Photochemical Generation of the 2,4,6-Trinitrobenzyl Anion

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Photolysis of aqueous solutions of 2,4,6-trinitrotoluene results in initial formation of the 2,4,6-trinitrobenzyl anion, 1. Evidence for this reactive intermediate, photogenerated in acidic or neutral media, is demonstrated by (1) its ability to exchange hydrogen for deuterium in photolyzed D_2O solutions, (2) by its facile condensation with p-nitroso-N,N-dimethylaniline to form a Schiff base, and (3) by its very rapid photonitrosation with nitrous acid to form, initially, syn-2,4,6-trinitrobenzaldoxime.

The existence of the 2,4,6-trinitrobenzyl anion (1) in aqueous systems has been considered by numerous investigators,[1-7] Previous work in this laboratory using deuterium exchange experiments has indicated that 1 is formed from 2,4,6-trinitrotoluene (TNT) in alkaline tetrahydrofuran–methanol solutions. This carbanion was then utilized as a nucleophile in halogen displacement reactions at aromatic carbon.[8]

Recently, Fyfe and Norris[9] have reported isolating 1 as its potassium or tetraphenylarsonium salt from cold heptane–isopropyl alcohol solutions using isopropoxide or methoxide ions as the bases. They were able to obtain NMR and UV–vis spectra of these salts; however, both salts of 1 were unstable at ambient temperature either as solids or in solution and could not be analyzed further.

Bernasconi[7] has also reported kinetic and spectroscopic evidence for the formation of a Janovsky complex between TNT and 1. He found that 1 formed as a transient species upon reaction of TNT with methoxide in methanol, ethoxide in ethanol, or hydroxide in 50% dioxane–water. However, no evidence of 1 was obtained by Bernasconi in a largely aqueous medium of 10% dioxane–water.

The light sensitive nature of o-nitrotolyl systems was recognized as early as 1904 by Sacks and Hilpert.[10] However, de Mayo[11] proposed hydrogen abstraction by the photoexcited nitro group as the major pathway for photochemistry of nitroaromatics. Flash photolysis experiments by Wettermark[12] of o-nitrotoluene, 2,4-dinitrotoluene, and 2,6-dinitrotoluene and similar experiments by Capellos and Suryanarayanan[13] on 2,4,6-trinitrotoluene provided spectroscopic evidence for formation of the aci-quinoid type intermediate (2) in nonpolar solvents and the subsequent formation of the anion 1 in polar solvents. These intermediates are presumed to arise by intramolecular hydrogen transfer in the triplet excited state of the o-nitro group.[12,13]

Wettermark has determined the pK_a values for the equilibrium between the aci-quinoid isomer and its conjugate base for 2-nitro- and 2,4- and 2,6-dinitrotoluenes and found them to be 3.7, 1.1, and 1.8,[12] respectively. On the basis of these values, the pK_a value for the ionization of aci-TNT would be expected to be <1.0. Therefore, photogeneration of the TNT anion even at low pH would be expected.

We wish now to offer evidence that 1 is photochemically generated in situ by irradiation of neutral and acidic aqueous solutions of 2,4,6-trinitrotoluene at wavelengths greater than 280 nm.

Results and Discussion

Photodeuterium Exchange Study. To test the possibility of a labile hydrogen being transferred in the

Scheme I
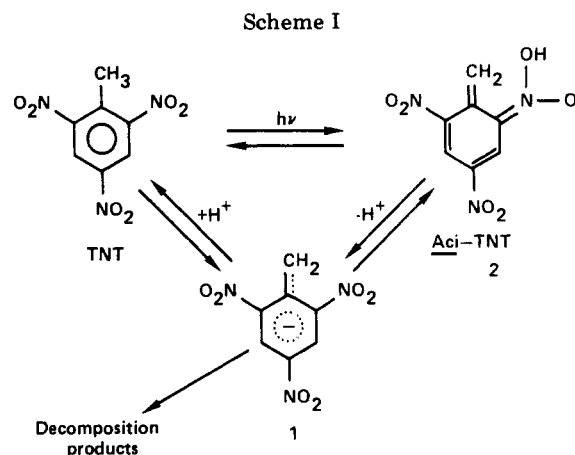
Table I. Photoexchange of 2,4,6-Trinitrotoluene in D_2O

pD^a	$10^4[TNT]_{60}{}^b$	% $D^{c,d}$	% photo-decomp.
1.5	3.31	53	17.5
4.0	2.82	47	29.6
7.0	1.85	30	53.8

^{a} Adjusted to pD 1.5 and 4.0 with D_2SO_4. ^{b} [TNT] after 60 min. Samples simultaneously irradiated by exposure to sunlight for 1 h. $10^4[TNT]_0 = 4.01$ M. ^{c} Deuterium assays by NMR of benzene-d_6 extracted photolysates. Calculated on the basis of $CH_3 \rightarrow CD_3$ equal to 100% exchange. ^{d} Solutions of TNT in D_2O and/or D_2SO_4 left in the dark for several days showed no deuterium in the TNT.

primary photosteps (Scheme I), D_2O solutions of 4×10^{-4} M TNT were irradiated for 1 h in sunlight at various acidities (Table I). Inspection of the mass spectra of the recovered TNT showed it to be a mixture of $PiCH_3$, $PiCH_2D$, $PiCHD_2$, and $PiCD_3$[14] as evidenced by sizable

(1) K. Bowden and R. Stewart, *Tetrahedron*, **21**, 261 (1965).
(2) E. Buncell, K. E. Russell, and J. Wood, *Chem. Commun.*, 252 (1968).
(3) R. E. Miller and W. F. R. Wynne-Jones, *J. Chem. Soc.*, 2375 (1959).
(4) J. A. Blake, M. J. B. Evans, and K. E. Russell, *Can. J. Chem.*, **44**, 119 (1966).
(5) E. F. Caldin and G. Long, *Proc. R. Soc. London, Ser. A*, **228**, 263 (1955).
(6) K. L. Servis, *J. Am. Chem. Soc.*, **89**, 1508 (1967).
(7) C. F. Bernasconi, *J. Org. Chem.* **36**, 1671 (1971).
(8) K. G. Shipp, L. A. Kaplan, and M. E. Sitzmann, *J. Org. Chem.*, **37**, 1966 (1972).
(9) C. A. Fyfe, C. D. Malkiewich, S. W. H. Damji, and A. R. Norris, *J. Am. Chem. Soc.*, **98**, 6983 (1976).
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(11) P. de Mayo, *Adv. Org. Chem.*, **2**, 367 (1960).
(12) M. E. Langmuir, L. Dogliotti, E. D. Black, and G. Wettermark, *J. Am. Chem. Soc.*, **91**, 2204 (1969), and references cited therein.
(13) K. Suryanarayanan and C. Capellos, *Int. J. Chem. Kinet.*, **6**, 89 (1974).

† Deceased.

increases in the intensity of the mass spectral lines at m/e 211, 212, and 213,[15] relative to unirradiated TNT. The amount of the deuterium incorporation was determined by NMR analysis using the singlet resonance from the ring protons of the photoexchanged TNT as the internal standard. Exchange of the ring protons was not expected, as was confirmed by oxidation of the recovered TNT to 1,3,5-trinitrobenzene (TNB)[16] and determination of its mass spectrum. The $(P + 1)/P$ ratio was identical with that of an authentic sample of TNB, confirming the absence of deuterium on the ring carbons.

The TNT → 2 → 1 → TNT mechanism for incorporation of deuterium into the methyl group of TNT conforms with the observations of Morrison and Migdalof[17] who upon irradiating D_2O/dioxane solutions of o-nitrotoluene and p-nitrotoluene found deuterium only in the methyl group of o-nitrotoluene.

The data in Table I also reveal that as the acidity increases, the decomposition of TNT decreases along with increased deuterium incorporation. This would be in accord with Scheme I where a more rapid return of the TNT anion (1) to either TNT or aci-TNT (2) would occur as the acidity increased. This suggests that the major pathway for photodecomposition is via the anion.

Trapping Photogenerated TNT Anions under Neutral Conditions. We have also photochemically generated and synthetically utilized the TNT anion in neutral aqueous solutions. In the presence of Pyrex-filtered light from a medium pressure Hg arc, 4.4×10^{-4} M TNT and 4.4×10^{-3} M N,N-dimethyl-p-nitrosoaniline afforded an 80% yield of N,N-dimethyl-N'-(2,4,6-trinitrobenzylidene)-p-phenylenediamine (3) after irradiating the reaction mixture for 45 min.[18] In a control reaction
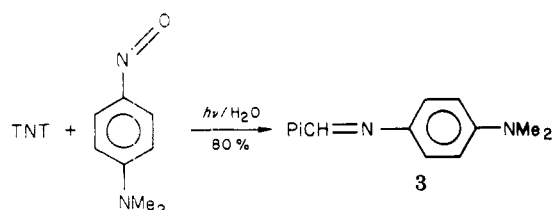
in the absence of light, 3 could not be detected. However, in the absence of light, but under alkaline conditions (piperidine catalyst), substantially smaller yields of 3 were produced due to formation of other alkaline degradation products of TNT such as $PiCH_2OH$, PiCHO, $PiCH_2CH_2Pi$, and PiH.[19]

This light-catalyzed method of generating a polynitrophenyl methide ion may have synthetic utility when use of a strong base would cause undesirable side reactions. We are at present attempting to extend this reaction to other substrates.

"Photonitrosation" of Trinitrotoluene. Further evidence for the photochemical formation of TNT anion comes from the rather facile "photonitrosation" of TNT in aqueous acidic nitrite solutions. While nitrous acid is in general unreactive with polynitrotoluenes, the presence of Pyrex-filtered light causes the methyl group of TNT to nitrosate very rapidly. Normally, TNT, when irradiated

Scheme II
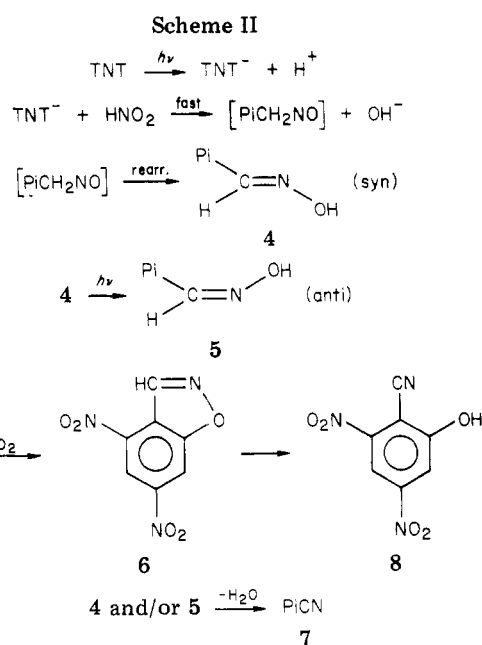
in water, slowly decomposes (70% in 60 min) to numerous products,[20] but when 5×10^{-4} M TNT is irradiated in pH 3.5 buffered aqueous 0.05 M nitrite solutions, all the TNT disappears within a few minutes time. In its place are formed five interrelated compounds, 4, 5, 6, 7, and 8 (see Scheme II), which we suggest originate from the same picrylnitrosomethane (9) intermediate. Compound 9 is tautomeric with the isolable syn oxime (4).[21]

In the presence of NO_2^- but at pHs greater than 5, none of these products are observed, indicating that the reacting species is HNO_2 whose pK_a is 3.5. An ionic mechanism is shown for the nitrosation step in Scheme II, but a radical or radical ion type mechanism cannot be ruled out at this point. The syn oxime 4 is the first isolable product which forms early in the photonitrosation but under the conditions of the experiment photoisomerizes slowly to the anti oxime (5) which in turn either cyclizes with displacement of nitrite to form the 4,6-dinitro[1,2]benzisoxazole (6) or eliminates the elements of water to form trinitrobenzonitrile (7). These products from the "photonitrosation" of TNT were isolated by preparative thin-layer chromatography and identified by either comparison with an authentic sample or by spectrometric methods.

In order to determine the relative rates of the photonitrosation and reprotonation steps of the photogenerated TNT anion, four photolyses were carried out in 1-cm UV cells containing 5×10^{-4} M TNT and 3.6×10^{-4} M HCl (pH 3.5) in D_2O at three different concentrations of nitrite. A blank run containing only TNT/HCl/D_2O was irradiated with Pyrex-filtered light from a 450-W mercury lamp. After 5 min only 8% decomposition had occurred but 75% deuterium was observed incorporated into the undecomposed TNT. However, when 0.005 M nitrite was added to the stock TNT/HCl/D_2O solution and then

(14) Pi = picryl = 2,4,6-trinitrophenyl.

(15) The base peak for TNT is m/e 210 (loss of OH), the intensity of the parent ion peak at m/e 227 is very low.

(16) H. L. Clarke and W. W. Hartman, "Organic Syntheses", Collect. Vol. I, Wiley, New York, 1941, p 543.

(17) H. Morrison and B. Migdalof, *J. Org. Chem.*, **30**, 3996 (1965).

(18) N,N-Dimethyl-p-nitrosoaniline is stable under these photoconditions.

(19) L. A. Kaplan and E. Kayser, unpublished results from the Naval Surface Weapons Center.

(20) Previous unpublished work by the authors has identified, in addition to the photonitrsation products, ten photodecomposition products in aqueous TNT photolysates (using sunlight or a Pyrex-filtered Hg lamp). The major ones are 2,4,6-trinitrobenzaldehyde, 1,3,5-trinitrobenzene, 2,4,6-trinitrobenzyl alcohol, 4,6-dinitroanthranil, 2-amino-4,6-dinitrobenzoic acid, 2,2'-dicarboxy-3,3',5,5'-tetranitroazobenzene, and 2-carboxy-3,3',-5,5'-tetranitro-NNO-azoxybenzene. As can be seen from these products no chemistry occurs at the para nitro position.

(21) 4 was also observed to be forming as an intermediate when 2,-4,6-trinitrotoluene was treated with NOCl in the presence of pyridine; M. E. Sitzmann and J. C. Dacons, *J. Org. Chem.*, **38**, 4363 (1973).
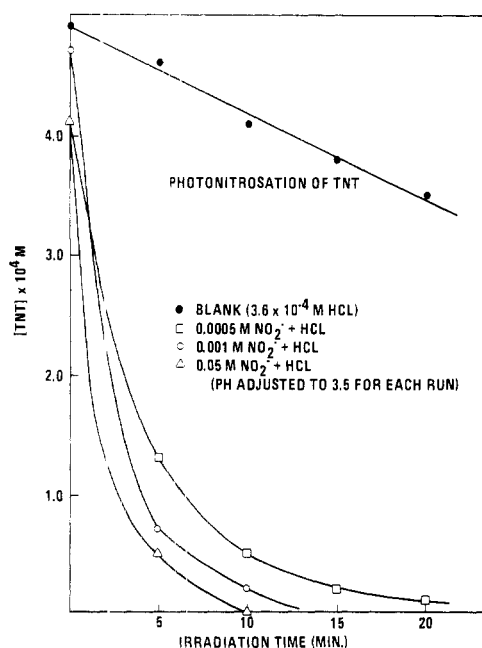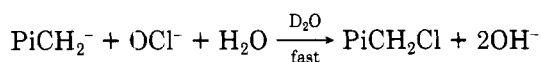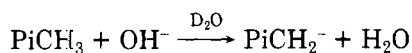
Figure 1.

irradiated for 5 min, analysis revealed 90% of the TNT had been nitrosated and the remaining 10% TNT had incorporated only 2 or 3% deuterium. Even at 0.0005 M nitrite, 69% photonitrosation occurred during the same irradiation period with approximately 25% deuterium found in the remaining 31% TNT. A third photolysis with an intermediate concentration of 0.001 M nitrite gave 85% photonitrosation and 5% deuterium exchange after 5 min. These data are outlined in Figure 1.

The TNT analyses were done by electron-capture gas chromatography of a benzene extract of the photolysate and the deuterium analysis by mass spectrometry of the TLC separated TNT.

Similar results were observed in earlier work at this laboratory[8] when a solution of TNT in tetrahydro-furan–methanol-d was rapidly added to D_2O–OD^- at 0 °C.

$$PiCH_3 + OH^- \xrightarrow{D_2O} PiCH_2^- + H_2O$$

$$PiCH_2^- + OCl^- + H_2O \xrightarrow[\text{fast}]{D_2O} PiCH_2Cl + 2OH^-$$

The mixture was immediately quenched in excess DCl–D_2O, and the recovered TNT was found to have exchanged 12.4% (by NMR analysis) of its methyl protons. Quenching the reaction after a 30-s equilibration increased the deuterium content to 25.5%. However, when the TNT anion was trapped by chlorination using hypochlorite in a deuterated solvent system, the resulting 2,4,6-trinitro-benzyl chloride product contained no deuterium in the α position.

Experimental Section

All photochemical reactions were conducted either in sunlight or with a 450-W medium-pressure mercury lamp using a no. 7740 Pyrex filter. The mercury lamp irradiations were carried out in a 500-mL Ace photoreactor equipped with a quartz cooling well.

The gas chromatographic analyses for TNT were performed on a Hewlett-Packard HP-5750 equipped with an electron-capture detector using a 4 ft $\times$ $^1/_4$ in. column containing 3% Dexsil 300 on Chromsorb W AW DMCS, 80/100 mesh. Dimethoxybenzene was used as an internal standard.

The mass spectrometry was conducted on a Varian MAT-111 GC/MS instrument, and the deuterium analyses and structure identification by NMR were done on a Varian HA-100 NMR spectrometer. The TNT used was recrystallized three times from

30% chloroform/carbon tetrachloride. TLC analyses were done using Merck silica gel 60 HF-254.

Photochemical Condensation of TNT and *p*-Nitroso-*N*,*N*-dimethylaniline to Form the Schiff Base *p*-Phenyl-enediamine-*N*,*N*-dimethyl-*N'*-(2,4,6-trinitrobenzylidene) (3). An aqueous solution (600 mL) of 4.4×10^{-4} M TNT and 4.4×10^{-3} M *p*-nitroso-*N*,*N*-dimethylaniline was irradiated for 1 h with Pyrex-filtered light for a 450-W mercury lamp in an Ace reactor vessel. The dark solid precipitate which formed was collected on filter paper, dried, and weighed, and a known weight of the sample was dissolved in acetone and analyzed quantitatively in UV at λ_{max} 510 nm. [The nitroso starting material has λ_{max} (acetone) of 410 nm]. Comparison of the optical density with that from a known pure sample of this Shiff base, prepared by the method of McGookin,[22] showed that we had obtained an 84% yield of **3** from TNT. Qualitative analyses were carried out by TLC of the photoproduct and compared to the authentic Schiff base where both gave purple spots at R_f 0.55 in benzene.

Photonitrosation of 2,4,6-Trinitrotoluene. A 600-mL aqueous solution of 4×10^{-4} M TNT and 0.05 M $NaNO_2$, adjusted to pH 3.5 with HCl, was irradiated with a mercury lamp for 20 min, after which time TNT could not be detected by GC. The photolysate was extracted with 600 mL of ether, and the ether extract was dried over Na_2SO_4 and then concentrated to ca. 1 mL. This procedure was repeated six times in order to obtain enough of the products. An analysis of the combined concentrated ether extracts is given below.

Identification of the Products from Photonitrosation of TNT. TLC of the above concentrated ether extracts revealed five components (R_f 0.75, 0.50, 0.25, 0.15, 0.00) and spraying with 20% EDA/Me_2SO aided in visualizing the spots and gave distinctive colors. The developing solvent was benzene.

(1) **4,6-Dinitro[1,2]benzisoxazole (6)**, R_f 0.75 (pink fading to yellow with EDA/Me_2SO). This product is slowly converted to **8** on a TLC plate but **6** can be isolated by preparative TLC if anhydrous solvents are used for chromatography and extraction. **6** has a mass spectrum (M^+, 209), an NMR spectrum [δ 9.64 (d, 1), 9.10 (q, 1), 8.97 (d, 1) (acetone-d_6)], and an IR spectrum very similar to the isomeric 4,6-dinitro-anthranil.[20] Hydrolysis of **6** gave **8** which is consistent with the known cleavage of benz-isoxazoles to ortho cyanophenols.[23]

(2) **2,4,6-Trinitrobenzonitrile (7)** [R_f 0.50 (red-brown with EDA/Me_2SO)] was isolated by preparative TLC using benzene as the extracting solvent. Evaporation of the benzene gave a white solid: mp 134 °C; MS (M^+, 238); NMR δ 9.35 (acetone-d_6). Comparison of **7**'s spectroscopic data with that of a known sample[24] of the nitrile (mp 135–136 °C) showed them to be identical.

(3) **syn-2,4,6-Trinitrobenzaldoxime (4)** (R_f 0.25, red-brown with EDA/Me_2SO) was isolated by preparative TLC (vida supra). On the TLC plate and in the presence of light, **4** is slowly transformed to **5**, **6**, and **7**. However, with benzene as the extracting solvent, and in the absence of light, **4** was isolated as a white solid: NMR (benzene-d_6) δ 7.92 (s, 1), 7.78 (s, 2), 6.90 (s, 1); MS (M^+, 256); IR (KBr) sharp band at 3525 cm^{-1}. The IR, NMR, and mass spectra of **4** were identical with those of an authentic sample prepared from 2,4,6-trinitrobenzaldehyde and hydroxylamine hydrochloride[25] (vida infra).

(4) **anti-2,4,6-Trinitrobenzaldoxime (5)**[26,27] (R_f 0.15, pink fading to yellow with EDA/Me_2SO). Attempted isolation of **5** via preparative TLC resulted in its transformation to **6** and **7**. However, irradiation of a benzene solution of **4** in sunlight gave a 1:1 equilibrium mixture of **4** and **5** (TLC analysis). Evaporation of the benzene left a white solid. IR of the mixture (KBr) was

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(23) (a) K. V. Auwers, *Ber. Dtsch. Chem. Ges. B*, **57**, 461 (1924); (b) H. Lindemann and H. Thiek, *Justus Liebigs Ann. Chem.*, **449**, 63 (1926); (c) H. Lindemann, H. Konitika, and S. Romanoff, *Justus Liebigs Ann. Chem.*, **456**, 284 (1927); (d) O. L. Brady and G. Bishop, *J. Chem. Soc.*, **127**, 1357 (1925).

(24) M. E. Sitzmann and J. C. Dacons, *J. Org. Chem.*, **38**, 4363 (1973).

(25) F. Sachs and W. Everding, *Ber. Dtsch. Chem. Ges.*, **36**, 961 (1904).

(26) L. Fieser and M. Fieser, "Advanced Organic Chemistry", Reinhold, New York, 1961, p 438.

(27) J. P. Vermes and R. Bengelmans, *Tetrahedron Lett.*, **25**, 2091 (1969).

the same as **4** but with an additional broad band at 3250 cm⁻¹.
NMR of the mixture (benzene-d_6): δ 7.92 (s, 1), 7.78 (s, 2), 7.38 (s, 1), 8.00 (s, 2). The hydroxyl proton NMR resonances were *not* present.

(5) 2-Hydroxy-4,6-dinitrobenzonitrile (8) (R_f 0.00, yellow turns green with EDA/Me₂SO) formed slowly from **6** in solution or on the TLC plate. It was isolated as a yellow acidic solid by preparative TLC [IR 3525 (OH), 2250 cm⁻¹ (CN); MS (M⁺, 209); NMR (acetone-d_6) pair of meta coupled doublets with 10-Hz couplings at δ 8.24 and 8.48]. Treatment of **8** with diazomethane gave 2-methoxy-4,6-dinitrobenzonitrile which was independently synthesized from reaction of 2,4,6-trinitrobenzonitrile with sodium methoxide. These two methoxy compounds had identical TLC, NMR, and MS data. The structural assignments for **6** and **8** are also supported by the reported[23] chemistry of substituted benzisoxazole formation and subsequent ring opening to the corresponding ortho cyanophenol.

(6) Reaction of 2,4,6-Trinitrobenzonitrile with Sodium Methoxide: 2-Methoxy-4,6-dinitrobenzonitrile, 4-Methoxy-2,6-dinitrobenzonitrile, and 2,4-Dimethoxy-6-nitrobenzonitrile. Sodium metal (0.6 g) was dissolved in 15 mL of methanol. A 5.5-mL aliquot of this solution was added dropwise, with stirring, to a boiling solution of 3.0 g (0.0125 mol) of 2,4,6-trinitrobenzonitrile in 30 mL of methanol. The red reaction mixture was allowed to cool and evaporate to half its original volume. Crystals formed and were isolated and recrystallized from benzene. TLC (in benzene) indicated mainly two compounds, one at R_f 0.35 and one at R_f 0.30. These were separated by column chromatography on silica gel-60 using benzene/hexane (1:1) at the start and gradually changing to benzene/hexane (3:1).

The component with an R_f value of 0.35 was found to be 2-methoxy-4,6-dinitrobenzonitrile: mp 120–121 °C (0.75 g isolated); NMR (acetone-d_6) δ 4.30 (s, 3), 8.58 (d, 1), 8.40 (d, 1); MS (M⁺, 223). Anal. Calcd for C₈H₅N₃O₅: C, 43.06; H, 2.26; N, 18.83. Found: C, 42.92; H, 2.21; N, 18.74.

The component at R_f 0.30 (0.5 g isolated) was 4-methoxy-2,6-nitrobenzonitrile: mp 133–134 °C; NMR (acetone-d_6) δ 8.10 (s, 2), 4.12 (s, 3); MS (M⁺, 223). Anal. Calcd for C₈H₅N₃O₅: C, 43.06; H, 2.26; N, 18.83. Found: C, 43.00; H, 2.21; N, 18.76.

When the mother liquor from the above monomethoxy compounds was further concentrated, a third compound, 2,4-dimethoxy-6-nitrobenzonitrile, crystallized out (yellow needles): mp 142–143 °C; NMR (acetone-d_6) δ 3.96 (s, 3), 4.01 (s, 3), 7.32 (d, 1), 7.07 (d, 1); MS (M⁺, 208). Anal. Calcd for C₉H₈N₂O₄: C, 51.93; H, 3.87; N, 13.46. Found: C, 51.88; H, 3.88; N, 13.34.

(7) Preparation of *syn*-2,4,6-Trinitrobenzaldoxime. To a solution of 14.4 g (0.06 mol) of the aldehyde in 300 mL of boiling ethanol was added 12.4 g of NH₂OH·HCl (0.18 mol) in 60 mL of water, followed by 120 mL of 5% NaHCO₃ added dropwise with stirring. Water was added until the solution became cloudy, then it was cooled to give 10.0 g of white solid, mp 156–157.6 °C (lit. 158 °C).[23] Upon concentrating the filtrate, another 3.3 g (mp 155.7 °C) was obtained to give a total yield of 88%. Determination of the structure to be the syn form was done by X-ray crystallography of a single crystal.

Reactions of *o*-Xylylenes Produced Photochemically from *o*-Alkylstyrenes[1a]

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The potential synthetic utility of *o*-xylylenes generated photochemically from *o*-alkylstyrenes has been investigated. The *o*-xylylenes produced from **3a**, **3b**, and **3c** were trapped with cyclohexene to yield octahydroanthracene derivatives in good yields (94, 86, and 63%, respectively). In the absence of cyclohexene, the *o*-xylylene from **3a** dimerized to produce **8**. Irradiation of **16** gave an *o*-xylylene which is an enol and which subsequently tautomerized to aldehyde **9**. Deuterium-labeling studies supported this mechanism. The quantum yield for formation of **9** upon direct irradiation of **16** was 0.085, and that for the xanthone photosensitized process was 0.027.

Because of their high reactivity as dienes in the Diels–Alder reaction, *o*-xylylenes (or *o*-quinodimethanes) are showing considerable promise as intermediates in organic synthesis.[2] Among the many methods for generating *o*-xylylenes, the one most used in synthesis is the thermolysis of benzocyclobutenes. Another method for generating *o*-xylylenes that has been used synthetically is

the photoenolization of *o*-alkylphenyl ketones, such as **1**.[3] The resulting photoenols **2** are readily trapped with reactive dienophiles. However, it has been reported[4] that
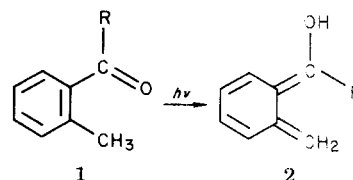
the photoenol derived from 2,4-dimethylbenzophenone cannot be trapped with weaker dienophiles such as cyclohexene. Presumably the proton tautomerization of **2**

(1) (a) For a preliminary communication of part of this work see J. M. Hornback, *Tetrahedron Lett.*, 3389 (1976); (b) NSF Undergraduate Research Participant, Summer 1976; (c) NSF Undergraduate Research Participant, Summer, 1978.
(2) For a few leading references see (a) T. Kametani et al., *J. Am. Chem. Soc.*, 100, 6218 (1978); (b) T. Kametani and K. Fukumoto, *Acc. Chem. Res.*, 9, 319 (1976); (c) R. L. Funk and K. P. C. Vollhardt, *J. Am. Chem. Soc.*, 99, 5483 (1977); (d) K. P. C. Vollhardt, *Acc. Chem. Res.*, 10, 1 (1977); (e) W. Oppolzer, *Angew. Chem., Int. Ed. Engl.*, 16, 10 (1977); (f) W. Oppolzer, *Synthesis*, 793 (1978); (g) J. R. Wiseman, N. I. French, R. K. Hallmark, and K. G. Chiong, *Tetrahedron Lett.*, 3765 (1978).

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