73245-21-3; **3h**, 73245-22-4; **3i**, 73245-23-5; **6d**, 17649-59-1; **6f**, 21483-46-5; **6g**, 50919-64-7; **6i**, 73195-01-4; **16a**, 73245-24-6; **16b**, 73195-02-5; **16c**, 73245-25-7; **16d**, 73245-26-8; **16e**, 73245-27-9; **16f**, 73245-28-0; **16g**, 73245-29-1; **16h**, 73245-30-4; **16i**, 73245-31-5; **17f**, 73195-03-6; **17g**, 73198-06-8; **18**, 73195-04-7; **19**, 73195-05-8; **20**, 73195-06-9; **21**, 73195-07-0; **22**, 73245-32-6; **23**, 73245-33-7; **24**, 73245-34-8; **25**, 73195-08-1; dimethyl acetylenedicarboxylate, 762-42-5; ethyl glycidate, 4660-80-4; ethyl lactate, 97-64-3.

Photodegradation of Some Alkyl *N*-Arylcarbamates[1]

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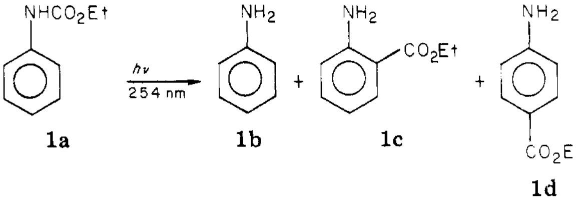
The UV photodegradation of a number of alkyl *N*-arylcarbamates in solution has been investigated. A mechanism for the photodegradation process is proposed. The initial excitation of the carbamate moiety involves a π,π^* transition into an excited singlet state. Chemical change from this excited state proceeds primarily via homolytic cleavage of the nitrogen to alkoxycarbonyl bond to provide a radical pair in a solvent cage. The quantum efficiency for carbamate disappearance is low. The major identifiable products are amines and photo-Fries rearrangement products (where formation is possible). The arylaminyl radical is proposed as a major reaction intermediate. It is suggested that the failure for the sum of quantum yields of formation for degradation products (amines and photo-Fries rearrangement products) to coincide with quantum yields for carbamate disappearance is due to reactions (e.g., coupling) of the aminyl radicals. The quantum yield for carbamate disappearance is independent of both methyl group substitution on the phenyl ring and excitation wavelength. In contrast, the quantum yield for the disappearance of the parent arylamine, a carbamate photodegradation product, does show dependence on these factors.

The photodegradation of urethanes based on aryl isocyanates has been the subject of a number of reports.[2-14] The earliest studies directed toward identification of the products formed were reported by Trecker et al.[2] and Bellus and Schaffner.[3] The latter found that irradiation of ethyl *N*-phenylcarbamate (**1a**) at 254 nm yielded ethyl *o*-aminobenzoate (**1c**), ethyl *p*-aminobenzoate (**1d**), and aniline (**1b**) (Scheme I). More recently, Beachell and Chang[4] also reported on the photodegradation of **1a**. In addition to products **1b**, **1c**, and **1d** they found CO_2. An intramolecular (concerted) rearrangement was proposed to account for the photo-Fries products (**1c** and **1d**).

Scheme I



Schwetlick and co-workers[5-10] confirmed the results of earlier workers with respect to the primary photodegradation products of **1a** in solution. They proposed, however, that the products were formed by N–C bond cleavage resulting in a solvent-caged radical pair. Within the solvent cage the ethoxycarbonyl radicals attacked the benzene ring at the ortho and para positions to give the reported photo-Fries products. Similarly, aniline was formed by diffusion of the anilinyl radical from the solvent cage followed by hydrogen abstraction. The existence of a cage effect was given credence when, upon photolysis of **1a** in the vapor phase, no photo-Fries products were detected.

Added support for a cage mechanism was obtained by Osawa et al.,[14] who reported ESR spectra as evidence for an anilinyl radical upon photolysis of the carbamate **1a**. Schwetlick et al.[8] determined the disappearance quantum yield of **1a** ($\Phi_D = 0.023$) and the quantum yield for formation of **1b** ($\Phi_{1b} = 0.009$), **1c** ($\Phi_{1c} = 0.008$), and **1d** ($\Phi_{1d} = 0.006$). The formation of **1b**, however, was not measured directly but was determined from the difference in the quantum yield of disappearance for **1a** and the sum of the quantum yields of formation for **1c** and **1d** [$\Phi_{1b} = \Phi_D(\mathbf{1a}) - (\Phi_{1d} + \Phi_{1c})$].

The current investigation is directed toward the photodegradation of simple urethanes **2a**–**5a** based upon aryl isocyanates bearing ring-substituted methyl groups. The effect of methyl-group ring placement on the photodegradation process and reaction products is of particular interest with respect to any analogies one may draw to the photodegradation of polymeric systems based on methyl phenylene diisocyanates.

Photolysis of carbamates **1a**–**5a** under a variety of conditions should yield interesting information concerning the

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(1) The nomenclature used follows that recommended by: Fletcher, J.; Dermer, O.; Fox, R. *Adv. Chem. Ser.* **1974**, No. 126.

(2) Trecker, D.; Foote, C.; Osborn, C. *Chem. Commun.* **1968**, 1034.

(3) Bellus, D.; Schaffner, K. *Helv. Chim. Acta* **1968**, *51*(1), 221.

(4) Beachell, H.; Chang, I. *J. Polym. Sci., Polym. Chem. Ed.* **1972**, *10*, 503.

(5) Schwetlick, K.; Noack, R.; Schmeider, G. *Z. Chem.* **1972**, *12*, 107.

(6) Noack, R.; Schwetlick, K. *Z. Chem.* **1972**, *12*, 108.

(7) Schwetlick, K.; Noack, R. *Z. Chem.* **1972**, *12*, 109.

(8) Noack, R.; Schwetlick, K. *Z. Chem.* **1972**, *12*, 143.

(9) Noack, R.; Schwetlick, K. *Z. Chem.* **1972**, *12*, 140.

(10) Noack, R.; Schwetlick, K. *Z. Chem.* **1973**, *14*, 99. Stumpe, J.; Melhorn, A.; Schwetlick, K. *J. Photochem.* **1978**, 1.

(11) Schultze, H. *Z. Naturforsch., B* **1973**, *28*, 339.

(12) Masilamani, D.; Hutchins, R.; Ohr, J. *J. Org. Chem.* **1976**, *41*, 3687.

(13) Schultze, H. *Makromol. Chem.* **1973**, *172*, 57.

(14) Osawa, Z.; Cheu, E.; Ogiwara, Y. *J. Polym. Sci., Polym. Lett. Ed.* **1975**, *13*, 535.

(15) Schulman, S.; Griepentrog, J. A. *Microchem. J.* **1962**, *6*(1), 179–97; *Chem. Abstr.* **1962**, *59*, 9848*d*.

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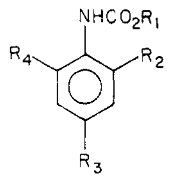

1a, $R_1 = Et; R_2 = R_3 = R_4 = H$
2a, $R_1 = Pr; R_2 = CH_3; R_3 = R_4 = H$
3a, $R_1 = Pr; R_3 = CH_3; R_2 = R_4 = H$
4a, $R_1 = Pr; R_2 = R_4 = CH_3; R_3 = H$
5a, $R_1 = Pr; R_2 = R_3 = R_4 = CH_3$

photodegradation mechanism of aromatic urethanes. Since several of the possibilities for the photo-Fries rearrangement process are excluded, a unique opportunity is provided to determine the effect of methyl blocking groups on the overall photodegradation of the aromatic urethane.

Experimental Section

General Methods. Ultraviolet spectra were recorded with a Beckman DK-2A spectrophotometer using 1-cm quartz cells. Infrared spectra were recorded with a Perkin-Elmer 451 infrared spectrophotometer. NMR spectra were recorded on a Jeolco Model JNM-4H-100 100-MHz spectrophotometer (using Me_4Si as an internal standard). The ultraviolet light source used was a 450-W Hanovia medium-pressure Hg lamp. Band-pass optical filters (254 and 280 nm) were from Baird-Atomic. A Hewlett-Packard Model 5710A GC with an FID was used for separation, detection, and quantification of products. The columns were 6 ft stainless-steel containing Carbowax 20-M on Chromosorb G.

Materials. Starting and Reference Materials. Isocyanates. Phenyl and *p*-tolyl isocyanates obtained from Eastman Organic Chemicals were distilled prior to use; fractions with boiling points of 64.5 °C (25 mm) and 61 °C (3.6 mm), respectively, were retained. *o*-Tolyl isocyanate (Eastman Organic Chemicals) and 2,6-dimethylphenyl and 2,4,6-trimethylphenyl isocyanates (Adams Chemical Co.) were used as received.

Amines. Aniline (**1b**) and *o*-toluidine (**2b**) (Eastman Organic Chemicals) were distilled, and fractions with boiling points of 67 °C (11 mm) and 90 °C (10 mm), respectively, were retained. *p*-Toluidine (**3b**) (Aldrich Chemical Co.) was purified by sublimation at 5 mm (bath temperature 90–100 °C), and material with a melting point of 43–45 °C was retained. 2,4,6-Trimethylaniline (**5b**) (Aldrich Chemical Co.) was distilled prior to use; bp 90–94 °C (1 mm). 2,6-Dimethylaniline (**4b**) (Aldrich Chemical Co.) was used as received.

Photo-Fries Rearrangement Products and Precursors. Ethyl *p*-aminobenzoate (**1d**) and methyl *o*-aminobenzoate from Aldrich Chemical Co. were used as received. 2-Amino-3-methyl-, 4-amino-5-methyl-, and 2-amino-5-methylbenzoic acids were obtained from Aldrich Chemical Co. 2-Amino-5-methylbenzoic acid was recrystallized two times from benzene in the presence of decolorizing charcoal and gave material melting at 180–181 °C.

Internal Standards. *n*-Eicosane (PolyScience Corp.) was used as received.

Solvents. Ethyl propionate (Aldrich Chemical Co.) was dried over magnesium sulfate (anhydrous) for 24 h and distilled at atmospheric pressure under a positive nitrogen pressure to give material with a boiling point of 95.5 °C; its UV spectrum showed no absorption above 260 nm. Spectrograde cyclohexane from Burdick and Jackson Laboratories was used in all photolysis reactions.

Miscellaneous. Boron trifluoride etherate (Aldrich Chemical Co.) was distilled prior to use; material with a boiling point of 125 °C (760 mm) was retained for use.

Preparative Procedures. 1. Preparation and Characterization of Alkyl *N*-Arylcarbamates. General Procedure. Dry propanol (100% molar excess) and a catalytic (1% by weight of isocyanate) amount of pyridine were placed in a flame-dried flask under a nitrogen atmosphere. A solution of the requisite isocyanate in ethyl acetate (dry) was added dropwise with stirring to the alcohol/pyridine solution. The extent of reaction was determined by following the intensity of the isocyanate band (ca. 2270–2240 cm^{-1}) in the IR. In some cases heating at 60 °C was necessary to speed the rate of isocyanate reaction (Table I).

When the isocyanate had completely reacted, the cooled reaction mixture was filtered to remove insolubles. In several cases ca. <0.5 g of an insoluble high-melting solid, most likely the corresponding urea, was isolated. The filtrate was concentrated and the crude carbamate purified by appropriate means (Table I). The structures assigned to the various carbamates were confirmed by NMR spectroscopy (Table I).

2. Preparation and Characterization of Photo-Fries Rearrangement Products. (a) Ethyl *o*- and *p*-Aminobenzoates (1c and 1d). The ethyl *p*-aminobenzoate (**1d**) was used as received. Ethyl *o*-aminobenzoate (**1c**) was obtained by transesterification of the methyl ester. The crude reaction product was distilled at 0.1 mm, and the fraction with a boiling point of 72.5–74 °C was retained. An NMR spectrum (Table II) confirmed the identity of the product.

(b) Amino- and Methyl-Substituted Benzoates. These compounds (**2c**, **2d**, and **3c**; see Table II) were prepared by esterification of their corresponding substituted benzoic acids by using boron trifluoride etherate as a catalyst.[16,17] The general procedure was as follows. Boron trifluoride etherate was added to a solution or slurry of the substituted benzoic acid in dry propanol. The addition rate was controlled, and external cooling was applied to maintain reaction temperatures below 30 °C. Upon completion of the addition, the reaction mixture was stirred at ambient temperatures for ca. 2 h. The reaction mixture was then heated to gentle reflux. Reflux temperatures were maintained for variable periods of time, depending on the starting substituted benzoic acid.

The cooled, pale to dark amber reaction mixtures were subsequently subjected to vacuum distillation (>30 mm) at a temperature not exceeding 100 °C. The still residues were cooled to ice–water-bath temperatures. After hydrolysis of residual boron trifluoride etherate and its complexes by careful addition of ice–water to the still residues, followed by neutralization with aqueous 10% sodium carbonate, the aqueous insolubles were extracted with ether. The combined and dried ether extracts were concentrated at reduced pressure. The crude propyl aminobenzoates were purified by fractional distillation in vacuo in the case of **2c** and **3c** and by recrystallization from hexane in the case of **2d** (Table II). Structural assignments were confirmed by NMR spectroscopy (Table II).

Photochemical Degradation. 1. Description of Apparatus. A 450-W, medium-pressure, Hanovia mercury lamp was focused through an appropriate band-pass filter (280 and 254 nm) on a 1 cm path length quartz cell. A blower was used to cool the mercury-lamp source. When desired, test solutions contained in the quartz cell could be purged with oxygen or helium. This was accomplished through the use of a needle-valve assembly attached to the tappered, quartz, cell neck.

2. Methods of Quantifying UV Photodegradation Products and Computing Photochemical Efficiencies. The loss of carbamate due to photodegradation and the amounts of known photodegradation products were determined quantitatively by GC using eicosane as an internal standard. The quantum yields of loss (Φ_D) and of product formation (Φ_p) were calculated by standard methods.[18]

Results

Ultraviolet Spectra. The ultraviolet spectral data of carbamates **1a**–**5a** and the resultant photoproducts expected from a process analogous to Scheme I are given in Table III. Concentration, absorbance, and extinction coefficients for peak maxima data are presented. For carbamates **1a**–**3a** the fine structure of the $S_1(\pi,\pi^*) \leftarrow S_0$ transition of benzene is retained. The 2,6-dimethyl-substituted (**4a**) and 2,4,6-trimethyl-substituted (**5a**) carbamates show little or no vibrational fine structure.

Quantum Yield (Φ_D) for Alkyl *N*-Arylcarbamate Degradation. Air-saturated solutions of the different

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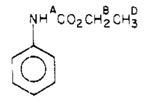
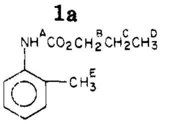
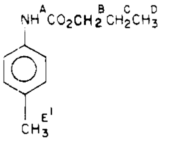
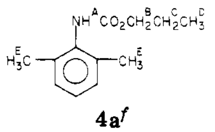
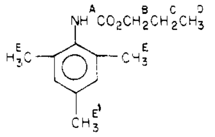
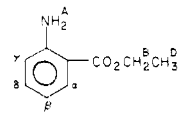
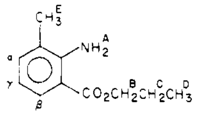
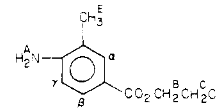
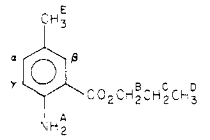
[16] Sowa, F.; Nieuwland, J. *J. Am. Chem. Soc.* **1936**, *58*, 271.
[17] Hallas, G. *J. Chem. Soc.* **1965**, 5770.
[18] Turro, N. J. In "Molecular Photochemistry"; W. A. Benjamin: Reading, MA, 1965; p 6.

Table I. Characterization of Alkyl *N*-Arylcarbamates[a]

			chemical shifts, δ[b]				
alkyl *N*-arylcarbamates	mp or bp (mm), °C	% yield	H^A	H^B	H^C	H^D	H^E (H^{E^1})
 **1a**	48-50[c]	quant[d]	6.95 (br s)	4.20 (q)		1.28 (t)	
 **2a**[f]	93.5-95.5 (0.1)	78.7[e]	6.46 (br s)	4.08 (t)	1.68 (m)	0.94 (t)	2.20 (s)
 **3a**	54-55[g]	quant[h]	6.79 (br s)	4.08 (t)	1.67 (m)	0.93 (t)	(2.26) (s)
 **4a**[f]	108-109 (0.2)	83[e]	6.30 (br s)	4.06 (t)	1.65 (m)	0.93 (t)	2.20 (s)
 **5a**[f]	64-65	82[e]	6.14 (br s)	4.07 (t)	1.65 (m)	0.93 (t)	2.19 (s) (2.24) (s)

[a] Satisfactory analytical data were reported for all new compounds listed in the table. [b] Me_4Si as reference, $CDCl_3$ as solvent. [c] Reported[4] melting point 52 °C. [d] Yield of crude product. **1a** was purified by sublimation at 0.2 mm (pot temperature 80-90 °C). [e] Yield of purified product. [f] Compounds previously unreported. [g] Reported[15] melting point 53.5-54 °C. [h] Yield of crude product. Purification was effected by recrystallization from an acetonitrile-hexane mixture.

Table II. Characterization of Amino- and Methyl-Substituted Propyl Benzoates[a]

			chemical shifts, δ[b]					
	mp or bp (mm), °C	% yield	H^A	H^B	H^C	H^D	H^E	H_{aryl}
 **1c**	72.5-74 (0.1)		5.76 (br s)	4.32 (q)		1.37 (t)		7.89 (m, H_α) 7.25 (m, H_β) 6.68 (m, H_γ, H_δ)
 **2c**	104-105[c] (0.15-0.2)	53	5.82 (br s)	4.20 (t)	1.75 (m)	1.00 (t)	2.11 (s)	7.15 (d, H_α) 7.79 (d, H_β) 6.55 (t, H_γ)
 **2d**	54-57[c]	52	4.10 (br s)	4.20 (t)	1.75 (m)	1.00 (t)	2.13 (s)	7.74 (m, H_α, H_β) 6.59 (d, H_γ)
 **3c**	83-84[c] (0.05-0.08)	36	5.56 (br s)	4.19 (t)	1.75 (m)	0.98 (t)	2.18 (s)	7.65 (s, H_α) 7.05 (dd, H_β) 6.53 (d, H_γ)

[a] Satisfactory analytical data were reported for all new compounds listed in this table. [b] Me_4Si as reference, $CDCl_3$ as solvent. [c] Compounds previously unreported.

urethanes (**1a**–**5a**) in cyclohexane were photolyzed to low conversions at 254 and 280 nm by using band-pass filters (Table IV). In the case of propyl *N*-*o*- and *N*-*p*-tolylcarbamates (**2a** and **3a**), the quantum yield for carbamate disappearance (Φ_D) was also determined in air-saturated solutions by using ethyl propionate as the solvent. Ethyl propionate was selected as a model solvent for photodegradation studies currently being carried out on simple urethanes in solid polymer matrixes of polymethyl and polypropyl methacrylate (PMMA and PPMA).[19] Photo-

Table III. UV Spectral Data

	λ_{ex_1},[a] nm	λ_{ex_2},[b] nm	concn, M	A_2[c]	$10^{-3}\epsilon_2$[d]
1a	<240	268, 274,[b] 287	6.99×10^{-4}	0.59	0.844
b	234	286	1.69×10^{-4}	0.26	1.54
c		333	3.13×10^{-5}	0.14	4.47
d	<230	278	3.09×10^{-5}	0.65	21.04
2a	<240	267, 279,[b] 281	7.0×10^{-4}	0.53	0.757
b	234	285	1.203×10^{-4}	0.20	1.66
c	245	333	4.87×10^{-5}	0.26	5.34
d	<230	271	3.16×10^{-5}	0.47	14.9
3a	236	280, 287,[b] 273	7.9×10^{-4}	0.69	0.873
b	238	295	2.0×10^{-4}	0.32	1.6
c	250	341	4.7×10^{-5}	0.19	4.04
4a	<240	259, 264,[b] 272	6.5×10^{-4}	0.17	0.261
b	234	282	1.6×10^{-4}	0.27	1.57
5a	<240	267	1.8×10^{-3}	0.47	0.262
b	236	290	1.15×10^{-4}	0.18	1.69

[a] λ_{ex_1} is the wavelength of the peak maximum for the $S_0 \rightarrow S_2(\pi,\pi^*)$ transition. [b] λ_{ex_2} is the wavelength of the peak maximum for the $S_0 \rightarrow S_1(\pi,\pi^*)$ transition. [c] A_2 is the absorbance for λ_{ex_2} at the concentration given. [d] ϵ_2 is the extinction coefficient for λ_{ex_2}.

Table IV. Quantum Yield (Φ_D) for Carbamate Degradation in Cyclohexane[a,b]

	$\Phi_{D,254}$	concn$_{254}$, M	$\Phi_{D,280}$	concn$_{280}$, M
1a	0.030	1.15×10^{-3}	0.027, 0.025,[c] 0.025[d]	9.44×10^{-4}
2a	0.022	1.4×10^{-3}	0.024	6.97×10^{-4}
3a	0.022	1.08×10^{-3}	0.029, 0.026,[c] 0.032[d]	8.07×10^{-4}
4a	0.030	6.5×10^{-4}		
5a	0.026	1.81×10^{-3}	0.024	1.81×10^{-3}

[a] All quantum yields were determined in air (unless otherwise noted) at low conversions to minimize any effects of product absorption or quenching. [b] Quantum yields calculated by using GC analysis with eicosane as an internal standard. [c] Solution continuously purged with N_2 or He during photolysis. [d] Solution continuously purged with oxygen during photolysis.

lysis of **2a** and **3a** at 280 nm in ethyl propionate gave disappearance quantum yields of 0.006 and 0.005, respectively—significantly lower than those obtained in cyclohexane (Table IV).

Effect of Oxygen on Quantum Yield (Φ_D) for *N*-Arylcarbamate Degradation. The quantum yield for loss was determined in the presence and absence of oxygen at 280 nm (Table IV). The values are comparable to those obtained for air-saturated solutions of the carbamates (**1a** and **3a**) under similar conditions of irradiation.

Quantum Yield for Product Formation (Φ_p). The quantum yields for product formation (Φ_p) from carbamates **1a**, **2a**, **3a**, and **5a** are summarized in Table V. No other nonvolatile products were identified. The sum of the product quantum yields (Φ_{total}) can be compared to the quantum yield for disappearance (Φ_D) of each of the carbamates (Table V) upon photolysis at 254 nm.

In a number of cases the effect of initial carbamate concentration on product formation was assessed from determination of quantum yields for products. In general, no concentration effect was observed. In a typical example, the quantum yield of ethyl *o*-aminobenzoate (**1c**) was unaffected upon a change in concentration of **1a** by 2 orders of magnitude (photolysis at 254 nm) (Table VI).

Table V. Quantum Yields (Φ_p) for Carbamate Photolysis Products Photolyzed at 254 nm in Cyclohexane[a,b]

carbamate	ArNH$_2$ Φ_b	*o*-PF Φ_c	*p*-PF Φ_d	Φ_{total}	Φ_D
1a	0.005	0.008	0.003	0.016	0.030
2a	0.005	0.003	0.008	0.016	0.022
3a	0.002	0.006		0.008	0.022
5a	0.000			0.000	0.024

[a] Φ_b, Φ_c, and Φ_d are the quantum yields for formation of the aromatic amine and the ortho photo-Fries and para photo-Fries products of the carbamate. Φ_{total} is the sum of Φ_b, Φ_c, and Φ_d. [b] Quantum yields were determined by using GC analysis and comparison with known concentrations of the particular product.

Table VI. Effect of Initial Carbamate 1a Concentration on the Quantum Yield (Φ_c) of its Ortho Photo-Fries Rearrangement Product (1c)

[1a], M	Φ_c of 1c[d]	$10^{-3}t_{irrad}$, s
6.5×10^{-2}	0.009[a]	1.8
6.5×10^{-3}	0.009[b]	1.8
1.15×10^{-3}	0.008[c]	1.8
7.0×10^{-4}	0.010[c]	1.98

[a] Determined from UV absorption of the ortho photo-Fries product. [b] Determined from both UV absorption and GC of the ortho photo-Fries product. [c] Determined by GC analysis. [d] At 254 nm.

Table VII. Effect of Products on Quantum Yield (Φ_D) of Carbamate 3a and Quantum Yield (Φ_c) of the Ortho Photo-Fries Product 3c upon Photolysis at 254 nm[a]

[3a], M	[3b], M	[3c], M	Φ_D	Φ_c of 3c
1.09×10^{-3}			0.023	0.004
1.09×10^{-3}	2.06×10^{-4}		0.021	0.004
1.09×10^{-3}		6.22×10^{-5}	0.023	0.003
1.09×10^{-3}	2.06×10^{-4}	6.22×10^{-5}	0.021	0.003

[a] Φ_D is the quantum yield for loss of carbamate 3a. Φ_c is the quantum yield for formation of 3c, the ortho photo-Fries product of carbamate 3a.

For the determination of the quenching effect of the photoproducts themselves on the degradation of the carbamate **3a**, the quantum yield of loss for **3a** was determined both in the absence and in the presence of the ortho photo-Fries product **3c** and the aromatic amine **3b** (Table VII). The quantum yield, Φ_c, for formation of the ortho photo-Fries product **3c** was also calculated under the same conditions. There was no change in either Φ_D for carbamate loss or Φ_c for formation of **3c** in the presence of either photoproduct.

Quantum Yield for Product Loss. The quantum yields for decomposition of the free aromatic amines (aniline, *p*-toluidine, etc.) are summarized in Table VIII for irradiation at 254 and 280 nm in either helium, oxygen, or air-saturated solutions. Since the parent arylamines (e.g., aniline from carbamate **1a**) are significant products of the urethane photodegradation at 254 and at 280 nm, it was important to examine their photochemistry. This was of particular interest, because in several cases it was found difficult to assess the extent of their formation.

The Φ_D values for the decomposition of the ortho and para photo-Fries products from carbamate **2a** were also determined and are quite low (**2c**, 1.4×10^{-4} M, $\Phi_D = 0.004$; **2d**, 8.1×10^{-5} M, $\Phi_D = 0.003$ at 254 nm).

Discussion

UV Spectral Interpretation for *N*-Arylcarbamates and Their Photodegradation Products. The ultraviolet

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(19) Unpublished results.

Table VIII. Quantum Yields (Φ_D) for Aromatic Amines Photolyzed at 254 and 280 nm in Cyclohexane[a]

	concn, M	$\Phi_{D,254nm}$	concn, M	$\Phi_{D,280nm}$
aniline (1b)	7.30×10^{-4}	0.031[b]	1.69×10^{-4}	0.007
	7.30×10^{-4}	0.031		
o-toluidine (2b)	7.19×10^{-4}	0.034	6.1×10^{-4}	0.014[c]
	7.19×10^{-4}	0.039[b]	6.1×10^{-4}	0.010
p-toluidine (3b)	6.91×10^{-4}	0.058	6.91×10^{-4}	0.037
			6.91×10^{-4}	0.038[b]
2,4,6-TMPA (5b)	1.15×10^{-4}	0.072[b]	1.15×10^{-4}	0.028
			7.68×10^{-4}	0.032[b,c]
2,6-DMPA (4b)			1.56×10^{-4}	0.016
			8.3×10^{-4}	0.012[b]

[a] In air-saturated cyclohexane except where noted. [b] In He-saturated cyclohexane. [c] In O_2-saturated cyclohexane.

spectral data for carbamates **1a**–**5a**, included in Table III, show two bands—one below 240 nm (~235 nm) and one near 280 nm. The 280-nm band is assigned to the $S_1(\pi,\pi^*) \leftarrow S_0$ transition of the phenyl ring shifted to the red by the $NHCO_2R$ urethane group.

The CO (n,π^*) transitions could not be identified for any of the carbamates regardless of the degree or position of methyl substitution. The absorption spectra and extinction coefficients of molecules **1a**–**5a** suggest that they all have similar excited states. The ultraviolet spectra of the arylamines **1b**–**5b** have extinction coefficients for the $S_1(\pi,\pi^*) \leftarrow S_0$ transition ($\lambda_{max} \approx 280$ nm, Table III) that are significantly larger ($\epsilon \sim 1.6 \times 10^3$) than the parent carbamates ($\epsilon < 1000$). This is probably due to the added interaction with the phenyl ring afforded by the amino group compared to the carbamate group. The $S_1(\pi,\pi^*) \leftarrow S_0$ bands of the para photo-Fries products **1d** and **2d** have much higher extinction coefficients than either the parent carbamates or the arylamines. These large values reflect the interaction of the amino and carboxylate groups when substituted para to one another on the phenyl ring. The position of the absorption band is approximately the same as for the parent carbamates and arylamines **1b**–**5b**. The red-shifted (>320 nm) absorbances of the ortho photo-Fries products (Table III) are attributed to a charge-transfer interaction of the adjacent amino and carboxylate groups. Such an interaction is not possible for the para photo-Fries products. Thus, the three ortho photo-Fries products **1c**–**3c** are unique in that the red-shifted absorption is due to a charge-transfer transition and not a $S_1(\pi,\pi^*) \leftarrow S_0$ transition.

Effect of Methyl Substitution. The quantum yields for decomposition (Φ_D) of carbamates **1a**–**5a**, shown in Table IV, are relatively insensitive to methyl group substitution on the phenyl ring. This fact is difficult to rationalize, as ring substitution of methyl groups ortho or para to the carbamate group eliminates the possibility for the photo-Fries rearrangement to these positions. A consideration of the quantum yields of the photoproducts for the carbamates may help explain the invariance of Φ_D with methyl substitution. In each case, for photolysis at 254 nm the sum (Φ_{total}) of the quantum yields for photoproducts (Φ_b, Φ_c, and Φ_d) obtained from cleavage of the N–C bond is less than the disappearance quantum yield (Φ_D) calculated from the loss of starting carbamate (see Table V). For carbamate **1a**, no positions are excluded to rearrangement by blocking methyl groups, and quantum yields are obtained for all three products (Φ_b, Φ_c, and Φ_d). Carbamate **2a** has one ortho position blocked, and there is an apparent decrease in Φ_c with an accompanying increase in Φ_d. In carbamate **3a**, the para position is blocked ($\Phi_d = 0$), and there is a subsequent increase in Φ_c. It appears that if one of the sites for rearrangement-product formation is blocked, then the alkoxycarbonyl radical simply proceeds to the other site or migrates from the solvent cage and decomposes. The parent arylamine then forms upon hydrogen abstraction in lieu of photo-Fries rearrangement. An anticipated increase in Φ_b for the arylamine (**3b**) was not observed. This may be due to the high reactivity of this arylaminyl radical, which will be discussed presently.

The reaction Scheme I depicts the formation of the parent arylamine and rearrangement products. For urethanes **1a**–**5a**, however, it does not account for the failure of Φ_b, Φ_c, and Φ_d to add up to Φ_D. Furthermore, Scheme I also fails to account for the lack of formation of amine **5b** upon photolysis of **5a** and the fact that Φ_D for **5a** is still of similar magnitude to the quantum efficiencies for the other carbamates studied. These apparent shortcomings lead one to consider the formation of other products that could arise from an alternate reaction path (process other than homolytic cleavage at the N–C bond) from the excited state of the carbamate.[20] Alternatively, the reactions of the arylaminyl radical (other than hydrogen abstraction to give amine) to give photolabile products could account for the difference between Φ_{total} and Φ_D.

Effect of Carbamate Concentration. The quantum yield for formation of **1c** (Φ_c, 254 nm) does not change with variation in concentration of **1a** over 2 orders of magnitude (Table VI). Even at concentrations less than 1×10^{-3} M, photo-Fries products and the parent arylamine are obtained upon irradiation of each of the carbamates **1a**–**4a**. This substantiates the results of Beachell and Chang,[4] who found product formation from **1a** at concentrations $<5 \times 10^{-4}$ M, which is contrary to a later report by Hutchins et al.[12] Thus there is no evidence for an intermolecular quenching process between excited-state and ground-state carbamate as had been proposed.[12] Such a process would result in a decrease of the photo-Fries product.

Effect of Oxygen and Irradiation Wavelength. Oxygen has little effect on the quantum yield for loss of carbamates **1a** or **3a** upon irradiation at 254 and 280 nm (Table IV). In addition, there is little difference in the quantum yield for disappearance (Φ_D) of carbamates **1a**–**5a** upon photolysis with 254- or 280-nm irradiation (Table IV). These results are interpreted from a consideration of the excited reactive states of the carbamates. As indicated previously, the carbamates **1a**–**5a** show a high-energy $S_2(\pi,\pi^*) \leftarrow S_0$ ($\lambda_{max} \approx 235$ nm) transition and a low-energy $S_1(\pi,\pi^*) \leftarrow S_0$ transition ($\lambda_{max} = 265$–285 nm). These states, along with the inoperative high-energy (n,π^*) and charge-transfer states, are depicted in the energy-level diagram (Figure 1). The absence of a wavelength effect on the Φ_D suggests an efficient internal conversion from the $S_2(\pi,\pi^*)$ state to the $S_1(\pi,\pi^*)$ state. The absence of an oxygen effect suggests a short-lived reactive state, S_1-

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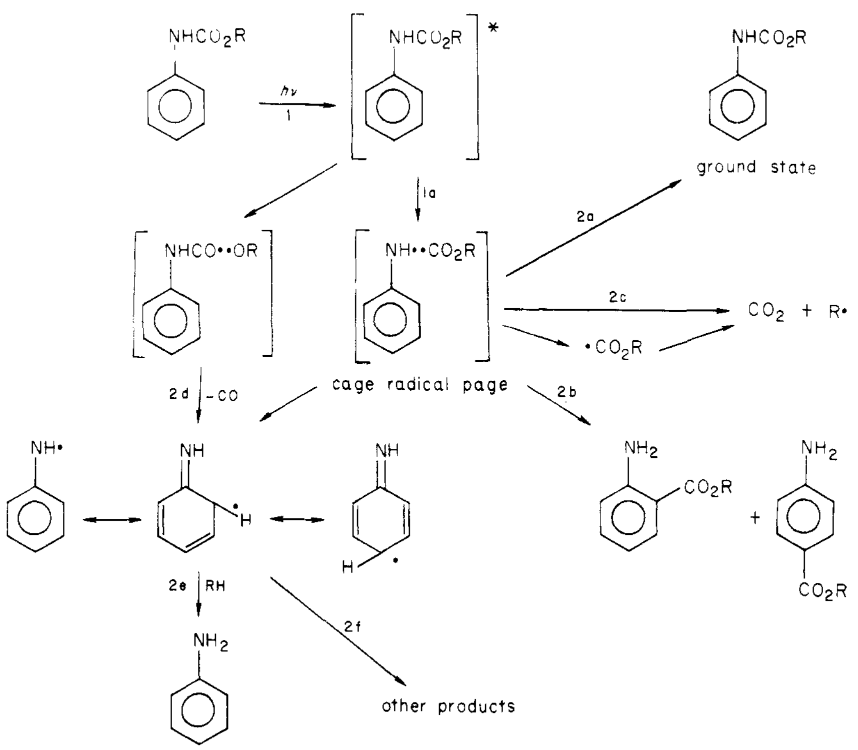
(20) The intermediacy of quinone imide methine-like structures is a possibility. The presence of such intermediates has been postulated by other investigators.

Scheme II. Photodegradation Process for Alkyl *N*-Arylcarbamates in Solution



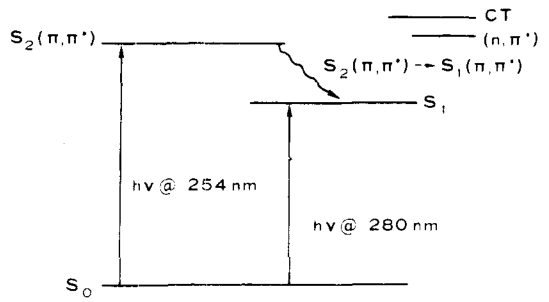


Figure 1. Energy-level diagram.

(π,π^*), leading to the parent arylamine and rearrangement products. The reaction from the triplet T_1 state has been excluded by Trecker et al.,[2] who found no decrease in the product yield of **1a** in the presence of triplet quenchers (e.g., *cis*-piperylene).

Effect of Solvent Polarity. The quantum yield for the disappearance of **2a** or **3a** is greatly diminished on going from the nonpolar cyclohexane to the relatively polar ethyl propionate solvent. Similar results for photolysis of carbamate **1a** have been obtained by Schwetlick et al.[7] Polar solvents can stabilize the $S_1(\pi,\pi^*)$ excited state, thereby decreasing the cleavage yield to give the "cage" radical pair. Furthermore, polar solvents may increase the rates for processes other than product formation. This effectively decreases the quantum yield for product formation.

Effect of Added Parent Arylamine and Rearrangement Products. A solution of carbamate **3a** was photolyzed in the presence of *p*-toluidine (**3b**) and the ortho photo-Fries product **3c**. The quantum yields for formation of **3c** and the disappearance of **3a** upon photolysis at 254 nm do not change with addition of **3b** or **3c**. At the concentrations of **3b** and **3c** employed, neither significantly influenced the photodegradation of **3a** by either competitive absorption or energy quenching.

Quantum Yields for Photodegradation of Rearrangement Products and Arylamines. A number of investigators have suggested that the products produced from photolysis of aromatic carbamates (i.e., **1a**) also degrade upon irradiation.[4,7] Indeed, we found that the arylamine **2b** and photo-Fries products **2c** and **2d** resulting from photolysis of **2a** degraded with disappearance quantum yields of 0.035, 0.004, and 0.003 for **2b**, **2c**, and **2d**, respectively, when irradiated at 254 nm. Thus, the photolability of the arylamine **2b** is much larger than for aminobenzoates **2c** and **2d**.

Due to the relatively large quantum yield for disappearance of *o*-toluidine (**2b**), a study of the photodegradation of aromatic amines **1b**–**5b** was initiated. The disappearance quantum yields at 280 nm increase in the order **1b**, **2b**, **4b**, **5b**, and **3b** (Table VIII). In fact, Φ_D at 280 nm for *p*-toluidine (**3b**) is on the order of 6 times greater than that for aniline (**1b**). Thus methyl substitution at the para position (e.g., **3b**) greatly enhances the disappearance quantum yield, while ortho substitution of a methyl group (e.g., **2b**) has a smaller but still significant effect. If methyl groups are substituted at both ortho positions (e.g., **4b**), there is a further increase in Φ_D. The Φ_D for **5b** is relatively close to the value obtained for **3b**. The large effect of the para-substituted methyl group on Φ_D can be attributed to an enhanced resonance effect. The effect of the *o*-methyl group is primarily inductive and less pronounced.

The Φ_D for arylamines at a given excitation wavelength was found to be oxygen independent (Table VIII). This observation eliminates the possibility of any arylamine–oxygen charge-transfer-complex effect on Φ_D at 254 and 280 nm.

For each aromatic amine, Φ_D increased when excited at 254 nm (compared to 280 nm). For aniline (**1b**) and *o*-toluidine (**2b**) this effect was substantial, $\Phi_{D,254}/\Phi_{D,280} \approx 4$ for aniline and $\Phi_{D,254}/\Phi_{D,280} \approx 3$ for *o*-toluidine. This may be attributed either to a difference in the rates for nonradiative (other than product formation) and radiative decay or to a change in the photoreaction process when exciting at 254 nm. These results are consistent with the dependence of the fluorescence (a singlet-state process) and phosphorescence (a triplet-state process) of aromatic

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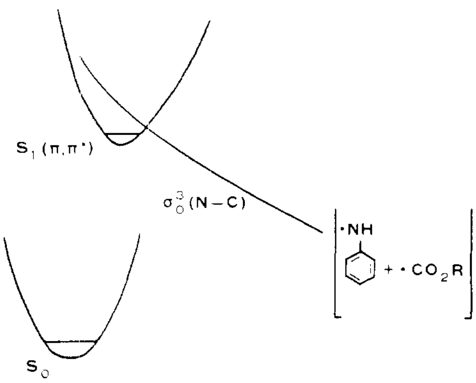

Figure 2. Surface diagram for photolysis of urethanes.

amines, such as aniline, on the wavelength of the exciting source.[21,22] Thus the photoprocesses of aromatic amines are wavelength dependent.

Proposed Mechanism for Alkyl *N*-Arylcarbamates in Solution. A lucid picture for the photodegradation of alkyl *N*-arylcarbamates in solution may now be presented from our results and from studies reported in the literature. Each phase or step of the photodegradation process will be considered with respect to Scheme II.

1. Excited State and Primary Reaction Processes. The absorption process of aromatic urethanes, as discussed previously, results in the formation of an excited molecule in the $S_1(\pi,\pi^*)$ energy level regardless of the exciting wavelength. From this state, the carbamate molecule can then dissociate to give a radical pair in a solvent cage or return to the ground state by a nonradiative or a radiative (fluorescence) decay process. The formation of a solvent-caged radical pair consisting of an aminyl radical and an alkoxycarbonyl radical arises from the surface crossing of the $S_1(\pi,\pi^*)$ excited state with the $\sigma_0{}^3$(N–C) repulsive surface (Figure 2), leading to a homolytic cleavage of the N–C bond (Scheme II, path 1a). A similar surface crossing of the $S_1(\pi,\pi^*)$ state with the $\sigma_0{}^3$(C–O) repulsive state leads to the formation of an alkoxyl and *N*-phenylformamoyl radical pair in a solvent cage (Scheme II, path 1b).

2. Formation of Primary Products. Primary reaction products are subsequently formed from reactions of the solvent-caged radical pair. As shown in Scheme II, path 2a, the radical pair can recombine to give the ground-state carbamate. Concurrently, the radical pair may combine to give photo-Fries rearrangement products (Scheme II, path 2b). These latter products are judged to be relatively photostable when compared to others that may form. Decomposition of the alkoxycarbonyl radical or the *N*-phenylformamoyl radical by decarboxylation and decarbonylation, respectively, can also occur (Scheme II, paths 2c and 2d). In the latter case this leads to a "free" anilinyl radical. These radicals also arise from disruption of the cage radical pair. It is the reactions of these anilinyl radicals that subsequently may account for most of the remaining primary reaction products. On the basis of our findings, the parent arylamine (e.g., aniline) is one of these products (except in the case of **5a**). It forms via hydrogen abstraction (Scheme II, path 2e). The fact that the sum of quantum efficiencies (Φ_{total}) for the parent amine and rearrangement products fails to coincide with the quantum efficiencies (Φ_D) for carbamate disappearance can be rationalized by postulating that the anilinyl radical can undergo reactions other than hydrogen abstraction.

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Registry No. **1a**, 101-99-5; **1b**, 62-53-3; **1c**, 87-25-2; **1d**, 94-09-7; **2a**, 73262-65-4; **2b**, 95-53-4; **2c**, 73262-66-5; **2d**, 73274-30-3; **3a**, 63379-16-8; **3b**, 106-49-0; **3c**, 73262-67-6; **4a**, 73262-68-7; **4b**, 87-62-7; **5a**, 73262-69-8; **5b**, 88-05-1.

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Influence of Fluorine and Oxygen Atoms at C-19 on the Previtamin D–Vitamin D Interconversion

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19,19-Difluorocholesteryl acetate (**6**), prepared by fluorination of 19-oxocholesteryl acetate (**5**), was converted to the respective 5,7-diene (**7**) which, on irradiation, gave both 19,19-difluoroprevitamin D_3 (**8**) and 19,19-difluorotachysterol (**9**). On the fluorinated previtamin did not rearrange to the corresponding vitamin D derivative (**4**) but isomerized, in part, to the tachysterol derivative **9**. On the other hand, 19-acetoxyprevitamin D_3 acetate (**11**), described previously by Moriarty et al.,[13] proved to be unstable, rearranging irreversibly to 19-acetoxyvitamin D_3 acetate (**12**).

The biogenetic route to vitamin D_3 (**3**) involves a photochemical conversion of 7-dehydrocholesterol (**1**) to previtamin D_3 (**2**) (Scheme I), followed by a thermal isomerization.[1] A similar route is commonly used for chemical synthesis of vitamin D_3 and its analogues since their respective 7-dehydrocholesterol derivatives are easily accessible.[1,2] However, the thermal isomerization of previtamin D_3 (**2**) to vitamin D_3 (**3**), which is shifted predominantly to the latter (20:80 at 80 °C), is sensitive to conformational and substitutional changes in the vicinity of the triene system,[3] which may thus preclude the formation of the

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