(25 g) and KI (75 g) were refluxed in 350 ml of methyl ethyl ketone. The solvent was evaporated, the residue washed with water, and recrystallized from benzene to give starting material.

Attempted Bromodechlorination of 2-Chloro-3-nitropyridine.—The molar ratio was 0.08 mol of aryl chloride and 0.416 mol of LiBr. In three experiments, methyl ethyl ketone, glacial acetic acid, and dimethyl sulfoxide were used as the solvent. Starting material was recovered when no acid was added to methyl ethyl ketone. In each case, the reaction mixture was refluxed for several hours, then the product isolated by pouring the reaction mixture on ice. If the product did not precipitate immediately, the solvent was removed by evaporation to obtain the solid product. The melting point of the product was 118–120°, and did not change with recrystallization. Potentiometric titration of the halide by silver nitrate showed the presence of both bromide and chloride ions.

Registry No.—Sulfuric acid, 7664-93-9; 2-bromo-5-nitropyridine, 4487-59-6; 2-chloro-3-nitropyridine, 5470-18-8; 2-iodo-5-nitropyridine, 19755-52-3; 2-bromo-3-nitropyridine, 19755-53-4.

The Photochemistry of Unsaturated Nitrogen Containing Compounds. II. The Mechanism of Benzonitrile and Benzaldimine Formation during Irradiation of Benzalazine

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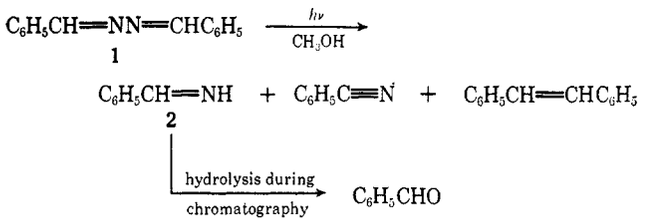
The photochemical reaction of benzalazine (1) to give benzonitrile and benzaldimine (2) was studied in the presence of various hydrogen donors in an effort to obtain information which would determine whether the mechanism for this photochemical transformation is inter- or intramolecular. These studies showed that with the addition of effective hydrogen donating agents such as benzhydrol and decyl mercaptan a definite decrease in product yield occurred; however, a limiting value in the decrease of this yield was reached beyond which further addition of trapping agents had no effect. These results are interpreted as indicative of both intra- and intermolecular reaction being operative in the photochemical conversion of benzalazine (1) to benzonitrile and benzaldimine (2). Mechanisms for these two processes are presented and discussed.

In the previous publication in this series[1] it was shown that benzalazine (1) reacted photochemically to produce benzonitrile, benzaldimine (2), and *trans*-stilbene. Benzaldimine (2) was discovered to be an

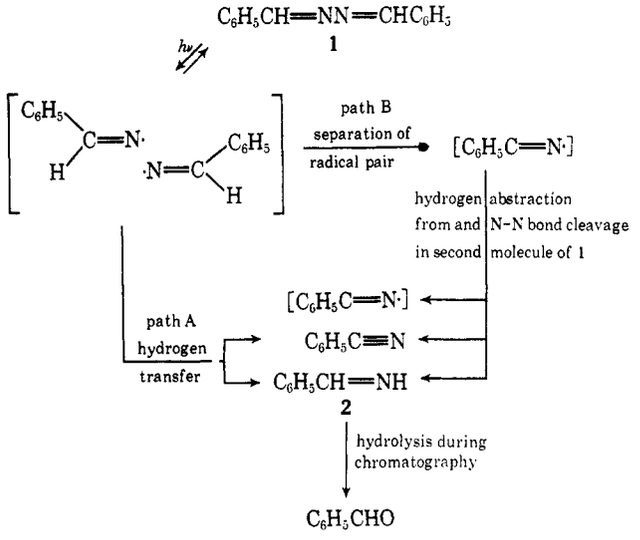


unstable photoproduct which hydrolyzed to benzaldehyde during chromatography. Two mechanisms were proposed at the time of the previous study in order to rationalize the apparently coupled benzonitrile–benzaldimine (2) formation (Scheme I); unfortunately, it was not feasible at that time with the evidence available to make a choice between these two mechanistic possibilities.

The fundamental difference between the two pathways under consideration (Scheme I) exists in the fact that path A postulates an intramolecular reaction mechanism with a hydrogen transfer which occurs within the solvent cage (a disproportionation within the solvent cage of the photochemically produced radical pair) while path B, in contrast, proposes an intermolecular reaction which requires the diffusion of the $C_6H_5CH{=}N$ radical through solution (*i.e.*, escape of the radical species from the solvent cage prior to further reaction) to react with a second molecule of benzalazine (1) in a hydrogen abstraction process. Accordingly, reaction *via* path A should be effectively insensitive to the presence of radical trapping agents in solution while a process such as that indicated by path B should show

SCHEME I

FORMATION OF BENZONITRILE AND BENZALDEHYDE FROM BENZALAZINE (1)



a change in reaction course in a solution where the $C_6H_5CH{=}N$ radical could be intercepted and could undergo reaction before reaching a benzalazine (1) molecule. As a basis for selection between these two possible pathways, a series of irradiations was undertaken in which alcohols with different hydrogen-donating abilities were used as reaction solvents; in addition, a number of reactions were also conducted in which decyl mercaptan was present in the reaction mixtures in various concentrations.

Results

The data given in Table I described the Vycor-filtered irradiations of benzalazine (1) with four dif-

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

TABLE I

PHOTOCHEMICAL REACTIVITY OF BENZALAZINE (1)[a]

Run no.	Time, hr	% completion	Solvent	Trapping agent	% yield of products[b] Benzonitrile	Benzaldehyde
1	11	25	2-Methyl-2-propanol	None	46	44
2	12	26	Methanol[c]	None	40	46
3	10	26	Ethanol	None	40	44
4	9	27	2-Propanol	None	35	48
5	10	25	2-Propanol	2.00 mmol of benzhydrol	25	48
6	10	22	2-Propanol	4.00 mmol of benzhydrol	25	52

[a] All runs made with a Vycor filter which removes light of wavelength shorter than 210 mμ. In each run 1.00 mmol of benzalazine was irradiated. [b] The per cent yield of a product is calculated by dividing the millimoles of product by millimoles of reactant consumed and multiplying by 100. [c] Product yield is slightly greater then reported earlier (ref 1) due to improved isolation procedure.

ferent alcohols as reaction solvents and irradiations in which a fifth alcohol was present in the reaction mixtures. A clear decrease in the yield of benzonitrile is apparent as one proceeds from run 1 to run 6 in Table I. The yield of benzaldehyde, on the other hand, shows little change under these different reaction conditions. (Since each molecule of benzalazine is potentially capable of producing both a molecule of benzonitrile and one of benzaldehyde, a 100% yield of each of these products is theoretically possible in any reaction.)

In Table II are listed the results of the irradiation of benzalazine (1) in 2-propanol with various amounts of added decyl mercaptan. An inspection of this table reveals that the addition of the mercaptan causes an initial decrease of 10% in the benzonitrile yield when compared to an irradiation run in pure 2-propanol; however, once the nitrile yield reaches 25% it remains constant and is not further changed by addition of more mercaptan. The effect of added decyl mercaptan on the yield of benzaldehyde is noticeably different from its effect on the benzonitrile yield since the amount of benzaldehyde isolated progressively decreases as more mercaptan is added.

TABLE II

THE PHOTOCHEMICAL REACTIVITY OF BENZALAZINE (1) IN THE PRESENCE OF DECYL MERCAPTAN

Run	Mercaptan concn, mmol/l.	% completion	% yield of products Benzonitrile	Benzaldehyde
1	0.00	27	35	45
2	0.10	25	27	44
3	0.33	25	24	40
4	0.66	25	25	40
5	3.33	25	25	33

Discussion

As was described in the introductory portion of this paper, the two proposed mechanisms for conversion of benzalazine (1) into benzonitrile and benzaldimine differ in that one occurs entirely within the solvent cage (path A, Scheme I) and the other requires escape from this solvent shell (path B, Scheme I). A logical method for distinguishing between these two possibilities consists of conducting irradiations of 1 in the presence of a substance capable of intercepting the $C_6H_5CH{=}N$ radical and, thereby, stopping any intermolecular process involving this species; unfortunately, selection of a suitable trapping agent is not an easy task since common free radical traps such as 2,2-diphenyl-1-picrylhydrazyl, galvinoxyl, and I_2 used in normal free radical reactions absorb light and are photochemically decomposed.[2] Two different types of compounds were found, however, which were acceptable as trapping agents under the conditions of these irradiations.

It is important to note in connection with the interpretation of the experimental results from this work that the yield of benzonitrile and not benzaldehyde is taken as the critical indicator of the ability of a trapping agent to affect the photochemical conversion of benzalazine (1). The reason for this choice can be seen from a consideration of Scheme I. In the proposed intermolecular reaction mechanism for decomposition of 1 (path B, Scheme I), the mechanism representing the reaction pathway assumed to be sensitive to radical traps, benzonitrile can only arise *via* diffusion of the $C_6H_5CH{=}N$ radical (or other radical species) through solution to abstract a hydrogen atom from a molecule of benzalazine (1); in contrast, benzaldimine (2), the precursor of benzaldehyde, might arise by hydrogen abstraction of the $C_6H_5CH{=}N$ radical from the solvent or other hydrogen donor present. Therefore, if path B is operative, only the yield of benzonitrile is necessarily dependent upon diffusion through solution of a radical species capable of abstracting a hydrogen atom from benzalazine (1). In considering B as a pathway for understanding benzonitrile production, it is important to emphasize that a hydrogen transfer resulting in benzonitrile formation can occur from benzalazine (1) to radical species other than the $C_6H_5CH{=}N$ radical; therefore, in order for the hydrogen donors used in this work to be effective radical traps, they must react with a $C_6H_5CH{=}N$ radical or other radicals present to give stable molecules and new radical species, ones which are not capable of abstracting a hydrogen atom from benzalazine (1).

The first method used in attempting to intercept the $C_6H_5CH{=}N$ radical consisted of a series of irradiations using various alcohols and mixtures of alcohols as reaction solvents. Unlike ionic reactions of alcohols in which an oxygen–hydrogen bond is generally more readily broken than carbon–hydrogen bond, radical-induced hydrogen atom abstractions favor loss of a hydrogen atom attached to the alcohol carbon if such a hydrogen exists;[3,4] presumably this phenomenon is

(2) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., New York, N. Y., 1967, p 603.

(3) W. H. Urry, F. W. Stacey, E. S. Huyser, O. O. Juveland, *J. Amer. Chem. Soc.*, **76**, 450 (1954).

(4) W. A. Pryor, "Free Radicals," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, p 219.

due to the ability of the hydroxyl group to participate in the stabilization of the radical center being formed.[5] With this fact in mind, methanol, ethanol, 2-propanol, and 2-methyl-2-propanol were closed as irradiation solvents. Of these four alcohols only 2-methyl-2-propanol has no hydrogen directly attached to an alcohol carbon; consequently, it among the four should be most resistent to free radical attack.[4,5] Methanol, ethanol, and 2-propanol, on the other hand, each have at least one hydrogen attached to the hydroxyl carbon and, therefore, are much more effective hydrogen donors.[6,7] Benzhydrol, which was added to two of the irradiations in 2-propanol, represents the most effective hydrogen donor of the alcohols used since in benzhydrol the radical center formed by hydrogen abstraction is not only adjacent to an OH group but it also stabilized by delocalization involving the benzene rings. Using these five alcohols as hydrogen donors provides at least three distinctly different levels of effectiveness in the hydrogen-donating ability of the reaction medium.

From an inspection of Table I it is clear that the yield of benzonitrile decreases as the hydrogen-donating ability of the solvent increases; however, even with benzhydrol present in a fourfold greater concentration than benzalazine (1), the yield of benzonitrile remains substantial. Comparing run 5 with run 6 of Table I reveals that a certain limiting value is apparently reached in the decrease of benzonitrile yield; thus, although addition of benzhydrol to an irradiation in 2-propanol reduces the benzonitrile formed, doubling the amount of benzhydrol present from 2.00 (run 5) to 4.00 mmol (run 6) does not change the yield further. It is necessary to be careful in placing too great an emphasis on reactions conducted in the presence of benzhydrol since it alone among the alcohols used absorbs light during irradiation. (In a control experiment benzhydrol also showed slight photochemical decomposition.) Although this fact does not necessarily negate the effectiveness of benzhydrol in these reactions, it does suggest that independent confirmation of these results by a second trapping agent would be valuable.

The second hydrogen donor selected as a trapping agent was decyl mercaptan. Mercaptans are well known for their ability to donate hydrogen atoms in radical abstraction reactions;[8] in addition, to this necessary qualification the problem of light absorption by the trapping agent is greatly reduced by the selection of this compound.

The results of irradiations of benzalazine (1) in the presence of various amounts of mercaptan are shown in Table II. A clear and significant parallel exists between the previously described irradiations using various alcohols and the results shown for the decyl mercaptan irradiations; namely, in each set of reactions the benzonitrile yield decreases until a limiting value is reached. This value is the same (25%) both in the presence of decyl mercaptan and in the presence of the most effective of the alcohols, benzhydrol.

On the basis of the considerations made thus far the following facts are clear. (a) The yield of benzonitrile in the photochemical reactions of benzalazine (1) is the best available indicator of the intervention of hydrogen donors in a potential intermolecular benzonitrile–benzaldimine (2) forming process. (b) The yield of benzonitrile decreases as the hydrogen-donating effectiveness of the medium increases; however, a limiting value exists beyond which further dimunition in yield does not occur. (c) The limiting value beyond which further reduction of yield of benzonitrile by hydrogen donors does not appear possible is the same whether benzohydrol of decyl mercaptan is used as the hydrogen-donating agent.

The first conclusion which reasonably can be drawn from these three facts is that since the majority of the benzonitrile (25%) arises *via* a pathway insensitive to effective hydrogen donors, the major reaction pathway is, logically, intramolecular. In terms of the mechanisms shown in Scheme I, therefore, the predominate mode of reaction can be represented by path A.

Although in path A a two-step sequence is proposed involving first the cleavage of a nitrogen–nitrogen bond and, second, the transfer of a hydrogen atom, there are no experimental facts requiring this particular timing. It is possible that these two processes could occur, at least in part, simultaneously. It is also conceivable that hydrogen transfer could precede nitrogen–nitrogen bond cleavage. The precise timing of these events is not known. The important factor is that the major process operative here occurs within the solvent cage and that path A (Scheme I) represents a reasonable conception for the mode of occurrence of such a reaction.

In addition to the portion of benzalazine (1) to benzaldimine (2) and benzonitrile reaction which gives evidence of being intramolecular, a substantial amount of this reaction is decidely influenced by the presence of solvents of different hydrogen-donating abilities and also by the addition of radical trapping agents to reaction mixture. The fact that a clear minimum in benzonitrile yield is reached beyond which further hydrogen donor addition has no effect argues well for the existence of an inter- as well as an intramolecular process. Clearly a reaction exists which is first hindered and then essentially stopped by the addition of hydrogen donors. If the benzonitrile yield were being decreased simply by an increase in the consumption of benzalazine (1) due to new reactions in the presence of effective hydrogen donors, the decrease in yield logically would have continued as greater amounts of hydrogen donors were added. Since such a continued decrease was not observed, the most reasonable explanation is that, in the absence of effective hydrogen donors, intermolecular reaction contributes to benzonitrile formation.

It is of interest to note two other studies on azine photochemistry. The vapor phase irradiation of both formaldazine[9] and acetaldazine[10] have been reported, although only the latter was studied in detail. Similar to benzalazine (1) irradiations, the major products from

(5) S. G. Cohen and H. M. Chao, *J. Amer. Chem. Soc.*, **90**, 165 (1968).

(6) 2-Propanol is probably the most widely used hydrogen atom source in photochemical reactions; in fact, it has been referred to in at least one text[7] as a "standard hydrogen donor."

(7) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1967, p 144.

(8) F. W. Stacey and J. F. Harris, Jr., in "Organic Reactions," Vol. 13, A. C. Cope, Ed., John Wiley & Sons, Inc., New York, N. Y., 1963, pp 166–167; (b) W. A. Pryor, "Free Radicals," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, p 216; (c) C. Walling, "Free Radicals in Solution," John Wiley & Sons, Inc., New York, N. Y., 1957, p 314.

(9) J. F. Ogilvil, *Chem. Commun.*, 359 (1965).

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

acetaldazine photolyses are acetonitrile and acetaldimine. In studying the mechanism of formation of these photoproducts[10] it was concluded that acetonitrile and acetaldimine were formed in these reactions in an intramolecular process. The differences in reaction medium and reactant structure make unprofitable at this time a comparison of the present work on benzalazine with that previously reported[10] for acetaldazine.

In summary, the results from study of the mechanism of the benzalazine (1) to benzonitrile–benzaldimine (2) conversion suggest that this reaction is capable of taking place *via* both intra- and intermolecular pathways. This conclusion is based primarily upon the fact that addition of radical trapping agents to the reaction mixtures decreases the amount of benzonitrile formation initially but a definite minimum is reached beyond which further addition of the trapping agents is ineffective.

Experimental Section[11]

Irradiation of Benzalazine (1) in 2-Methyl-2-propanol Using a Vycor Filter.—In a typical run 208.3 mg (1.000 mmol) of benzalazine[12] (1) in 300 ml of 2-methyl-2-propanol at 25.0° was irradiated with constant stirring for 11 hr using a 100-W Hanovia high-pressure quartz mercury-vapor lamp which had been lowered into a water-cooled quartz immersion well. A Vycor filter was introduced between this light source and the reaction mixture. Prepurified nitrogen was passed through the solution for 1 hr prior to irradiation and a slow stream of nitrogen was continued during photolysis.

After 11 hr, the solvent was removed by distillation *in vacuo* below 30° producing a distillate which was transparent in the uv spectrum and leaving a yellow solid. This solid was chromatographed on an 80 × 2.5 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 90–122 yielded 156 mg of benzalazine (1) as yellow crystals, mp 92–94°. Fractions 123–133 afforded 11.7 mg (44%) of clear oil which gave the ir spectrum of benzaldehyde. Treatment of these fractions with semicarbazide hydrochloride according to the method of Shriner, Fusion, and Curtin[13] produced benzaldehyde semicarbazone, mp 219–222° (lit.[13] mp 222°). Fractions 134–170 gave 11.8 mg (46%) of a clear oil identical in ir and iv spectra with a known sample of benzonitrile. Control experiments concerned with the stability of the reactant and products under isolation conditions have been previously described.[1]

Irradiation of Benzalazine (1) in Methanol Using a Vycor Filter.—The procedure and material involved were the same as those described for the irradiation in 2-methyl-2-propanol. The only change was methanol was used as the reaction solvent.

Fractions 81–120 produced 160 mg of yellow solid, mp 86–89°, recrystallized from hexane to give 153 mg of benzalazine, mp 90–93°. Fractions 121–134 gave 12.7 mg of benzaldehyde, identified by ir spectroscopy. Fractions 135–154 afforded 10.7 mg of benzonitrile, identified by ir and uv spectroscopy.

Irradiation of Benzalazine (1) in Ethanol Using a Vycor Filter.—The procedure and materials used were the same as those described for the irradiation in 2-methyl-2-propanol except ethanol was used as the reaction solvent.

Fractions 89–119 gave 155 mg of benzalazine, mp 91°. Fractions 121–134 afforded 11.4 mg of benzaldehyde, identified by ir spectroscopy. Fractions 139–159 produced 10.7 mg of benzonitrile, identified by ir and uv spectroscopy.

Irradiation of Benzalazine (1) in 2-Propanol Using a Vycor Filter.—The procedure and substances used were the same as those described for the irradiation in 2-methyl-2-propanol. The only change was that 2-propanol was used as the solvent.

Fractions 91–125 afforded 162 mg of yellow solid, mp 80–85°, recrystallized from hexane to give 152 mg of benzalazine, mp 90–91°. Fractions 126–135 gave 13.0 mg of benzaldehyde, identified by ir spectroscopy. Fractions 140–160 gave 9.5 mg of benzonitrile, identified by ir and uv spectroscopy.

Irradiation of Benzalazine (1.00 Mmol) and Benzhydrol (2.00 Mmol) in 2-Propanol Using a Vycor Filter.—Benzalazine (208.3 mg, 1.000 mmol) and benzhydrol (358 mg, 2.00 mmol) in 300 ml of 2-propanol at 25.0° were irradiated in the normal manner. The isolation scheme was the same as that used in the irradiation run in 2-methyl-2-propanol.

Fractions 60–83 gave 320 mg of benzhydrol, mp 60–65°. Fractions 95–122 yielded 146 mg of benzalazine, mp 90–94°. Fractions 123–135 afforded 14.4 mg of benzaldehyde identified by ir spectroscopy. Fractions 136–154 gave 7.5 mg of benzonitrile, identified by ir and uv spectroscopy.

Irradiation of Benzalazine (1.00 Mmol) and Benzhydrol (4.00 Mmol) Using a Vycor Filter.—The procedure and materials used were the same as in the above irradiation with added benzhydrol except that the benzhydrol concentration was doubled. The isolation procedure and results were essentially the same.

Irradiation of Benzalazine (1.00 Mmol) and Decyl Mercaptan (1.00 Mmol) in 2-Propanol.—Benzalazine (208.3 mg, 1.00 mmol) and decyl mercaptan (174 mg, 1.00 mmol) in 300 ml of 2-propanol at 25.0° were irradiated in the usual manner. The isolation procedure was the same as that used in the irradiation run in 2-methyl-2-propanol.

Fractions 22–40 afforded 144 mg of decyl mercaptan, identified by ir spectroscopy. Fractions 90–121 gave 167 mg of yellow solid, mp 85–89°, recrystallized from hexane to give 146 mg of benzalazine, mp 89–91°. Fractions 122–135 produced 14.1 mg of benzaldehyde, identified by ir spectroscopy. Fractions 136–160 produced 7.5 mg of benzonitrile, identified by ir and uv spectroscopy.

Irradiation of Benzalazine (1.00 Mmol) and Decyl Mercaptan (2.00 Mmol) in 2-Propanol.—The procedure and materials used were the same as in the above irradiation with added decyl mercaptan except that the mercaptan concentration was doubled. The isolation procedure and results were essentially the same.

Irradiation of Benzalazine (1.000 Mmol) and Decyl Mercaptan (10.0 Mmol) in 2-Propanol.—The procedure and materials used were the same as in the above irradiation with added decyl mercaptan except that the mercaptan concentration was doubled. The isolation procedure and results were essentially the same.

Registry No.—1, 588-68-1; 2, 16118-22-2; benzonitrile, 100-47-0.

Acknowledgment.—Appreciation is gratefully expressed to the Research Corp. for support of this work.

(11) All melting points were taken on a Fisher-Johns block and are corrected.

(12) T. Curtius and R. Jay, *J. Prakt. Chem.*, **39**, 45 (1889).

(13) R. L. Shriner, R. C. Fusion, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley & Sons, Inc., New York, N. Y., 1956, pp 218 and 283.