Photochemistry of Aryl Carbamates

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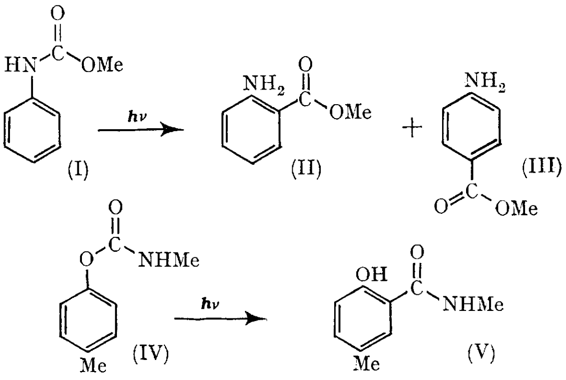
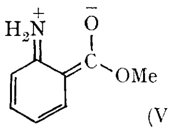
WE report a unique photochemical rearrangement of aryl carbamates. Ultraviolet irradiation of *N*-aryl and *O*-aryl carbamates in dilute solution was observed to form aminobenzoates and hydroxybenzamides, respectively. Thus, irradiation of 0·25M-methyl *N*-phenylcarbamate (I) in t-butyl alcohol for 96 hr. with a 200 w medium-pressure mercury arc (quartz vessel) resulted in a 5% conversion into methyl 2-aminobenzoate (II) (53%), methyl 4-aminobenzoate (III) (14%), and aniline (10%). Similar irradiation of 0·21M-*p*-tolyl *N*-methylcarbamate (IV) for 72 hr. provided a 25% conversion into *p*-cresol (21%) and *N*-methyl 2-hydroxy-5-methylbenzamide [(V) (57%); ν_{max} 3480, 1643, 1595, 1547, 868, 832, and 814 cm.$^{-1}$; τ 7·75 (s, tolyl Me), 7·02 (d, *J* 2·5 Hz, N-Me), 3·11 (d, *J* 4 Hz, 4-phenyl H), and 2·80 (coincident d, *J* 4 Hz, 3- and 6-phenyl H's)].

These novel rearrangements are formally similar to the photo-Fries reaction of aryl esters and the analogous rearrangement of anilides.[1,2] Like the photo-Fries reaction,[3] they were unresponsive to triplet quenchers (1·1 × 10^{-2} M-ferric acetylacetonate,[4] 5 × 10^{-3} M-naphthalene[5]), indicating that rearrangement proceeds from an upper singlet or very short-lived triplet state.




(VI)

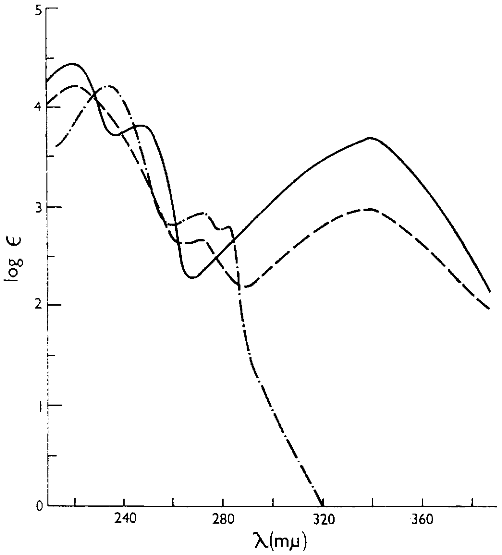


FIGURE. *U.v. absorption spectra (in* t-BuOH) *of methyl* N-*phenylcarbamate* (I) (—·—·) *and methyl* 2-*aminobenzoate* (II), *alone* (——) *and in the presence of* 1·8 M-*hydrochloric acid* (— — —).

Also like many photo-Fries rearrangements,[1,2] both reactions were self-terminating. This was particularly noticeable in the reaction of (I), where rearrangement stopped after only 5% conversion. We attribute this self-extinguishing feature to competitive absorption of light by the products (II) and (III). As observed with 4-aminobenzophenones,[6] a strong "charge-transfer" band (λ_{max} 340 mμ, log ϵ 3·68) appeared in the u.v. absorption spectrum of (II) (Figure). This is ascribed to a "charge-transfer" state designated as (VI).

Protonation of (II) with hydrochloric acid, and consequent quaternization of the amino-group, suppressed the absorption band at 340 mμ (Figure), an effect also observed with 4-aminobenzophenone.[6] This effect was amplified in the photochemistry of (I). Irradiation under acidic conditions (1·8 M-HCl) produced a two-fold enhancement in the yields of (II) and (III), an apparent consequence of the reduced absorptivity of protonated (II).

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