of colorless distillate. To the distillate was added 50 ml of xylene and cyclohexane to afford a total volume of 1500 ml. The solution was then subjected to irradiation as shown above. The results of five recyclings are listed in Table I.

Registry No.—I, 931-87-3; II, 931-89-5; III, 111-78-4.

A Reexamination of the Effect of Benzophenone on Benzalazine Photochemistry[1]

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Several years ago it was reported that the irradiation of a mixture of benzalazine and benzophenone in cyclohexane led in moderate yield to benzonitrile.[2] The authors of this report accounted for their observation by proposing the four-step sequence given in eq 1–4.

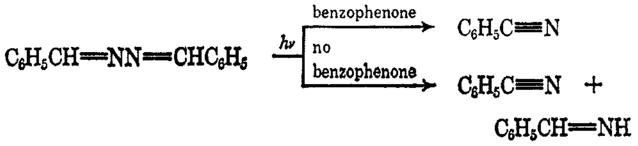
$$(C_6H_5)_2C{=}O \overset{h\nu}{\rightleftharpoons} (C_6H_5)_2C{=}O^* \qquad (1)$$

$$(C_6H_5)_2C{=}O^* + C_6H_5CH{=}NN{=}CHC_6H_5 \rightleftharpoons C_6H_5C{=}NN{=}CHC_6H_5 + (C_6H_5)_2COH \qquad (2)$$

$$C_6H_5\dot{C}{=}NN{=}CHC_6H_5 + (C_6H_5)_2C{=}O \longrightarrow 2\ C_6H_5C{\equiv}N + (C_6H_5)_2\dot{C}OH \qquad (3)$$

$$2\ (C_6H_5)_2\dot{C}OH \longrightarrow \text{benzpinacol} \qquad (4)$$

More recently, other studies[3,4] have shown that, in the absence of benzophenone, benzalazine still reacts photochemically to give benzonitrile, although in lower yield; however, with reactions run with no benzophenone present, an approximately equal amount of benzaldimine (isolated as benzaldehyde, its hydrolysis product) also is formed. In an effort to understand the unusual influence of benzophenone upon the photochemistry of benzalazine, a detailed study of this reaction was undertaken.



When benzophenone and benzalazine were jointly irradiated in cyclohexane under nitrogen (run 1, Table I), the starting materials rapidly disappeared, but surprisingly, only trace amounts (<1%) of benzonitrile were formed. Since the original description of this reaction[2] did not comment on the exclusion of oxygen, a second set of experiments was conducted in which oxygen was purposely added during photolysis. In the presence of oxygen, the reported benzonitrile yield was realized, although a significant quantity of benzaldehyde was still isolated[5] (run 2, Table I). These second experiments clearly suggested that the critical factor in this reaction was the presence of oxygen and not benzophenone. To confirm this suggestion, benzalazine was irradiated under oxygen without benzophenone and was found to produce benzonitrile in high yield (run 3, Table I).

TABLE I

IRRADIATIONS OF BENZALAZINE IN CYCLOHEXANE[a]

Run	Atmosphere	Substance added	Time, hr	Completion	Product Yield,[b] mg	
					Benzonitrile	Benzaldehyde
1	Nitrogen	Benzophenone[c]	4.0	100	Trace	Trace
2	Oxygen	Benzophenone[c]	20.0	44	43 mg	15 mg
3	Oxygen	None	20.0	39	55 mg	15 mg
4	Nitrogen	None	10.0	40	15 mg	18 mg

[a] One millimole of benzalazine was irradiated in each run. [b] Product yield is given in mg of product per 100 mg of reactant consumed to avoid confusion, since each molecule of reactant can produce two molecules of product. [c] Two millimoles of benzophenone were added.

On the basis of these results, it is concluded that (a) the critical element responsible for the increased benzonitrile yield in the photochemistry of benzalazine is the presence of oxygen and not benzophenone; (b) the mechanism previously proposed[2] involving benzophenone in the photodecomposition of benzalazine is incorrect.

The observed influence of oxygen on this reaction is understandable in terms of the mechanism previously proposed for benzalazine decomposition under direct irradiation.[3] This mechanism, which has been shown to be consistent with the effect of hydrogen donors on benzalazine photolysis,[4] suggests that excitation of benzalazine results in a homolytic cleavage the nitrogen–nitrogen bond, producing two $C_6H_5CH{=}N$ radicals which may either react directly (a disproportionation reaction) to give benzonitrile and benzaldimine or may diffuse apart in solution. If the existence of $C_6H_5CH{=}N$ radicals in solution is combined with the fact that radicals of this type are known to be oxidized by molecular oxygen to nitriles[6] (eq 5),

$$RCH{=}NH + Cu(II) \longrightarrow H^+ + Cu(I) + [RCH{=}N\cdot] \xrightarrow{O_2} RC{\equiv}N + HO_2\cdot \qquad (5)$$

the increased benzonitrile yield from the oxygenated irradiations of benzalazine is the logical result of the interaction between oxygen and $C_6H_5CH{=}N$ radical species.

Experimental Section

The irradiation and isolation procedure used in each of the reactions described in the text was identical; therefore, only one of these reactions will be described in detail.

Direct Irradiation of Benzalazine in Cyclohexane under Oxygen.—Benzalazine (208.3 mg, 1.0000 mmol) in 300 ml of cyclohexane was irradiated at 25.0° with constant stirring for 20.0 hr, using a 100-W Hanovia high-pressure quartz mercury-vapor lamp which had been lowered into a water-cooled quartz immersion well. Oxygen was passed through the solution for 1 hr prior to irradiation and a slow stream of oxygen was continued during photolysis.

After 20 hr, the solvent was removed by distillation *in vacuo* below 30°, producing a yellow oil. This oil was chromatographed

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[1] Part IV in a series entitled "The Photochemistry of Unsaturated Nitrogen-Containing Compounds."

[2] J. E. Hodgkins and J. A. King, *J. Amer. Chem. Soc.*, **85**, 2680 (1963).

[3] R. W. Binkley, *J. Org. Chem.*, **34**, 2311 (1968).

[4] R. W. Binkley, *ibid.*, **34**, 2072 (1969).

[5] All attempts to isolate the benzhydrol indicated (ref 2) to be a reaction product (eq 4) have at present been unsuccessful. No evidence could be obtained for the formation of benzpinacol.

[6] W. Brackman and P. J. Smit, *Rec. Trav. Chim.*, **82**, 757 (1963).

on a 100 × 2.2 cm Florisil column slurry packed in 1:9 ether–hexane; 20-ml fractions were collected. The column was eluted as follows: 0.5 l. of hexane; 0.5 l. of 1:99 ether–hexane; 0.5 l. of 1:49 ether–hexane; 1.0 l. of 1:24 ether–hexane; 0.5 l. of 1:12 ether–hexane; and 0.5 l. of 1:6 ether–hexane.

Fractions 82–119 yielded 117 mg of benzalazine as yellow crystals, mp 91–94°. Fractions 121–131 gave 13.8 mg of a clear oil identified as benzaldehyde by comparison of ir and uv spectra with those of a known sample. Fractions 134–168 afforded 39.4 mg of a clear liquid identified as benzonitrile also by comparison of the ir and uv spectra of the photoproduct with those of a known sample of benzonitrile.

Registry No.—Benzophenone, 119-61-9; benzalazine, 588-68-1.

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Deoxygenation and Chlorination of Azoxybenzene by Acidic Halides[1]

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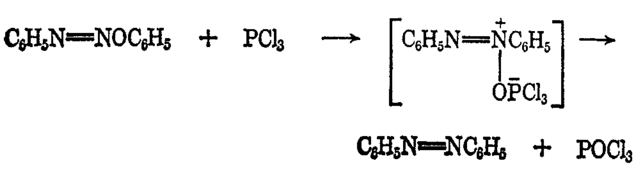
Recent investigations[2–4] of the mechanism of the Wallach rearrangement[5] of azoxybenzene to *p*-hydroxyazobenzene induced by chlorosulfonic acid led to the identification of small amounts of azobenzene and *p*-chloroazobenzene as additional products of this reaction.[6] This suggested the possibility of the initial formation of an intermediate product through chlorosulfonation of the oxygen of azoxybenzene followed either by rearrangement and decomposition to *p*-chloroazobenzene or by direct decomposition to azobenzene. This also indicated the possibility of a much simpler general method for preparing halogenated azo compounds than those that are now available.

Deoxygenation of Azoxybenzene.—Azoxybenzene is deoxygenated to azobenzene by certain acidic halides which can undergo oxidation. Scheme I, which suggests a possible way in which this transformation may occur in the deep red reaction mixture, shows phosphorus trichloride being oxidized to phosphorus oxychloride as azoxybenzene is reduced to azobenzene practically quantitatively. Other observations which appear in the Experimental Section show similar results that were obtained with several other inorganic acidic halides. Acetyl bromide and acetyl iodide also yield azobenzene in this reaction below 20°. At higher temperatures, these halides lead to the formation of some aniline and benzidine in addition to azobenzene.

SCHEME I

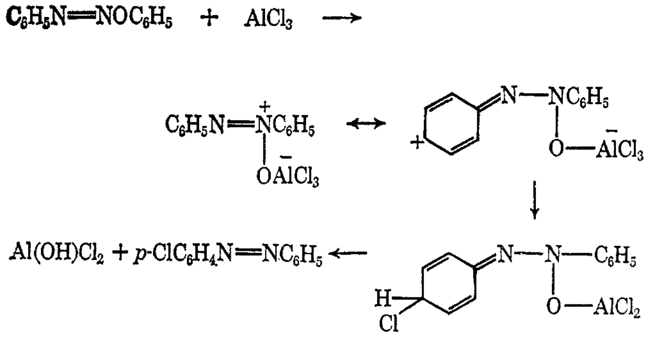


$$C_6H_5N{=}NOC_6H_5 + PCl_3 \longrightarrow \left[C_6H_5N{=}\overset{+}{N}C_6H_5\ (\bar{O}PCl_3)\right] \longrightarrow C_6H_5N{=}NC_6H_5 + POCl_3$$

Deoxygenation of Azoxybenzene with Chlorination.—The unusual deoxygenation and chlorination of azoxybenzene by aluminum chloride was observed under various conditions. A solid mixture of aluminum chloride and azoxybenzene reacts spontaneously and highly exothermically after a brief induction period. This reaction is violent at 40° in molten azoxybenzene. However, in refluxing carbon disulfide the red reaction mixture yields *p*-chloroazobenzene in 83% yield *via* a smooth reaction. Similar results are obtained in a refluxing acetyl chloride solution of molar equivalent amounts of azoxybenzene and aluminum chloride. Both of these procedures are recommended for the preparation of *p*-chloroazobenzene over the Curtin and Ursprung[7] method because of their simplicity and high yield of product.

Ferric chloride may replace aluminum chloride in this reaction, but the yield of *p*-chloroazobenzene is usually smaller. However, aluminum bromide and aluminum iodide reduce azoxybenzene to azobenzene even under mild conditions (0°). It was also noted that aluminum chloride fails to convert azoxybenzene to *p*-chloroazobenzene if any halide that deoxygenates azoxybenzene is present in the reaction mixture. This suggests that preferential deoxygenation of azoxybenzene by reducing halides prevents the aluminum chloride from reacting as proposed in Scheme II, which attempts to present a possible rationalization of the manner in which this reaction occurs under mild conditions.

SCHEME II



The reaction of azoxybenzene in benzenesulfonyl chloride in the presence of ferric chloride is more complex. A small amount of *p*-chloroazobenzene and a product which was characterized as a sulfone are formed in this reaction. As ferric chloride appears to function as a Friedel–Crafts catalyst in this reaction as well as the chlorinating agent, the yield of *p*-chloroazobenzene is improved by increasing the concentration of ferric chloride in the reaction mixture. Aluminum chloride is much less effective than ferric chloride in this reaction.

Azoxybenzene, aluminum chloride, and sulfuryl chloride react to form *p*-chloroazobenzene and *p,p′*-dichloroazobenzene. An increase in the molar ratio of alu-

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(1) Supported in part by the Research Committee of the Graduate School of the University of Wisconsin from special funds voted by the State Legislature and by a research grant from the University of Wisconsin Center System.

(2) M. Shemyakin, V. Maimind, and B. Vaichunaite, *Chem. Ind.* (London), 755 (1958).

(3) M. Shemyakin, V. Maimind, and Ts. E. Agaadzhanyan, *ibid.*, 1223 (1961).

(4) P. Gore, *ibid.*, 191 (1959).

(5) O. Wallach and L. Belli, *Ber.*, **13**, 525 (1880).

(6) I. Pearl and A. Ronzio, *J. Org. Chem.*, **12**, 785 (1947).

(7) D. Curtin and J. Ursprung, *ibid.*, **21**, 1221 (1956).