

PHOTOSENSITIVE PROTECTING GROUPS

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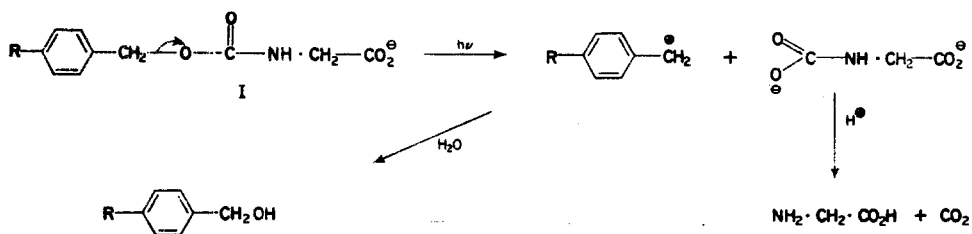
THE observation that benzyloxycarbonylglycine (I, R=H) appeared to liberate free glycine on irradiation with ultra-violet light led us to investigate more fully the action of ultra-violet light on various amino-acid derivatives. After irradiation of an aqueous solution of the sodium salt of benzyloxycarbonylglycine the following products were detected: (i) benzyl alcohol (characterized as the 3:5-dinitrobenzate; (ii) a solid material, having physical properties suggestive of a polymer, which analysed as  $(C_7H_8O)_n$ ; (iii) glycine (isolated and characterized as hippuric acid); (iv)  $\beta$ -phenylethylamine (isolated as its hydrochloride); (v) N-benzylglycine (not isolated, but detected by comparative paper chromatography).

TABLE 1

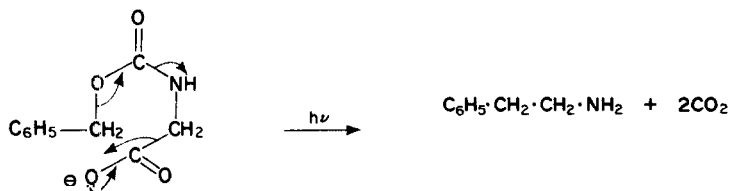
Compound	Q
Benzyloxycarbonylglycine	0.15
p-Nitrobenzyloxycarbonylglycine	0.005
p-Bromobenzyloxycarbonylglycine	0.075
p-(4-Methoxyphenylazo) benzyloxycarbonylglycine	0
Cinnamyloxycarbonylglycine	0.12
$\beta$ -Phenylethyloxycarbonylglycine	0
Benzyl glycine-N-dithiocarbamate	0.084
Ethyl glycine-N-dithiocarbamate	0.024
Thiobenzoylglycine	0
Hippuric acid	0
Aceturic acid	0
Benzylsulphonaminoacetic acid	0.18

Glycine was found to be the major N-containing product and was obtained in yields of up to 75 per cent. The quantum yield of glycine in this photolytic fission was found to be 0.15. The values for the quantum yields (Q) of glycine formed on irradiation of a variety of related glycine derivatives with the 2537 Å mercury line are summarized in Table 1.

These results, together with the nature of the products isolated from the irradiation of benzyloxycarbonylglycine, suggest that the photolytic fission involves a heterolysis of the benzyl-oxygen bond in the sense indicated below:



The formation of  $\beta$ -phenylethylamine may proceed via an intramolecular cyclic mechanism viz:



Further studies of the detailed mechanism of photolysis are currently being made.

It is hoped that these investigations will lead to the development of a variety of photosensitive protecting groups - i.e. groups capable of being removed by irradiation with light of the appropriate wavelength.

This method of removing the carbobenzyloxy group has proved of value in the detection of benzyloxycarbonyl aminoacids on paper. The paper chromatogram, after drying, is irradiated with a medium pressure mercury arc for a period of 30 min to 4 hr depending upon the nature of the benzyloxycarbonyl aminoacid, and the paper is then sprayed with ninhydrin in the usual way.