Photochemical Addition of Amines to Styrenes

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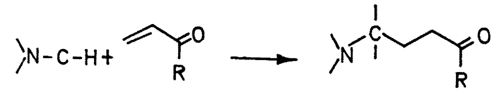
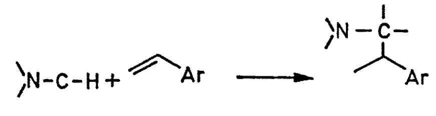
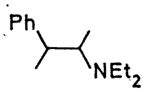
TERTIARY amines add photochemically[1] to conjugated carbonyl compounds (R = alkyl or OMe) to join C-1 of the amine to the β-carbon atom of the unsaturated compound:



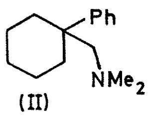
Irradiation of styrenes in amines with unfiltered light from a medium-pressure mercury lamp, in contrast, causes addition of C-1 of the amine to the α-carbon atom of the double bond:



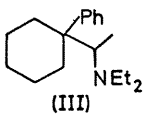
Thus styrene itself with triethylamine gives the adduct (I); 1-phenylcyclohexene gives (II) with trimethylamine and (III) with triethylamine; 1-phenylcyclopentene gives (IV) and indene (V) with triethylamine. Isopropylamine reacts with 1-phenylcyclohexene to form a mixture of the C-(VI) and the N-adduct (VII) in the proportion of 58:37 (the remaining 4·9% of basic product consisting of a third component of undetermined structure).



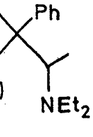
(I)



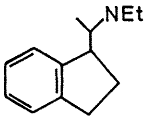
(II)



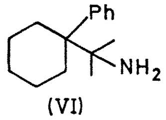
(III)



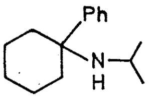
(IV)



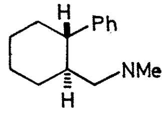
(V)



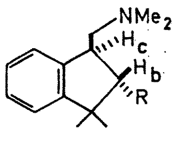
(VI)



(VII)



(VIII)



(IX) R = H_a
(X) R = D

The structures of the adducts were determined by i.r., u.v., and n.m.r. spectroscopy, and in some cases confirmed by independent synthesis. The styrene adduct (I) was identical with the mixture of stereoisomers formed by irradiation of 1-phenylethyl benzoate in triethylamine.[2] 1-Phenylcyclohexyl cyanide[3] was reduced with lithium aluminium hydride and the primary amine methylated to (II) with formalin and formic acid. [There was no trace in the photochemical product of the isomer (VIII), a reference sample of which was obtained from the Diels–Alder adduct of butadiene and *trans*-cinnamic acid.[4]] Compound (III) was made from 1-acetyl-1-phenylcyclohexane[5] by reductive amination to the primary amine[6] which was then ethylated by two successive cycles of acetylation and reduction with lithium aluminium hydride. The amine (VII) was made by addition of phenyl-lithium to isopropyliminocyclohexane, obtained by condensation of isopropylamine with cyclohexanone.

As in the photochemical addition of amines to conjugated esters and ketones,[1] the adducts were accompanied by the dihydro-derivatives of the olefins, and as before, increase in the reaction temperature increased the yield of the dihydro-compounds.

The Table shows the yields under comparable conditions. Some of the ideas suggested by the trend in the figures are being tested by further experiments.

The stereochemistry of the photo-addition was shown to be stereospecifically *cis* by n.m.r. study† of the adducts (IX) and (X) between trimethylamine and 3,3-dimethylindene and its 2-deuterio-analogue. Of the two protons H_a(1·90 p.p.m.) and H_b(1·44 p.p.m.) in (IX), the one at lower field disappeared in (X) showing that the upfield proton H_b must be *cis* to the dimethylaminomethyl group.[7] (In 1,1,3-trimethylindane, similarly, the 2-proton *cis* to the 3-methyl group appears at 1·37 p.p.m. and the one *trans* at 2·00 p.p.m.). At the same time the signal from H_b changed from a doublet of doublets in (IX) to a simple broadened doublet (J_{bc} 3·3 Hz.) in X. The 100 MHz. spectrum revealed none of the *trans*-adduct.

TABLE

	Reaction products (%)		
Olefin	Amine	Dihydro-	Recovered olefin
Indene	(V) 43	45	3
Phenylcyclopentene	(IV) 20	13	33
Phenylcyclohexene	(III) 11	3	46
Styrene	(I) 5·5	1	30

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† Figures are quoted for solutions in CCl_4 containing Me_4Si.

[1] R. C. Cookson, J. Hudec, and N. A. Mirza, *Chem. Comm.*, 1968, 180.

[2] R. C. Cookson, J. Hudec, and N. A. Mirza, *Chem. Comm.*, 1967, 824.

[3] C. H. Tilford, *J. Amer. Chem. Soc.*, 1947, **69**, 2903.

[4] J. Klein, *Tetrahedron*, 1964, **20**, 475.

[5] R. Jacquier and H. Cristol, *Bull. Soc. chim. France*, 1957, 346.

[6] *cf.* P. A. S. Smith and D. R. Baer, *J. Amer. Chem. Soc.*, 1954, **76**, 4561.

[7] L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, Oxford, 1959, pp. 116—117; also D. T. Longone and A. H. Miller, *Chem. Comm.*, 1967, 447; A. Segre and J. I. Musher, *J. Amer. Chem. Soc.*, 1967, **89**, 706.