Novel Photochemical Reactions of Diphenylacetylene and Stilbenes in Amines

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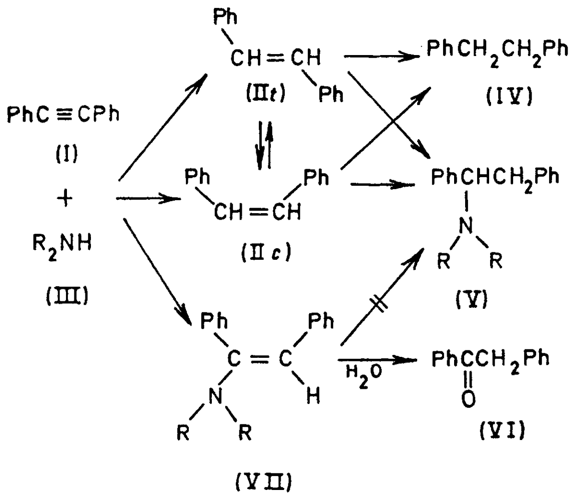
Summary Photoexcited diphenylacetylene (I) reacts with secondary amines (III) to give 1,2-diphenylethane (IV), saturated tertiary amines (V), and enamines of deoxybenzoin (VII), whereas photoexcited *trans*- and *cis*-stilbenes (II*t* and II*c*) give (IV) and (V) in both cases.

Photochemical addition of alcohol or carboxylic acid to diphenylacetylene (I) has been reported.[1,2] We now describe novel photochemical reactions of (I) as well as *trans*- and *cis*-stilbenes (II*t* and II*c*) with secondary amines (III) which give a completely hydrogenated product, 1,2-diphenylethane (IV), together with saturated tertiary amines (V) and enamines of deoxybenzoin (VII), in contrast to the results obtained with hydroxylic nucleophiles.[1]



When a solution (0·15 M) of (I) in (III; R = Et) was irradiated in a quartz vessel by high pressure Hg lamp under N_2 until (I) disappeared and the reaction mixture was chromatographed (silica gel) after evaporation of the excess of amines, (IV), (V; R = Et), and deoxybenzoin (VI) were obtained. All the reaction products were identified by direct comparison with authentic specimens. (I) as well as (VI) was absent from the photolysate prior to chromatography and another product was obtained by preparative g.l.c.; this was identified as (VII; R = Et). Therefore, (VI) is regarded as the secondary product of (VII) produced during the chromatographic treatment. The structure of (VII; R = Et) was established by direct comparison with an authentic sample prepared according to the published method.[3]

The progress of the reaction was followed by g.l.c. and the results showed (i) that the quantity of (VII; R = Et) as well as that of (IV) and (V; R = Et) increased at the expense of (I), thus (VII; R = Et) cannot be an intermediate because irradiation of a solution of (VII; R = Et) in diethylamine could not induce any appreciable change, (ii) that two transient small peaks appeared at the beginning of the reaction. Compounds corresponding to each peak were isolated by g.l.c. and their mass spectra were superimposable with those of (II*t*) and (II*c*); therefore the intermediates were established as (II*t*) and/or (II*c*).

The reaction of (I) with other secondary amine gave analogous results (Table). The photoreaction of (II*t*) in diethylamine proceeded 10 times as quickly as that of (I) to give (IV) and (V).

Table. *Photolysis of* (I) *in* (III)[a]

(III)		(IV) (%)	(V) (%)	(VI) (%)
Diethylamine	..	32[b]	14[b]	20[b]
Morpholine ..	..	6	20	43
Pyrrolidine ..	..	27	24	32
Piperidine ..	..	8	18	28

[a] Conversion of (I) was 100%. [b] Numbers signify isolation yields.

The photoreaction of (I) was not affected by the presence of pyrene (triplet quencher) or triphenylene (triplet sensitizer).[4] Irradiation of (I) in triethylamine or *N*-methylmorpholine led to complete recovery of (I). The photodimer of (I) was not detected; this is believed to be the product formed through the triplet excited state of (I).[5] Irradiation of (II*t*) or (II*c*) in the same amines led only to *cis–trans* isomerisation. No detectable amounts of either phenanthrene[2,6] or the dimer of (II)[7] existed at any reaction stage.

We believe, therefore, that a singlet excited state of (I) is implicated, and that the reduction of (I) involves ionic, rather than radical[8,9] intermediates.

We thank Professor Hitosi Nozaki for help and encouragement.

(*Received*, 13*th December* 1971; *Com.* 2121.)

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