Extraction with chloroform (2 × 15 mL) and the usual workup gave 0.86 g (72%) of a 3:2 mixture (by ^{1}H NMR) of 3-*exo*-nitro-5-*exo*-(perchloryloxy)nortricyclene (**12**) and 3-*exo*-nitro-5-*endo*-(perchloryloxy)nortricyclene (**13**). Silica gel column chromatography (elution with 1:3 mixture ethyl acetate–hexane) gave pure 5-exo isomer **12** [R_f 0.4; decomposition at 100 °C; IR 1550, 1370, 1275, 1250, 840 cm^{-1}; ^{1}H NMR (60 MHz, CCl_4) 5.02 (1 H, s, $HCOClO_3$), 4.58 (1 H, s, $CHNO_2$), 2.98 (2 H, m), 2.2–1.7 (10 H, m)] and pure 5-endo isomer **13**: R_f 0.3; decomposition at 90 °C; IR 1550, 1375, 1275, 1245, 840, 800 cm^{-1}; ^{1}H NMR (60 MHz, CCl_4) 5.37 (1 H, m, $CHNO_2$), 5.15 (1 H, m, $HCOClO_3$), 2.98 (2 H, m), 2.2–1.7 (10 H, m).

Registry No. **1**, 81971-79-1; **2**, 81971-80-4; **3**, 81971-81-5; **4**, 81971-82-6; **5**, 81971-83-7; **6**, 81971-84-8; **7**, 81971-85-9; **8**, 78053-17-5; **9**, 78053-18-6; **10**, 81971-86-0; **11**, 81971-87-1; **12**, 78053-20-0; **13**, 78088-38-7; $LiClO_4$, 7791-03-9; ethylene, 74-85-1; 1,2-dichloroethane, 107-06-2; 1,2-dibromoethane, 106-93-4; 1-chloro-2-nitroethane, 625-47-8; 1-heptene, 592-76-7; 1,2-dichloroheptane, 10575-87-8; 1,2-dibromoheptane, 42474-21-5; cyclohexene, 110-83-8; 1,2-dichlorocyclohexane, 1121-21-7; 1,2-dibromocyclohexane, 5401-62-7; 3-nitrocyclohexene, 6925-08-2; 4-nitrocyclohexene, 4883-68-5; norbornadiene, 121-46-0.

Photochemical Beckmann Rearrangements. Correspondence between Substituent Effects in Oximes and Oxaziridines[1]

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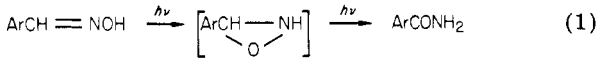
The relative migratory tendencies of hydrogen and aryl groups in the photochemical Beckmann rearrangement of benzaldoximes **2a–c** were compared with those in the photochemical rearrangement of 2-alkyl-3-aryloxaziridines **3a–f**. The migratory tendencies depended on the nature of the aryl substituent and were similar in **2a–c** and **3a–c**, implying that the photochemical Beckmann rearrangement proceeds through an oxaziridine intermediate. A similar order of migratory tendencies was not found in the *tert*-butyloxaziridines **3d–f**, presumably because of steric effects.

The photochemical rearrangement of oximes to amides, or the photochemical Beckmann rearrangement,[2-6] has been shown to proceed by intramolecular oxygen transfer through studies of ^{18}O-labeled oximes.[2b] Accordingly, it has been postulated that the rearrangement goes through an intermediate oxaziridine, **1** (eq 1). Evidence for this



(1)

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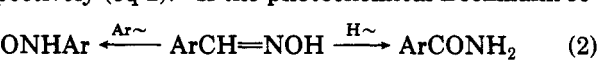
type of intermediate is provided by the low-temperature photolysis of *p*-anisaldoxime, which gave an unstable material containing activie oxygen and with a UV absorption maximum near 235 nm. These properties suggest an oxaziridine, although the material was not thoroughly characterized.[2b]

The rearrangement of aryl aldoximes can lead to aryl carboxamides or to *N*-arylformamides, depending on whether the migration involves hydrogen or the aryl group, respectively (eq 2). If the photochemical Beckmann rearrangement proceeds through an oxaziridine intermediate, then these relative migration tendencies should parallel those in similar oxaziridines. Since oxaziridines of the type **1** are too unstable to isolate, we have prepared and studied the photolysis of several 2-methyl- and 2-*tert*-butyl-3-aryloxaziridines (**3a–f**) to compare the migratory tendency of the aryl group with that of aryl aldoximes with the same aryl substituents.



(2)

Table I. Photolysis of Oximes ArCH=NOH

compd	Ar	irrad time, h	% yield of products: $ArCONH_2$	% yield of products: $ArNH_2$
2a	C_6H_5	3.5	21	
2b	p-$CH_3OC_6H_4$	25	34	4.1
2c	p-ClC_6H_4	4	25,[a] 40	

[a] $C_6H_5CONH_2$.

Results and Discussion

Photolysis of Aryl Aldoximes. Ethanol solutions of aryl aldoximes **2a–c** were irradiated with UV light through quartz, with the results shown in Table I. Benzaldoxime (**2a**) and *p*-chlorobenzaldoxime (**2c**) gave only amides via hydrogen migration. In the latter case, the product was a mixture of *p*-chalorobenzamide and benzamide, the latter arising from photochemical dechlorination of *p*-chlorobenzamide, as was shown by an independent photolysis of *p*-chlorobenzamide under the same conditions. Photolysis of *p*-anisaldoxime (**2b**) gave *p*-anisamide and *p*-anisidine in a ratio of 8.3:1. Since independent photolysis showed that *N*-formyl-*p*-anisidine was converted into *p*-anisidine about 10 times as efficiently as was **2b**, we conclude that the formamide was formed initially in the oxime rearrangement and then photolyzed to *p*-anisidine. It appears that the ratio of hydrogen to aryl group migration in this rearrangement is about 8:1. Although our analysis of the product from photolysis of **2b** did not reveal any *N*-formyl-*p*-anisidine, its presence has been reported.[2]

Photolysis of 2-Alkyl-3-aryloxaziridines. Oxaziridines **3a–f** were irradiated under nitrogen in the same way

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Table II. Photolysis of Oxaziridines ArCH—N(R)O

oxaziridine	Ar	R	irrad time, h	% yield of products: ArCONHR (4)	ArNRCOH (5)	ArCH=NR (6)
3a	C_6H_5	CH_3	2	20		8
3b	p-$CH_3OC_6H_4$	CH_3	1	26	3	
3c	p-ClC_6H_4	CH_3	1.5	57		17
3d	C_6H_5	t-C_4H_9	3	51		9
3e	p-$CH_3OC_6H_4$	t-C_4H_9	1.5	27		
3f	p-ClC_6H_4	t-C_4H_9	2	34,[a] 40		

[a] $C_6H_5CONHC_4H_9$-t.

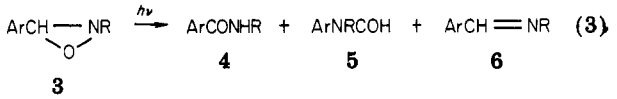
Table III. Quantum Yields and Photostationary States (pss) in Photolysis of Oximes ArCH=NOH

compd	Ar	$([Z]/[E])_{pss}$	Φ_{E-Z}	Φ_{rearr}
2a	C_6H_5	1.32	0.47	0.022
2b	p-$CH_3OC_6H_4$	0.75	0.19	0.010
2c	p-ClC_6H_4	0.72	0.15	0.028

Table IV. Quantum Yields in Photorearrangement of Oxaziridines ArCH—N(R)O

compd	Ar	R	light absorbed, einsteins × 10^{-4}: 1.17/ Φ	2.34/ Φ	5.84/ Φ
3a	C_6H_5	CH_3	1.9	1.5	0.71
3b	p-$CH_3OC_6H_4$	CH_3		0.31	0.33
3c	p-ClC_6H_4	CH_3	1.8	1.4	0.62
3d	C_6H_5	t-C_4H_9	0.39	0.30	0.20
3e	p-$CH_3OC_6H_4$	t-C_4H_9	0.51	0.35	0.27
3f	p-ClC_6H_4	t-C_4H_9		0.12	0.14

as the oximes. In all cases the photorearrangement was very rapid and gave higher yields of products than were obtained from the oximes (Table II), suggesting that an oxaziridine intermediate would not survive in the photolysis of an oxime. As with the oximes, the formation of amides (4, eq 3) is the sole process for all oxaziridines



(3)

except the 2-methyl-3-p-anisyl derivative **3b**, where the ratio of hydrogen to aryl migration is again about 8:1. No product of aryl migration was observed with the 2-*tert*-butyl-3-p-anisyl derivative **3e**, possibly because of steric hindrance by the bulky *tert*-butyl group.

The photorearrangements of **3c** and **3f** were accompanied by some photodechlorination, as was that of **2c**. We could not determine whether the dechlorination occurred prior to rearrangement because photolysis of amide **4f** gave a quantitative yield of **4d** in less time than was required for photorearrangement of oxaziridine **3d**.

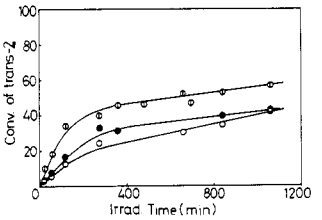


Figure 1. Time–conversion curves for photolysis of *trans*-aryl aldoximes **2** with 254-nm light: circle with vertical bar for **2a**, solid circle for **2b**, and open circle for **2c**.

The parallel migratory tendencies of hydrogen and aryl groups in these oximes and oxaziridines implies that the photochemical Beckmann rearrangement may proceed through an oxaziridine intermediate.

Quantum Yields in Photorearrangements. Quantum yields in the photorearrangements of **2** and **3** were determined to furnish a basis for assessing the correspondence in the migratory tendencies of the substituent groups. Quantum yields were determined by irradiating ethanol solutions of the compounds with 254-nm light, and the results are shown in Tables III and IV.

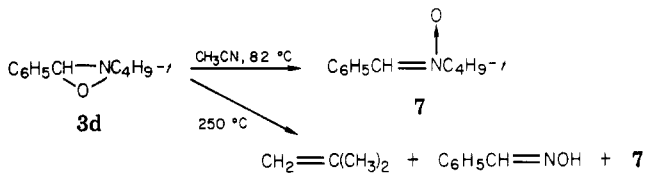
The photorearrangement of **2** was followed by HPLC. In the early stage, efficient trans–cis isomerization of the aldoxime hides the less efficient oxime–amide rearrangement. Time–conversion curves (Figure 1) are composed of both the initial rapid E–Z isomerization and the slower oxime–amide rarrangement. The former is estimated to be 5–20 times as efficient as the latter. Photostationary states (pss) of the trans (E)–cis (Z) isomerizations were attained within 400 min. After attainment of the pss, irradiation was continued to 1200 min, effecting slow rearrangement of the oxime and keeping the pss unchanged. Quantum yields of the oxime–amide rearrangement were determined from the slopes of the time–conversion curves after establishment of the pss. The rather low quantum yields suggest that excited aldoxime is largely directed to the E–Z isomerization, while the rearrangement to amide is a less effective process. The quantum yields for both processes in **2a** dissolved in ethanol are comparable to those reported in dioxane solution.[2]

Table V. Properties of Oxaziridines ArCH—N(R)O

compd	Ar	R	λ_{max} (CH_2Cl_2), nm (log ε)	purity, %[a]	isomer composition,[b] %: cis	trans
3a[c]	C_6H_5	CH_3	245 (3.08)	93.5	35	65
3b	p-$CH_3OC_6H_4$	CH_3	257 (3.57)	87.5	29	71
3c	p-ClC_6H_4	CH_3	281 (3.68), 276 (3.69)	90.9	36	64
3d[d]	C_6H_5	t-C_4H_9	245 (2.82)	100		100
3e[e]	p-$CH_3OC_6H_4$	t-C_4H_9	265 (2.78), 249 (2.84)	90.9		100
3f[e]	p-ClC_6H_4	t-C_4H_9	281 (3.38), 275 (3.40)	100		100

[a] Estimated from ratio of areas of NMR peaks of aldehyde proton to those of R protons. [b] Estimated from areas of NMR peaks of R protons. [c] References 2b and 15. [d] References 7, 8, and 16. [e] Reference 16.

Scheme I

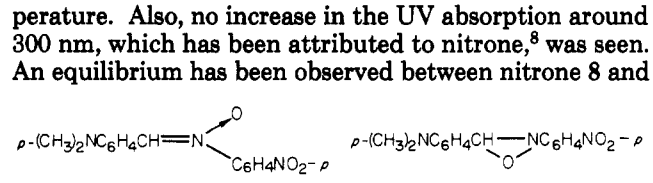


Quantum yields for the rearrangement of oxaziridines were measured by following the remaining active oxygen by iodometry,[7] and are shown in Table IV. The methyloxaziridines **3a** and **3c** have quantum yields >1 at low light-absorption levels, suggesting that they may rearrange by a radical chain mechanism initiated by aldehyde impurities (see Table V).[2] This hypothesis is supported by the dependence of quantum yield on light quanta absorbed. The lower quantum yield of **3b** is attributed to the effect of the methoxy substituent in lower the rate of hydrogen abstraction in the excited state.

The quantum yields for the *tert*-butyloxaziridines **3d–f** are all <1, suggesting that a radical chain mechanism is not important in these compounds despite their contamination with small amounts of the corresponding aromatic aldehydes. The order of reactivity in the *tert*-butyl series is different from that of the methyl series, and the order in the latter seems more appropriate than that in the former for comparison with the order of reactivity of the oximes because **3e** did not yield an aryl-migration product owing to steric hindrance.

The order of the quantum yields in the rearrangement of the oxaziridines, **3a > 3c > 3b**, resembles that for the oximes. It is important to note that the oxaziridines used in this study are over 10 times as labile toward UV light as the oximes. If the photorearrangement of oxime to amide is assumed to require two photons, one for conversion of the oxime to oxaziridine and another for conversion of oxaziridine to amide, the overall process should be relatively inefficient. However, the quantum efficiency for the rearrangement of oxime to oxaziridine is not known.

Attempts to isolate 3-*p*-anisyloxaziridine (**1**) during photolysis of **2b** at dry ice–acetone temperature failed, presumably because of its thermal instability. It has been reported that the thermal stability of oxaziridines depends on the substituent and the solvent.[7,8] It has been reported that **3d** is converted into nitrone **7** on refluxing in CH_3CN (Scheme I), whereas in the gas phase at 250 °C it yields isobutylene (60%), benzaldoxime (36%), and nitrone **7** (12%).[7] However, no conversion of any of **3a–f** to a nitrone was detected by NMR when their solutions in CCl_4 or EtOH were examined after 3 h in the dark at room temperature. Also, no increase in the UV absorption around 300 nm, which has been attributed to nitrone,[8] was seen. An equilibrium has been observed between nitrone **8** and



the corresponding oxaziridine **9**,[8] but this phenomen is not general for 2-alkyloxaziridines. It seems to be necessary for the oxaziridine–nitrone isomerization that the oxaziridine have an electron-donating substituent on the ring carbon and an electron-withdrawing substituent on the ring nitrogen, since the reaction probably proceeds by heterolytic carbon–oxygen bond fission, which develops positive charge on the carbon and negative charge on the nitrogen.

Ozaziridines with alkyl groups on either or both the ring carbon and nitrogen atoms are sufficiently stable to be isolated. On the other hand, aryl substituents on the nitrogen tends to make them less stable,[8] and attempts to prepare 2-phenyl-3-fluorenyloxaziridine led only to *N*-phenylfluorenylnitrone, apparently because of low stability of the oxaziridine.[9a] The products from thermolysis of oxaziridines are also dependent on the nitrogen substituent; **3d** yields the oxime and isobutylene,[7] whereas oxaziridines with phenyl on the nitrogen isomerize to the amides.[8] Since the oxaziridines in this study are alkyl-substituted, the conversion of **3** into **4** or **5** is apparently a photochemical process rather than a thermal one in view of the thermolysis of **3d** to the oxime but not the amide. In the thermolysis of a series of 2-phenyl-3-aryloxaziridines, the tendency for aryl migration increases with an increase in electron-donating ability of the substituent on the aryl group.[8]

Since we obtained a product of aryl migration only with the *p*-anisyloxaziridine **3b**, we attempted to prepare 2-methyl- and 2-*tert*-butyl-3-[*p*-(dimethylamino)phenyl]oxaziridines, which should also show some aryl migration. However, our preparations contained only 14% and 33% active oxygen, respectively, and their photochemistry was not studied.

We also attempted to effect the photochemical Beckmann rearrangement of benzophenone oxime, *p*-methoxybenzophenone oxime, and fluorenone oxime by irradiation in ethanol or acetic acid solutions, but niether amide nor anilide was formed, although slow decomposition of the oximes was observed. In view of the suggestion that photolysis of 10-phenylphenanthridine *N*-oxide and fluorenone anil *N*-oxide to amides proceeds through oxaziridines,[9b] our negative results with these ketoximes imply that they are not readily converted to the oxaziridines.

Experimental Section

Mass spectra were recorded on a JEOL GC/MS double-focussing mass spectrometer by using a silicone OV-1 column (2 m), Model MJS D-300. NMR spectra were recorded on a Hitachi NMR Model R-24B. GLC analyses were performed with a Yanagimoto gas chromatograph, Model G-180, equipped with an FID detector and using either a silicone OV-1 or PEG 20M column. Product yields were determined by using naphthalene as an internal standard, and product identification was made by comparison with retention volumes of authentic samples or by GC/MS analysis.

Materials. Oximes were prepared by reaction of in the following: ketones with NH_2OH; their melting points matched those reported.[10-14] 2-Alkyl-3-aryloxaziridines **3a–f** were prepared by condensation of the benzaldehydes with alkylamines followed by oxidation with *m*-chloroperbenzoic acid in CH_2Cl_2.[7,8,15,16] Oxaziridines **3a–c,e** were contaminated with small amounts of the starting aldehydes; their purity and cis/trans ratios, estimated from NMR peaks, are shown in Table V. Purities estimated by iodometric determination of active oxygen were within 3% of those estimated by NMR.[7,15,17,18] The assignment of cis and trans isomers was based on the empirical rule that the NMR peaks of the 2-alkyl hydrogens in the cis isomer should be shifted upfield owing to the anisotropic effect of the aryl ring.[17,18]

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The properties of **3a,d-f** correspond to those reported (see Table V for references).

2-Methyl-3-*p*-anisyloxaziridine (**3b**): mass spectrum, (70 eV), *m/e* (relative intensity) 165 (M^+, 60), 136 (25), 135 (100), 107 (43), 78 (68); NMR δ 2.30 (s, 0.87 H), 2.73 (s, 2.13 H), 3.70 (s, 2.13 H), 3.75 (s, 0.87 H), 4.15 (s, 0.71 H), 4.90 (s, 0.29 H), 6.9 (m, 4 H); active oxygen calcd for $C_9H_{11}NO_2$ 9.7%, found 9.4% (corrected for purity).

2-Methyl-3-*p*-chlorooxaziridine (**3c**): mass spectrum, (70 eV), *m/e* (relative intensity) 169 (M^+, 60), 168 (63), 141 (33), 139 (100), 110 (10); NMR δ 2.35 (s, 1.08 H), 2.82 (s, 1.92 H), 4.28 (s, 0.64 H), 5.03 (s, 0.36 H), 7.30 (s, 2.56 H), 7.37 (s, 1.44 H); active oxygen calcd for $C_8H_{10}NOCl$ 9.4%, found 9.4% (corrected for purity).

Amides were prepared by reaction of benzyl chlorides with NH_3 or alkylamines in the presence of NaOH. Melting points corresponded to those reported as follows: **4a**,[19] **4b**,[22] **4c**,[23] **4d**,[20] *p*-anisamide,[21] and *p*-chlorobenzamide.[21] N-*tert*-Butyl-*p*-anisamide: mp 140-141.5 °C; mass spectrum, *m/e* 207 (M^+). N-*tert*-Butyl-*p*-chlorobenzamide: mass spectrum, *m/e* 213 (M^+).

N-Arylformamides were prepared by condensation of anilines with ethyl formate. Melting or boiling ranges corresponded to those reported in the following: *N*-methylformanilide,[24] *p*-anisylformamide,[2b,25] p-chlorophenylformamide.[26]

N-Methyl-*N*-*p*-anisylformamde (**5b**): UV (MeOH) λ_{max} 237 nm (log ϵ 3.96); bp 160-171 °C (4 mm); mass spectrum, *m/e* (relative intensity) 165 (M^+, (30), 136 (9), 125 (8), 124 (100), 122 (56), 108 (9), 96 (3), 94 (3), 43 (22).

Photolyses. Solutions of oximes or oxaziridines ($\sim 10^{-2}$ M) in ethanol were irradiated with UV light from a 300-W high-pressure Hg lamp (Halos HIP 300). Photolyses of oximes were followed by monitoring the disappearance of starting material by TLC, and product analyses were carried out by GLC. Photolyses of oxaziridines were performed under nitrogen with irradiation through a quartz filter. The progress of the reaction was monitored by iodometric determination of active oxygen, and reaction products were analyzed by GLC and GC/MS.

Quantum Yields. Quantum yields in photolyses were measured by irradiating 35 mL of ethanol solutions of substrates ($\sim 2 \times 10^{-2}$ M) in 40-mL quartz tubes in a merry-go-round apparatus equipped with a 60-W low-pressure Hg lamp that emitted 254-nm light. Light intensities were measured with a potassium ferrioxalate actinometer.[27] The amount of light quanta absorbed was 3.58×10^{-6} einstein/min. Disappearance of substrate was followed by HPLC for oximes and by iodometry for oxaziridines. The HPLC analyses were performed on a JASCO high-performance liquid chromatograph (Twincle) equipped with a Finepack Sil NH_2 column eluted with dioxane at a flow rate of 1 mL/min. A UV detector at 250 nm was used. The *E* aldoximes (trans) have retention times t_R of 3.6, 3.7, and 3.5 min for **2a**, **2b**, and **2c**, respectively.

Registry No. (*E*)-**2a**, 622-31-1; (*Z*)-**2a**, 622-32-2; (*E*)-**2b**, 3717-21-3; (*Z*)-**2b**, 3717-22-4; (*E*)-**2c**, 3717-24-6; (*Z*)-**2c**, 3717-23-5; *cis*-**3a**, 39245-63-1; *trans*-**3a**, 40264-03-7; *cis*-**3b**, 82044-36-8; *trans*-**3b**, 82044-37-9; *cis*-**3c**, 82044-38-0; *trans*-**3c**, 82044-39-1; *trans*-**3d**, 3585-81-7; *trans*-**3e**, 82079-47-8; *trans*-**3f**, 82044-40-4; 2-methyl-3-[*p*-(dimethylamino)phenyl]oxaziridine, 82044-41-5; 2-*tert*-butyl-3-[*p*-(dimethylamino)phenyl]oxaziridine, 82044-42-6; benzophenone oxime, 574-66-3; *p*-methoxybenzophenone oxime, 54150-63-9; fluorenone oxime, 2157-52-0.

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Nucleophilic Catalysis of the Hydrolysis of Phenyl Acetates by the Succinimide Anion in Aqueous Solution

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Kinetic studies were conducted on the disappearance of some phenyl acetates in aqueous solutions buffered by succinimide/succinimide anion at 30 °C. The most reasonable mechanistic scheme, compatible with the data, is that shown in Scheme I involving nucleophilic displacement by the succinimide anion on the ester. The rate equation (eq 2) may be derived from the mechanism of Scheme I. The values of pseudo-first-order rate constants which were determined may be predicted by eq 2 and the constants of Table I with an error of 7% or less (see Table II). Phenyl acetate was the only substrate that had no buffer-dependent disappearance. Although succinimide is converted to succinamic acid by hydrolysis in the buffered solutions used, only about 6% or less of succinimide is lost during the time required for substrate disappearance. The nucleophilic role for the succinimide anion was assigned on the basis of a high Hammett ρ value (2.25) for the three phenyl acetates studied and the low solvent deuterium isotope rate effect of 1.13 obtained for the *p*-nitrophenyl acetate substrate. The low value for the nucleophilic rate constant obtained by *p*-nitrophenyl acetate cannot be ascribed to ground-state charge delocalization as estimated by MINDO-3 calculations utilizing frontier molecular orbital theory. This observed low reactivity is therefore thought to be the result of a tight anionic solvation shell in the aqueous solutions employed. Media studies in different salts on this reaction show little effects. Finally, the absence of third-order rate terms involving succinimide in this reaction is due to the inability of the succinimide anion to have its nucleophilicity increased by proton removal in the transition state.

The nucleophilicity of imide anions is well-documented by the Gabriel synthesis of primary amines, involving the S_N2 displacement of halogen atoms from primary alkyl halides.[1]

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