To test this intermediate, we fortified the reaction with $HgCl_2$. There was no evidence found to indicate any *n*-alkyl chloride formed.

Experimental Section

Preparation of Br_2O.—A solution of Br_2O in CCl_4 was prepared by mechanically stirring 6.8 ml (19.9 g, 0.125 mol) of Br_2, 60 g (0.278 mol) of red HgO, and 300 ml of CCl_4 in a 500-ml round-bottom flask fitted with a reflux condenser. The solution was maintained at 45° and light was excluded. After 90 min, the solution was cooled to −20° by a Dry Ice–methanol bath and 80 g (0.359 mol) of fresh HgO was added. Stirring was continued for 30 min followed by filtration to remove the $HgBr_2$ and unreacted HgO.

The filtrate was then connected to a vacuum line and the contents transferred slowly at −25°. The CCl_4 and Br_2 transfers first leaving a brownish green solid which when transferred and collected gives the uv spectrum reported for Br_2O.[3]

Preparation of the Alkyl Halide.—In a typical experiment, the Br_2O in CCl_4 solution is added, via a pressure equalized dropping funnel, to 250-ml flask containing 4.4 g (0.043 mol) of *n*-pentanoic acid which is dissolved in 50 ml of CCl_4. The solution was refluxed in the dark during the addition of Br_2O which took approximately 75 min. The solution was then allowed to reflux for an additional 15 min. Products were analyzed by isolation and vapor phase chromatography.

Registry No.—Br_2O, 21308-80-5.

(3) (a) W. Brenschede, and H. J. Schumaker, *Z. Physikol. Chem.*, **29B**, 356 (1935); (b) W. Brenschede, and H. J. Schumaker, *Z. Anorg. Chem.*, **226**, 370 (1936).

Photoisomerization of *cis*-Cyclooctene to *trans*-Cyclooctene[1]

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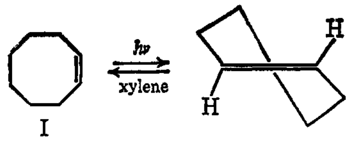
The need for modest quantities of *trans*-cyclooctene in connection with exploratory work in these laboratories coupled with the length of conventional syntheses[2,3] prompted us to explore a short direct route to this compound. The known benzene, toluene, and xylene sensitized isomerization of olefins[4] suggested the photosensitized isomerization of *cis*-cyclooctene as a potential route to the *trans* isomer. Since benzene is known to afford high yields of adduct when irradiated in the presence of cyclooctene,[5] xylene was chosen as sensitizer.



I II

Irradiation of a solution of xylene and cyclooctene in purified cyclohexane followed by silver nitrate extraction and decomposition of the silver nitrate complex with concentrated ammonium hydroxide gave a two-component mixture. Preparative vpc isolation of the compounds followed by direct comparison with authentic materials showed the major product to be *trans*-cyclooctene (II) and the minor component to be 1,5-cyclooctadiene (III). That the 1,5-cyclooctadiene was not a photochemical product in this system was evident from the decrease in the percentage of III in the recycled irradiation mixtures (Table I). The dramatic decrease in III upon repeated photolysis suggests that it is a minor impurity in commercial cyclooctene which coextracts with II.

Table I

Yield of *trans*-Cyclooctene and 1,5-Cyclooctadiene as a Function Recycling Photolysis Mixture

Number of cycles	Total yield, g	% II	% III
1	2.2	82	18
2	2.1	90	10
3	2.4	95	5
4	2.1	97	3

This method has proven useful in conveniently preparing up to 2.5 g of *trans*-cyclooctene per irradiation cycle. Although initial irradiations yield mixtures of II and III, the high reactivity of II still renders the material synthetically useful. Continued irradiation of samples with an intervening distillation to remove higher boiling material affords II in good purity (>97%). The method, although limited in the amount of material obtained, requires only a small amount of manipulative operations and thus should be useful in preparation of modest amounts of II for exploratory and mechanistic work.

Experimental Section

Cyclooctene (600 ml) in 900 ml of olefin-free cyclohexane was extracted four times with 100 ml of 30% aqueous silver nitrate. After the extract was washed with water, dried over Drierite, and distilled through a 3-in. column, 150 ml of xylene was added to form the irradiation mixture. The material was irradiated in 500-ml portions for 36 hr under nitrogen using a 450-W Hanovia medium pressure source and a Corex filter sleeve. The use of a Vycor filter gave faster conversions initially but led to buildup of polymer on the immersion well. The combined irradiation solutions were extracted four times with 80 ml of 20% aqueous silver nitrate; the silver nitrate solution was washed with pentane twice, 70 ml) and decomposed by dropwise addition into 150 ml of concentrated ammonium hydroxide at 0°. The oily aqueous solution was extracted with pentane (thrice, 75 ml), the pentane layer dried, and the pentane distilled through a 6-in. Vigreux column. Short-path distillation of the remaining light yellow liquid afforded 2.2 g (0.02 mol) of colorless liquid, bp 75–6° (75 mm). Vpc inspection (20% β,β-oxydipropionitrile on 60–80 Chrom P, 10 ft × 0.25 in., 70°) showed three components with retention times of 10, 12, and 28 min. These products were identified as *cis*-cyclooctene, *trans*-cyclooctene, and 1,5-cyclooctadiene. The percentage of *cis*-cyclooctene in seven individual runs varied from 1 to 3% of the *trans* isomer.

For recycling, the light yellow photolysis solution was distilled at atmospheric pressure through a short column to yield 1400 ml

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(1) A grant from the Eli Lilly Co., Indianapolis, Ind., is gratefully acknowledged.

(2) A. C. Cope, R. A. Pike, and C. F. Spencer, *J. Amer. Chem. Soc.*, **75**, 3212 (1953); E. J. Corey and J. I. Shulman, *Tetrahedron Lett.*, 3655 (1968); E. J. Corey, F. A. Carey, R. A. E. Winter, *J. Amer. Chem. Soc.*, **87**, 934 (1965); E. J. Corey and R. A. Winter, *ibid.*, **85**, 2677 (1963).

(3) A recent improvement over these methods has been reported: J. N. Hines, M. J. Peagram, G. H. Whitham, and M. Wright, *Chem. Commun.*, 1593 (1968).

(4) For leading references, see P. J. Kropp and H. J. Krauss, *J. Amer. Chem. Soc.*, **89**, 5199 (1967).

(5) D. Bryce-Smith, A. Gilbert, and B. H. Orger, *Chem. Commun.*, 512 (1966).

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.

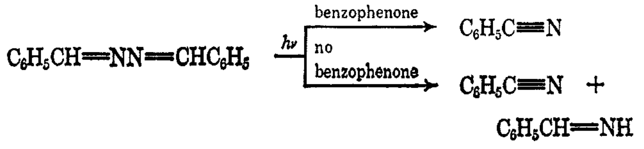
$$(C_6H_5)_2C{=}O \overset{h\nu}{\rightleftharpoons} (C_6H_5)_2C{=}O^* \qquad (1)$$

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

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

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

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.



$$C_6H_5CH{=}NN{=}CHC_6H_5 \xrightarrow{h\nu} \begin{cases} \xrightarrow{\text{benzophenone}} C_6H_5C{\equiv}N \\ \xrightarrow[\text{benzophenone}]{\text{no}} C_6H_5C{\equiv}N + C_6H_5CH{=}NH \end{cases}$$

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	Product Yield,[b] mg 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).