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PHOTOCHEMICAL TRANSFORMATION OF N-(*p*-TOLUENESULFONYL)DIPHENYLCYCLOPROPENIMINE

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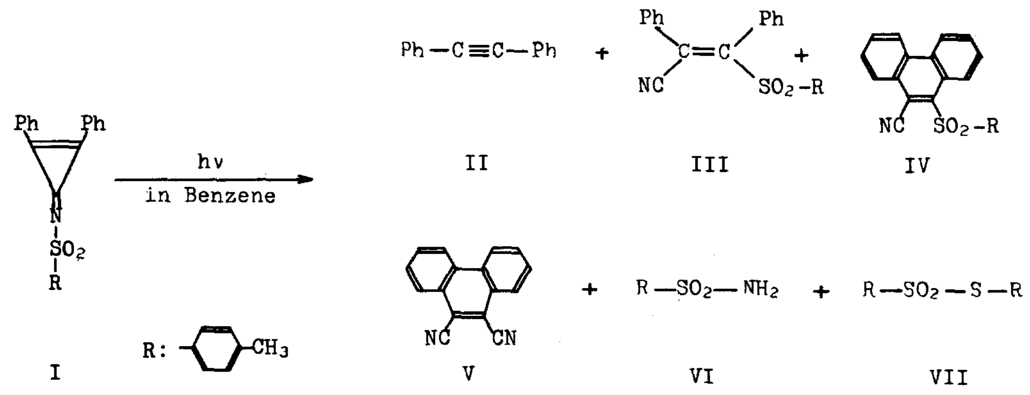
There have been reported some interesting results on the photochemical transformations of cyclopropene derivatives: 3-acyl-1,2-diphenylcyclopropene(1) and 1,3,3-trimethylcyclopropene(2) undergoes dimerizations at the strained double bond while diphenylcyclopropenone takes a route of α-cleavage to the formation of a quantitative amount of diphenylacetylene(3).
Now we wish to report other types of the photochemical conversion of a cyclopropene derivative.

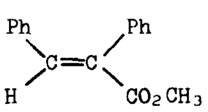
Irradiation of N-(*p*-toluenesulfonyl)diphenylcyclopropenimine (I)(4) in dry benzene under a nitrogen stream by a high pressure mercury lamp for 4 hours resulted in the formations of the following products: diphenylacetylene(5a) (II, 45 %), 1-cyano-2-*p*-toluenesulfonyl-*cis*-stilbene (III, mp 165-165.5°, 5 %), 9-cyano-10-*p*-toluenesulfonylphenanthrene (IV, mp 226-227°, 3 %), 9,10-dicyanophenanthrene(5b) (V, mp 290-291°, 8%), *p*-toluenesulfonylamide(5c) (VI, mp 137°, 13 %), and *p*-tolyl *p*-toluenetiolsulfonate(5d) (VII, mp 75-75.5°, 7 %). The structures of II, V, VI and VII were firmely established by comparisons with authentic samples (5a-d).

The compounds III and IV showed satisfactory elemental analyses and molecular weight determinations as those expected from $C_{22}H_{17}NSO_2$ and $C_{22}H_{15}NSO_2$, respectively. In their IR spectra, there was observed characteristic absorptions of $C\equiv N$ (at 2220 cm^{-1} for III and 2215 cm^{-1} for IV) and SO_2 group (at 1150 cm^{-1} for both compounds). The results indicate that there are a cyano group and *p*-toluenesulfonyl group in these compounds. The *cis*-stilbene structure for III and phenanthrene for IV are clearly shown by their UV and NMR spectra. The

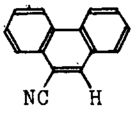


compound III exhibits a broad maximum at 287 mμ (logε 4.01), which is that expected from *cis*-stilbene chromophore(6a). On the other hand, the compound IV exhibits characteristic maxima in this region: at 208 mμ (logε 4.42), 234 mμ (4.46), 261 mμ (4.59), 330 mμ (4.09), 358 mμ (3.42) and 375 mμ (3.38)(6b). Moreover, its NMR spectrum exhibits characteristic low field signals at 1.4 τ (m, 2 H), 2.2 τ (m, 6 H), and 2.8 τ (m, 4 H), which are the feature of phenanthrene derivatives(7). In addition to these results, the structure of III and IV are consistent with the observation that the compound IV has been produced in a reasonable yield when III was irradiated under the same condition as above. The formation of phenanthrene skelton from *cis*-stilbene has been known to occur specifically in the absence of oxidants when the carbonyl group is conjugated with the unsaturated system(8).

Irradiation of I in methanol gave also a mixture of II-VII but two more products were isolated in this case: namely, metyl α-phenylcinnamate(9a) (VIII, mp 75-76°, 2 %) and 9-cyanophenanthrene(9b) (IX, mp 112-113°, 2.5 %). The structures of VIII and IX were determined by comparisons with authentic specimens(9a-b).

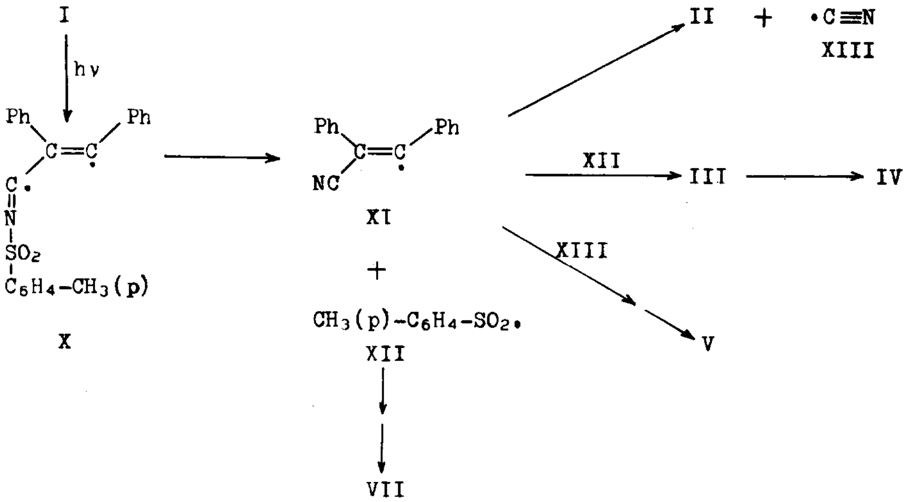


VIII



IX

Now, it is to be noted that there have been obtained a number of the products in addition to a most significant route to produce diphenylacetylene, which is a sharp contrast to the observation that diphenylacetylene has been a sole reaction product in the photoreaction of diphenylcyclopropenone. In the present case, the diradical X, which has been derived from an α-cleavage of I, can be stabilized by a loss of p-toluenesulfonyl radical (XII) to give a cyanostilbenyl radical XI. This radical may split into diphenylacetylene and a cyano radical (XIII).



The radical XI will couple with the radical XII to give III, and III gives IV on further irradiation. A coupling of XI with XIII will be a route of the formation of V(10). A coupling of XII will give VII followed by deoxygenation. In methanol, both X and XI stabilized by abstraction of hydrogen from the solvent and they have been isolated as VIII and IX.

There is a possibility of the formation of p-toluenesulfonylisonitrile during the reaction since the formations of II and VI might be rationalized by a such route, also. In the formation of II and VI, some of the additional experiments are required and they are in progress.

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(10) Photochemical transformation of *cis*-stilbene derivatives to phenanthrene derivatives was more effective in 1,2-dicyano-*cis*-stilbene than in 1-cyano-2-*p*-toluensulfonyl-*cis*-stilbene.