The Photochemistry of Unsaturated Nitrogen-Containing Compounds. I. Irradiation of Benzalazine

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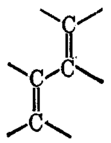
The direct irradiation of benzalazine (**7**) in methanol or benzene is shown to produce, after chromatographic separation of the irradiation mixture, *trans*-stilbene, benzonitrile, and benzaldehyde. The benzaldehyde is not present in the reaction mixture immediately after irradiation but results from a reaction occurring during isolation. Evidence is presented identifying benzaldimine (**8**) as the photochemically produced precursor of benzaldehyde. This observation is incorporated into a proposed reaction mechanism. The inability of triphenylene to sensitize this process is discussed both in terms of the excited state responsible for reaction and also in light of the previously determined capability of benzophenone to initiate photochemically the decomposition of **7**.

During the past several years one of the active areas of organic photochemistry has been the study of systems which contain two conjugated double bonds. Within this general classification of compounds the three types of molecules which have attracted the majority of attention are the dienes (**1**), the enones (**2**), and the diones (**3**). Irradiation of each of these three types of systems has produced a different and highly varied set of photochemical reactions.[1]



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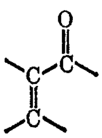

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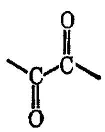

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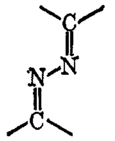
In contrast to the three types of systems mentioned above, the azines (**4**), the enimines (**5a,b**), and the diimines (**6a,b**) constitute several additional classes of compounds which possess two conjugated double bonds but which have been the subject of little photochemical investigation.[2-5] Since each of the three classifications of conjugated compounds already under study has produced an important series of photochemical processes in which the type of reaction observed varies considerably from one class of compounds to the next, a systematic consideration of the remaining, nitrogen containing systems is a logical and potentially valuable undertaking. The work reported here on the photochemistry of benzalazine (**7**) represents the initial phase of such investigation.



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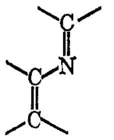

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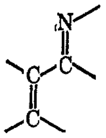

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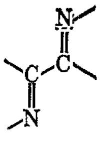

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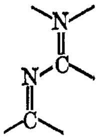

6b

Before describing the results of a photochemical study of benzalazine (**7**) it is necessary to note that previous mention of the irradiation of **7** has appeared twice in the literature.[5,6] The first instance,[6] an account of work done in connection with a study of the thermal decomposition of **7**, contained the report that **7** was unreactive when exposed to light of wavelength greater than 250 mμ. In the second paper,[5] which describes an observation arising from the study of the reactions of phenyldiazomethane, it was recorded that **7**, upon irradiation in the presence of benzophenone, was decomposed to yield benzonitrile. In neither of these studies was the photochemistry of benzalazine (**7**) the primary goal of the research conducted; therefore, although several interesting observations were made, a comprehensive study of the excited-state reactions of **7** did not ensue.

Results

Direct irradiation of a methanol solution of **7** under a nitrogen atmosphere produced upon removal of solvent a deep yellow oil. Chromatography on Florisil separated the reaction mixture into four fractions: unreacted starting material, benzonitrile (38%),[7] benzaldehyde (39%), and *trans*-stilbene (4%). The product yields remained constant for different low conversions; however, irradiations in which essentially all of the starting material was consumed resulted in lower yields, presumably owing to the photochemical decomposition of the products (see Table I). A significant change in product yield was noted when the relatively inert benzene was used as the reaction solvent.[8] In this case the reaction mixture after chromatography gave, in addition to unreacted starting material, benzonitrile (90%), benzaldehyde (90%), and *trans*-stilbene (7%).

$$\underset{\mathbf{7}}{C_6H_5CH{=}NN{=}CHC_6H_5} \xrightarrow[\text{2. chromatographic separation}]{\text{1. } h\nu \text{ in benzene or methanol}} C_6H_5C{\equiv}N + C_6H_5CHO + C_6H_5CH{=}CHC_6H_5$$

Irradiation of either a benzene or methanol solution of **7** with light previously passed through a Pyrex

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[1] (a) O. L. Chapman, *Advan. Photochem.*, **1**, 381 (1963); (b) K. Schaffner, *ibid.*, **4**, 81 (1966); (c) R. Srinivasan, *ibid.*, **4**, 113 (1966); (d) R. O. Kan, "Organic Photochemistry," McGraw-Hill Book Co., New York, N. Y., 1966, pp 32–57, 93–94, 105–150; (e) W. G. Dauben and W. T. Wipke, *Pure Appl. Chem.*, **9**, 539 (1965).

[2] P. Beak and J. L. Miesel, *J. Amer. Chem. Soc.*, **89**, 2375 (1967).

[3] R. A. Mitsch and P. M. Ogden, *Chem. Commun.*, 59 (1967).

[4] (a) R. K. Brinton, *J. Amer. Chem. Soc.*, **77**, 842 (1955); (b) J. F. Ogilvil, *Chem. Commun.*, 359 (1965).

[5] J. E. Hodgkins and J. A. King, *J. Amer. Chem. Soc.*, **85**, 2679 (1963).

[6] H. E. Zimmerman and S. Somasekhara, *ibid.*, **82**, 5865 (1960).

[7] All yields corrected for unreacted starting material.

[8] See footnote *d*, Table I.[9]

[9] (a) L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *ibid.*, **88**, 3666 (1966); (b) J. Saltiel and L. Metts, *ibid.*, **89**, 2233 (1967).

TABLE I

IRRADIATIONS OF BENZALAZINE (7)

Reacn no.	Time, hr	% completion	Filter	Sensitizer	Solvent	% yield of products[a]		
						Benzonitrile	Benzaldehyde	*trans*-Stilbene
1	12	21	None	None	Methanol	38	40	3
2	20	31	None	None	Methanol	38	39	4
3	75	100	None	None	Methanol	33	26	5
4	60		Pyrex[b]	None	Methanol		No reaction	
5	41	31	Vycor[c]	None	Methanol	36	38	3
6	40	9	None	None[d]	Benzene	90	90	7
7	60		Pyrex	None	Benzene		No reaction	
8	60		Pyrex	Triphenylene	Benzene		No reaction	
9[e]	*f*	*g*	Pyrex	Benzophenone	Cyclohexane	85	0	0

[a] Corrected for unreacted starting material. [b] Removes light of wavelength shorter than 280 mμ. [c] Removes light of wavelength shorter than 210 mμ. [d] It is probable that the solvent was participating in energy transfer in this reaction; however, its exact role is unclear. See ref 9a and b. [e] See ref 5. [f] Time not reported; see ref 5. [g] Per cent completion was not given but apparently was near 100; see ref 5.

filter (no transmittance at wavelengths shorter than 280 mμ) resulted in quantitative recovery of starting material. When a Vycor filter (no transmittance at wavelengths shorter than 210 mμ) was used, the reaction took place in the same manner as in the unfiltered irradiation; however, the photolysis time was doubled in order to reach the same degree of completion. For a second time no reaction was observed when an experiment was conducted using triphenylene as a triplet-state sensitizer.[10]

The photochemical reactions of benzalazine (**7**) are summarized in Table I.

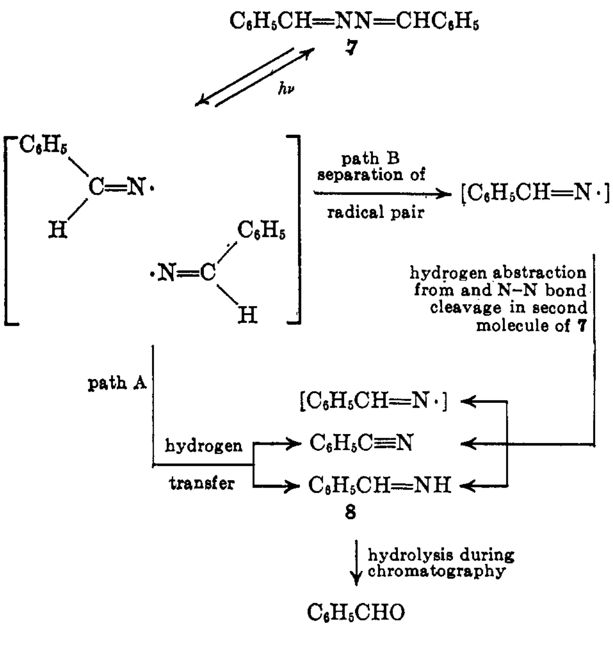
Although benzaldehyde appeared to be one of the photoproducts, its characteristic absorption at 5.91 μ ($CHCl_3$) was absent in the ir spectrum of the crude irradiation mixture;[11] therefore, benzaldehyde must have been the product of some reaction occurring during chromatography. Control experiments showed that the starting material and the chromatographically obtained products were not affected by the isolation procedure, thus suggesting the intermediacy of some unstable photoproduct which was being transformed to benzaldehyde. Although the characteristic benzaldehyde absorption was missing, the crude ir spectrum of the irradiation mixture showed an absorption band at 6.12 μ which was present in neither the starting material nor the products but could be identified in the spectrum of a known sample of benzaldimine[12] (**8**). When the volatile products from the reaction mixture were distilled *in vacuo* at room temperature, the ir spectrum of the distillate appeared to be that of a mixture of benzonitrile and **8**. Since one of the two established derivatives of **8** is benzaldimine hydrochloride,[12] several attempts were made to obtain this salt by saturation of the above-mentioned distillate with hydrogen chloride gas; however, no solid product could be separated from the mixture. The other established derivative of **8** is the corresponding aldehyde resulting from hydrolysis. After treatment of the distillate with water, its ir spectrum resembled that of a known mixture of benzonitrile and benzaldehyde. Reacting the hydrolysis product from the irradiation mixture with either semicarbazide hydrochloride or 2,4-dinitrophenylhydrazine resulted, respectively, in the precipitation of the semicarbazone and 2,4-dinitrophenylhydrazone of benzaldehyde; in this manner, the identity of the hydrolysis product was established to be benzaldehyde. A final but necessary requirement for the intermediacy of **8** in the proposed reaction sequence was met when **8** was converted into benzaldehyde during a control chromatography run. Thus, on the basis of spectroscopic evidence, direct hydrolysis to benzaldehyde, and chromatographic behavior, the unstable intermediate produced upon irradiation of benzalazine (**7**) is identified as benzaldimine (**8**).

Discussion

A proposed mechanism for the photochemical formation of benzonitrile and benzaldehyde from benzalazine (**7**) is given in Scheme I. In this process it is postulated that the initial step is the photochemical cleavage of the nitrogen–nitrogen bond in **7** to produce a radical pair. The reactive species resulting from this fission can either proceed directly *via* a hydrogen transfer to give benzonitrile and benzaldimine (**8**) (path A)

SCHEME I

FORMATION OF BENZONITRILE AND BENZALDEHYDE FROM BENZALAZINE (7)



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[10] W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 4537 (1964).

[11] The ir spectra of known mixtures showed that less that 2 mg of benzaldehyde would have been detected under these conditions; in addition, combining 2 mg of benzaldehyde with the reaction mixture at this time caused the appearance of the easily detectable carbonyl band at 5.91 μ.

[12] T. L. Tolbert and B. Houston, *J. Org. Chem.*, **28**, 695 (1963).

or they may react by an alternative route beginning with escape from the solvent cage and leading to reaction with a second molecule of **7** (path B). In reaction through path B the abstraction of a hydrogen atom from **7** produces **8** while the subsequent (or simultaneous) nitrogen–nitrogen bond cleavage in **7** leads to benzonitrile and generates a new free-radical species capable of repeating the hydrogen abstraction process. In either paths A or B, the final step in the sequence is the hydrolysis of **8** to benzaldehyde during chromatography.

In considering the justification for the proposed mechanism, several factors are of importance. First, the formation of the radical pair shown in Scheme I has considerable analogy in the photochemistry of the related α-diketone systems where the photocleavage of the central (carbon–carbon) bond is one of the frequently occurring processes.[13-17] Photochemically producing the radical pair as outlined above has the effect of creating immediately adjacent to each other, two species either one of which can act as a hydrogen source or a hydrogen acceptor in a disproportionation reaction; therefore, the transfer of a hydrogen atom at this point as depicted by path A represents a logical subsequent step. Reaction *via* path A is analogous to the reaction pathway proposed for the gas phase irradiation of acetaldazine.[4a] The alternative or, perhaps, additional mode for understanding product formation, path B, merits certain consideration owing to its resemblence to the previously suggested mechanism for the photochemical decomposition of benzalazine (**7**) in the presence of benzophenone[5] (Scheme II).

SCHEME II

PHOTOCHEMICAL FORMATION OF BENZONITRILE FROM BENZALAZINE (7) IN THE PRESENCE OF BENZOPHENONE[5]

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

$$C_6H_5CH{=}N{-}N{=}CHC_6H_5 + (C_6H_5)_2C{=}O^* \rightleftharpoons C_6H_5\dot{C}{=}N{-}N{=}CHC_6H_5 + (C_6H_5)_2\dot{C}OH$$

$$C_6H_5\dot{C}{=}N{-}N{=}CHC_6H_5 + (C_6H_5)_2C{=}O \rightleftharpoons 2C_6H_5C{\equiv}N + (C_6H_5)_2\dot{C}OH$$

$$2(C_6H_5)_2\dot{C}OH \rightleftharpoons \text{benzpinacol}$$

Since reaction by either path A or B leads to a result which is consistent with the experimental finding that benzonitrile and the precursor of benzaldehyde must form with equal probability (equal molar quantities of benzonitrile and benzaldehyde are always isolated when the photochemical reaction is run to different low conversions), a definitive statement concerning the relative importance of these two processes must await the further investigation now in progress. The validity of the final portion of the proposed reaction mechanism, namely, the existance of benzaldimine (**8**) as a photoproduct and its subsequent conversion to benzaldehyde, rests in the demonstration given earlier in detail (see results) that **8**, and not benzaldehyde, is present in the reaction mixture immediately after irradiation of **7** and is totally converted into benzaldehyde during chromatography.

It is informative to compare certain portions of this work with the previously mentioned irradiation of benzalazine (**7**) in the presence of benzophenone.[5] Since excited benzophenone is capable not only of hydrogen abstraction but also of triplet energy transfer,[18] benzonitrile could have resulted either from a hydrogen abstraction process such as that given in Scheme II or by a transfer of triplet energy from benzophenone to **7** followed by a different series of reactions, possibly similar with those shown in Scheme I. One method for resolving this problem consists of replacing benzophenone (E_t = 69 kcal/mol[9a]) with a compound such as triphenylene (E_t = 67 kcal/mol[9a]) which is capable of transferring triplet excitation of essentially equal energy but is not readily able to hydrogen abstract. When an experiment was run using triphenylene as a sensitizer, no measurable amount of photochemical reaction was observed; thus, a clear indication is provided that hydrogen abstracting ability is an important element in the light induced formation of benzonitrile from benzalazine (**7**)–benzophenone mixtures. This experiment, however, provides no evidence concerning other aspects of the mechanism shown in Scheme II.

The identity of the excited state responsible for the observed photochemical reaction is as yet unknown; however, the existing experimental data do provide some information pertaining to this question. It is reasonable to assume that the triplet energy for benzalazine (**7**) is not considerably greater than those values found in the related diene-type, systems shown in Table II.[19-23] On the basis of such a comparison it would appear unlikely that the triplet energy of **7** would be greater than that of triphenylene; consequently, in a sensitization experiment triphenylene should easily transfer triplet excitation to **7**. Since no reaction was observed when triphenylene was used as an energy transfer agent, it seems reasonable to conclude that the lowest energy triplet state of **7** is not capable of reaction. In comparison with the

TABLE II

TRIPLET ENERGIES IN DIENE-TYPE SYSTEMS

Compd No.	Compd Name	Triplet energy, kcal/mol	Ref
1	Butadiene	59.6	*a*
2	Isoprene	60.0	*a*
3	1,3-Hexadiene	53.5	*a*
4	Biacetyl	57.2	*b*
5	Benzil	57.3	*b*
6	Cyclohexenone	61	*c*

[a] See ref 21 and 22. [b] See ref 9a. [c] See ref 23.

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(13) H. A. Staab and J. Ipaktschi, *Tetrahedron Lett.*, 583 (1966).

(14) H. A. Staab and J. Iptaktschi, *Angew. Chem., Intern. Ed. Engl.*, **5**, 320 (1966).

(15) P. A. Leermakers, P. C. Warren, and G. F. Vesley, *J. Amer. Chem. Soc.*, **86**, 1768 (1964).

(16) N. C. Yang and A. Morduchowitz, *J. Org. Chem.*, **29**, 1654 (1964).

(17) G. S. Hammond, P. A. Leermakers, and N. J. Turro, *J. Amer. Chem. Soc.*, **83**, 2395 (1961).

(18) L. B. Jones and G. S. Hammond, *ibid.*, **87**, 4219 (1965).

(19) Although it would be of interest to determine whether the lowest triplet state of benzalazine (**7**) is n − II* or II − II* in nature, this is not necessarily a critical feature in comparing the triplet energy of **7** with those of the compounds listed in Table II since this group contains triplet states which are both of the II − II* (butadiene, isoprene, and 1,3-hexadiene) and n − II* (biacetyl[20]) variety.

(20) H. E. Zimmerman, R. W. Binkley, J. J. McCullough, and G. A. Zimmerman, *ibid.*, **89**, 6589 (1967).

(21) D. F. Evans, *J. Chem. Soc.*, 1735 (1960).

(22) R. S. H. Liu, N. J. Turro, and G. S. Hammond, *J. Amer. Chem. Soc.*, **87**, 3406 (1965).

(23) E. Y. Lam, D. Valentine, and G. S. Hammond, *ibid.*, **89**, 3482 (1967).

lowest triplet state, the lowest energy singlet is no more reactive. Irradiation of 7 with light of wavelength greater than 280 mμ produced no reaction even though there was considerable absorption of light by 7 due to the long wavelength absorption band ($\lambda_{\max}$ 303 mμ (methanol)). Combining the two observations described above leads to the unusual conclusion that the reactivity of 7 is derived from an excited state other than the lowest singlet or triplet.

Although *trans*-stilbene is a minor product resulting from the irradiation of 7, the mechanism for its formation is of interest owing to the existance of several possible reaction pathways each of which finds some precedent in the chemical literature. Work designed to select among these several possibilities is now in progress.

Experimental Section[24]

Direct Irradiation of Benzalazine (7) in Methanol.—In a typical run 208.3 mg (1.000 mmol) of benzalazine[25](7) in 300 ml of anhydrous methanol[26] was irradiated for 20 hr at 23° with constant stirring using a 100-W Hanovia high-pressure quartz mercury-vapor lamp which had been lowered into a water-cooled quartz immersion well. Prepurified nitrogen was passed through the solution for 1 hr prior to irradiation and a slow stream of nitrogen was continued during photolysis. No filter was used.

After 20 hr, the solvent was removed by distillation *in vacuo* below 40°, producing a distillate which was transparent in the uv spectrum and leaving a yellow oil. The residual oil was chromatographed on a 78 × 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; 1.0 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 16–30 yielded 2.4 mg (4%) of crystalline *trans*-stilbene, mp 121–122° (lit.[27] mp 124°). This material was identical in ir spectrum and showed no mixture melting point depression with a known sample. Fractions 90–120 yielded 144 mg of benzalazine (7) as yellow crystals, mp 92–93°. Fractions 123–139 afforded 12.7 mg (39%) of a slightly yellow oil which gave the ir spectrum of benzaldehyde. Treatment of these fractions with semicarbazide hydrochloride according to the method of Shriner, Fuson, and Curtin[28] produced benzaldehyde semicarbazone, mp 220–222° (lit.[28] mp 222°). Fractions 140–167 gave 12.0 mg (38%) of a clear oil identical in ir and uv spectra with a known sample of benzonitrile.

Irradiation of Benzalazine (7) in Methanol Using a Vycor Filter.—The type and amount of materials used and the irradiation procedure were identical with that described in the direct irradiation in methanol except that a vycor filter was placed between the light source and the reaction mixture and the irradiation time was increased to 41 hr.

The irradiation mixture was chromatographed on a 76 × 2.5 cm Florisil column slurry packed in 1:9 ether–hexane; 500 ml fractions were collected. The column was eluted as follows: 3.5 l. of 1:19 ether–hexane and 0.5 l. of 1:9 ether–hexane.

Fraction 1 gave 2.0 mg (3%) of crystalline *trans*-stilbene, mp 120–122°. Fractions 2 and 3 gave 144 mg of benzalazine (7) as a yellow solid, mp 90–93°, yielding, after 1 recrystallization from petroleum ether (35–60°), 139 mg of benzalazine (7), mp 93–94°. Fractions 5 and 6 afforded 12.7 mg (38%) of benzaldehyde, identified by ir spectroscopy. Fractions 7 and 8 yielded 11.5 mg (36%) of benzonitrile, identified by ir spectroscopy.

Irradiation of Benzalazine (7) in Methanol Using a Pyrex Filter.—The procedure and the identity and quantity of the compounds used corresponded exactly to the direct irradiation in methanol except that a Pyrex filter was placed between the light source and the reaction mixture and the irradiation time was increased to 60 hr. The chromatographic adsorbent and elution scheme were the same as used in the direct irradiation.

Fractions 90–135 afforded 207 mg of crystalline benzalazine (7), mp 92–93°.

Direct Irradiation of Benzalazine (7) in Benzene.—The type and amount of compounds used and the experimental procedure were the same as in the direct irradiation in methanol except that the reaction solvent was benzene and the irradiation time became 40 hr.

The irradiation mixture was chromatographed on a 76 × 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; 0.5 l. of 1:24 ether–hexane; and 1.0 l. of 1:12 ether–hexane.

Fractions 15–35 yielded 1.1 mg (7%) of crystalline *trans*-stilbene. Fractions 96–115 gave 190 mg of benzalazine (7) as a crystalline yellow solid, mp 91–93°. Fractions 116–125 afforded 8.6 mg (90%) of benzaldehyde which was identified by ir spectroscopy. Fractions 126–150 yielded 8.1 mg (90%) of benzonitrile, also identified by ir spectroscopy.

Irradiation of Benzalazine (7) in Benzene Using a Pyrex Filter.—The procedure and the identity and quantity of the compounds used were exactly that employed in the direct irradiation in methanol except that a Pyrex filter was placed between the light source and the reaction mixture, benzene was used as an irradiation solvent, and the irradiation time was 60 hr. The chromatographic adsorbent and the elution scheme were the same as used in the direct irradiation in methanol.

Fractions 95–130 afforded 206 mg of crystalline benzalazine (7), mp 92–93°.

Irradiation of Benzalazine (7) in Benzene Using Triphenylene as a Sensitizer.—In a typical run 52.1 mg (0.25 mmol) of benzalazine (7) and 280 mg (1.22 mmol) of triphenylene in 300 ml of benzene were irradiated for 60 hr. The experimental procedure used, including the chromatographic separation, was the same as that used in the direct irradiation in methanol except that a Pyrex filter was placed between the light source and the reaction mixture.

Fractions 100–127 from the chromatography yielded 53.7 mg of yellow solid, mp 89–93°, producing after recrystallization from petroleum ether, 52.0 mg of benzalazine (7), mp 92–94°.

Test of the Stability of Benzalazine (7) under the Reaction and Isolation Conditions.—Benzalazine (7) (208.3 mg, 1.000 mmol) was dissolved in 300 ml of anhydrous methanol and stirred for 60 hr at 25°, and the solvent was removed by distillation *in vacuo* below 40°. The residual solid was chromatographed on a 77 × 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 90–135 yielded 206 mg of benzalazine (7), mp 93–94°.

Test of the Stability of Benzonitrile during Chromatography.—Benzonitrile (63 mg, 0.61 mmol) was chromatographed on a 79 × 2.5 cm column of Florisil slurry packed in 1:9 ether–hexane; 500-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; 0.5 l. of 1:24 ether–hexane; and 2.0 l. of 1:12 ether–hexane.

Fractions 7 and 8 gave 59 mg of benzonitrile identified by ir spectroscopy.

Test of the Stability of Benzaldehyde during Chromatography.—Benzaldehyde (52 mg, 0.49 mmol) was chromatographed on a 78 × 2.5 cm column of Florisil slurry packed in 1:9 ether–hexane; 500-ml fractions were collected. The column was eluted as follows: 0.5 l. of hexane; 0.5 l. of 1:49 ether–hexane; 0.5 l. of 1:24 ether–hexane; and 2.5 l. of 1:12 ether–hexane.

Fraction 8 gave 52 mg of benzaldehyde identified by ir spectroscopy.

Identification of Benzaldimine[12] (8) as an Intermediate in the Photolysis of Benzalazine (7).—A 208.3-mg (1.000 mmol) sample of benzalazine (7) in 300 ml of anhydrous methanol was irradiated according to the procedure described in the direct irradiation in methanol. After 75 hr, the solvent was removed by distillation *in vacuo* below 40°, giving a distillate which was transparent in

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[24] All melting points were taken on a Fisher–Johns block and are corrected.

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

[26] In methanol benzalazine shows absorption maxima at 303 (ε 37,800) and 217 mμ (ε 17,900) with shoulders at 324 (ε 17,200) and 309 (ε 34,000) mμ.

[27] A. Michaelia and H. Lange, *Ber.*, **8**, 1314 (1875).

[28] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1956, pp 218 and 283.

the uv spectrum and leaving a residual yellow oil. The ir spectrum of this oil showed no absorption at 5.91 μ (C=O in benzaldehyde) but did exhibit absorption at 6.12 μ [(C=N in benzaldimine (**8**)]. The volatile photoproducts were removed *in vacuo* from the reaction mixture at 25° leaving a solid yellow residue and giving as a distillate a clear oil. The ir spectrum of the oil was that of a mixture of benzonitrile and **8** with no benzaldehyde present.[29] Addition of 1.0 ml of water to the distillate, stirring for 10 hr, extraction with ether, and evaporation of the ether gave a second oil whose ir spectrum appeared to be that of a mixture of benzaldehyde and benzonitrile. Treatment of this oil with semicarbazide hydrochloride according to the method of Shriner, Fuson, and Curtin[28] led to the isolation of benzaldehyde semicarbazone, mp 220-222° (lit.[28] mp 222°).

Conversion of Benzaldimine (8) into Benzaldehyde during Chromatography.—Benzaldimine (**8**) (52.1 mg, 0.49 mmol) was chromatographed on a 76 × 2.5 cm column of Florisil 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; and 0.5 l. of 1:12 ether-hexane.

Fractions 120-140 afforded 45 mg of benzaldehyde, identified by ir spectroscopy and its semicarbazone derivative, mp 218-220° (lit.[28] mp 222°).

Registry No.—**7**, 588-68-1; **8**, 16118-22-2.

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(29) The benzaldimine used for comparison was synthesized according to the procedure given in ref 12.

Arylation by Aromatic Nitro Compounds at High Temperatures. IV. Nitrobenzene with Toluene and Toluene-α-d_3

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Nitrobenzene reacts with toluene at 600° to give the arylation product, methylbiphenyl, in addition to biphenyl and the toluene dehydro dimers (bibenzyl, methyldiphenylmethane, and dimethylbiphenyl). Most of the biphenyl contains one benzene ring from toluene and nitrobenzene each; some consists of benzene rings solely from one reactant. Toluene and toluene-α-d_3, pyrolyzed at low conversion, give only the dehydro dimers. The total amount and distribution differ markedly from that resulting in the nitrobenzene reaction. Apparently, in the absence of added free radicals, toluene pyrolyzes largely by a nonradical mechanism.

Earlier papers described the reactions of nitrobenzene with benzene[1] and with its fluorinated derivatives.[2] To extend these studies to compounds containing benzylic hydrogens, we examined the reactions of aromatic nitro compounds with a series of methylated benzenes and naphthalenes. This paper describes the reactions of nitrobenzene with toluene and toluene-α-d_3 and of nitrobenzene-d_5 with toluene, as well as the pyrolysis of toluene-α-d_3 alone.

Experimental Section

Materials. The reagents and standards for gas chromatography, except as noted below, were purchased from Aldrich Chemicals and used as received. Where purity was critical, the reagent was analyzed and, if necessary, purified by distillation, crystallization, and gas chromatography.

Table I shows the source and melting (or boiling) points of the ten $C_{14}H_{14}$ isomers used as gas chromatography standards. Methyldiphenylmethanes were prepared from methylbenzyl bromides rather than the chlorides as Senff described.[3] Reaction with benzene in the presence of ferric chloride was vigorous, and careful addition was necessary to keep the reaction under control.

Dimethylbiphenyls were prepared by stirring and refluxing mixtures of iodotoluenes and copper at atmospheric pressure for 24 hr, instead of in a bomb tube as described by Ullmann.[4] Unsymmetrical dimethylbiphenyls were made from equimolar mixtures of two iodotoluenes. They were not isolated; their retention times were determined by comparison with authentic symmetrical dimethylbiphenyls.

TABLE I

Compound	Synthesized according to	Yield, mol %	Mp (bp), °C	
			Found	Lit.
Bibenzyl	Purchased, Aldrich	...	52	52
2-Methyldiphenylmethane	*a*	54	(279-281)	(279-282)
3-Methyldiphenylmethane	*a*	48	(265-269)	(268-269)
4-Methyldiphenylmethane	*b*	38	(280-282)	(279-280)
2,2'-Dimethylbiphenyl	*c*	33	15-17	17.8
2,3'-Dimethylbiphenyl	*c*	...	...	(265-267)
2,4'-Dimethylbiphenyl	*c*	...	...	(272-260)
3,3'-Dimethylbiphenyl	*c*	38	(285-287)	(286-287)
3,4'-Dimethylbiphenyl	*c*	...	...	(288-289)
4,4'-Dimethylbiphenyl	Purchased, Aldrich	...	120-121	122

[a] See ref 3. [b] A. Behr and N. A. van Dorp, *Ber.*, **7**, 18 (1874). [c] See ref 4.

Toluene-α-d_3 was prepared in 45 mol % yield by reduction of benzotrichloride in D_2O with zinc dust.[5] It had the following isotopic composition: 2.3% d_2, 96.2% d_3, 1.0% d_4, 0.3% d_5, and 0.2% d_6. Nitrobenzene-d_5 was prepared in 50 mol % yield by nitrating benzene-d_6 with nitrogen pentoxide in carbon tetrachloride according to Haines and Adkins.[6] Its isotopic composition was 96.9% d_5 and 3.1% d_4.

Procedure.—Arylations were run in a Vycor tube filled with Vycor beads in an electric furnace maintained at 600 ± 1° under pure dry nitrogen with contact times of 9-12 sec. The vapors were condensed in a bulb at −60°, the condensate was distilled to recover unreacted material, and the residue was analyzed.

In a typical experiment, a solution of 5.011 ml (0.05 mol) of nitrobenzene in 26.6 ml (0.25 mol) of toluene was passed through a Vycor tube at 600° under nitrogen flowing at 20 cc/minute. Contact time was 9.5 sec. The vapors were condensed in a bulb at −60°; the condensate was distilled to recover 20 ml of toluene and give 6.9 g of products, the composition of which is shown in Table II.

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(1) E. K. Fields and S. Meyerson, *J. Amer. Chem. Soc.*, **89**, 3224 (1967).

(2) E. K. Fields and S. Meyerson, *J. Org. Chem.*, **32**, 3114 (1967).

(3) P. Senff, *Ann.*, **220**, 230 (1883).

(4) F. Ullmann and G. H. Meyers, *ibid.*, **332**, 42 (1904).

(5) E. K. Fields and S. Meyerson, forthcoming publication.

(6) L. B. Haines and H. Adkins, *J. Amer. Chem. Soc.*, **47**, 1419 (1925).