# A Comparative Study of the Photolytic Decompositions of 2-Azidoacetophenone and 3-Methylanthranil

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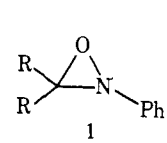
**Abstract:** The photolyses of 2-azidoacetophenone and 3-methylanthranil in degassed methanol at 313 nm proceed with quantum yields of 0.63 ± 0.04 and 0.16 ± 0.03, respectively. These quantum efficiencies are unaffected by solvent changes to cyclohexane and benzene. When these photolyses are conducted in piperidine at 300 nm, 3-acetyl-2-piperidino-3*H*-azepine is formed in a virtually quantitative yield from 3-methylanthranil, while 3-acetyl-2-piperidino-3*H*-azepine plus an almost equal amount of a new azepine, 7-acetyl-2-piperidino-3*H*-azepine, are isolated from 2-azidoacetophenone. Yields of 2-aminoacetophenone are <3%. Neither of these reactions could be quenched with oxygen or piperylene. An esr signal for a triplet arylnitrene is found for 2-azidoacetophenone but not for 3-methylanthranil after photolysis in a solvent matrix at −196°. Photosensitization with benzene and triphenylene is singlet in nature. Triplet photosensitization occurs with acetophenone, xanthone and 3-methoxyacetophenone yielding 2-aminoacetophenone as the major product. Evidence excluding chemical sensitizations by photochemically generated ketyl radicals is presented. The course of these photochemical reactions is discussed from the standpoint of multiplicity, reversibility, selectivity, and observed thermal reactions.

Studies of photochemical and thermal reactions in which an arylnitrene has been postulated, or appears to be possible,[1-9] have been an area of widespread past and present interest. Once generated, arylnitrenes yield a wide variety of products resulting from ring modifications, hydrogen abstractions, and insertion reactions. Less certain about these reactions are the mechanistic details which include the spin multiplicity of the intervening nitrene as well as the factors influencing the subsequent pathway by which the nitrene is converted into the isolated products. Photochemical rather than thermal generation of potential arylnitrenes provides the advantage of isolation of thermally unstable products.[10] Nevertheless, a detailed mechanistic investigation can be complicated by crossing from the singlet to the triplet manifold in the arylnitrene precursor as well as in the nitrene itself, by chemical[5d] as well as electronic quenching, by singlet energy transfer,[11] and by possible photoinduced, free-radical reductions[5d,12] of the arylnitrene precursor.

We were particularly interested in the pathway by which photochemically produced arylnitrenes ring expand to the 3*H*-azepines.[5a] This study was stimulated by the report[8] that photosensitization of 3-substituted 2-phenyloxaziridine (**1**) and phenylazide gave triplet phenylnitrene which abstracted hydrogen from the solvent to give aniline. These results suggested that singlet and triplet arylnitrenes underwent different reactions, since direct photolysis of phenylazide in diethylamine gave[5a] an azepine in high yield. Unfortunately, the problems posed by possible chemical sensitization were not considered.

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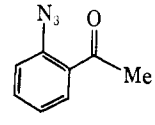


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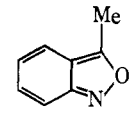


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A photolytic study of the model compounds 2-azidoacetophenone (**2**) and 3-methylanthranil (**3**) was initiated in order to examine the various factors influencing ring expansion to 3*H*-azepines for the following reasons. (1) 3*H*-Azepines were known[9] to be formed in high yields from the photolysis of anthranils. (2) Although 2-azidoacetophenone and 3-methylanthranil can, in principle, yield the same arylnitrene, **4** (R = acetyl), it was expected that the radically different precursors would dramatically affect the subsequent photolytic pathways. Specifically, if the rate of intersystem crossing for 2-azidoacetophenone approached the value of $10^{10}$ $sec^{-1}$ reported[13] for acetophenone, decomposition through a singlet must be very fast to escape decomposition through the triplet manifold.[14] (3) 2-Azidoacetophenone undergoes a facile thermal decomposition[15] to yield 3-methylanthranil thus providing a pos-

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(3) J. I. G. Cadogen, *et al.*, *J. Chem. Soc.*, 2808, 2813, 2819 (1969), and references therein.

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(5) (a) W. von E. Doering and R. A. Odum, *Tetrahedron*, **22**, 81 (1966); (b) A. Reiser and R. Marley, *Trans. Faraday Soc.*, **64**, 1806 (1968), and references therein; (c) R. A. Odum and A. M. Aaronson, *J. Amer. Chem. Soc.*, **91**, 5680 (1969); (d) J. S. Swenton, T. J. Ikeler, and B. H. Williams, *ibid.*, **92**, 3103 (1970); (e) R. J. Sundberg, M. Brenner, S. R. Suter, and B. P. Das, *Tetrahedron Lett.*, 2715 (1970).

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(7) (a) R. A. Odum and M. Brenner, *ibid.*, **88**, 2074 (1966); (b) R. J. Sundberg, *ibid.*, **88**, 3781 (1966).

(8) J. S. Splitter and M. Calvin, *Tetrahedron Lett.*, 1445 (1968).

(9) (a) M. Ogata, H. Kano, and H. Matsumoto, *Chem. Commun.*, 397 (1968); (b) M. Ogata, H. Matsumoto, and H. Kano, *Tetrahedron*, **25**, 5205 (1969).

(10) M. Ogata, H. Matsumoto, and H. Kano, *ibid.*, **25**, 5217 (1969).

(11) F. D. Lewis and J. C. Dalton, *J. Amer. Chem. Soc.*, **91**, 5260 (1969).

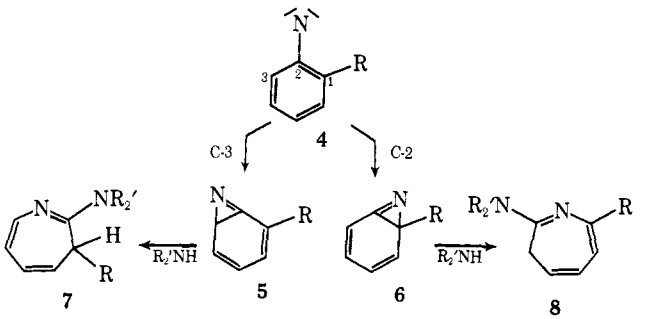
(12) (a) B. M. Monroe and S. A. Weiner, *ibid.*, **91**, 450 (1969); A. Padwa, W. Bergmark, and D. Pashayon, *ibid.*, **91**, 2653 (1969).

(13) A. A. Lamola and N. J. Turro, "Energy Transfer and Organic Photochemistry," Wiley, New York, N. Y., 1969, p 198.

(14) The failure of 4-azidoacetophenone or 4,4′-diazidobenzophenone to exhibit[5b] phosphorescence does not exclude triplet population, since the absence of phosphorescence may be due to high quantum efficiencies for decomposition and/or radiationless decay from the lowest triplet state.

(15) The thermal decomposition of 2-azidoacetophenone in methanol either at 65° or in the injection port of the glpc equipment proceeds readily to give 3-methylanthranil. No azepine could be detected.

sible competing process to azepine formation. (4) The generation of an arylnitrene from 2-azidoacetophenone is an irreversible process and reversible in the 3-methylanthranil case. (5) The potential arylnitrene intermediate, **4** (R = acetyl), formed from either 2-azidoacetophenone or 3-methylanthranil allowed the selectivity of the 3*H*-azepine formation to be examined since two azabicyclo[4.1.0]hepta-2,4,6-trienes[16] (**5** and **6**, R = acetyl) can be envisaged from the competition of C-1 *vs.* C-3 ring closure.




Prior to the completion of this work, a brief report[5c] pertaining to the photolysis of a variety of 4-substituted phenylazides in dimethylamine appeared. The results of this study are in overall agreement but there are some major differences and additions.

## Results

**Absorption Spectra.** The ultraviolet absorption spectrum of 2-azidoacetophenone in methanol exhibits maxima at 234 (log $\epsilon$ = 4.19), 264 (log $\epsilon$ = 3.43), and 305 nm (log $\epsilon$ = 3.43). In cyclohexane an additional shoulder of low intensity appears at 317 nm on the main peak at 302 nm (log $\epsilon$ = 3.41). 3-Methylanthranil displays a maximum at 317 nm (log $\epsilon$ = 3.79 in methanol, log $\epsilon$ = 3.73 in cyclohexane).

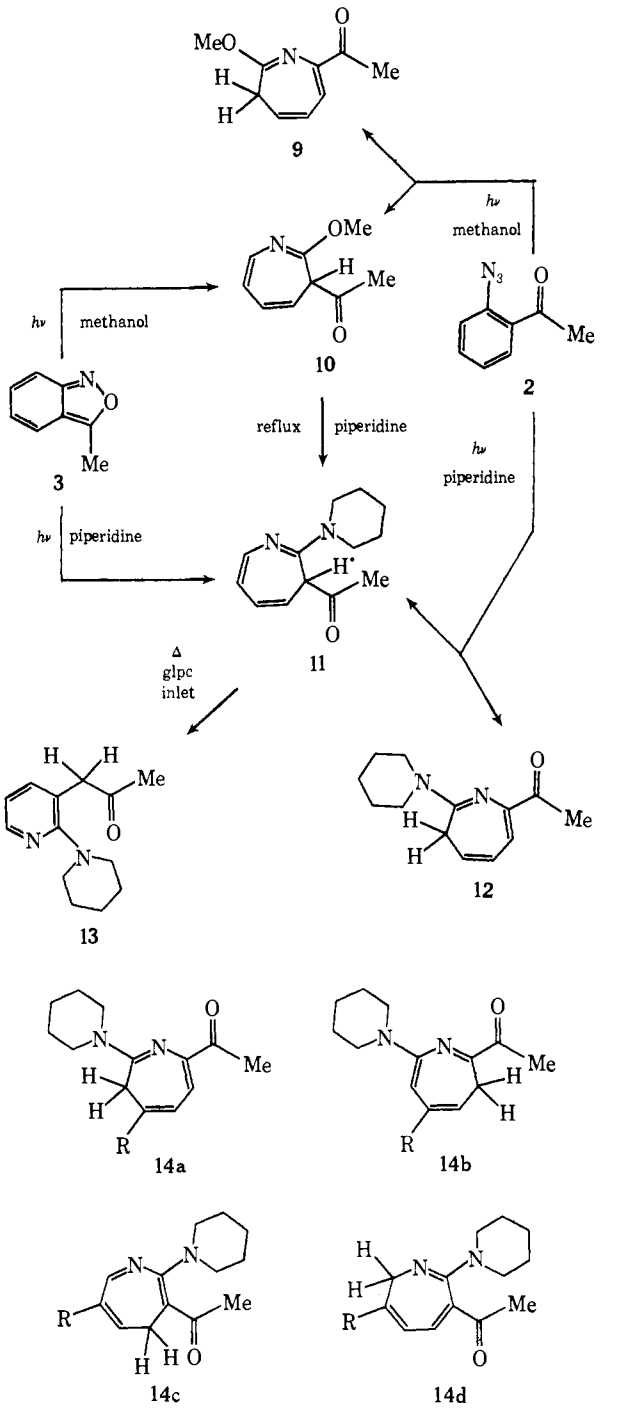
**Direct Photolyses.** These results are depicted in Scheme I and summarized in Table I. The disappearance of 3-methylanthranil at 313 nm in methanol proceeded with a quantum efficiency of 0.16 ± 0.03 yielding 3-acetyl-2-methoxy-3*H*-azepine (**10**) in a 58% yield. The yield of 2-aminoacetophenone was less than 3%. The quantum yield for disappearance of 3-methylanthranil was unaffected by a switch to cyclohexane or benzene as solvent. Glpc analysis failed to show significant product yields in nonnucleophilic solvents. Only polymeric materials could be isolated. When the photolysis was conducted in piperidine, 3-acetyl-2-piperidino-3*H*-azepine (**11**) was formed in a virtually quantitative yield and could be isolated by column chromatography along with traces of 7-acetyl-2-piperidino-3*H*-azepine (**12**). 3-Acetyl-2-piperidino-3*H*-azepine, unlike the methoxy derivative, underwent a rapid thermal rearrangement[17] to 3-acetonyl-2-piperidinopyridine (**13**) in the injection port during glpc analysis. 3-Acetyl-2-methoxy-3*H*-azepine could easily be converted to 3-acetyl-2-piperidino-3*H*-azepine by reflux in piperidine.

The disappearance of 2-azidoacetophenone upon direct photolysis with 313-nm light in methanol or cyclohexane proceeded with a quantum yield of 0.63 ± 0.04.

(16) These intermediates have been widely postulated as short-lived precursors to azepines. See ref 1, 2b, 3, 5, and 9.

(17) This interesting rearrangement has been the subject of a more detailed report. See ref 10.

**Scheme I**




With methanol as solvent, 3-acetyl-2-methoxy-3*H*-azepine was formed in a 37% yield. The yield of 3-acetyl-2-methoxy-3*H*-azepine was found to be a linear function of the disappearance of azide up to 51% consumption with no apparent induction period. Glpc analysis indicated no other significant peaks except for 3-methylanthranil.[18] The yield of 2-aminoacetophenone was less than 3%. Uv spectral analysis, however, suggested the presence of an additional product ab-

(18) Unlike the photolyses in methanol for which uv analysis was suitable for monitoring azide disappearance at low conversions, no method was totally acceptable with piperidine as solvent. Uv, ir, $N_2$ evolution, and glpc analysis were all tried and the glpc technique was used as the best compromise. The use of glpc depends on the ability to monitor azide disappearance by the 3-methylanthranil generated from it in the injection port.[15] This measurement is obscured to the extent that anthranil is formed as a primary photoproduct.

**Table I.** Direct Photolyses[a] of 2-Azidoacetophenone and 3-Methylanthranil

| Reactant | $\Phi_d$[b] | Solvent | % disappearance % reactant | Product yields[c] (theor[d]), % 9 | 10 | 11 | 12 |
|---|---|---|---|---|---|---|---|
| **3** | 0.16 ± 0.03 | Methanol | 14 ± 2[e] | ?[f] | 7 ± 1 (58 ± 3) | | |
| **3** | | Methanol | 54 ± 4[e] | ?[f] | 30 ± 2 | | |
| **3** | 0.16 ± 0.03 | Cyclohexane | 15 ± 1[g] | Only polymeric material isolated | | | |
| **3** | 0.15 ± 0.03 | Benzene | 20 ± 1[g] | Only polymeric material isolated | | | |
| **3** | | Piperidine | 26 ± 2[e] | | | 23 ± 2 (98 ± 5) | Trace[h] |
| **3** | | Piperidine | 56 ± 4[e] | | | 52 ± 4 | Trace[h] |
| **2** | 0.65 ± 0.04 | Cyclohexane | 21 ± 2[g] | Only polymeric material isolated | | | |
| **2** | 0.63 ± 0.04 | Methanol | 18 ± 1[g] | ?[f] | 5 ± 1 (37 ± 3) | | |
| **2** | | Methanol | 30 ± 2[g] | ?[f] | 11 ± 2 | | |
| **2** | | Piperidine | ~15[i] | | | 6 ± 1 | 5 ± 1 |
| **2** | | Piperidine | ~40[i] | | | 18 ± 2 | 17 ± 2 |

[a] Degassed 0.05 *M* samples using Rayonet photochemical reactor with 300-nm lamps. [b] Quantum yields for disappearance of reactant. Done separately at 313 nm [c] Determined by glpc with internal standard where **11** was by necessity measured at **13**. Yields are based on total amount of **2** or **3** and are not corrected for unreacted starting material. [d] Theoretical yields obtained using the slope method plotting product yields *vs.* the decrease in reactant at five points up to 55% reactant disappearance. [e] Glpc analysis. [f] Product **9** falls under or is poorly separated from **3** upon glpc analysis under a variety of columns and conditions. [g] Uv analysis, solutions allowed to stand 2 hr before analysis. [h] Identified by glpc collection and ir comparison with **12** produced from **2**. Less than 2% of theoretical yield. [i] By glpc analysis.[18]

sorbing at 300–320 nm, a region in which 3-methylanthranil absorbs strongly. Nevertheless, samples of the 3-methylanthranil glpc peak failed to yield superimposable spectra when subjected to an infrared comparison with authentic material. Nmr analysis indicated the presence of an additional azepine. Attempts to isolate this azepine by column chromatography or glpc were unsuccessful. The same problems were encountered with the ethoxy derivative. The use of piperidine as solvent was more successful and based upon the nmr analysis and the results with 2-azido-4 methylacetophenone, the unknown was assigned the structure 7-acetyl-2-methoxy-3*H*-azepine (**9**).

Photolysis of 2-azidoacetophenone in piperidine yielded two major products, which could be separated by column chromatography. One of these was 3-acetyl-2-piperidino-3*H*-azepine. Even though nmr and ir analyses indicated that the other product was an isomeric azepine having a conjugated keto function and a basic carbon framework consisting of a methylene group attached to a diene structure possessing $\alpha$, $\beta$, and $\gamma$ vinyl protons, its structure could not be unambiguously established. If all the possibilities arose through the opening of the azirines **5** and **6** (R = acetyl) by piperidine, four azepines, **14a–d** (R = hydrogen), fit the nmr splitting patterns. To simplify the problem, 2-azido-4-methylacetophenone was photolyzed in piperidine and the equivalent unknown product was isolated. The collapse of the methylene proton signal from the doublet observed at 2.56 ppm for the azepine formed from 2-azidoacetophenone to the singlet observed at 2.57 ppm for the azepine formed from 2-azido-4-methylacetophenone rules out structures **14b** + **c**. Structure **14d** can be excluded on the basis of the chemical shift of the methylene protons as well as the failure to observe line broadening for them. Accordingly, the structures of the second azepine isolated in the photolysis of 2-azidoacetophenone and 2-azido-4-methylacetophenone were assigned as **9**, **12**, and **14a** (R = methyl). In piperidine, azepine yields based upon azide disappearance[18] could not be obtained with accuracy at low azide conversions but accounted for ~60% of the material balance upon prolonged irradiation.

**Esr Measurements.** The esr spectra obtained after a 15-min irradiation of 2-azidoacetophenone with 300-nm light at −196° in a variety of solvents gave the following signals: toluene (6710 G), ethylbenzene (6630 G), and tetrahydrofuran (6630 G). The signal persists for over 24 hr if the sample is maintained at −196°. 3-Methylanthranil failed to yield a similar signal under the same conditions.

**Quenching and Sensitization Studies.** These results are summarized in Tables II and III. The disappearance of 2-azidoacetophenone and 3-methylanthranil as well as the appearance of their photoproducts could not be quenched with oxygen or moderate and high concentrations of piperylene. Whether or not these results are consistent with a singlet or very rapidly reacting triplet pathway could be determined if the triplet states could be populated *via* triplet photosensitization. The aromatic sensitizers, benzene and triphenylene, were tried initially in order to avoid potential complications associated with the photoreduction of aromatic ketones. The photolysis of either 2-azidoacetophenone or 3-methylanthranil in 3:1 benzene–methanol at 254 nm under conditions whereby the benzene was absorbing >98% of the light led to the formation of 3-acetyl-2-methoxy-3*H*-azepine. With 254-nm light triphenylene sensitized the disappearance of 3-methylanthranil but not 2-azidoacetophenone and again azepine was formed. Nevertheless, the failure to quench this latter process with added piperylene suggested that a singlet pathway was responsible.

2-Azidoacetophenone was shown to suppress the phosphorescence of xanthone in EPA at −196° with approximately the same efficiency as piperylene. Irradiation of methanolic solutions of azide at 350 nm under conditions whereby xanthone absorbed virtually all of the light led to an immediate discoloration

**Table II.** Quenching Attempts on the Photodecomposition of 2-Azidoacetophenone and 3-Methylanthranil

| Reactant (conc[a]) | $h\nu$[b] | Quencher (concn[c]) | % photolysis[d] | Quenched/unquenched ratios: Reactant disappearance | 12 | 12/11 |
|---|---|---|---|---|---|---|
| **3** (2.8, MeOH) | 313 | $O_2$ (atm) | 14 ± 2 | 1.03 ± 0.05 | | |
| **2** (3.7, MeOH) | 313 | $O_2$ (atm) | 16 ± 2 | 1.02 ± 0.05 | | |
| **3** (2.8, MeOH) | 313 | Piperylene (0.15) | 20 ± 2 | 0.95 ± 0.05 | | |
| **3** (2.8, MeOH) | 313 | Piperylene (1.0) | 10 ± 1 | 0.97 ± 0.05 | | |
| **2** (3.7, MeOH) | 313 | Piperylene (0.15) | 50 ± 3 | 0.96 ± 0.05 | | |
| **2** (50, piperidine) | 300 | Piperylene (1.0) | 40 ± 4[f] | | 1.04 ± 0.06[e] | 1.03 ± 0.06[e] |
| **2** (50, piperidine) | 300 | Piperylene (1.0) | 50 ± 5[f] | 1.06 ± 0.06[f] | | |

[a] Concentration of reactant × $10^3 M$, solvent; degassed except with oxygen as quencher. [b] Wavelength of excitation. The 313-nm source was provided by a Bausch and Lomb high intensity monochrometer with super pressure mercury lamp and the 300-nm source by a Rayonet photochemical reactor with 300-nm lamps. [c] Concentration (molar) of quencher. [d] Obtained by uv analysis unless noted otherwise. [e] Obtained by glpc where **11** must necessarily be measured as **13**. [f] Measured by monitoring glpc peak associated with 3-methylanthranil.[18]

**Table III.** Sensitized Photolyses[a] of 2-Azidoacetophenone and 3-Methylanthranil

| Reactant (concn, $M$) | Solvent | Sensitizer (concn, $M$) | $h\nu$[b] | % disappearance: **2** or **3**[c] | % disappearance: Sensitizer[d] | % appearance of 2-aminoacetophenone[c] |
|---|---|---|---|---|---|---|
| **2** (0.0) | 1:1 PhH–MeOH[e] | Xanthone (0.075) | 350 | 80 ± 5 | ~1–2 | 26 ± 4 |
| **2** (0.01) plus 1 $M$ piperylene | 1:1 PhH–MeOH[e] | Xanthone (0.075) | 350 | 15 ± 3[f] | ~1–2 | 4 ± 3 |
| None | 1:1 PhH–MeOH[e] | Xanthone (0.075) | 350 | | 10 ± 2 | |
| **2** (0.013) | Piperidine | Xanthone (0.075) | 350 | 94 ± 6 | | 87 ± 5 |
| **3** (0.013) | Piperidine | Xanthone (0.075) | 350 | 63 ± 5 | | 75 ± 5 |
| **2** (0.052) | MeOH | 3-Methoxyacetophenone (2) | 300 | 46 ± 5[g] | | Not measured |
| **2** (0.052) plus 1 $M$ piperylene | MeOH | 3-Methoxyacetophenone (2) | 300 | 6 ± 3[g,f] | | Not measured |
| None | MeOH | 3-Methoxyacetophenone (0.01) | 300 | | <4 | |
| **2** (0.050) | MeOH | 3-Methoxyacetophenone (2) | 254 | 46 ± 5[g] | | Not measured |
| **2** (0.050) | MeOH | Acetophenone (2) | 254 | 64 ± 5[g] | | Not measured |
| **2** (0.025) | MeOH | 3-Methoxyacetophenone (2) | 254 | 36 ± 5[g] | | Not measured |
| **2** (0.025) | MeOH | Acetophenone (2) | 254 | 55 ± 5[g] | | Not measured |
| **2** (0.050) | Piperidine | 3-Methoxyacetophenone (2) | 254 | 42 ± 5[g] | | 75 ± 10 |
| **2** (0.050) | Piperidine | Acetophenone (2) | 254 | 60 ± 5[g] | | 67 ± 10 |

[a] Degassed, 10-ml quartz vessels; brackets indicate those runs which received equal amounts of light. [b] Rayonet photochemical reactor with 254-, 300-, and 350-nm lamps. [c] Determined by glpc[18] except where noted. Amine yields are based on amount of disappearance of **2** or **3**. [d] Determined by uv analysis. [e] Benzene–methanol mixture needed because of insolubility of xanthone. [f] Uncorrected for small amount of azepine formed. Azepine yields ~0 after adjusting for yield expected from the nonsensitized, direct absorption by the azide. [g] Determined by ir analysis of absorption in the 2050–2150-$cm^{-1}$ region.

which failed to occur when xanthone was irradiated without azide present. Glpc analysis indicated that 2-aminoacetophenone was being formed in low yields at the expense of the azide. Further, this sensitization could be dramatically quenched with added piperylene. The use of piperidine as solvent led to increased yields of amine. The yields of azepines with xanthone as sensitizer were <2% of theoretical and were not quenched in the presence of 1 $M$ piperylene. Simultaneous xanthone sensitizations at 350 nm of equal concentrations of 2-azidoacetophenone and 3-methylanthranil in piperidine under conditions where both received the same amount of light indicated that the disappearance of the 3-methylanthranil glpc peak[18] and appearance of 2-aminoacetophenone were slightly faster for 2-azidoacetophenone. 3-Methoxyacetophenone was shown to sensitize the disappearance of 0.05 $M$ solutions of azide with ~70% the efficiency of acetophenone. The sensitizers were both receiving >96% of the 254-mm light under these conditions. The possibility that these results might be due to differences in the absorption spectra of 3-methoxyacetophenone and acetophenone or to the lack of a purely monochromatic light source were eliminated by using lower concentrations of azide without affecting this efficiency relationship. The 3-methoxyacetophenone-sensitized disappearance of azide was quenchable with piperylene and was shown to proceed about 50 times faster than the disappearance of sensitizer photolyzed with no azide present. Sensitization of 2-azidoacetophenone with either 3-methoxyacetophenone or acetophenone gave high yields of 2-aminoacetophenone in piperidine.

## Discussion

The lack of a solvent dependence for $\Phi_d$ excludes solvent involvement except as a trapping agent. Three factors argue against the mechanism

$$\mathbf{2} \xrightarrow{h\nu} \mathbf{3} \xrightarrow{h\nu} \text{azepine}$$

for the photolysis of 2-azidoacetophenone. (1) The distribution of the 3$H$-azepine isomers differs from the distribution observed for the photolysis of 3-methylanthranil. (2) Straight-line plots of azide disappearance *vs.* the appearance of 3-acetyl-2-methoxy-3$H$-azepine are obtained. (3) A higher quantum yield is

observed for formation[19] of 3-acetyl-2-methoxy-3*H*-azepine from 2-azidoacetophenone ($\Phi = 0.23 \pm 0.04$) than from 3-methylanthranil/($\Phi = 0.09 \pm 0.03$).

The most striking feature of the direct photolysis of 2-azidoacetophenone is the observed exclusive singlet pathway, since triplet sensitization leads to formation of 2-aminoacetophenone. The rate of photodecomposition of 2-azidoacetophenone must, therefore, be greater than the rate of intersystem crossing to the triplet state, the multiplicity from which most photochemistry is initiated for the unsubstituted acetophenone. The shoulder of low intensity which appears at 317 nm on a main peak at 302 nm in the uv spectrum of 2-azidoacetophenone in cyclohexane very probably is an $n \rightarrow \pi^*$ transition; however, in methanol, the expected blue shift for this shoulder leaves only the intense ($\pi,\pi^*$) band[20] at 305 nm. While we have no evidence to exclude the possibility that the photodecomposition of 2-azidoacetophenone in polar solvents may be from an $S_1(n,\pi^*)$ state buried in the tail of the intense ($\pi,\pi^*$) band, $S_1(\pi,\pi^*)$ states have intrinsically shorter[21] lifetimes than $S_1(n,\pi^*)$ states, thus requiring a rate of intersystem crossing faster than that needed to capture $S_1(n,\pi^*)$ states in order to efficiently populate the triplet manifold.

The failure of either 2-azidoacetophenone or 3-methylanthranil to react in an available triplet pathway removes any ambiguity[5b] in reducing the possible states through which these molecules must pass prior to decomposition to just those occurring in the singlet manifold subsequent to population of $S_1$, since the $\sigma$ NN or $\sigma$ NO bond to be broken is not directly perturbed[5b] in the $S_1$ state. The formation of 3*H*-azepines in high yields from the photolysis of 2-azidoacetophenone, when thermolysis[15] yields exclusively 3-methylanthranil, does not constitute evidence against participation of a vibrationally excited ground state, since conventional ground-state kinetic selectivity favoring the pathway with lowest energy requirements does not apply to a vibrational level population of $S_0$ from $S_1$. Nevertheless, invoking a vibrationally excited ground-state mechanism, even when such a pathway is clearly available, must be tentative in view of the difficulties[22] that arise in attempting to exclude all other possible mechanisms competing for $S_1$. Since fluorescence for 2-azidoacetophenone and 3-methylanthranil could not be detected, the pathway competing for $S_1$, regardless of mechanism, must be proceeding at a rate faster than their inherent radiative lifetimes which are calculated[21] to be $4 \times 10^{-10}$ sec for 2-azidoacetophenone and $2 \times 10^{-10}$ sec for 3-methylanthranil assuming that the lowest excited singlet is ($\pi,\pi^*$) in nature.

The esr signal observed at 6710 G upon photolysis of 2-azidoacetophenone at $-196°$ is very similar in its characteristics to the reported[23] signal at 6701 G for triplet phenylnitrene obtained from phenylazide under similar conditions. Neither of these molecules has a significant triplet pathway[5a] for photolysis in solution at room temperature so that detection of an esr triplet nitrene signal must be due to the suppression of the chemical degradation reactions competing for singlet nitrene at these low temperatures. Although the failure to detect a similar signal for 3-methylanthranil may be used as an argument against an arylnitrene participating in this case, it should be noted that some azides show similar behavior.[23] Recombination of the initially generated arylnitrene formed from 3-methylanthranil may explain the esr results as well as the decreased quantum efficiency[24] over that observed for the azide. It is clear from the identity of $\Phi_d$ for 3-methylanthranil in methanol and benzene that reversibility need be considered only prior to closure at C-3 to form azirine **5** (R = acetyl) and that this azirine will be diverted to pathways other than re-formation of anthranil if it is not captured by a nucleophile. Reversibility will not, however, explain why an arylnitrene generated from 3-methylanthranil which manages to escape recombination does not exhibit the same selectivity with regard to closure and capture at C-1 to give azepines **9** and **12** *vs.* closure and capture at C-3 to give azepines **10** and **11** as observed for those formed from 2-azidoacetophenone. We are continuing our studies of this curious result.[25]

Many of the interpretations proposed for the results of this study rest upon establishing the validity of the triplet-sensitized decompositions of 2-azidoacetophenone and 3-methylanthranil. The observed quenching of xanthone disappearance by the 4-substituted phenylazides[5c] is a necessary but not conclusive requirement[12b] for triplet energy transfer. Purely aromatic sensitizers were tried initially in this study in the hope of avoiding the complication of chemical sensitization by ketyl radicals.[12b] Whenever benzene or triphenylene ($E_T$ = 85 and 67 kcal mol$^{-1}$, respectively)[26] sensitized the disappearance of 2-azidoacetophenone or 3-methylanthranil, 3*H*-azepines were formed. The failure to quench this sensitization with added piperylene suggests that singlet energy transfer is responsible. Such a process has been reported[11] for the phenanthrene-sensitized disappearance of alkylazides. The aromatic ketones, acetophenone, 3-methoxyacetophenone, and xanthone photosensitized the disappearance of 2-azidoacetophenone and 3-methylanthranil to give 2-aminoacetophenone rather than 3*H*-azepines. Triplet energy transfer and not chemical sensitization appears to be involved for the following reasons. (1) The photosensitization reaction is quenchable with piperylene. (2) The disappearance of 2-azidoacetophenone and concurrent formation of 2-aminoacetophenone is proceeding almost as fast with the sensitizer 3-methoxyacetophenone as with acetophenone even though 3-methoxyacetophenone produces ketyl radicals with ~1% the efficiency of acetophenone.[27] The slight differ-

(19) Obtained by multiplying $\Phi_d \times$ per cent yield.

(20) 3-Acetoxy and 3-methoxy substituents attached to the aromatic ring of butyrophenone lower $S(\pi,\pi^*)$ levels to the point where the $S(n,\pi^*)$ state cannot be detected in the absorption spectra: J. N. Pitts, Jr., D. R. Burley, J. C. Mani, and A. D. Broadbent, *J. Amer. Chem. Soc.*, **90**, 5902 (1968).

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(24) That $\Phi_d$ for 3-methylanthranil is four times less efficient than for 2-azidoacetophenone is consistent with this interpretation but not necessarily required by it.

(25) The behavior of 3-methylanthranil is quite similar to other anthranils,[9b] which yield azepines resulting from nucleophilic capture of azirines formed by an overwhelming preference for C-3. Interestingly, the azepines formed from the photolysis of 2-azidoacetophenone result from an almost equal preference for C-1 and C-3, in distinct contrast to the observed preference for C-3 in both 2-azidotoluene[6] and 2-azidobiphenyl.[6e]

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ences could be totally due to the failure to achieve a diffusion-controlled rate of energy transfer because of the expected[28] proximity of the donor and acceptor $E_T$ levels. In such a case, differences of ~1 kcal mol[27,28] can have a two- or threefold influence on the rate of disappearance of acceptor. (3) The disappearance of 2-azidoacetophenone is proceeding approximately 50 times faster than the disappearance of 3-methoxyacetophenone ($\Phi_d \simeq 0.006$)[27] irradiated simultaneously with no azide present.

## Experimental Section

**General.** The light sources were provided by a Bausch and Lomb high intensity monochromator with a super pressure mercury lamp and a Rayonet photochemical reactor equipped with either 254-, 300-, and 350-nm lamps. Spectroquality solvents were employed with the exception of piperidine, which was distilled immediately prior to use. The sensitizers were all commercially available. Triphenylene and xanthone were recrystallized twice from benzene. 3-Methoxyacetophenone and acetophenone were redistilled once. Piperylene was distilled immediately prior to use. 2-Aminoacetophenone and 2-nitroacetophenone were commercially available and were used without further purification. 2-Amino-4-methylacetophenone was obtained[29] from 3-methylacetanilide. 2-Azidoacetophenone[30] and 2-azido-4-methylacetophenone were obtained from the corresponding amines by known procedures.[31] 3-Methylanthranil[32] was prepared from 2-nitroacetophenone and purified by two recrystallizations of the mercuric chloride complex from ethanol. The anthranil was obtained by subsequent treatment of this complex with concentrated potassium chloride solution, extraction, and distillation. All glpc was accomplished with a Varian Model 700 unit. The glpc of the photolyses carried out in methanol was done with a 10 ft, 0.250-in. diameter aluminum column with 10% Carbowax on 60–80 mesh Chromosorb W. Analyses for 3-methylanthranil and 2-aminoacetophenone in the photolyses done in piperidine were accomplished with a 6 ft, 0.250 in. diameter aluminum column with 3% STAP on 100–120 mesh Aeropack 30. The glpc for the piperidinoazepines was conducted on a 6 ft, 0.250 in. diameter aluminum column with 10% SE-30 on 60–80 mesh Chromosorb W. Elemental composition of products was determined by high resolution mass spectroscopy[33] and elemental analysis.[34] Potassium ferrioxalate actinometry was used.[35] Quantum yields for disappearance of 2-azidoacetophenone and 3-methylanthranil were run to 10–15% completion as determined by uv analysis. The disappearance of the anthranil was measured at 317 nm and the azide at 234 nm. The reported quantum efficiencies represent the average of two measurements. After the initial measurement, the sample cell was then used as the actinometer cell and the actinometer cell as the sample cell and the photolysis was repeated.

**Direct Photolysis of 2-Azidoacetophenone in Methanol.** 2-Azidoacetophenone (1.61 g, 0.01 mol) was dissolved in 200 ml of methanol and irradiated overnight while nitrogen was bubbling through the solution in a Rayonet photochemical reactor equipped with 300-nm bulbs. A clear liquid having an identical ir spectrum and glpc retention time as 3-acetyl-2-methoxy-3*H*-azepine[9b] was isolated by preparative glpc of the crude photolysis mixture obtained after removal of methanol under reduced pressure. The ir and nmr spectra of the material obtained by glpc collection of the broadened 3-methylanthranil peak revealed that important absorption bands other than those expected for 3-methylanthranil were present: ir (neat) 1680 $cm^{-1}$; nmr ($CCl_4$, for regions not obscured by 3-methylanthranil) $\delta$ 6.34 (doublet of a doublet, 1, $J$ = 6.0 and 9.0 Hz), 5.42 (doublet of a triplet, 1, $J$ = 6.5 and 9.0 Hz), 3.71 (s, 3, $OCH_3$), 2.58 (d, 2, $J$ = 6.5 Hz), and 2.29 ppm (s, 3, $O{=}CCH_3$). The ir and nmr evidence were interpreted to indicate that a new azepine possessing a conjugated keto function as well as a methylene group attached to a diene structure with $\alpha$, $\beta$, and $\gamma$ vinyl protons was present under the 3-methylanthranil peak. Further attempts to purify this product by column chromatography and glpc were unsuccessful.

**Direct Photolysis of 3-Methylanthranil in Piperidine.** 3-Methylanthranil (1.33 g, 0.01 mol) was dissolved in 200 ml of freshly distilled piperidine and irradiated overnight under the Rayonet 300-nm light source while nitrogen bubbled through the solution. After removal of most of the piperidine under reduced pressure, the crude brown residue was chromatographed on 100 g of grade IV, neutral alumina using hexane as solvent. Unphotolyzed starting material was collected prior to the main fraction which consisted of a slightly yellow oil. Rechromatography of this oil under the same conditions gave a pale yellow liquid which solidified upon standing. Recrystallization from cyclohexane gave 322 mg (15% based on the total amount of anthranil used) of a white solid identified as 3-acetyl-2-piperidine-3*H*-azepine: mp 67–68°; ir ($CCl_4$) 1720 and 1570 $cm^{-1}$; uv max (cyclohexane) 220 (log $\epsilon$ = 4.11) and 298 nm (log $\epsilon$ = 3.88); nmr ($CCl_4$) $\delta$ 6.83 (d, 1, $J$ = 8.0 Hz, vinyl proton at C-7), 6.33 (doublet of a doublet, 1, $J$ = 6.0 and 9.0 Hz, vinyl proton at C-5), 5.53 (doublet of a doublet, 1, $J$ = 6.0 and 8.0 Hz, vinyl proton at C-6), 5.26 (m, 1, not clearly separated from doublet appearing at lower ppm associated with vinyl proton at C-6, assigned as the vinyl proton at C-4), 4.42 (d, 1, $J$ = 9.0 Hz, methylene proton at C-3), 3.37 (m, 4, $CH_2NCH_2$), 1.80 (s, 3, $O{=}CCH_3$), and 1.56 ppm (broad singlet, 6, methylene protons not adjacent to nitrogen); spin decoupling at C-6 collapsed the proton signals at C-7 and C-5 to a singlet and doublet, respectively. Decoupling at C-4 collapsed the methylene proton at C-3 to a singlet; high-resolution mass spectrum (70 eV) *m/e* (rel intensity) molecular ion: 218.1404 (21.45), $C_{13}H_{18}N_2O$; 201.1407 (13.31), $C_{13}H_{17}N_2$; and 175.1246 (100.00), $C_{11}H_{15}M_2$.

*Anal.* Calcd for $C_{13}H_{18}N_2O$: C, 71.53; H, 8.31; N, 12.83. Found: C, 7.156; H, 8.21; N, 12.90.

**3-Acetyl-2-piperidino-3*H*-azepine.** 3-Acetyl-2-methoxy-3*H*-azepine (82.4 mg, 0.5 mol) was dissolved in 25 ml of piperidine and refluxed for 4 hr in a $N_2$ atmosphere. After removal of piperidine under reduced pressure, the residue was chromatographed on 100 g of grade IV, neutral alumina using hexane as solvent. A solid was isolated which after recrystallization from cyclohexane gave a material (64 mg, 74%) which possessed the same ir spectra and failed to depress the melting point of the 3-acetyl-2-piperidino-3*H*-azepine formed in the photolysis of 3-methylanthranil in piperidine.

**3-Acetonyl-2-piperidinopyridine.** A solution of 3-acetyl-2-piperidino-3*H*-azepine (109 mg, 0.05 mol in 0.25 ml of cyclohexane) was injected in ten equal portions into the glpc inlet port. Collection of the one major peak and subsequent distillation in a short-path microstill at 0.05 mm with a pot temperature of 100° yielded a clear liquid (32 mg, 29%): ir (neat) 1730 and 1580 $cm^{-1}$; nmr ($CCl_4$) $\delta$ 8.13 (doublet of a doublet, 1, $J$ = 2.0 and 5.0 Hz, aromatic proton at C-6), 7.32 (doublet of a doublet, 1, $J$ = 2.0 and 7.5 Hz, aromatic proton at C-4), 6.82 (doublet of a doublet, 1, $J$ = 5.0 and 7.5 Hz, aromatic proton at C-5), 3.57 (s, 2, $O{=}CCH_2{-}$), 2.92 (m, 4, $-CH_2NCH_2-$), 1.97 (s, 3, $O{=}CCH_3$), and 1.59 ppm (broad singlet, 6, methylenes not adjacent to nitrogen); high-resolution mass spectrum (70 eV) *m/e* (rel intensity) molecular ion: 218.1405 (28.12), $C_{13}H_{18}N_2O$: 175.1240 (38.07), $C_{11}H_{15}N_2$; and 84.0816 (100.00), $C_5H_{10}N$.

*Anal.* Calcd for $C_{13}H_{18}N_2O$: C, 71.53; H, 8.31; N, 12.83. Found: C, 71.49; H, 8.23; N, 12.96.

**Direct Photolysis of 2-Azidoacetophenone in Piperidine.** 2-Azidoacetophenone (1.61 g, 0.01 mol) was dissolved in 200 ml of piperidine and irradiated overnight under the Rayonet 300-nm light source with nitrogen bubbling through the solution. After removal of most of the solvent under reduced pressure, the crude brown residue was chromatographed on 100 g of grade IV neutral alumina using hexane as solvent. Unphotolyzed azide preceded two main fractions, each of which was rechromatographed twice under the same conditions in order to achieve better purity. The second fraction was 3-acetyl-2-piperidino-3*H*-azepine based upon an ir comparison with a known sample. The first fraction was distilled in a short-path microstill at 100° (0.05 mm) to give a slightly yellow liquid (263 mg, 12% based upon the total amount of azide used) which was identified as 7-acetyl-2-piperidino-3*H*-

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azepine based upon the results of the photolysis of 2-azido-4-methylacetophenone: ir ($CCl_4$) 1680 and 1550 $cm^{-1}$; uv max (cyclohexane) 222 (log $\epsilon$ = 4.17), 256 (log $\epsilon$ = 4.00), and 324 nm (log $\epsilon$ = 3.68); nmr ($CCl_4$) $\delta$ 6.68 (d, 1, $J$ = 6.5 Hz, vinyl proton at C-6), 6.34 (doublet of a doublet, 1, $J$ = 6.5 and 8.5 Hz, vinyl proton at C-5), 5.24 (has the appearance of a quartet, but upon higher resolution appears to be a doublet of a triplet, 1, $J$ = 7.0 and 8.5 Hz, vinyl proton at C-4), 3.48 (m, 4, $-CH_2NCH_2-$), 2.56 (d, 2, $J$ = 7.0 Hz, methylene protons at C-3), 2.29 (s, 3, O=CC$H_3$), and 1.57 ppm (broad singlet, 6, methylene protons not adjacent to nitrogen); high-resolution mass spectrum (70 eV) *m/e* (rel intensity) molecular ion: 218.1400 (31.42), $C_{13}H_{18}N_2O$; 135.0696 (100.00) $C_8H_9NO$; and 84.0860 (41.06), $C_5H_{10}N$.

*Anal.* Calcd for $C_{13}H_{18}N_2O$: C, 71.53; H, 8.31; N, 12.83. Found: C, 71.67; H, 8.28; N, 12.63.

**2-Azido-4-methylacetophenone.** Using 2-amino-4-methylacetophenone[29] as starting material, the procedure of Mallory[31] was followed yielding a white solid upon recrystallization from hexane: mp 36–37°; ir ($CCl_4$) 2118, 1680, and 1605 $cm^{-1}$; uv max (methanol) 238 (log $\epsilon$ = 4.30), 264 (log $\epsilon$ = 4.07), and 307 nm (log $\epsilon$ = 3.48); nmr ($CDCl_3$) $\delta$ 7.62 (d, 1, $J$ = 8.0 Hz, aromatic proton at C-6), 6.84–7.08 (m, 2, unresolved aromatic protons at C-3 and C-5), 2.58 (s, 3, O=CC$H_3$), and 2.36 ppm [s (finely split), 3, methyl protons at C-4].

*Anal.* Calcd for $C_9H_9N_3O$: C, 61.70; H, 5.18; N, 23.99. Found: C, 61.53; H, 5.30; N, 23.89.

**Direct Photolysis of 2-Azido-4-methylacetophenone in Piperidine.** 2-Azido-4-methylacetophenone (1.75 g, 0.01 mol) was dissolved in 200 ml of piperidine and irradiated overnight under the Rayonet 300-nm light source with nitrogen bubbling through the solution. After removal of the solvent under reduced pressure, the crude residue was chromatographed three times as before in order to separate the two azepine fractions. The fraction preceding the 3-acetyl-6-methyl-2-piperidino-3*H*-azepine was isolated and distilled in a short-path microstill at 110° (0.05 mm) to yield a clear liquid: ir, uv, and glpc properties strongly resemble those of the equivalent azepine isolated from the 2-azidoacetophenone photolysis; nmr ($CCl_4$) 6.63 (d, 1, $J$ = 6.0 Hz, vinyl proton at C-6), 6.12 [d (each finely split into two quartets), 1, $J$ = 6.0 Hz, vinyl proton at C-5], 3.54 (m, 4, $-CH_2NCH_2-$), 2.57 (s, 2, methylene protons at C-3), 2.31 (s, 3, O=CC$H_3$), 1.96 [s (finely split into a doublet), 3, methyl protons at C-4], and 1.61 ppm (broad singlet, 6, methylene protons not adjacent to nitrogen).

*Anal.* Calcd for $C_{14}H_{20}N_2O$: C, 72.38; H, 8.68; N, 12.06. Found: C, 72.33; H, 8.51; N, 11.94.

**Yield Determinations in Direct Photolysis Experiments.** The following general procedure was used. Five quartz vessels were filled with the appropriate solutions (10 ml, 0.05 *M*) of either 2-azidoacetophenone or 3-methylanthranil, degassed by the freeze–thaw method, and irradiated in a merry-go-round apparatus at 300 nm. The vessels were removed from the light source in such a manner as to achieve varying degrees of photolysis from 10 to 60% disappearance of reactant. Fluorene was then added as an internal standard and the solvent was removed under reduced pressure. The residue was analyzed by glpc for the appearance of the appropriate azepines, 2-aminoacetophenone, and 3-acetonyl-2-piperidinopyridine, and the disappearance of 3-methylanthranil. Plots of the disappearance of reactant *vs.* the appearance of products gave straight lines with slopes equal to product yields. Control experiments demonstrated that known mixtures of reactants and products could be accurately determined by this method. With methanol as solvent, reactant disappearance was more conveniently determined *via* uv analysis. Table I summarizes the results.

**Quenching Runs.** The decrease in concentration of reactants was monitored by uv: 3-methylanthranil, 317 nm; 2-azidoacetophenone, 234 nm. Piperylene was removed prior to uv analysis by the following method: 25 ml of methanol was added to the 10 ml sample at the completion of the photolysis and the solvent was removed under reduced pressure at room temperature until ~2 ml of solution remained. The sample was then diluted to exactly 5 ml with methanol and the uv measurement was made. Control experiments showed that virtually all of the piperylene could be removed under these conditions without effecting a significant change in the azide concentration. In order to examine the effect of quencher on product formation, more concentrated solutions requiring the higher light intensity provided by the Rayonet 300-nm source were used. In the glpc procedure, 3-acetyl-2-piperidino-3*H*-azepine was measured as its thermal rearrangement product, 3-acetonyl-2-piperidinopyridine. The reported results for all quenching studies represent the average of two runs in which the vessel with quencher present became the vessel without quencher in the duplicate experiment.

**Sensitization Studies.** The reported results are averages obtained by the interchange method used in the quenching studies. With xanthone as sensitizer, fluorene was added as a glpc standard to the photolyzed 10-ml solution and the sample concentrated to ~0.5 ml under reduced pressure. The starting material, standard, and products were then taken up in hexane, a solvent in which xanthone is only sparingly soluble. The hexane solution was concentrated under reduced pressure and its contents were analyzed by glpc for the decrease in the 3-methylanthranil peak[12] as well as the appearance of other product peaks. 2-Aminoacetophenone was identified by collection of a sample by glpc and ir comparison with an authentic sample. With acetophenone and 3-methoxyacetophenone as sensitizers, the photolyzed solution was concentrated at room temperature under reduced pressure until all the solvent was removed. The remaining liquid was then analyzed by ir for the disappearance of the azide. The procedure involved matching the intensity of the observed azide absorption in the 2050–2150-$cm^{-1}$ region with standard solutions of azide in sensitizer. The standard solutions ranged from 0 to 100% of the initial amount of azide in increments of 20%. The observed intensity after photolysis was measured by weighing the area of the peak in the 2050–2150-$cm^{-1}$ region as well as the areas corresponding to the two closest standard solutions. Interpolation between the 20% range allowed the decrease in azide concentration to be measured. Control experiments established that this method could determine decreases in azide concentrations at the 50% disappearance level with about ±5% accuracy. Glpc analysis was used in the benzene and triphenylene sensitizations. The majority of the triphenylene was removed prior to analysis by the same method used for the xanthone sensitizations. The disappearance of sensitizer for all these experiments was monitored by uv analysis.

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