The Effect of Light on Electron-Transfer Substitution at a Saturated Carbon Atom¹

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Quantum yields have been determined for four electron-transfer substitution reactions at a saturated carbon atom: azide and quinuclidine displacement of chloride ion from p-nitrocumvl chloride, azide displacement of nitrite ion from α , p-dinitrocumene, and displacement of nitrite ion from ethyl α -nitroisobutyrate by the salt of 2-nitropropane. The values range from 3.5 for the quinuclidine-p-nitrocumyl chloride reaction to 6000 for the azide-p-nitrocumyl chloride reaction. A study of the wavelength dependence of the quantum yields supports the view that photochemical initiation involves a charge-transfer complex between the nucleophile and the compound in which substitution takes place.

That light may speed up a radical anion substitution process was first recognized during a study of the reactions of p-nitrobenzyl chloride.² Since then numerous examples of light effects have been found, some of them very large;³⁻⁶ all that is required is illumination by diffuse daylight or by ceiling lights. There can be no question, then, that light often has a profound effect on the rate of electron-transfer substitution reactions.⁷ But beyond this rudimentary fact there is no information regarding related questions such as quantum yields and the intermediacy of charge-transfer complexes. This paper is concerned with upgrading the earlier, rather primitive, observations with a more sophisticated photochemical study; toward that end we have determined the quantum yields of four representative electron-transfer chain substitution reactions that take place at a saturated carbon atom. Furthermore, by studying the wavelength dependence of the quantum yields, we have obtained evidence for the view that photochemical initiation proceeds by way of a charge-transfer complex derived from the nucleophile and the compound in which substitution occurs.⁸

We discuss first the reaction of α , *p*-dinitrocumene with sodium azide at room temperature in hexamethylphosphoramide (HMPA) solution. When conducted in normal room light a 94% yield of pure p-nitrocumyl azide is obtained in 2 h (eq 1); if the reaction is carried out under



two 20-W white fluorescent lights it proceeds to completion in less than 10 min.¹ However, in the dark there is no detectable reaction after 48 h.

It is of interest that on mixing a colorless HMPA solution of α ,*p*-dinitrocumene with a colorless HMPA solution of sodium azide, an orange-yellow solution is immediately produced. This color is not due to product formation since the product, p-nitrocumyl azide, is colorless and, indeed, it exhibits a spectrum nearly identical with that of α , pdinitrocumene; it is transparent at wavelengths greater than 410 nm. Nor does the new band derive from ionic strength effects; the absorption spectrum of α , p-dinitrocumene is unchanged by the presence of 0.2 M sodium perchlorate.

The electronic absorption spectra of Figure 1 provide quantitative information. It will be seen that a new ab-

Table I. Wavelength Dependence of the Quantum Yield for the Reaction of α , *p*-Dinitrocumene with Sodium Azide

wave- length, nm	quantum yield	relative light intensity ^a	major light absorbing species
510	283, 325	10.2	charge-transfer complex
470	244, 328	10.5	charge-transfer complex
366	55, 65	7.7	α -p-dinitrocumene

^a The absolute value of an average light intensity, in mEinsteins per hour, may be obtained by multiplying by 2.12×10^{-4} .

Table II. Dependence of Quantum Yield on Light Intensity for the Reaction of α , *p*-Dinitrocumene with Sodium Azide

wavelength, nm	quantum yield	relative light intensity ^a
470	244, 328	10.5
	544, 587	1.0
366	14, 14	89.7
	55, 65	7.7

^a The absolute value of an average light intensity, in mEinsteins per hour, may be obtained by multiplying by 2.12×10^{-4} .

sorption, not exhibited by sodium azide (which is transparent at wavelengths greater than 300 nm) or by α , pdinitrocumene, is present in a solution that contains both of these reagents; the broad and featureless nature of the

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⁽¹⁾ This, paper 30 in the series "Substitution Reactions Which Proceed via Radical Anion Intermediates", is based on the Ph.D. thesis of P. A. Via radical Anion intermediates, is based on the Ph.D. thesis of P. A.
Wade, Purdue University, 1973. For the preceding paper, see: Kornblum,
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(2) Russell, G. A.; Danen, W. C. J. Am. Chem. Soc. 1966, 88, 5663.
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 ⁽⁴⁾ Kornblum, N.; Stuchal, F. W. J. Am. Chem. Soc. 1967, 89, 725.
 (4) Kornblum, N.; Stuchal, F. W. J. Am. Chem. Soc. 1970, 92, 1804. (5) Kornblum, N.; Davies, T. M.; Earl, G. W.; Greene, G. S.; Holy, N. L.; Kerber, R. C.; Manthey, J. W.; Musser, M. T.; Snow, D. H. J. Am. Chem. Soc. 1967, 89, 5714.

⁽⁶⁾ Kornblum, N.; Boyd, S. D.; Ono, N. J. Am. Chem. Soc. 1974, 96,

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⁽⁷⁾ It should be emphasized that in many instances light is not necessary for the reaction to occur; but even here it often provides significant rate acceleration.

⁽⁸⁾ For reviews of this subject, see: (a) Kornblum, N. Angew. Chem., Int. Ed. Engl. 1975, 14, 734. (b) Kornblum, N. In The Chemistry of Functional Groups, Supplement F: The Chemistry of Amino, Nitroso and Nitro Compounds and Their Derivatives; Patai, S., Ed.; Wiley: New York, 1982; p 361. (c) Norris, R. K. In *The Chemistry of Functional Groups, Supplement D*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1983; p 681. (d) It should be noted that subsequent to the completion of this work (see footnote on page 739 of ref 8a), studies that support the view that photostimulated substitution reactions of iodobenzene and bromobenzene by anions proceed via charge-transfer complexes have been published; see for example: Fox, M. A.; Younathan, J., Fryxell, G. E. J. Org. Chem. 1983, 48, 3109 and references therein cited.



Figure 1. Electronic absorption spectra at l = 0.01 cm for 0.1 M α ,p-dinitrocumene in HMPA (--); 0.1 M α ,p-dinitrocumene with 0.2 M NaN₃ in HMPA (--).

new absorption is typical of charge-transfer complexes.⁹ The spectrum of 0.1 M α ,p-dinitrocumene is completely on scale when a sample cell with a light path length (l) of 10^{-3} cm is used: λ_{max} 265 nm; ϵ_{max} ca. 10⁴. The absorption curve obtained with this 10^{-3} cm cell for α ,p-dinitrocumene plus sodium azide (with absorption due to the salt itself subtracted out) is experimentally indistinguishable from that of α ,p-dinitrocumene. Thus the weak charge-transfer absorption depicted in Figure 1 is the only absorption due uniquely to the combination of reagents.

Monochromatic 470-nm light is very effective in initiating the reaction of α ,p-dinitrocumene with sodium azide (eq 1). At this wavelength quantum yields as high as ca. 570 are observed. A quantum yield of 570 denotes a minimum average chain length of 570 but it would not be surprising if the actual chain length were considerably longer, for it is a relatively rare photochemical reaction that proceeds in the absence of energy-wasting processes.

The quantum yield for the reaction of eq 1 depends both on wavelength and light intensity. The wavelength dependence is given in Table I. It will be seen that at 470 nm and 510 nm, where only the charge-transfer complex absorbs, the quantum yield is high (ca. 295). However, at 366 nm where α,p -dinitrocumene is the major absorbing species, the quantum yield is unambiguously lower (ca. 60). This result is consistent with the view that light induces reaction of α,p -dinitrocumene with sodium azide via a sequence involving a charge-transfer intermediate.

Table II summarizes the dependence of quantum yield on light intensity in the reaction of eq 1. It will be seen that when the light intensity is high, the quantum yield is low. At high light intensity, the concentrations of the *p*-nitrocumyl free radical (1) and the azido radical (2) are relatively high¹ and, as a result, chain termination processes, e.g., that of eq 2, will occur more often. This, of course, results in shorter chains and lower quantum yields.



The reaction of p-nitrocumyl chloride with sodium azide (eq 3) is very fast. After a 10-min exposure to room light



Figure 2. Electronic absorption spectra at l = 0.01 cm for 0.1 M *p*-nitrocumyl chloride in HMPA (--); 0.1 M *p*-nitrocumyl chloride with 0.2 M NaN₃ in HMPA (--).

the reaction is complete and a 95% yield of pure p-nitrocumyl azide is isolated.^{1,10}



Upon mixing *p*-nitrocumyl chloride with sodium azide in HMPA, an orange-yellow color immediately develops. The electronic absorption spectra of Figure 2 provide quantitative data concerning this phenomenon. It will be noted that these spectra are quite similar to those obtained with α ,*p*-dinitrocumene (Figure 1). A new absorption, not present for either sodium azide or for *p*-nitrocumyl chloride, is produced by a combination of these reagents. When the spectra are taken so that the absorption curves are on scale, (i.e., with a cell light path of 10^{-3} cm), one sees no change in the 250–400-nm region. In short, *p*-nitrocumyl chloride behaves in exactly the same way as α ,*p*dinitrocumene and we again attribute the orange-yellow absorption to a charge-transfer complex.

Monochromatic light with a wavelength of 470 nm is exceedingly effective in initiating the reaction of *p*-nitrocumyl chloride with sodium azide. At this wavelength the quantum yield is ca. 6000. Thus, the reaction of eq 3 has a chain length of at least 6000. Since 470-nm light is not absorbed by *p*-nitrocumyl chloride, but only by the charge-transfer complex, it is clear, as in the previous case, that initiation derives from a photochemical process involving the charge-transfer complex.

The third reaction investigated is that which occurs between quinuclidine and p-nitrocumyl chloride (eq 4). In



the dark there is no substitution even after 12 h. However,

⁽⁹⁾ Vars, R.; Tripp, L. A.; Pickett, L. W. J. Phys. Chem. 1962, 66, 1754.

⁽¹⁰⁾ In the dark this reaction is ca. 50% complete after 7.8 h and the major product is *p*-nitrocumyl azide (45% yield) with about 5% of the dehydrohalogenation product—*p*-nitro- α -methylstyrene. However, the *p*-nitrocumyl azide obtained from the dark reaction derives principally from an ionic process with only a small fraction being produced via the electron-transfer chain mechanism: P. A. Wade, Doctoral Dissertation, Purdue University, 1973.



Figure 3. Electronic absorption spectra at l = 1.00 cm for 0.1 M *p*-nitrocumyl chloride in Me₂SO (—); 0.1 M *p*-nitrocumyl chloride with 0.2 M quinuclidine in Me₂SO (--).

with a 10-h exposure to two 20-W fluorescent lights, a 90% yield of the quaternary salt is obtained.^{1,4} It has been proposed that this reaction proceeds via a one-electron chain sequence in which a radical anion and a radical cation are produced in the initiation process (eq 5-9).⁴



$$\begin{array}{c} + \overset{+}{N} \overset{+}{\bigcirc} \\ \bigcirc \\ & & \\$$

When Me₂SO solutions of *p*-nitrocumyl chloride and quinuclidine are mixed, a pale yellow color is immediately produced. The electronic absorption spectra of Figure 3 provide quantitative data. Quinuclidine does not absorb at wavelengths greater than 320 nm and consequently is not depicted. It will be noted that *p*-nitrocumyl chloride by itself has no absorption above ca. 435 nm. But the combination of these two reagents unambiguously absorbs 435-480-nm light; this new absorption is presumed to be due to a charge-transfer complex. In contrast to the charge-transfer complex with azide ion, the absorbance of this species is weak (ca. one-fiftieth as great). Whether

 Table III. Wavelength Dependence of the Quantum Yield for the Reaction of p-Nitrocumyl Chloride with Quinuclidine

wave- length, nm	quantum yield	relative light intensity ^a	major light absorber
435	3.0, 3.9	36.9	charge-transfer complex
366	1.2, 1.1	26.5	p-nitrocumyl chloride

 a The absolute value of an average light intensity, in mEinsteins per hour, may be obtained by multiplying by 2.12 \times 10⁻⁴.

this is so because the charge-transfer complex actually possesses a smaller extinction coefficient than that of the complex with azide ion or whether the concentration of the charge-transfer species is considerably lower is not known.

Monochromatic 435-nm light is effective in initiating the reaction of p-nitrocumyl chloride with quinuclidine but the quantum yield is only 3.5. This relatively low quantum yield may derive from two causes; either photochemical initiation (eq 5 and 6) is inefficient or the chain length of eq 7–9 is short. The fact that as little as 1 mol % of oxygen is an effective inhibitor for this reaction⁴ suggests that the former of these two possibilities is the more important. If we assume that initiation of the reaction of *p*-nitrocumyl chloride with quinuclidine proceeds by way of a chargetransfer complex and that this is photochemically energized so that complete transfer of one electron from the quinuclidine moiety to the *p*-nitrocumyl chloride occurs, then the result is the formation of a radical cation and a radical anion (eq 6). Here the coulombics of the initiation step, in contrast to the corresponding step with an anionic nucleophile, would clearly be unfavorable. Furthermore, the radical anion and radical cation, even when formed, are more likely to recombine than a radical anion and free radical. On this basis, energy-wasting processes could compete more successfully here. If this is so, then, even with a relatively long chain sequence, the overall quantum yield for substitution would be low.

The quantum yield for the reaction of p-nitrocumyl chloride with quinuclidine shows wavelength dependence (see Table III). At wavelengths where only the charge-transfer complex absorbs, the quantum yield is ca. 3.5. However, at wavelengths where p-nitrocumyl chloride is the major absorbing species, the quantum yield is only one-third as great—i.e., 1.1. This result is consistent with the view that photochemical initiation proceeds preferentially via a charge-transfer complex.

The fourth reaction studied is the purely aliphatic transformation of eq 10. This reaction gives a 95% yield of the pure β -nitro ester and it exhibits a substantial light effect.¹¹

$$\begin{array}{cccc} & & & & & & & \\ NO_2 & & & & & \\ H_3C - C - CO_2C_2H_5 & + & Li^{\dagger}(H_3C)_2\overline{C} - NO_2 & & & \\ I & & & & \\ CH_3 & & & \\ CH_3 & & & \\ CH_3 & & & \\ \end{array}$$
(10)

A solution of the lithium salt of 2-nitropropane in HMPA is colorless and remains so for at least 75 h, provided the solvent is rigorously deoxygenated *prior* to dissolution of the salt. Such a solution when freshly prepared and also after standing for 75 h exhibits the electronic absorption spectrum of Figure 4. When this colorless solution and a colorless solution of the α -nitro ester are mixed, the resulting solution is also colorless. This, of course, is not what is observed when *p*-nitrocumyl

⁽¹¹⁾ Kornblum, N.; Boyd, S. D.; Stuchal, F. W. J. Am. Chem. Soc. 1970, 92, 5783.



Figure 4. Electronic absorption spectra at l = 1.00 cm for 0.2 M Li⁺(H₃C)₂CNO₂⁻ in HMPA (----); 0.1 M ethyl α -nitroisobutyrate in HMPA (---); 0.2 M Li⁺(H₃C)₂CNO₂⁻ with 0.1 M ethyl α -nitroisobutyrate in HMPA (the spectrum of Li⁺(H₃C)₂CNO₂⁻ was subtracted out) (----).

Table IV. Wavelength Dependence of the Quantum Yield for the Reaction of Ethyl α -Nitroisobutyrate and the Lithium Salt of 2-Nitropropane

wave- length, nm	quantum yield	relative light intensity ^a	major light absorbing species
400	260, 185	11.4	charge-transfer complex
366	39, 32	7.9	lithium salt of 2-nitropropane
320	30, 43	3.6	α -nitro ester

^a The absolute value of an average light intensity, in mEinsteins per hour, may be obtained by multiplying by 2.12×10^{-4} .

chloride and α , *p*-dinitrocumene are employed.

It is apparent from Figure 4 that both the nitroparaffin salt and the α -nitro ester exhibit major absorptions only at wavelengths shorter than 400 nm—i.e., in the near-ultraviolet. The spectrum for a combination of these reagents, with the absorption of the nitroparaffin salt subtracted out, shows a small amount of new absorption at longer wavelengths. This new absorption is not due to product formation, for the β -nitro ester of eq 10 is transparent at wavelengths greater than 385 nm. We attribute it to formation of a charge-transfer complex, as observed in previous examples. Consistent with this view are the results obtained in quantum yield-wavelength dependence studies.

Monochromatic 400-nm light is very effective in initiating the reaction of ethyl α -nitroisobutyrate with the lithium salt of 2-nitropropane (eq 10). At this wavelength the quantum yield is ca. 220, which provides strong support for the proposed chain mechanism.¹¹ It is also noteworthy that the quantum yield for this reaction shows a marked wavelength dependence which is summarized in Table IV. At 400 nm, where it appears likely that a major portion of the absorption is due to a charge-transfer complex, the quantum yield is high (ca. 220). In contrast, at 366 nm where the lithium salt of 2-nitropropane is the major light absorber, the quantum yield is relatively low-i.e., 36. Finally, at 320 nm, where the α -nitro ester is the major light absorber, the quantum yield is again relatively low-i.e., 36. These results support the view that here, as well as with *p*-nitrocumyl chloride and α ,*p*-dinitrocumene, photochemical initiation proceeds preferentially via a charge-transfer intermediate.

Experimental Section

Electronic absorption spectra were obtained on a Cary 14-R spectrophotometer. Absorbances measured for actinometry were performed on a Beckman DUR spectrophotometer. Chloride ion titrations were performed on a Buchler-Cotlove model 4-2008 chloridometer. NMR spectra were recorded on a Varian A-60 spectrometer. Vapor-phase chromatography (GLC) was performed on an Aerograph A-350-B instrument equipped with dual columns [5% SF-96 on Chrom G]. Reactions using α , p-dinitrocumene were analyzed at 185 °C (10 ft \times 0.25 in. column); reactions using ethyl α -nitroisobutyrate were analyzed at 135 °C (5 ft \times 0.25 in. column). All reactions were run in a darkroom under only safelite illumination (Kodak #2 filter): $\lambda > 630$ nm. Sources of stray light were rigorously excluded. Glassware was oven-dried and cooled in a dessicator prior to assembly. Unless otherwise noted, HMPA reactions were worked up by addition to water (400 mL) layered with benzene (125 mL). The layers were separated and the aqueous layer was further extracted with two 75-mL portions of ether. The combined organic layers were washed (five 200-mL portions of water), dried (anhydrous MgSO₄), and concentrated at reduced pressure. Me₂SO reactions were worked up similarly except only three 150-mL portions of water were used to wash the combined organic layers. Water layers were diluted to 1000 mL before Cl⁻ was titrated.

Materials. Me₂SO was distilled at reduced pressure from CaH₂ and was stored under N₂. HMPA was distilled at reduced pressure through a 33-cm helipak column and was stored under argon: bp 65 °C [0.4 mm]; transparent at $\lambda > 310$ nm. Preparations of *p*-nitrocumyl chloride,¹² α ,*p*-dinitrocumene,¹³ ethyl α -nitroisobutyrate,¹⁴ *p*-nitrocumyl azide,¹ N-(*p*-nitrocumyl)quinuclidinium chloride,¹ ethyl 3-nitro-2,2,3-trimethylbutyrate,¹¹ and the lithium salt of 2-nitropropane⁶ have been described elsewhere. Quinuclidine was sublimed from sodium¹ prior to use: mp 161–163 °C (sealed tube) [lit.¹ mp 161–163 °C (sealed tube)].

Deoxygenation Procedures. Reactions with Quinuclidine. A reaction set-up consisting of a photochemical cell and a gas inlet-vacuum take-off adaptor connected to a four-necked, round-bottomed flask was purged with N_2 . A side-arm solid addition tube containing quinuclidine (weighed out in a drybox) and a second addition tube containing *p*-nitrocumyl chloride were attached to the flask. Me₂SO was added to the flask and freeze-pump-thaw deoxygenated. The freeze-pump-thaw cycle consisted of keeping the *p*-nitrocumyl chloride and quinuclidine (dry ice-acetone baths) while freezing the Me₂SO (liquid N₂ bath) under argon, evacuating the set-up (<1 mm), melting the Me₂SO, and reintroducing argon. This cycle was repeated three additional times to ensure removal of oxygen.

Reactions with the Lithium Salt of 2-Nitropropane. The same reaction set-up and freeze-pump-thaw cycle as above was used. It was necessary to cool the addition tube containing volatile ethyl α -nitroisobutyrate in liquid N₂ during the freeze-pump-thaw cycles.

Reactions with Sodium Azide. Sodium azide and HMPA were added to a N_2 -purged three-necked round-bottomed flask outfitted with a photochemical cell and gas inlet-vacuum take-off adaptor. An addition tube containing the substrate was attached to the third neck and the flask contents were subjected to four freeze-thaw cycles as described above.

Photochemical Apparatus. UV-vis light was obtained from a Hanovia 200-W, 20-25-V Hg-Xe arc lamp powered by a 9-amp dc source. Wavelengths were isolated by using a Bausch & Lomb high intensity monochromator (exit/entrance slit ratio set at 0.56; exit slit 1.50 mm, unless otherwise noted) equipped with a diffraction grating having a 200-700-nm range (1200 grooves/mm, blazed at 220 nm). A band pass width of 11.1 nm was calculated¹⁵ for the typical monochromator settings. A 2.03-mm Corning Pyrex filter (7740) was placed after the lamp to remove second-order wavelengths (>90% absorbance at $\lambda < 277$ nm). Two matched custom-built (Lab Glass: transparent at $\lambda > 350$ nm; 30% absorbance at 320 nm) cylindrical Pyrex cells (5.5-cm long) were used as reaction cells and for actinometry; the 5.5-cm lightpath of the cells was sufficiently large for reaction and actinometer

⁽¹²⁾ Kornblum, N.; Ackermann, P.; Swiger, R. T. J. Org. Chem. 1980, 45, 5294.

 ⁽¹³⁾ Kornblum, N.; Cheng, L.; Kerber, R. C.; Kestner, M. M.; Newton,
 B. N.; Pinnick, H. W.; Smith, R. G.; Wade, P. A. J. Org. Chem. 1976, 41, 1560.

⁽¹⁴⁾ Kornblum, N.; Blackwood, R. K.; Powers, J. W. J. Am. Chem. Soc. 1957, 79, 2507.

⁽¹⁵⁾ Johns, H. E.; Rauth, A. M. Photochem. Photobiol. 1965, 14, 673.

solutions to absorb >95% of the incident light in all cases, unless otherwise stated.

Actinometry. Calculated light intensities were the average of values determined just prior and directly subsequent to a quantum yield determination. Two different actinometers were used: at $\lambda \leq 470$ nm, the ferrioxalate actinometer,¹⁶ and at $\lambda >$ 470 nm, the Reinecke's salt actinometer.^{16b,17} At 470 nm, the actinometers were compared and a difference of <2% was noted. The aqueous ferrioxalate solutions used at $\lambda < 420$ nm were 0.006 M and at $\lambda > 420$ nm, 0.15 M. Reinecke's salt, K[Cr(NH₃)₂(S-CN)₄], was dissolved just prior to use as an 0.005 M aqueous solution. The reported quantum yields were interpolated where necessary.

Quantum Yields for the Reaction of p-Nitrocumyl Chloride and Sodium Azide. In the darkroom for each run, p-nitrocumyl chloride (0.798 g, 4.0 mmol) was added from the addition tube to the deoxygenated solution of NaN_3 (0.52 g, 8.0 mmol) in HMPA (40 mL), and the resulting solution was stirred. Two control reactions stirred in the dark were worked up after 19 min and the water layer titrated for Cl⁻: 6.2% and 10.1%reaction. The organic products (0.7934 g and 0.7991 g) were a mixture of two materials: p-nitrocumyl chloride (94% and 89%) and a small amount of p-nitrocumyl azide (6% and 11%, respectively, by NMR).

Another stirred reaction solution was irradiated for 14.6 min with 470-nm light. Workup after 19 min gave an oil (0.7895 g), which was 40% p-nitrocumyl chloride and 60% p-nitrocumyl azide by NMR. Titration of the water layer for Cl⁻ indicated 57.5% reaction. The average (8.2% reaction) of the dark reactions was subtracted and the quantum yield determined: $\phi = 6480$. Two duplicate runs gave $\phi = 6700$ and 4480.

Quantum Yields for the Reaction of α , p-Dinitrocumene with Sodium Azide. Wavelength Dependence. In the darkroom, α ,p-dinitrocumene (0.84 g, 4.0 mmol) was added to the solution of NaN₃ (0.52 g, 8.0 mmol) in HMPA (40 mL), and the resulting solution was stirred. Five control reactions were run in the dark and were worked up from 30 to 84 min after mixing. From 0.772 to 0.8404 g (93% to 99% recovery) of off-white solids, which in each case were α ,*p*-dinitrocumene (>99% purity; GLC and NMR), were obtained.

A stirred solution of the reactants was irradiated ($I = 2.16 \times$ 10^{-3} mEinstein/h) at $\lambda_{max} = 510$ nm for 29.6 min. Workup gave 0.8371 g of an off-white solid, a mixture of α, p -dinitrocumene (91.4 wt %; GLC and NMR) and p-nitrocumyl azide (8.6 wt %;): ϕ = 325. A duplicate run gave similar results: ϕ = 283.

Another solution of the reactants was irradiated ($I = 2.22 \times$ 10^{-3} mEinstein/h) at $\lambda_{max} = 470$ nm for 29.4 min. Workup gave 0.8215 g of an off-white solid, a mixture of α , p-dinitrocumene (93.3 wt %; GLC and NMR) and *p*-nitrocumyl azide (6.7 wt %): $\phi =$ 244. A duplicate run gave similar results: $\phi = 328$.

Another solution of the reactants was irradiated ($I = 1.90 \times$ 10^{-2} mEinstein/h) at $\lambda_{max} = 366$ nm for 22.1 min. Workup gave 0.8265 g of an off-white solid, a mixture of α ,p-dinitrocumene (97.6 wt %; GLC and NMR) and p-nitrocumyl azide (2.4 wt %): $\phi =$ 14. A duplicate run gave identical results: $\phi = 14$.

Quantum Yields for the Reaction of α , p-Dinitrocumene with Sodium Azide. Intensity Dependence. These experiments complement results obtained in the wavelength study above. A solution of the reactants was irradiated with low intensity (I = 2.2×10^{-4} mEinstein/h; monochromator exit slit: 0.50 mm) light at $\lambda_{max} = 470$ nm for 82.2 min. Workup gave 0.8049 g of an off-white solid, a mixture of α , p-dinitrocumene (95.6 wt %; GLC and NMR) and p-nitrocumyl azide (4.4 wt %): $\phi = 587$. A duplicate run gave similar results: $\phi = 544$.

A solution of the reactants was irradiated with low intensity $(I = 1.63 \times 10^{-3} \text{ mEinstein/h})$ light at $\lambda_{\text{max}} = 470 \text{ nm}$ for 28.9 min. Workup gave 0.8142 g of an off-white solid, a mixture of α , pdinitrocumene (98.9 wt %; GLC and NMR) and p-nitrocumyl azide (1.1 wt %): $\phi = 55$. A duplicate run gave similar results: $\phi = 65.$

Quantum Yields for the Reaction of p-Nitrocumyl Chloride and Quinuclidine. In the darkroom, quinuclidine (0.89 g, 8.0 mmol) and p-nitrocumyl chloride (0.798 g, 4.0 mmol) were added from addition tubes to deoxygenated Me_2SO (40 mL), and the resulting solution was stirred. One control reaction run in the dark was worked up after 10.2 h: 1.2% reaction (Cl⁻ titration of the water layer). NMR of the water-insoluble products (0.8011 g) indicated *p*-nitrocumyl chloride and a small amount of quinuclidine (<3 wt %). A second control reaction, run for 8.1 h, gave 1.4% reaction (Cl⁻ titration).

A stirred reaction solution was irradiated (I = 7.38 mEinstein/h)for 10.1 h at $\lambda_{max} = 435$ nm. A second cell containing ferioxalate solution was placed in tandem after the reaction cell, since a 5.5-cm sample path length was not sufficient to absorb all of the incident light. The reaction solution absorbed 78% ($5.77 \times 10^{-2} \text{ mE}$) of the incident light. After workup, Cl⁻ titration of the water layer indicated 6.8% reaction; the % dark reaction was subtracted: ϕ = 3.9. A water-insoluble oil (0.7732 g) containing p-nitrocumyl chloride and quinuclidine (3 wt %) was obtained but the water-soluble quinuclidine salt was not isolated. A duplicate experiment gave similar results: $\phi = 3.0$.

Another solution was irradiated $(I = 5.95 \times 10^{-3} \text{ mEinstein/h})$ at λ_{max} = 366 nm for 8.0 h. Cl⁻ titration of the water layer indicated 2.8% reaction: $\phi = 1.2$. A duplicate run gave similar results: $\phi = 1.1$.

Quantum Yields for the Reaction of Ethyl a-Nitroisobutyrate and the Lithium Salt of 2-Nitropropane. Wavelength Dependence. In the darkroom, the lithium salt of 2nitropropane (0.76 g, 8.0 mmol) was added to deoxygenated HMPA (40 mL), and the resultant mixture was stirred for 10 min to obtain solution. Ethyl α -nitroisobutyrate (0.644 g, 4.0 mmol) was then added to provide the reaction solution. A control reaction stirred in the dark for 33 min was poured into water (400 mL) layered with pentane (100 mL). The layers were separated and the aqueous layer was further extracted with two 75-mL portions of pentane. The combined pentane extracts were washed (four 250-mL portions of water), dried (anhydrous MgSO₄), and concentrated in the cold $(0-5 \circ C)$ at reduced pressure to give an oil (0.5488 g), which consisted of ethyl α -nitroisobutyrate (96.7 wt %, GLC and NMR) and β -nitro ester, ethyl 3-nitro-2,2,3-trimethylbutanoate (3.3 wt %). Two duplicate runs gave similar results: 3.4 wt % and 3.5 wt % of β -nitro ester, respectively.

A stirred reaction solution was irradiated (I = 2.10×10^{-3} mEinstein/h) for 29.5 min at $\lambda_{max} = 400$ nm. A second cell containing ferrioxalate solution was placed in tandem after the reaction cell, since a 5.5-cm sample path length was not sufficient to absorb all of the incident light. The reaction solution absorbed 63% (6.52 × 10⁻⁴ mE) of the incident light. After a 33-min reaction time, workup as in the control reaction gave an oil (0.5452 g), which consisted of ethyl α -nitroisobutyrate (92.2 wt %, GLC and NMR) and β -nitro ester (7.8 wt %). The amount of dark reaction (3.3%) was subtracted: $\phi = 185$. A duplicate reaction gave $\phi = 260$.

Another reaction solution was irradiated ($I = 1.62 \times 10^{-3}$ mEinstein/h) for 29 min at $\lambda_{max} = 366$ nm and was worked up as above. An oil (0.588 g) was isolated and consisted of ethyl α -nitroisobutyrate (95.4 wt %, GLC and NMR) and β -nitro ester (4.6 wt %): $\phi = 39$. A duplicate reaction gave $\phi = 32$.

Another reaction solution was irradiated ($I = 9.12 \times 10^{-4}$ mEinstein/h) for 29.7 min at $\lambda_{max} = 320$ nm and was worked up as above. An oil (0.5386 g) was isolated and consisted of ethyl α -nitroisobutyrate (96.1 wt %, GLC and NMR) and β -nitro ester (3.9 wt %): $\phi = 30$. A duplicate reaction gave $\phi = 43$.

Electronic Absorption Spectra. Spectra taken with a 1.0-cm path length employed standard fused silica cells. Spectra taken with a 0.010-cm path length utilized 1.000-cm cells equipped with a 0.990-cm spacer. Spectra taken at 0.001 ± 0.0003 cm employed concave plates (Helma). Subtraction spectra were determined by placing a solution of one component in the reference beam and a solution of multiple components in the sample beam.

Spectra for samples containing the lithium salt of 2-nitropropane were taken in freeze-pump-thaw deoxygenated HMPA. Deoxygenated 0.2 M HMPA solutions of the salt were stable for at least 75 h and were colorless: λ_{max} 350 nm, ϵ_{max} 4.2; $\lambda < 305$, $\epsilon > 10$. Introduction of 0.25 equiv of O₂ resulted in a yellow solution within 1 h and after 75 h a much different spectrum: λ $< 445 \text{ nm}, \epsilon > 10.$

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Registry No. Azide, 14343-69-2; quinuclidine, 100-76-5; 2nitropropane anion, 20846-00-8; α , p-dintrocumene, 3276-35-5; p-nitrocumyl chloride, 14500-58-4; $\alpha\text{-nitroisobutyrate},$ 5342-77-8; 2-nitropropane lithium salt, 3958-63-2; sodium azide- α ,p-dinitrocymene charge-transfer complex, 108592-01-4; sodium azide-p-nitrocumyl chloride charge-transfer complex, 108592-02-5; quinuclidine-p-nitrocumyl chloride charge-transfer complex, 108617-76-1; α -nitroisobutyrate-HMPA charge-transfer complex, 108592-03-6.

Modification of Photochemical Reactivity by Cyclodextrin Complexation: **Consequences of Restricted Rotation of Norrish Type II 1,4-Diradicals from Aryl Alkyl Ketones**

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Photochemical behavior of any alkyl ketones complexed to β -cyclodextrin both in aqueous solution and in the solid state have been investigated. Comparison of the above behavior with that in isotropic solvents reveals that cyclodextrin inclusion provides an environment wherein photoreactions may be carried out with consequences different from those observed in homogeneous solution. Products of elimination and cyclization resulting from the Norrish type II hydrogen abstraction were monitored. The ratio of these products was dependent on the length but not on the bulkiness of the alkyl substituent. These observations are rationalized on the basis of the steric constraints by the cyclodextrin cavity on the rotational motions of the 1,4-diradical.

Introduction

The past decade has witnessed an ever-increasing interest in the effects of organized assemblies on photochemical reactions.¹ Reactants accommodated in molecular assemblies such as micelles, microemulsions, liquid crystals, and organic crystals often achieve a greater degree of organization compared to homogeneous solution, a feature which may promote unique reaction features. A specific subarea that has attracted recent interest concerns the reactivity of molecules incorporated into "host-guest" systems. Cyclodextrin, which is a cyclic oligosaccharide containing six or more D-(+)-glucopyranose units, is one of the most important host systems. Each cyclodextrin molecule has a toroidal, hollow, truncated cone with primary and secondary hydroxyl groups crowning the narrower and wider rims, respectively. The interior of each cyclodextrin cavity contains two rings of C-H groups and a ring of glucose oxygen atoms. Hence, the interior is relatively hydrophobic, whereas the exterior is relatively hydrophilic. It is this feature that enables cyclodextrins to extract, hold, and protect hydrophobic molecules from aqueous solutions. The application of cyclodextrins as an organizing microenvironment in photochemical reactions has been initiated recently and has revealed selectivity in product distributions.² During the last few years, our group has been investigating the influence of cyclodextrin

Chart I

cavity on photochemical reactions.³ The goal is to achieve selectivity in photochemical reactions using this unusual

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