

with benzene-chloroform (90-10) 0.99 g (26%) of phenyl-(4-pyridyl)-1-deuteriomethyl acetate: n_D^{20} 1.5621; nmr (CDCl_3) τ 7.94 (s, 3, acetate methyl protons), a hint of a peak at 3.15 (benzylic proton), 2.82 (doublet) partially hidden under the multiplet with a sharp peak at 2.73 (total intensity 7, β protons in pyridine and phenyl protons), 1.47 (d, 2, α protons in pyridine).

Anal. Calcd for $\text{C}_{14}\text{H}_{12}\text{DNO}_2$:¹⁵ C, 73.67; H, 5.74; D, 7.69 atom % excess. Found: C, 74.03; H, 5.85; N, 9.05 atom % excess.

Continued elution with chloroform-methanol (90-10) gave 0.80 g (25%) of 4-(α,α -dideuteriobenzyl)pyridine N-oxide: mp 103-105°; nmr (CDCl_3) identical with that of the authentic sample. A sample was recrystallized from ethyl acetate for analysis, mp 105-106°.

Anal. Calcd for $\text{C}_{12}\text{H}_9\text{D}_2\text{NO}$:¹⁵ C, 76.97; H, 5.92; D, 18.18 atom % excess. Found: C, 76.58; H, 6.03; D, 21.80 atom % excess.

Registry No.—Phenyl-4-pyridylmethyl acetate, 24929-18-8; phenyl-4-pyridylmethyl acetate picrate, 24866-72-6; 1,4-dimethylpyridinium methosulfate, 24866-73-7; 1-acetoxy-4-benzylpyridinium perchlorate, 24866-74-8; 4-(α,α -dideuteriobenzyl)pyridine N-oxide, 24866-75-9; phenyl-(4-pyridyl)-1-deuteriomethyl acetate, 24866-76-0.

Photochemistry of Unsaturated Nitrogen Containing Compounds.

VII. Photolysis of Phenylhydrazones¹

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The photochemistry of benzaldehyde phenylhydrazone (1), benzophenone hydrazone (2), benzaldehyde diphenylhydrazone (3), benzophenone phenylhydrazone (4), and benzophenone diphenylhydrazone (5) has been investigated. The products formed from these irradiations indicate that hydrazones are capable of two types of reaction. First, the nitrogen-nitrogen bond of the hydrazone system may be cleaved in a process which results in the formation of an amine and an imine (isolated in most cases as the corresponding aldehyde or ketone). In cases where the hydrazone is derived from an aldehyde, this same reaction pathway also produces a nitrile. The second type of reaction, observed only for benzaldehyde phenylhydrazone (1) and benzophenone hydrazone (2), is one which reduces the hydrazone system to a hydrocarbon; hence, this latter reaction type is a photochemical analog of the Wolff-Kishner reduction. Possible mechanisms for these two reaction processes are proposed and discussed.

As a part of a continuing study of the photochemistry of unsaturated systems containing nitrogen,² the light-induced reactions of a series of five hydrazones (1-5) have been investigated. Interest in these molecules was stimulated by recent findings arising from the photochemistry of a related group of compounds, the azines (6). Several studies during the past few years³⁻⁵ have indicated that the photolysis of azines leads either to cleavage of the nitrogen-nitrogen bond in the azine system, the major reaction pathway, or complete loss of nitrogen from the molecule, a minor process. The structural similarity between the azine (6) and hydrazone (7) systems suggested a possible similarity in their photochemical reaction.

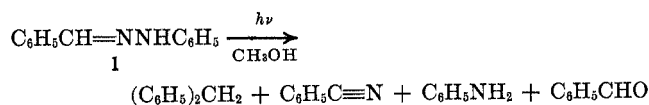


Of the five compounds studied, only benzaldehyde phenylhydrazone (1) has been mentioned previously in the chemical literature as a reactant in light-initiated processes. In these earlier reports the interest in 1 centered around the observation that it is photochromic^{6,7} and that it may undergo a photochemical *cis*-

trans isomerization;⁸ however, in no case was a general study of the photochemistry of this compound conducted. Thus, in order to establish and extend the knowledge of the photochemical reactions of hydrazones as well as to compare hydrazone (7) and azine (6) photochemistry, the following results from the photolyses of hydrazone systems 1-5 are reported.

Results

Vycor-filtered irradiation of a methanol solution of benzaldehyde phenylhydrazone (1) under nitrogen produced upon solvent removal a reddish-brown oil. Chromatography on Florisil separated the reaction mixture into five fractions, one of which was unreacted starting material. The other four were diphenylmethane (14%), benzonitrile (8%), benzaldehyde (15%), and aniline (17%). [The identity of the photo-



products in this and subsequent reactions was established in each case by comparison of the spectral properties (ir, nmr, uv) of the photoproducts with those of independently obtained samples; where possible, mixture melting point comparisons were also made.] The remainder of the reaction mixture stayed as a dark brown band at the top of the chromatography column. Elution with several different solvents failed to move

(1) For paper VI, see J. I. Sarkisian and R. W. Binkley, *J. Org. Chem.*, **35**, 1228 (1970).

(2) Part of this work has been reported in a preliminary form; see R. W. Binkley, *Tetrahedron Lett.*, 1893 (1969).

(3) R. K. Brinton, *J. Amer. Chem. Soc.*, **77**, 842 (1955).

(4) J. F. Ogilvie, *Chem. Commun.*, 359 (1965).

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

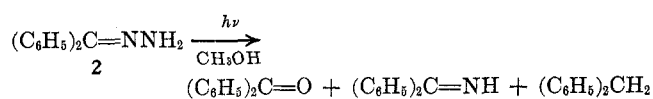
(6) G. Wettermark and A. King, *Photochem. Photobiol.*, **4**, 417 (1965).

(7) M. Padoa and T. Minganti, *Atti. Accad. Naz. Lincei, Mem., Cl. Sci. Fis. Mat. Natur. Sez. 2a*, **22**, 500 (1914).

(8) G. Condorelli and L. L. Costanzo, *Boll. Sedute Accad. Gioenia Sci. Natur. Catania*, **8** [4], 753 (1969).

this material. The course of reaction was not markedly altered by conducting the photolyses in the nonhydroxylic solvent benzene. Unfiltered irradiation of benzaldehyde phenylhydrazone (1) in methanol produced a reaction whose product yields were similar to, although generally lower than, those from the Vycor-filtered irradiation. Photolysis of a methanol solution of 1 through a Pyrex filter resulted in a gradual disappearance of starting material with benzaldehyde and aniline being the only products isolated. Benzaldehyde phenylhydrazone (1), as well as the other hydrazones studied, were subjected to the reaction conditions in the absence of light and found to be stable.

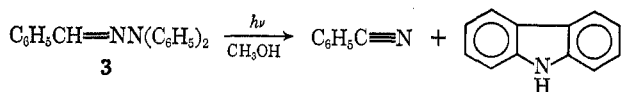
The photolysis of benzophenone hydrazone (2) in methanol under nitrogen through a Vycor filter produced, in addition to unreacted starting material, three products: benzophenone (34%), benzophenone imine (21%), and diphenylmethane (16%). The total yield of benzophenone and benzophenone imine was constant; however, the relative amounts of these two products fluctuated considerably. The yields men-



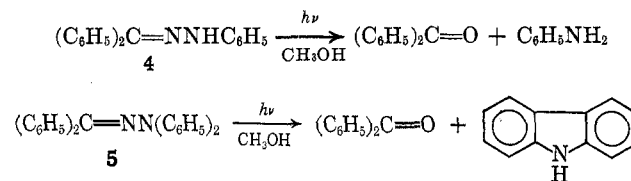
tioned for this reaction represent the highest percentage of benzophenone imine obtained. If the reaction mixture was allowed to stand overnight before work-up, no benzophenone imine was isolated. An independently synthesized sample of benzophenone imine⁹ reverted upon standing overnight to benzophenone.¹⁰ As with the irradiation of benzaldehyde phenylhydrazone (1), unfiltered photolysis of benzophenone hydrazone (2) yielded essentially the same result as the Vycor-filtered irradiation, although the yield of diphenylmethane decreased slightly. Photolysis of a mixture of hydrazine and benzophenone did not produce any of the reactions found from irradiation of benzophenone hydrazone (2). The only process observed in this mixed photolysis was a photoreduction reaction leading to benzpinacol.

Two different sets of reaction conditions had detectable effect upon the yield of diphenylmethane from irradiation of benzophenone hydrazone (2). The first of these consisted of conducting the photolyses of 2 in benzene where the yield of diphenylmethane increased to 39%. Unfortunately, the diphenylmethane formed during irradiation in benzene was difficult to separate from other hydrocarbon material which resulted from photochemical reactions of benzene itself. The second set of conditions which altered the yield of diphenylmethane from photolysis of 2 resulted when sodium hydroxide was added to the usual Vycor-filtered reaction in methanol. This modification increased the diphenylmethane yield to 31%.

Vycor-filtered irradiation of benzaldehyde diphenylhydrazone (3), the third in this series of hydrazones studied, resulted in formation of benzonitrile (30%) and carbazole (56%). No di- or triphenylmethane or di-



phenylamine¹¹ was detected in the reaction mixture. Similar Vycor-filtered irradiation of benzophenone phenylhydrazone (4) in methanol resulted in the isolation of benzophenone (19%) and aniline (17%) while benzophenone diphenylhydrazone (5) led to benzophenone (43%) and carbazole (76%).



Discussion

Since one of the goals of the present study is a comparison between azine and hydrazone photochemistry, a logical place to begin discussion of the experimental findings from this work is with the similarities which exist between the photochemical reactions of these two systems. The major reaction pathway recorded for the various aldazines which already have been investigated begins with nitrogen-nitrogen bond cleavage in the azine system and ends with the formation of a nitrile and an imine³⁻⁵ (Scheme I). The imine, in at least one case, hydrolyzes readily to the corresponding aldehyde.

Each of the five hydrazones investigated undergoes a photochemical reaction which is similar to the azine decomposition pictured in Scheme I. A ketone and an amine result from ketone hydrazone photolyses while an aldehyde, an amine, and a nitrile form when aldehyde hydrazones are irradiated. The carbonyl compounds isolated from these reactions appear to result from hydrolysis during isolation of imines formed during photochemical reaction. This proposed C=N to C=O conversion is supported by the fact that benzophenone imine can be isolated from the irradiation of benzophenone hydrazone (2) when the reaction is quickly analyzed; however, the imine thus isolated is converted to benzophenone simply upon standing in the air. A less rapid work-up of the benzophenone hydrazone (2) reaction mixture results only in isolation of benzophenone with no imine being detected. Benzaldimine, the imine anticipated from photolyses of hydrazones 1 and 3, has previously been shown to hydrolyze to benzaldehyde under the chromatographic conditions.⁶ The similarity in product identity from azine and hydrazone photolyses suggests a similarity in reaction course.

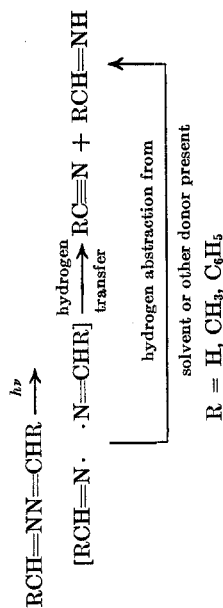
Shown in Scheme II is a mechanistic proposal for the formation of aniline, benzaldehyde, and benzonitrile from the photolysis of benzaldehyde phenylhydrazone (1). A similar process is assumed to be operative in the formation of the corresponding products from photolyses of the other four hydrazones (2-5). To the extent that these two mechanisms (Schemes I and II) are correct, the most important photochemical reaction in both hydrazone and azine photochemistry is a nitrogen-nitrogen bond cleavage. The fact that this type of reaction is observed in the photochemistry of both hydrazones and azines suggests that in other types of compounds which contain a nitrogen-nitrogen single

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

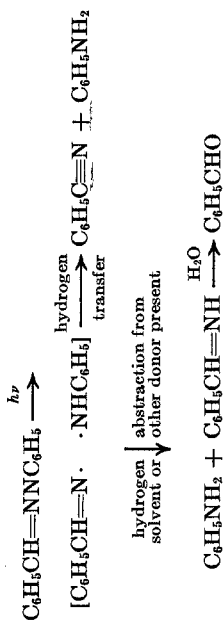
(10) A. Lachman, *Org. Syn.*, **10**, 28 (1930).

(11) Diphenylamine is converted photochemically to carbazole: see K. Grellmann, G. M. Sherman, and H. Linschitz, *J. Amer. Chem. Soc.*, **85**, 1882 (1963).

SCHEME I
FORMATION OF NITRILES AND IMINES FROM
ALDAZINE PHOTOLYSES



SCHEME II
FORMATION OF ANILINE, BENZALDEHYDE, AND BENZONITRILE
FROM BENZALDEHYDE PHENYLHYDRAZONE PHOTOLYSIS



SCHEME III
PROPOSED MECHANISM FOR PHOTOCHEMICAL
WOLFF-KISHNER REDUCTION

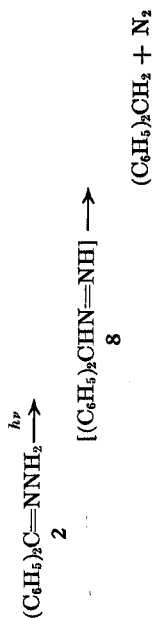
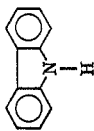


TABLE I
PHOTOCHEMICAL REACTIONS OF HYDRAZONES

Run	Hydrazone	Irradiation time, hr	Filter	% completion	Solvent	(C ₆ H ₅) ₂ CH ₂	C ₆ H ₅ C≡N	C ₆ H ₅ CHO	C ₆ H ₅ NH ₂	(C ₆ H ₅) ₂ CO
1	Benzaldehyde (1)	2.0	Vycor ^b	68	Methanol	14	8	15	17	
2	phenylhydrazone	2.0	Vycor	64	Benzene	14		12	7	
3	Benzaldehyde	1.0	None	52	Methanol	11	7	7	7	
4	phenylhydrazone	22.0	Pyrex ^c	29	Methanol	None	None	19	Trace	
5	Benzophenone (2)	4.0	Vycor	41	Methanol	26				34 ^d
6	hydrazone	4.0	Vycor	51	Methanol, NaOH	31				5 ^e
7	Benzophenone (2)	4.0	None	43	Methanol	16				17 ^f
8	hydrazone	4.0	Vycor	40	Benzene	39				45
9	Benzaldehyde (3)	2.0	Vycor	100	Methanol		30			56
10	diphenylhydrazone	4.0	Vycor	62	Methanol				17	19
11	phenylhydrazone	2.0	Vycor	100	Methanol					69
	Benzophenone (5)									39
	diphenylhydrazone									44 ^g

^a Product yields based on reacted starting material. ^b Transmits above 205 nm. ^c Transmits above 280 nm. ^d 21% benzophenone imine isolated. ^e 48% benzophenone imine isolated. ^f 44% benzophenone imine isolated.



Fractions 8–11 yielded 35 mg (0.21 mmol, 14%) of diphenylmethane, identical in ir and nmr spectra with an authentic sample²⁰ of diphenylmethane. Fractions 20–24 gave 5 mg of a deep red solid which was not further characterized. Fractions 33–36 afforded 23 mg (0.22 mmol, 15%) of benzaldehyde, identical in ir and uv spectra with an authentic sample²⁰ and forming, according to the method of Shriner, Fuson, and Curtin,²¹ benzaldehyde semicarbazone, mp 219–222° (lit.²² mp 222°). Fractions 37 and 38 produced 12 mg (0.12 mmol, 8%) of benzonitrile, identical in ir and uv spectra with a known sample of benzonitrile.²⁰ Fractions 42–50 gave 147 mg of yellow solid, mp 140–149°, recrystallized from ethanol–water to give 137 mg (0.698 mmol) of yellow crystalline benzaldehyde phenylhydrazone (1), mp 154–155° (lit.¹⁹ mp 153°). Fractions 52–56 afforded 23 mg (0.25 mmol) of yellow oil identical in ir spectrum with a known sample of aniline²⁰ and forming, upon reaction with benzoyl chloride, benzanilide, mp 160° (lit.²³ mp 163°).

Pyrex-Filtered Irradiation of Benzaldehyde Phenylhydrazone (1) in Methanol.—Benzaldehyde phenylhydrazone (221 mg, 1.12 mmol) was irradiated under exactly the same conditions as described for the Vycor-filtered irradiation in methanol except that a Pyrex filter was placed between the lamp and the reaction mixture and the irradiation time was increased to 22.0 hr. The chromatographic procedure was also the same as that described above.

The first 20 fractions contained no material. Fractions 21–24 gave 7 mg of a deep red solid, which was shown by tlc analysis to contain at least two compounds. This red material was not further characterized. Fractions 37–38 afforded 7 mg (0.07 mmol, 19%) of benzaldehyde, identified by ir spectroscopy. Fractions 39–47 yielded 156 mg (0.79 mmol) of benzaldehyde, phenylhydrazone (1), mp 150–154°. Fractions 50–55 gave a trace (less than 2 mg) of material which had the same uv spectrum as aniline.

Direct Irradiation of Benzaldehyde Phenylhydrazone (1) in Methanol.—Benzaldehyde phenylhydrazone (483.4 mg, 2.46 mmol) was irradiated under the same conditions as the Vycor-filtered irradiation of 1 except that no filter was used and the irradiation time was reduced to 1.0 hr. The chromatographic procedure was the same as that described above.

Fractions 6–10 gave 25 mg (0.15 mmol, 11%) of diphenylmethane, identified by ir spectroscopy. Fractions 17–21 gave 3 mg of red solid which was not identified. Fractions 30–32 produced 10 mg (0.09 mmol, 7%) of benzaldehyde, identified by ir and uv spectroscopy. Fractions 33 and 34 afforded 10 mg (0.09 mmol, 7%) of benzonitrile, identified by ir and uv spectroscopy. Fractions 38–48 gave 280 mg of yellow-brown solid, mp 131–139°, recrystallized from ethanol–water to give 264 mg (1.34 mmol) of benzaldehyde phenylhydrazone, mp 154°. Fractions 50–52 yielded 9 mg (0.09 mmol, 7%) of aniline, identified by ir spectroscopy.

Vycor-Filtered Irradiation of Benzaldehyde Phenylhydrazone (1) in Benzene.—Benzaldehyde phenylhydrazone (3.964 mg, 2.02 mmol) was irradiated under the same conditions as in the Vycor-filtered irradiation in methanol except that benzene was used as the reaction solvent. The chromatographic procedure was also the same.

Fractions 7–14 afforded 93.2 mg of colorless oil which appeared by ir spectroscopy to be impure diphenylmethane. These fractions were rechromatographed (see below). Fractions 22–25 gave 5 mg of a deep red solid which was not examined further. Fractions 35–40 yielded 16 mg (0.16 mmol, 12%) of benzaldehyde, identified by ir spectroscopy. Fractions 42–49 gave 254 mg (1.29 mmol) of benzaldehyde phenylhydrazone, mp 150–155°. Fractions 55–60 produced 9 mg (0.09 mmol, 7%) of aniline, identified by ir spectroscopy.

Rechromatography of fractions 7–14 from the above chromatography column in the same manner on silicic acid gave 17 mg (0.10 mmol, 14%) of diphenylmethane, identified by ir spectroscopy, in fractions 8–10.

Stability Test of Benzaldehyde Phenylhydrazone (1) under Reaction and Isolation Conditions.—Benzaldehyde phenylhydrazone (216.2 mg, 1.10 mmol) was subjected to the same reaction

and isolation conditions as described in the Vycor-filtered irradiation in methanol except that the lamp was not turned on. Unreacted starting material was recovered quantitatively.

Vycor-Filtered Irradiation of Benzaldehyde Diphenylhydrazone (3) in Methanol.—Benzaldehyde diphenylhydrazone²⁴ (271.1 mg, 0.995 mmol) was irradiated in the same way as described for the Vycor-filtered irradiation of benzaldehyde phenylhydrazone in methanol. The chromatography procedure was also the same.

The first 27 fractions contained no material. Fractions 28–36 yielded 92 mg (0.56 mmol, 56%) of carbazole, mp 244° (lit.²⁵ mp 238°). The photochemically produced carbazole was identical in ir spectrum and showed no mixture melting point depression with an authentic sample.²⁰ Fractions 38–41 afforded 31 mg (0.30 mmol, 30%) of benzonitrile, identified by ir spectroscopy.

Stability Test of Benzaldehyde Diphenylhydrazone (3) under Reaction and Isolation Conditions.—Benzaldehyde diphenylhydrazone (3) was subjected to the same reaction and isolation conditions as described in the Vycor-filtered irradiation in methanol except that the lamp was not turned on. Unreacted starting material was recovered quantitatively.

Vycor-Filtered Irradiation of Benzophenone Phenylhydrazone (4) in Methanol.—Benzophenone phenylhydrazone²⁶ (504.4 mg, 1.85 mmol) was irradiated in the same manner as that described for the Vycor-filtered irradiation of benzaldehyde phenylhydrazone (1) in methanol except that the irradiation time was 4.0 hr. The chromatographic procedure was the same as in the previous experiments.

Fractions 1–15 contained no material. Fractions 16–23 yielded 194 mg of unreacted benzophenone phenylhydrazone (4), mp 132–135° (lit.²⁶ mp 137°). Fractions 30–35 afforded 23 mg (0.27 mmol, 19%) of benzophenone, identified by ir spectroscopy. Fractions 50–55 afforded 23 mg (0.24 mmol, 17%) of aniline, identified by ir spectroscopy.

Stability Test of Benzophenone Phenylhydrazone (4) under Reaction and Isolation Conditions.—Benzophenone phenylhydrazone was subjected to the same reaction and isolation conditions as described in the Vycor-filtered irradiation of benzaldehyde phenylhydrazone (1) in methanol except that the lamp was not turned on. Unreacted starting material was recovered quantitatively.

Vycor-Filtered Irradiation of Benzophenone Diphenylhydrazone (5) in Methanol.—Benzophenone diphenylhydrazone²⁷ (359.6 mg, 1.03 mmol) was irradiated in the same manner as described for the Vycor-filtered irradiation of benzaldehyde phenylhydrazone (1) in methanol. The chromatographic procedure was also the same.

The first 18 fractions contained no material. Fractions 19–21 gave 7 mg of unreacted benzophenone diphenylhydrazone, mp 139–145° (lit.²⁷ mp 145°). Fractions 30–35 yielded 130 mg (0.78 mmol, 76%) of carbazole, mp 240–244°, identical in ir spectrum with an independent sample. Fractions 36–42 afforded 80 mg (0.44 mmol, 43%) of benzophenone, identified by ir spectroscopy.

Stability Test of Benzophenone Diphenylhydrazone (5) under Reaction and Isolation Conditions.—Benzophenone diphenylhydrazone was subjected to the same reaction and isolation conditions as described in the Vycor-filtered irradiation of benzaldehyde phenylhydrazone (1) in methanol except that the lamp was not turned on. Unreacted starting material was recovered quantitatively.

Vycor-Filtered Irradiation of Benzophenone Hydrazone (2) in Methanol.—Benzophenone hydrazone²⁸ (385.2 mg, 1.97 mmol) was irradiated in the same manner as described for the Vycor-filtered irradiation of benzaldehyde phenylhydrazone (1) in methanol except that the irradiation time was 4.0 hr. The chromatographic procedure was the same as in the previous experiments.

Fractions 8–11 yielded 28 mg (0.17 mmol, 26%) of diphenylmethane, identified by ir and nmr spectra. Fractions 34–38 gave 39 mg (0.22 mmol, 34%) of benzophenone, identified by comparison of the ir and uv spectra. Fractions 43–48 gave 24 mg (0.13 mmol, 21%) of benzophenone imine, identical in ir spectrum with that of an independently prepared sample⁹ and decomposing to benzophenone upon standing in the air. Frac-

(20) Aldrich Chemical Co., Inc., Milwaukee, Wis. 53210.

(21) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," Wiley, New York, N. Y., 1956, pp 218, 283.

(22) J. Thiele, *Justus Liebigs Ann. Chem.*, **270**, 34 (1892).

(23) H. Hubner, *ibid.*, **208**, 201 (1881).

(24) E. Fischer, *ibid.*, **190**, 179 (1878).

(25) C. Graebe and C. Glaser, *Ber.*, **5**, 12 (1872).

(26) M. Pickel, *Justus Liebigs Ann. Chem.*, **232**, 228 (1886).

(27) W. Schlenk and E. Bergmann, *ibid.*, **463**, 311 (1928).

tions 50-59 gave 260 mg (1.17 mmol) of unreacted benzophenone hydrazone, mp 95-96° (lit.²⁸ mp 98°).

Direct Irradiation of Benzophenone Hydrazone (2) in Methanol.—Benzophenone hydrazone (476 mg, 2.46 mmol) was irradiated in the same manner as described for the Vycor-filtered irradiation of benzaldehyde phenylhydrazone (1) in methanol except that no filter was used and the irradiation time was extended to 4.0 hr. The chromatographic procedure was the same as in the previous experiments.

Fractions 7-10 yielded 28 mg (0.17 mmol, 16%) of diphenylmethane, identified by ir and nmr spectroscopy. Fractions 35-39 gave 33 mg (0.18 mmol, 17%) of benzophenone, identified by ir spectroscopy. Fractions 45-51 gave 83 mg (0.46 mmol, 44%) of benzophenone imine, identified by ir spectroscopy and by spontaneous conversion to benzophenone upon standing. Fractions 52-59 produced 273 mg (1.39 mmol) of unreacted benzophenone hydrazone, mp 94-97°.

Vycor-Filtered Irradiation of Benzophenone Hydrazone (2) in Benzene.—Benzophenone hydrazone (339.1 mg, 1.73 mmol) was irradiated in the same manner as described for the Vycor-filtered irradiation of benzaldehyde phenylhydrazone (1) in methanol except that benzene was the reaction solvent and the irradiation time was extended to 4.0 hr. The chromatographic procedure was the same as in the previous experiments.

Fractions 5-10 gave 69 mg of material whose ir spectrum indicated it to be impure diphenylmethane. These fractions were rechromatographed (see following paragraph). Fractions 29-34 afforded 56 mg (0.31 mmol, 45%) of benzophenone, identified by ir spectroscopy. Fractions 43-50 produced 204 mg (1.04 mmol) of unreacted benzophenone hydrazone, mp 92-94°.

Rechromatography of fractions 5-10 under the same conditions

(28) T. Curtius and E. Rauterberg, *J. Prakt. Chem.*, **44** [2], 194 (1891).

gave 39 mg (0.23 mmol, 39%) of diphenylmethane, identified by ir spectroscopy, in fractions 5-8.

Vycor-Filtered Irradiation of Benzophenone Hydrazone (2) in Methanol Containing Sodium Hydroxide.—Benzophenone hydrazone (398 mg, 2.03 mmol) and sodium hydroxide (20 mg, 0.50 mmol) were irradiated in the same manner as described for the Vycor-filtered irradiation of 1 in methanol. The chromatographic analysis of the reaction mixture was also conducted in the same manner.

Fractions 6-8 afforded 53 mg (0.32 mmol, 31%) of diphenylmethane, identified by ir spectroscopy. Fractions 29-31 gave 9 mg (0.05 mmol, 5%) of benzophenone, identified by ir spectroscopy. Fractions 33-39 produced 89 mg (0.49 mmol, 48%) of benzophenone imine, identified by ir spectroscopy and by conversion to benzophenone upon standing. Fractions 42-52 gave 197 mg of unreacted benzophenone hydrazone (2), mp 90-94°.

Pyrex-Filtered Irradiation of Benzophenone and Hydrazine in Benzene.—Benzophenone (180 mg, 1.00 mmol) and hydrazine (128 mg, 4.00 mmol) were irradiated in the same manner as described for the Pyrex-filtered irradiation of 1 except that benzene was the solvent. The ir spectrum of the crude reaction mixture was the same as that of benzopinacol.

Registry No.—1, 588-64-7; 2, 5350-57-2; 3, 966-88-1; 4, 574-61-8; 5, 3746-21-2.

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Reactions of Ketones and Related Compounds with Solid Supported Phosphoric Acid Catalyst. IV. Rearrangement Studies of Trimethylacetaldehyde-1-¹⁴C and 3-Methyl-2-butanone-2-¹⁴C¹

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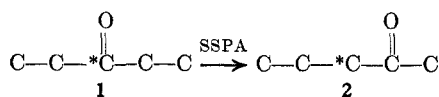
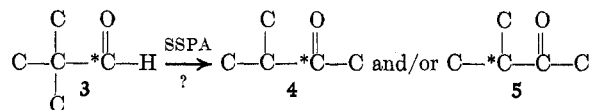
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Solid supported phosphoric acid (SSPA) treatment of trimethylacetaldehyde-1-¹⁴C at 230° gives 3-methyl-2-butanone-2-¹⁴C (4) and no 3-methyl-2-butanone-3-¹⁴C (5); no oxygen-function rearrangement takes place. Further SSPA treatment of 4 did not result in rearrangement to 5. These and related experiments where oxygen-function rearrangement does take place are rationalized in terms of relative stabilities of proposed carbonium ion intermediates.

Solid supported phosphoric acid (SSPA) is an effective catalyst for the rearrangement of aldehydes and ketones to isomeric ketones.² In agreement with previous work,³ trimethylacetaldehyde was found² to rearrange quantitatively to 3-methyl-2-butanone.

Since the 2-pentanone formed from 3-pentanone-3-¹⁴C (1) by SSPA treatment had all of the carbon-14

the SSPA-catalyzed rearrangement of trimethylacetaldehyde to 3-methyl-2-butanone.



label in the 3 position,⁴ it was of interest to see if a similar oxygen-function rearrangement would take place in

Trimethylacetaldehyde-1-¹⁴C (3), synthesized by the method of Brown and Tsukamoto,⁵ was passed once through a SSPA column² at 230°, and the resulting 3-methyl-2-butanone-X-¹⁴C was degraded to isopropyl acetate by *m*-chloroperbenzoic acid oxidation. Derivatives of the acid and alcohol parts of the ester were prepared and assayed for radio activity. The results of these experiments are shown in Table I.

Since all of the radioactivity was found in the acetanilide and none in the isopropyl derivative, it is clear that oxygen-function rearrangement does not take place during the conversion of trimethylacetaldehyde to 3-methyl-2-butanone, *i.e.*, 3 → 4 and not 5.

(1) Supported by U. S. Atomic Energy Commission Contract AT-(40-1)-3234. Paper III in this series: F. Juge and A. Fry, *J. Org. Chem.*, **35**, 1876 (1970).

(2) W. H. Corkern and A. Fry, *J. Amer. Chem. Soc.*, **89**, 5888 (1967).

(3) S. N. Danilov and E. D. Venus-Danilova, *Ber.*, **59B**, 377 (1926); H. Hopff, C. D. Nenitzescu, D. A. Isacescu, and I. P. Cantuniar, *ibid.*, **69B**, 2244 (1936).

(4) A. Fry and W. H. Corkern, *J. Amer. Chem. Soc.*, **89**, 5894 (1967).

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