after 24 hr of exposure, less than half of the hydrazone remained, while sensitizer concentration had not diminished. However, no products could be observed by vpc, and column chromatography yielded only tars in addition to sensitizer and starting material. A control sample without sensitizer had not reacted after 48 hr of irradiation. Moreover, triplet energy transfer was confirmed by the fact that, at concentrations where triphenylene was absorbing essentially all of the light, benzophenone hydrazone quenched triphenylene phosphorescence (EPA, 77°K). Since diphenylmethane is photochemically stable under the sensitized reaction conditions, it was concluded from the above that singlet hydrazone is the excited-state intermediate responsible for the formation of diphenylmethane.

The mechanism of diphenylmethane formation has been described as a photochemical Wolff-Kishner reduction involving an initial hydrogen migration to form the azo compound, followed by loss of nitrogen and radical recombination.⁵



Since it was of interest to us to determine whether the reduction was an entirely intramolecular process,

(7) The photochemistry of benzophenone imine has been studied by E. S. Huyser.⁸ Degassed photolyses of benzophenone azine under the outlined reaction conditions resulted only in unreacted starting material and tars.

(1) M. Fischer, *Tetrahedron Lett.*, 5273 (1966).

(2) R. W. Binkley, *J. Org. Chem.*, **33**, 2311 (1968).

(3) E. S. Huyser, R. S. H. Wang, and W. T. Short, *ibid.*, **33**, 4323 (1968).

(4) A. Padwa, W. Bergmark, and D. Pashayan, *J. Amer. Chem. Soc.*, **91**, 2653 (1969).

(5) R. W. Binkley, *Tetrahedron Lett.*, 1893 (1969).

(6) Roughly one-fourth of the starting material reacted in 48 hr in *n*-hexane; 72 hr was required for the same per cent reaction in benzene and methanol.

TABLE I
 DEGASSED PHOTOLYSES OF BENZOPHENONE HYDRAZONE AT 2537 Å

Solvent	Time, hr	Products, % ^{a,b}					Total
		(C ₆ H ₅) ₂ CH ₂	(C ₆ H ₅) ₂ CO	(C ₆ H ₅) ₂ CNH	(C ₆ H ₅) ₂ CN ₂ C-(C ₆ H ₅) ₂	(C ₆ H ₅) ₂ CNNH ₂	
Methanol	4	1.2	Trace	Trace	0.8	98	All
	12	4.0	Trace	Trace	4.0	71.2	79.2
	24	7.6	0.7	1.5	1.8	54.7	66.4
	48	15.9	1.1	2.4	1.5	42.9	63.8
Benzene	4					100	All
	12	1.7	Trace	1.1	1.9	82.5	87.2
	24	2.7	Trace	1.3	1.6	59.0	64.6
	48	6.5	1.0	2.9	1.8	41.9	54.1
<i>n</i> -Hexane	4	1.2	5.4	3.0	3.1	87.3	All
	8	3.1	7.9	5.1	9.2	74.7	All
	12	4.4	7.0	4.0	6.2	47.3	68.9
	20	8.4	6.2	3.8	6.0	18.4	42.8
	24	10.2	5.6	2.8	1.8	13.1	33.5

^a Based on vpc analysis. ^b Values are accurate to ±10%.

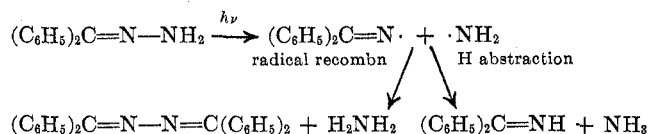
 TABLE II
 NONDEGASSED PHOTOLYSES OF BENZOPHENONE HYDRAZONE AT 2537 Å

Solvent	Time, hr	Products, % ^a						Total	
		(C ₆ H ₅) ₂ CH ₂	(C ₆ H ₅) ₂ CO	(C ₆ H ₅) ₂ CNH	(C ₆ H ₅) ₂ CHOCH ₂	(C ₆ H ₅) ₂ CN ₂ C-(C ₆ H ₅) ₂	(C ₆ H ₅) ₂ CN ₂ CH ₂		(C ₆ H ₅) ₂ CNNH ₂
Methanol	4	Trace	9.5	Trace	1.6	7.4	9.9	59.4	87.8
	8	0.6	8.3	Trace	2.2	14.0	10.5	41.4	77.0
	12	1.6	7.4	1.6	3.0	18.4	6.0	26.7	64.7
Benzene	4	0.8	8.8	4.1		5.8		76.2	95.7
	8	1.4	10.9	4.2		10.4		54.9	81.8
	12	2.5	11.0	4.2		12.2		47.6	77.5
<i>n</i> -Hexane	4	1.3	23.4	9.4		16.2		46.0	96.3
	8	6.6	24.0	7.1		8.3		6.2	52.2

^a ±10% accuracy.

or whether hydrogen abstraction from solvent was involved, the reaction was run in 99.5% hexadeuterio-benzene. Product analysis was achieved by high resolution mass spectroscopy of a sample whose vpc retention time corresponded to diphenylmethane. The P + 1 peak for pure diphenylmethane (*m/e* 168) is calculated to be approximately 15% the intensity of the parent ion.⁸ Sample analysis resulted in a relative intensity of 43%, indicating the presence of monodeuterated diphenylmethane. No evidence for the dideuterated compound was found since the peak at *m/e* 170 was of the expected intensity for a combination of the P + 2 peak of diphenylmethane and the P + 1 peak of the monodeuterated product. These results indicate that hydrogen abstraction from solvent is competitive with radical recombination in the second stage of the reaction. No attempt was made to determine the fate of the phenyl radicals which would be generated by hydrogen abstraction.

Benzophenone, benzophenone imine, and benzophenone azine can result from several competing reaction mechanisms. Benzophenone imine and azine can both be formed by initial cleavage of the N-N bond, followed by radical recombination or hydrogen abstraction from either solvent or starting material.



(8) R. I. Reed, "Applications of Mass Spectrometry to Organic Chemistry," Academic Press, New York, N. Y., 1966, p 19.

One would also expect to find benzonitrile; however, this product was not observed.

Azine could also be formed by condensation of benzophenone with starting material. Benzophenone can result from the hydrolysis of imine, azine, or starting material, or from direct photooxidation of the latter by residual traces of oxygen in solution. The second process was felt to be significant when solutions were not sufficiently degassed. This conclusion was based upon the previously reported high yield of benzophenone from this photolysis⁹ and upon our noticeably higher yields of azine and benzophenone in *n*-hexane (Table I) which is difficult to degas effectively. Therefore, in an effort to verify or eliminate some of the possible reaction routes to these products, non-degassed samples were photolyzed. Results are summarized in Table II.

Photooxidation.—The increased yields of benzophenone listed in Table II are felt to be almost entirely due to photooxidation of starting material. This conclusion is based upon the following evidence. (1) Photolysis of nondegassed benzophenone azine solutions under conditions identical with those used for benzophenone hydrazone produced no benzophenone. A slight amount of decomposition occurred in methanol, the azine completely disappeared with only polymer formation in 24 hr in *n*-hexane and no reaction occurred in benzene. These results are completely consistent with the data in Table II for benzophenone azine. (2) Use of solvents not subjected to further drying gave no change in product ratios, thus eliminating hydrolysis as a significant process.

Condensation of benzophenone with starting material readily explains the increase in benzophenone azine. Somewhat surprising, however, was the observed increase in the rate of formation of diphenylmethane and benzophenone imine in both *n*-hexane and benzene relative to that observed in degassed samples. In addition, two new products, benzhydryl methyl ether and benzophenone azine with formaldehyde, were isolated from the methanol photolysis.

A careful consideration of the above data led to the conclusion that all of these results could be explained by hydrogen abstraction by excited benzophenone and subsequent hydrogen transfer to various species in solution in a process analogous to that observed by Padwa, *et al.*, in the photoreduction of aryl *N*-alkylimines.⁴ In order to test this hypothesis, a benzene solution containing 10:1 benzophenone:hydrazone (mole per cent) was photolyzed at 3500 Å. After 3 hr, less than 15% hydrazone remained (vpc analysis). As had been expected, azine was the major product; however, diphenylmethane (7%) was also present. These two products, together with unreacted ketone and hydrazone, quantitatively accounted for starting material. To rule out possible sensitization by azine, an azine:hydrazone mixture was photolyzed under the same conditions and at 3130 Å. No reaction occurred. The possibility of direct sensitization by benzophenone had been previously eliminated by the results of triphenylene sensitization.

Scheme I outlines the proposed reaction sequence for the air-exposed photolysis of benzophenone hydrazone in methanol. Steps 1 and 2 are the photo-processes observed in degassed solutions and, owing to their low quantum efficiency, are considered subordinate to steps 3 and 4 in air-exposed solutions. Steps 5–12 list the possible routes for hydrogen abstraction and transfer. Step 5 is likely to predominate in methanol, with step 9 being more significant in solvents where hydrogen abstraction is more difficult. This view is supported by the increase in the rate of diphenylmethane formation in *n*-hexane and benzene. The fact that such an increase is not observed in methanol is explained by the presence of more kinetically favorable reaction paths, such as step 7.

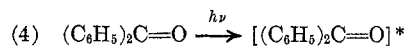
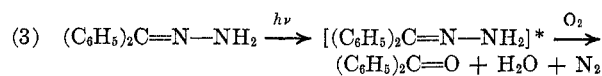
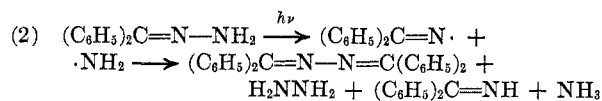
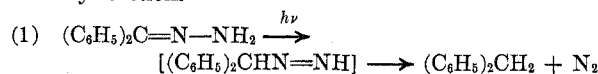
Hydrogen transfer from benzhydroxyl radical to the imino radical, step 6 is felt to be the reason for the observed increase in benzophenone imine. Although reaction between any two of the four radicals in step 6 is theoretically possible, the fact that benzhydrylidenebenzhydroxylamine⁹ is not formed in any observable amount is attributed to the low efficiency of imino radical formation (Table II).

The presence of benzhydryl methyl ether can only be explained by the mechanism outline in steps 9, 11, and 12. Both the ether and benzophenone azine are known to result from photolysis of diphenyldiazomethane.^{10,11}

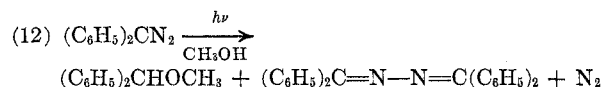
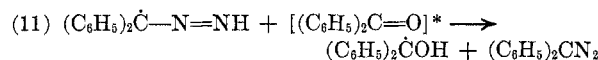
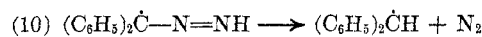
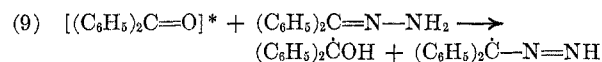
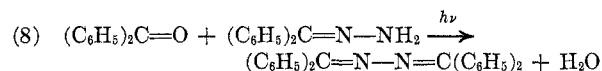
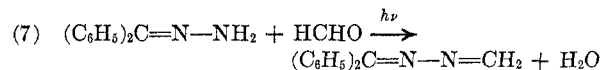
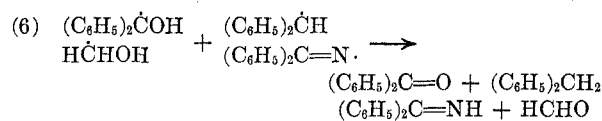
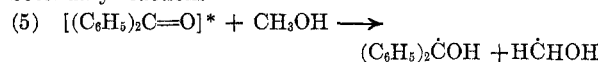
We conclude from the above that, although it is extremely inefficient, "true" photolysis of benzophenone hydrazone does occur and results primarily in a Wolff-Kishner type reduction to diphenylmethane. This con-

SCHEME I
AIR-EXPOSED PHOTOLYSIS OF BENZOPHENONE HYDRAZONE
IN METHANOL

A. Primary reactions



B. Secondary reactions



clusion is based upon the observed slower rate of formation and larger yield of diphenylmethane in degassed solutions, and the fact that, although benzophenone is present in degassed methanol, the amount ($\approx 1\%$) must be considered insufficient for significant light absorption, since no benzhydryl methyl ether or benzophenone azine with formaldehyde was observed. If, however, oxygen is not scrupulously excluded from the system, the principal result will be photooxidation of starting material to benzophenone with subsequent hydrogen abstraction and transfer by the latter.

Experimental Section

General.—All melting points are uncorrected and were determined using a Mel-Temp apparatus. Infrared spectra were obtained using a Beckman IR-4 instrument. Liquid samples were run as neat films and solids were run in liquid cells with carbon tetrachloride as solvent. Nmr spectra were recorded on a Varian HR-60 spectrometer in deuterio chloroform with tetramethylsilane as internal standard. Mass spectral analyses of photoproducts were performed by Battelle Memorial Institute, Columbus, Ohio. All commercial chemicals used were Matheson Coleman and Bell products, and all solvents were Spectrograde. The latter were dried by the following methods: (1) benzene was allowed to stand over sodium for at least 24 hr before use, (2) *n*-hexane was placed over molecular sieve, (3) methanol was

(9) See reference in footnote 7.

(10) H. Staudinger, E. Anthes, and F. Pfenninger, *Ber.*, **49**, 1936 (1916).(11) W. Kirmse, L. Horner, and H. Hoffmann, *Justus Liebigs Ann. Chem.*, **614**, 19 (1958).

distilled over magnesium according to the procedure of Fieser,¹² and (4) deuteriobenzene was distilled and dried over molecular sieve.

Benzophenone Hydrazone.—The extraction thimble of a Soxhlet extractor was filled with 20 g of molecular sieve; 9.1 g (0.050 mol) of benzophenone and 8.8 g (0.176 mol) of 99–100% hydrazine hydrate were refluxed overnight (16–24 hr). The hot alcoholic solution was filtered, and evaporation of solvent yielded 7.2 g (73%) of crude product, mp 90–94°. After one recrystallization from ethanol, the product melted at 98–99° (lit.¹³ mp 97–98°).

Photolysis of Benzophenone Hydrazone.—Samples consisting of 0.2 mmol of hydrazone in 10 ml of solvent were irradiated in a Rayonet chamber reactor equipped with a "merry-go-round," at 2537 and 3000 Å. Degassed samples were evacuated to 10⁻⁵–10⁻⁴ mm in four to five freeze-thaw cycles on a high-vacuum line, and helium was pumped through the samples for 5 min after the final cycle. Sample tubes were sealed with a high-vacuum stopcock. Aliquots were periodically withdrawn for vpc analysis through a side arm equipped with serum cap. Analyses were carried out on a Varian Model 1200 flame ionization gas chromatograph using a 5 ft × 1/8 in. column packed with 3% SE-30 on 100/120 Varaport 30. Samples for product identification were collected by column chromatography on Florisil and by preparative vpc on a Varian Model 700 using a 10 ft × 3/8 in. 10% SE-30 on 30–60 Chromosorb W column.

Diphenylmethane and benzophenone were identified by comparison of vpc retention times and ir and nmr spectra with those of commercial samples.

Benzophenone azine was prepared according to the procedure of Szmant and McGinnis, mp 163–164° (lit.¹³ mp 164°). A mixture melting point with a sample of photoproduct collected by column chromatography showed no depression, and the infrared spectra of the samples were identical.

Benzophenone imine was prepared from the Grignard reaction of phenyl bromide and benzonitrile,¹⁴ bp 85–86° (0.2 mm) [lit.¹⁴ bp 127° (3.5 mm)]. Infrared spectra of prepared and col-

lected samples had characteristic bands at 3.1 and 6.4 (NH) and 6.25 μ (C=N).

Benzhydryl methyl ether, prepared according to the method of Welch and Smith,¹⁵ had bp 129–130° (2 mm) [lit.¹⁵ bp 153.2–153.5 (14.5 mm)]. The infrared spectrum was identical with that of the photoproduct ether, showing strong CO absorption at 9.1 μ.

Benzophenone azine with formaldehyde was prepared by a procedure similar to that used for starting material. Refluxing 0.8 g (0.004 mol) of benzophenone hydrazone with 0.25 g (0.008 formula wt) of paraformaldehyde in 20 ml of methanol in a Soxhlet extractor (molecular sieve) for 3 hr resulted in a quantitative yield of benzophenone azine with formaldehyde, bp 97–98° (0.03 mm), ir 3.34 and 3.42 (CH₂), and 5.98 and 6.25 μ (C=N). The nmr resonance peak for the methylene group was not observed and was felt to be part of the phenyl multiplet at δ 7–8, since no other peaks were present in the spectrum.

Quantum Yield Studies.—A 0.006 M solution of potassium ferrioxalate, prepared according to the method of Calvert and Pitts,¹⁶ and a 0.002 M degassed solution of benzophenone hydrazone in methanol were simultaneously irradiated for 2 hr through a 2540 Å band-pass filter using a 450-W Hanovia high-pressure mercury lamp. During this time, <5% of the hydrazone and >95% of the ferrioxalate reacted, and it was therefore impossible to accurately determine the reaction quantum yield by this technique.

Sensitization Studies.—All sensitized reactions were carried out with a 10:1 concentration ratio of sensitizer:hydrazone. Benzene solutions of triphenylene and hydrazone were degassed to <5 × 10⁻⁵ mm and allowed to stand 24 hr prior to irradiation. Photolyses at 3500 Å were run in a Rayonet reactor. Azine-hydrazone mixtures were photolyzed using the Hanovia lamp with a 3130-Å band-pass filter.

Registry No.—Benzophenone hydrazone, 5350-57-2.

Acknowledgment.—The authors wish to thank Dr. Roger Foltz, Battelle Memorial Institute, Columbus, Ohio, for his mass spectral analyses.

(15) C. M. Welch and H. A. Smith, *J. Amer. Chem. Soc.*, **72**, 4748 (1950).

(16) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., New York, N. Y., 1966, p 785.

(12) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1957, p 289.

(13) H. H. Szmant and C. McGinnis, *J. Amer. Chem. Soc.*, **72**, 2890 (1950).

(14) P. L. Pickard and T. L. Tolbert, *J. Org. Chem.*, **26**, 4886 (1961).

Photochemistry of Thiophenes. IX.¹ Rearrangements of Alkylthiophenes and the Dithienyls

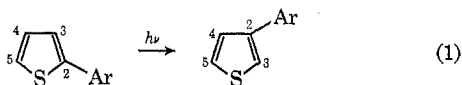
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Irradiation of 2-methyl-, benzyl-, neopentyl-, and *t*-butylthiophenes leads to their irreversible transformation to the corresponding 3-substituted derivatives. Yields vary from 8 to 27%. 2,5-Di-*t*-butylthiophene rearranges irreversibly to 2,4-di-*t*-butylthiophene which compound is remarkably stable under the reaction conditions. Irradiation of 2,2'-dithienyl leads to 2,3'-dithienyl and a small amount of benzo[*b*]thiophene. 2,3'-Dithienyl affords 3,3'-dithienyl and benzo[*b*]thiophene as major products. 5,5'-Dideuterio-2,2'-dithienyl gives 5,5'-dideuterio-2,3'-dithienyl upon irradiation while 2',5'-dideuterio-2,3'-dithienyl gives 2,5'-dideuterio-3,3'-dithienyl and 4,7'-dideuteriobenzo[*b*]thiophene. A valence bond isomerization reaction is proposed to account for the results.

We reported previously that arylthiophenes transpose ring atoms upon irradiation.² For 2-arylthiophenes these valence bond isomerizations are characterized both by an irreversible interchange of the 2- and 3-carbon atoms of the thiophene ring (eq 1) and main-



(1) Paper VIII: R. M. Kellogg and H. Wynberg, *Tetrahedron Lett.*, 5895 (1968).

(2) H. Wynberg, R. M. Kellogg, H. van Driel, and G. E. Beekhuis, *J. Amer. Chem. Soc.*, **89**, 3501 (1967), for a summary.

tenence of structural integrity in the migrating substituent.

Experiments with arylalkyl-disubstituted thiophenes indicated that the aryl group migrates in preference to the alkyl group.³ In this paper we show that simple alkylthiophenes may also rearrange, although usually in somewhat lower yield. Moreover, we find that heteroaromatic substituted thiophenes (*i.e.*, dithienyls) undergo photochemical interconversion.

(3) H. Wynberg, G. E. Beekhuis, H. van Driel, and R. M. Kellogg, *ibid.*, **89**, 3498 (1967).