Photochemical Addition of Amines to Diarylcyclopropanes

By STEPHEN S. HIXSON
(*Chemistry Department, University of Massachusetts, Amherst, Massachusetts* 01002)

Summary The photochemical addition of amines to diarylcyclopropanes occurs with predominant retention of configuration most likely *via* a mechanism involving initial complex formation.

WE have recently reported studies concerning the photochemical addition of methanol to diarylcyclopropanes,[2] an anomalous polar process occurring concomitantly with other reactions which seem best rationalized as proceeding *via* radical-like species. In order to examine further the behaviour of the excited states of arylcyclopropanes and to study the dichotomy between polar and non-polar reaction paths, we have examined the interaction of the cyclopropanes with amines. We now report that amines add photochemically to diarylcyclopropanes in a stereoselective fashion.

Irradiation† of diphenylcyclopropane (**1**) in cyclohexylamine afforded 30% of adduct (**2a**) with small amounts of other, previously observed,[3] photoproducts of (**1**). Photolysis in n-butylamine proceeded similarly to form (**2b**). Upon irradiation of (**1**) in the secondary amine piperidine, 31% of (**2c**) was produced. In this case 20% of 1,3-diphenylpropane (**3**) was found; only traces of (**3**) could be detected in the photolyses in the primary amines. Separate irradiation of (**2c**) in piperidine afforded significant amounts of (**3**). Thus, much, but probably not all, of the (**3**) formed is derived from (**2c**).

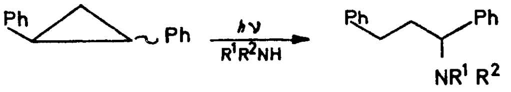
Attempts to sensitize the addition of cyclohexylamine to (**1**) using both acetophenone and xanthone failed. In both cases net *trans* to *cis* isomerization of (**1**) was observed, indicating the sensitizer had transferred triplet energy. We conclude that the pathway leading to amine addition does not pass through the triplet state of (**1**).

The reaction stereochemistry was studied by irradiation of dibenzotricyclo[3,3,0,$0^{2,8}$]octadiene (**4**) in cyclohexylamine. The addition proceeded stereoselectively to give 78% of a mixture of (**5**) and (**6**) consisting of 80% of *syn*-isomer (**5**) and 20% of *anti*-isomer (**6**).‡ Compounds (**5**) and (**6**) were independently prepared *via* reaction of cyclohexylamine with *anti*- and *syn*-4-bromodibenzobicyclo-[3,3,0]octadiene,[4] respectively. Thus, as in the addition of methanol,[1] the reaction proceeds with a preference for

---

† All irradiations were carried out under N_2 using Corex-filtered light from a Hanovia 450 W medium-pressure mercury arc.

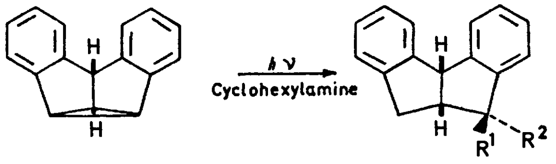
‡ The ratio of (**5**) : (**6**) remained relatively constant on conversions of (**4**) of 16% (where product absorption is minimal) to 53% (where product absorption is more significant).



(1)

(2)

a; $R^1 = H, R^2 =$ cyclohexyl
b; $R^1 = H, R^2 =$ n-butyl
c; $R^1R^2 = C_5H_{10}$



(4)

(5) $R^1 = H, R^2 = C_6H_{11}NH$
(6) $R^1 = C_6H_{11}NH, R^2 = H$

retention of configuration at the site of nucleophilic attack, a preference not dictated by steric factors since the major product (**5**) is the more hindered one.§

In order to determine the deuterium isotope effect on the addition cyclohexane solutions of (**1**) containing 1·0 M-n-butylamine or $[NH_2\text{-}^2H_2]$-n-butylamine (98·5% $^2H_2$) were irradiated simultaneously on a turntable apparatus. No isotope effect was observed ($\phi_H/\phi_D = 0{\cdot}99 \pm 0{\cdot}04$).

The low acidity of amines, and the absence of an observable isotope effect argue against a mechanism involving initial protonation by amine. Attack by amine on a ring-opened (zwitterionic) species is rendered doubtful by the observed preference for *syn*-stereochemistry (but not eliminated entirely since stereoselective addition to a partially opened species may perhaps be envisaged). A radical reaction would be expected to occur at the α-carbon of the amine. Importantly, the absence of an isotope effect in the addition suggests that hydrogen transfer is not involved in the rate-determining step. Initial rate-determining complex formation between amine and cyclopropane followed by collapse of the complex to product is a likely possibility.

We acknowledge support from the Petroleum Research Fund, administered by the American Chemical Society.

(*Received, 7th August* 1972; *Com.* 1387.)

---

§ The n.m.r. spectra of (**5**) and (**6**) do not allow a determination of the stereochemistry of protonation to be made.

[1] S. S. Hixson, *J. Amer. Chem. Soc.*, 1971, **93**, 5293; S. S. Hixson and D. W. Garrett, *ibid.*, p. 5294.

[2] C. S. Irving, R. C. Petterson, I. Sarkar, H. Kristinnson, C. S. Aaron, G. W. Griffin, and G. J. Boudreaux, *J. Amer. Chem. Soc.*, 1966, **88**, 5675.

[3] G. W. Griffin, J. Covell, R. C. Petterson, R. M. Dodson, and G. Klose, *J. Amer. Chem. Soc.*, 1965, **87**, 1410.

[4] S. Cristol, W. Y. Lim, and A. R. Dahl, *J. Amer. Chem. Soc.*, 1970, **92**, 4014.