Photochemical 1-Alkylation of Amines by Benzoic Esters

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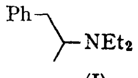
THE preceding Communication described the photochemical reaction of a diallylic compound involving the excited singlet state, rather than the triplet state and cleavage into two radicals. We now describe a photochemical reaction of allylic esters that does seem to involve radicals.

Irradiation of benzyl benzoate and trimethylamine through silica with light from a medium-pressure mercury lamp gives β-phenylethyldimethylamine and benzoic acid in good yield. Similarly benzyl benzoate yields benzoic acid and (I) with triethylamine, (II) with isopropylamine, and

(III) with isopropyl alcohol. Although the yields are lower than those from benzyl or allyl benzoates, some alkyl benzoates also undergo the reaction: t-butyl benzoate and triethylamine, for example, give the amine (IV). Unsymmetrical allyl benzoates lead to mixtures of but-3-enylamines, so the isomeric allylic benzoates (V) and (VI) on irradiation in triethylamine each produce an almost identical mixture of the amines (VII) and (VIII) in a ratio of 4 : 1. Many other allylic benzoates behave in the same way.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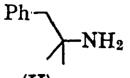
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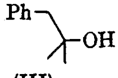
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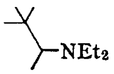
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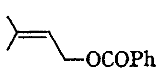
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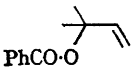
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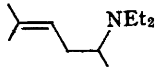
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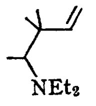
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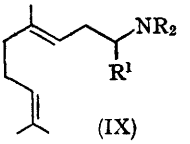
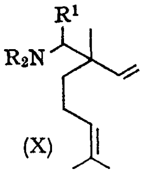
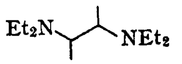

(IX)

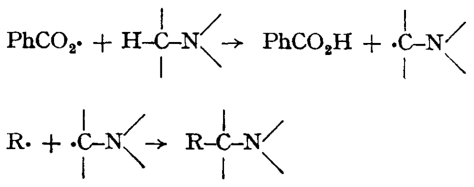

(X)


(XI)

The reaction sometimes provides a useful method of synthesis of amines or substances derived from them, which are hard to make otherwise. For example, neryl, geranyl, or linaloyl benzoate with trimethylamine each gives the *cis*- and *trans*-isomers of the amine (IX; R = Me, R^1 = H) (separable by gas chromatography) in about 60% yield, accompanied by small amounts of the isomer (X; R = Me, R^1 = H). With triethylamine, the corresponding compounds are formed where R = Et and R^1 = Me.

Since nearly all the benzoate appears as benzoic acid, the benzoyloxy-radical in the original radical pair that we suppose is produced must abstract a hydrogen atom from a molecule of amine faster than it loses carbon dioxide. The photo-reaction is probably related to the thermal reaction of benzoyl peroxide with amines,[1] with the allyl radical filling the role of the second benzoyloxy-radical in the latter:

$$\text{R-OCOPh (triplet)} \rightarrow \text{R}\cdot + \cdot\text{OCOPh}$$



$$\text{PhCO}_2\cdot + \text{H-C-N}\langle \rightarrow \text{PhCO}_2\text{H} + \cdot\text{C-N}\langle$$

$$\text{R}\cdot + \cdot\text{C-N}\langle \rightarrow \text{R-C-N}\langle$$

Only small amounts of products from dimerisation of the radical R· are usually produced, but the alkylated amine is always accompanied by the dehydro-dimer of the amine and related products: triethylamine, for example, is converted into the *meso* and racemic isomers of the diamine (XI). Low temperatures (presumably by reducing the speed of diffusion of the radicals apart) favour photo-alkylation of the amine at the expense of formation of dehydro-dimer and polymer. Not all the dehydro-dimer arises from the aminomethyl radicals generated in the hypothetical scheme above, because not only benzoates but a wide range of other aromatic compounds, including benzene itself, induce this dehydro-dimerisation on irradiation.[2] The first step may be transfer of an electron from the amine,[3] either directly into the antibonding aromatic orbital or, more likely, to the triplet state of the aromatic compound. Applications of chromophoric derivatives other than benzoates will be reported later.

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[1] C. Walling, "Free Radicals in Solution", Wiley, New York, 1957, p. 590; L. Horner, *J. Polymer Sci.*, 1955, **18**, 438.

[2] Miss S. M. de Brito Costa, unpublished experiments.

[3] H. Leonhardt and A. Weller, *Z. phys. Chem.* (*Frankfurt*), 1961, **29**, 277.