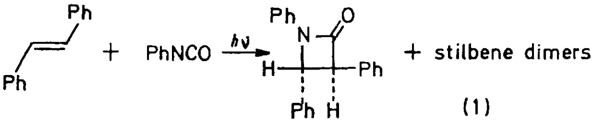
The Photocycloaddition of Stilbene to Phenyl Isocyanate

By TADATOSHI KUBOTA* and HIROSHI SAKURAI

(*The Institute of Scientific and Industrial Research, Osaka University, Suita, Osaka, Japan*)

Summary Irradiation of stilbene in phenyl isocyanate gave *trans*-1,3,4-triphenylazetidin-**2**-one in a 45% yield.

IT is well known that nucleophilic olefins such as enamines react with phenyl isocyanate to form four-membered ring lactams which are 1,2-cycloaddition products of the isocyanate across olefinic double bonds.[1] Stilbene, however, does not react even with the very reactive isocyanate such as chlorosulphonyl isocyanate.[2] We found that the photoexcited stilbene reacted with phenyl isocyanate to give a β-lactam.



(1)

A solution of *trans*-stilbene (0·4 g) in phenyl isocyanate (20 g) was irradiated in a Pyrex tube for 4 days with a 350 W high-pressure mercury lamp.† Chromatography on silica gel gave *trans*-1,3,4-triphenylazetidin-2-one (45%) and stilbene dimers (20%), see reaction (1). Irradiation of *cis*-stilbene gave the same azetidinone in a 40% yield. The structure of the azetidinone was established by the identity of its spectroscopic data with those of an authentic sample[3] and mixed m.p. The *cis*-azetidinone, which is a possible product, could be neither isolated nor detected in the n.m.r. spectrum of the crude azetidinone separated by chromatography.[3] After heating a mixture of *cis*- or *trans*-stilbene and phenyl isocyanate for 19 h at 180°,‡ the azetidinone was not detected by g.l.c. Thus, this azetidinone does not appear to be produced thermally. Since most of light is absorbed by stilbene [PhNCO λ_{max} 275 nm (ϵ 405), stilbene *trans* (ϵ 26,000), *cis* (ϵ 5000) at 310 nm], azetidinone formation is considered to be due to the reaction between phenyl isocyanate and an excited stilbene. A photostationary state of 75% *cis*- and 25% *trans*-stilbene was reached at *ca.* 5% conversion. Therefore, it is to be expected that the same product was obtained regardless of the stilbene initially used (*cis* or *trans*). The photolysis of a β-lactam is known to give an olefin and an isocyanate, or a keten and an imine.[4] In fact, this azetidinone under irradiation also decomposed gradually in the absence of stilbene, but under our experimental conditions it decomposed only very slowly since most of light is absorbed by a small amount of stilbene which is present in the reaction system. Therefore, this fragmentation will not lower the yield so much.

Methyl isocyanate did not react with stilbene, perhaps because of the lower reactivity of methyl isocyanate.§

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† The solution must be deoxygenated with nitrogen. If not so, the yield will decrease to *ca.* 20%.

‡ Under these conditions the azetidinone did not decompose.

§ In the thermal reactions of isocyanate with olefins, it is known that alkyl isocyanate is less reactive than aryl isocyanate.[5]

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[3] O. L. Chapman and W. R. Adams, *J. Amer. Chem. Soc.*, 1968, **90**, 2333.
[4] M. Fischer, *Chem. Ber.*, 1968, **101**, 2669.
[5] S. Hünig, K. Hübner, and E. Benzing, *Chem. Ber.*, 1962, **95**, 926.