Quantum Yield Evidence for a Chain Reaction in the Photochemical Decomposition of Phenyl Azide

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On the basis of their use as photoaffinity labels, as polymerization initiators, and in preparing photoresists, azides have been the subject of extensive investigation. Recent studies have concentrated upon the photochemical behavior of aryl azides, with particular attention being paid to the mechanistic details of the decomposition of phenyl azide.[1,2]

Irradiation of phenyl azide at 77 K results in the loss of molecular nitrogen and formation of phenyl nitrene[3] (eq 1). The quantum yield of phenyl nitrene formation ($\phi_{-\mathrm{N}_2}$), determined by monitoring the production of molecular nitrogen, is temperature independent,[3-5] being somewhat higher in nonpolar ($\phi_{-\mathrm{N}_2} = 0.52$)[5] than in polar ($\phi_{-\mathrm{N}_2} = 0.43$)[3,4] solvents. In neutral solvents, azobenzene,[6] the known thermolysis product,[7] and an intractable polymeric material[8,9] are the major photoproducts. Azepines and anilines are produced upon irradiation of phenyl azide in solutions containing ammonia, organic amines, or other nucleophilic reagents.[8,10,11]

Azobenzene can be formed via the dimerization of two phenyl nitrene intermediates (eq 2) or via the reaction of a phenyl azide molecule with a phenyl nitrene intermediate to form a 1,2-diphenyltetraazadiene[12] (eq 3), which is thought to readily decompose into azobenzene and molecular nitrogen (eq 4). Reaction 3 also affords 1,4-diphenyltetraazadiene, which is thought to decompose by forming molecular nitrogen and *two* phenyl nitrene intermediates (eq 5). Any phenyl nitrene intermediates formed via reaction 5 could combine to form azobenzene (eq 2) or diffuse from the solvent cage with *each* reacting with a molecule of phenyl azide (eq 3). Owing to the possibility that such a chain reaction could occur upon irradiation of phenyl azide, we have made a quantitative investigation of its solution photochemistry. In particular, we have determined the quantum yields of phenyl azide disappearance ($\phi_{-\mathrm{PhN}_3}$) in polar and nonpolar solvents as a function of concentration and a variety of experimental conditions.

Scheme I

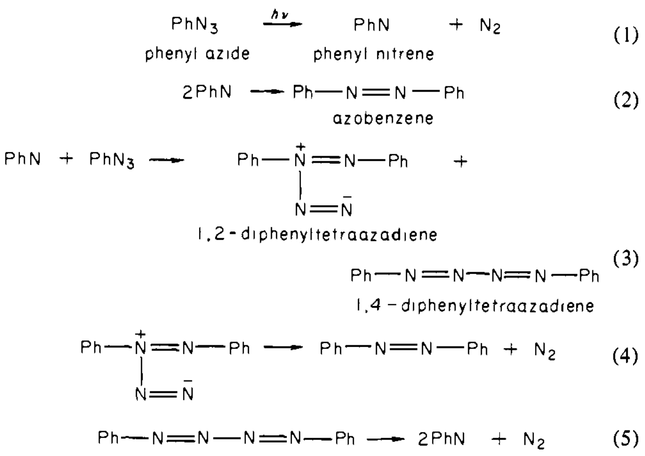

Table I. Quantum Yields of Disappearance of Phenyl Azide upon 254-nm Irradiation

	$\phi_{-\mathrm{PhN}_3}$[b]			
concn, M[a]	N_2[c]	air	O_2[c,d]	quencher[d]
3×10^{-2}	300	10	12	2.7[e]
3×10^{-3}	52	2	0.8	0.6[e]
3×10^{-4}	3.5	0.7	0.9	
3×10^{-5}	3.0	0.8		0.4[f]

[a] Acetonitrile solutions at room temperature. [b] $\phi_{-\mathrm{PhN}_3}$ ± 10%. [c] Saturated by bubbling the acetonitrile solutions with nitrogen or oxygen gas. [d] Corresponding concentrations are 2×10^{-2}, 2×10^{-3}, 2×10^{-4} M. [e] An equimolar concentration of 2,3-dimethylbutene was added to an aerated solution. [f] An equimolar concentration of tetracyanoethene was added to a 3.6×10^{-5} M aerated solution.

Phenyl azide, 2-methyl-, 4-methyl-, 2-ethyl-, and 2-nitrophenyl azide were synthesized according to literature procedures[13,14] from commercial starting materials, purified by column chromatography and/or vacuum distillation, and characterized by ultraviolet-visible absorption (Perkin-Elmer 575 UV-vis), infrared absorption (Perkin-Elmer 580 IR + Interdata 6/16 computer), and nuclear magnetic resonance (Perkin-Elmer R24B and Bruker WM 300 NMR) spectroscopy. Irradiations were accomplished by using either a 450-W Hg lamp and chemical filters[15] or a 1000-W Hg-Xe lamp and Bausch & Lomb high-intensity monochromator to isolate 254-nm radiation. Quantum yields of disappearance of phenyl azide ($\phi_{-\mathrm{PhN}_3}$) were determined by measuring the decrease in ultraviolet absorbance of phenyl azide solutions (while an isosbestic point was maintained) upon irradiation. The light flux was calibrated by using potassium ferrioxalate as a chemical actinomer.[15] $\phi_{-\mathrm{PhN}_3}$ for phenyl azide solutions >ca. 10^{-3} M were similarly determined, but after quantitative dilutions. Photoproducts (other than the polymeric material) were isolated by high-pressure liquid chromatography using a Waters ALC/GPC 204 LC, Waters μporasil column (12 × 0.25 in.), 2% anhydrous ether in hexane, 2 mL/min flow rate, 1500 psi, and 280-nm absorbance detection. They were characterized by UV, NMR, and/or mass (Varian MAT 112 + SS200 data system) spectroscopy and by comparison to commercial samples. Alternatively, photoproducts were isolated by gas chromatography (Varian 1400 GC, 10% SP 2100 stainless steel column (6 ft × 0.125 in.)) and characterized by mass spectroscopy. 3-Methylpentane (99+%, Phillips Petroleum) was distilled from Dri-Na (Baker) prior to use. Acetonitrile (UV, Burdick and Jackson) was used directly as the solvent for all photochemical experiments unless otherwise noted.

Irradiation with 254-nm light of a 10^{-4} M solution of phenyl azide in 3-methylpentane at 77 K results in the loss of phenyl azide absorption; $\phi_{-\mathrm{PhN}_3} = 0.49$, a value in excellent agreement with that measured by Reiser and Marley[5] in a hydrocarbon matrix. The absorption spectrum recorded upon irradiation at 77 K is very similar to that reported by Reiser et al.[3] for phenyl nitrene. Irradiation of phenyl azide in a room temperature, aerated 3-methylpentane solution (1.5×10^{-4} M) results in a decrease in phenyl azide absorbance (250 nm) and increase in absorbance in the 270-360-nm region. An isobestic point (261 nm) is initially established but is destroyed upon prolonged irradiation. At short irradiation times and small conversions of phenyl azide, azobenzene is the only photoproduct; however, a polymeric material is also a major photoproduct upon prolonged irradiation. $\phi_{-\mathrm{PhN}_3} = 0.9 \pm 0.1$, a value somewhat higher than that previously determined by monitoring the evoultion of moleular nitrogen ($\phi_{-\mathrm{N}_2} = 0.53$).[5]

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In deaerated 3-methylpentane solutions,[16] it was found that $\phi_{-\mathrm{PhN}_3}$ was dependent upon the concentration of phenyl azide ([PhN_3]) whereby $\phi_{-\mathrm{PhN}_3}$ increased with increasing [PhN_3]. At [PhN_3] = 1.8×10^{-4}, 2.1×10^{-3}, and 1.8×10^{-2} M, $\phi_{-\mathrm{PhN}_3} = 1.0 \pm 0.08$, 1.4, and 2.8, respectively. Quantum yield values of greater than unit efficiency are indicative of a chain reaction, thus further studies were made in a solvent that might promote such a reaction. Acetonitrile was selected, and notably high $\phi_{-\mathrm{PhN}_3}$ values were obtained.

Upon irradiation of a room temperature, aerated solution of phenyl azide in acetonitrile, it was observed that the $\phi_{-\mathrm{PhN}_3}$ *is quite sensitive to the exact experimental conditions.* For example, $\phi_{-\mathrm{PhN}_3}$ = 0.7 at [PhN_3] = 3×10^{-4} M but is notably larger at higher [PhN_3] or when $\phi_{-\mathrm{PhN}_3}$ is determined in deaerated solutions.[16] Indeed, *quantum yields of photodecomposition greater than unit efficiency can consistently be measured.* Under optimum experimental conditons, $\phi_{-\mathrm{PhN}_3}$ = 300! Table I is a summary. Note that the high values of $\phi_{-\mathrm{PhN}_3}$ are substantially decreased (a) when [PhN_3] is decreased, (b) upon introduction of molecular oxygen to the solution at constant [PhN_3], or (c) upon addition of an equimolar amount of 2,3-dimethylbutene or tetracyanoethene. At [PhN_3] = 2×10^{-4} M, $\phi_{-\mathrm{PhN}_3}$ is independent (±9%) of temperature in the 24 to −35 °C range.

Quantum yields of photodecomposition greater than unit efficiency were also measured for four phenyl azide derivatives that were examined. In a deaerated acetonitrile solution, $\phi_{-\mathrm{PhN}_3}$ = 210 for 2-methylphenyl azide (6.9×10^{-2} M) and $\phi_{-\mathrm{PhN}_3}$ = 60 for 4-methylphenyl azide (6.6×10^{-2} M). In addition, $\phi_{-\mathrm{PhN}_3}$ = 2.6 and 2.1 for aerated acetonitrile solutions of 2-nitrophenyl azide (1.5×10^{-1} M) and 2-ethylphenyl azide (1.6×10^{-1} M), respectively. That these latter two aryl azides have $\phi_{-\mathrm{PhN}_3}$ values greater than unity is quite interesting since each nitrene can undergo an intramolecular reaction affording a bicyclic product.[14,17-19]

Acetonitrile is not a significant participant in the photochemical decomposition of phenyl azide. Analysis of ^{15}N NMR and mass spectral data obtained for irradiated solutions or for the isolated photoproducts of phenyl azide reveal that *cis*- and *trans*-azobenzene and the polymeric material are the primary products.[20] No products derived from reaction with acetonitrile (unless incorporated into the as yet uncharacterized polymeric material) or from hydrogen abstraction processes (i.e., anilines) are detected. High-pressure liquid chromatography would have allowed for their separation from the photochemical reaction mixture.

The notably high quantum yields of disappearance of phenyl azide upon irradiation in concentrated acetonitrile solutions can be rationalized based upon the suggestion of Smith[12] whereby a chain reaction occurs as a result of reaction of phenyl nitrene with phenyl azide to form 1,4-diphenyltetraazadiene (eq 3), which then decomposes into *two* phenyl nitrene intermediates (eq 5) which react further. Experimental evidence of the existence of 1,4-diphenyltetraazadiene is derived from the reaction of organometallics with aryl azides, which yield stable cobalt,[21] nickel, and platinum[22] complexes of 1,4-diaryltetraazadiene. Also, McDonald and Chowdhury[23] have employed quadrupole mass spectroscopic techniques to study the gas-phase reaction of phenyl nitrene anion radical with phenyl azide. The results suggest that the anion radical of 1,4-diphenyltetraazadiene is formed.

Alternatively, it is possible that phenyl nitrene reacts with phenyl azide to form molecular nitrogen and a second phenyl nitrene without formation of a 1,4-tetraazadiene intermediate (eq 6).

$$\mathrm{PhN} + \mathrm{PhN}_3 \longrightarrow 2\mathrm{PhN} + \mathrm{N}_2 \qquad (6)$$

Were reaction 6 to occur, it would also account for the high $\phi_{-\mathrm{PhN}_3}$ values that are measured since it would act as the chain propagation step (instead of reactions 3 and 5) via continued formation of phenyl nitrene.[24]

Dimerization (eq 2) or polymerization reactions would compete with reaction 6 or reactions 3 and 5 to limit the chain. In 3-methylpentane, it is possible that hydrogen atom abstraction reactions also limit the chain, thus accounting for the lower $\phi_{-\mathrm{PhN}_3}$ values measured in that solvent at corresponding [PhN_3]. We are continuing to investigate the photochemically initiated chain decomposition reaction of phenyl azide in order to elucidate mechanistic details of this reaction.

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Registry No. Phenyl azide, 622-37-7; 2-methylphenyl azide, 31656-92-5; 4-methylphenyl azide, 2101-86-2; 2-ethylphenyl azide, 35774-47-1; 2-nitrophenyl azide, 1516-58-1.

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[16] Phenyl azide solutions were deaerated either by using a multiple freeze/pump/thaw vacuum line cycle or by bubbling with dry nitrogen gas (West-Penn Laco) for 3 min at 0 °C.

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Synthetic Studies on Arene–Olefin Cycloadditions. 4.[1] Total Synthesis of (±)-Modhephene[†]

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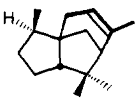
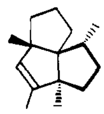
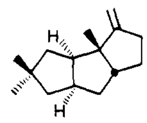
The arene–olefin meta cycloaddition[3] was shown in our previously described syntheses of (±)-α-cedrene (**1**),[1a] (±)-isocomene (**2**),[1b] and (±)-hirsutene (**3**)[1c] to offer a fundamentally new and particularly efficient approach to three distinct tricycloundecane skeletons.[4] We report herein its extension to a fourth structural



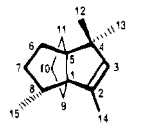
1
α-Cedrene



2
Isocomene



3
Hirsutene



4
Modhephene

[†] Dedicated to Professor Gilbert Stork on the occasion of his 60th birthday.

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