Photochemical Addition of Amines to Conjugated Olefins

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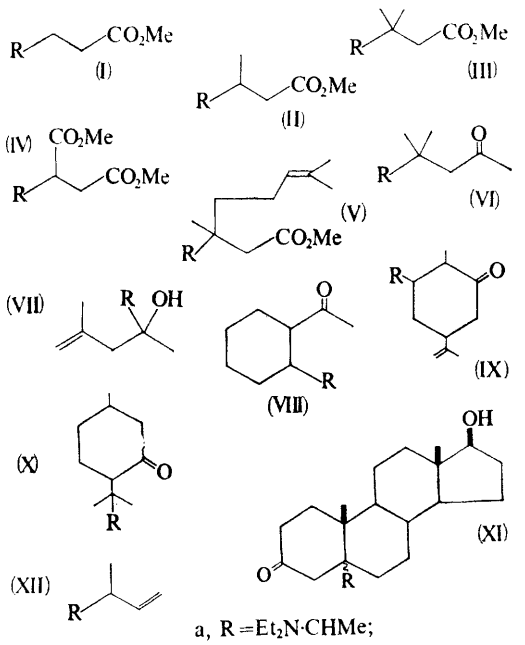
TERTIARY AMINES add to conjugated olefins in a reaction, related to the photochemical α-alkylation of amines by benzoic esters, that was recently reported.[1] For example, irradiation of the following αβ-unsaturated esters in triethylamine with a 500w medium pressure mercury arc through silica gave the adducts shown: methyl acrylate (Ia), methyl crotonate (IIa), methyl ββ-dimethylacrylate (IIIa), methyl fumarate (IVa), and methyl geranate (Va). αβ-Unsaturated ketones reacted in the same way: 4-methylpent-3-enone (VIa + VIIa), acetylcyclohexene (VIIIa), carvone (IXa), pulegone (Xa), and 17β-hydroxyandrost-4-en-3-one (XIa). Activation of the $n \rightarrow \pi^*$ transitions of the ketones by use of a Pyrex filter led to the same adducts in the same yields, but more slowly.



a, R = $Et_2N{\cdot}CHMe$;
b, R = H

The structures of the adducts were established mainly by spectroscopic methods. Reduction of the amino-ester (IIa) with lithium aluminium hydride and dehydration of the resulting alcohol with alumina in pyridine[2] at 175—180° produced the unsaturated amine (XIIa) that had already been made by irradiation of crotyl benzoate in triethylamine.[1] The adducts (IIa, IVa, Va, VIIIa, IXa, Xa, and XIa) were formed as mixtures of stereoisomers. An important competing reaction was reduction of the conjugated double bond: the yields of the amine adducts and of the αβ-dihydro-compounds are shown in the Table.

TABLE

Percentage yields

	a	b		a	b
(I) ..	16	9	(VII) ..	6·0	—
(II) ..	30	10	(VIII) ..	28	15
(III) ..	16	13	(IX) ..	33	23
(IV) ..	36	12	(X) ..	44	11
(V) ..	6·6	25	(XI) ..	39	14
(VI) ..	25	14			

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[1] R. C. Cookson, J. Hudec, and N. A. Mirza, *Chem. Comm.*, 1967, 824.
[2] *Cf.* E. Von Rudloff, *Canad. J. Chem.*, 1961, **39**, 1860.