

(m, 1 H, arom), 7.28–7.45 (m, 5 H, arom), 7.85–8.20 (m, 2 H, arom), coupling constants verified by decoupling experiments; mass spectrum (70 eV) m/e (rel intensity) 418 (40), 387 (15), 386 (37), 261 (11), 248 (35), 247 (100), 231 (13), 219 (13).

Anal. Calcd for $C_{27}H_{30}O_4$: C, 77.48; H, 7.23. Found: C, 77.31; H, 7.08.

A solution of **23** (11 mg, 0.026 mmol) in 11 ml of CH_3OD containing 14 mg (0.26 mmol) of sodium methoxide was refluxed for 6 hr under a nitrogen atmosphere. The cooled solution was neutralized with 5 ml of D_2O containing CF_3CO_2D and then diluted with water (50 ml) and extracted with ether (3×25 ml). The combined ether layers were washed with water, dried ($MgSO_4$), and evaporated, and the residue was recrystallized from methanol to give 7 mg (64%) of **23- d_4** : pmr ($CDCl_3$) as for **23** except that the four methylene signals at δ 2.21, 2.37, 2.79, and 2.94 were absent;³⁷

(37) Hb does not exchange under these conditions; approach by the base to Hb may be hindered, or formation of the enolate anion at that site would bring the bulky ester side chain in a position which interacts severely with the *gem*-dimethyl group on the seven-membered ring.

mass spectrum (70 eV) m/e (rel intensity) 422 (9), 391 (8), 390 (15), 248 (49), 247 (100).

When the autoxidation of **18** was carried out as described above but using CH_3OD and Na_2O in D_2O and the resulting acid was esterified directly with diazomethane, the resulting **23** contained six deuterium atoms (mass spectrum), the four methylene protons, and the methine protons Hb and Hd being labeled.

Autoxidation of 16. When **16** (85 mg, 0.228 mmol) was autoxidized using exactly the procedure described for the oxidation of **18**, there was isolated only 9 mg (10%) of the acid **22** (identical by ir and nmr with the autoxidation product of **18**), the remainder of the material being neutral. However, when **16** was first treated as described for the isomerization of **16** to **18** (*vide supra*) and the reaction mixture was subsequently refluxed for an additional 4 hr with air rather than nitrogen bubbling through the solution, acid **22** was isolated in 80% overall yield.

Acknowledgment. We are indebted to the National Science Foundation and the National Institutes of Health for grants which supported this research.

Arylcyclopropane Photochemistry. The Photochemical Addition of Amines to 1,2-Diarylcyclopropanes

Stephen S. Hixson

Contribution from the Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01002. Received January 12, 1974

Abstract: Photolysis of 1,2-diphenylcyclopropane (**1**) in primary or secondary amines resulted in addition of the N–H bond of the amine across the C–1–C–2 bond of the cyclopropane. Irradiation of dibenzotricyclo[3.3.0.0^{2,8}]octadiene (**15**) in cyclohexylamine produced a 4:1 mixture of *syn*- and *anti*-4-cyclohexylaminodibenzobicyclo[3.3.0]octadienes (**16** and **17**), indicating a preference for the formation of the more hindered isomer. Sensitization studies indicate that the additions to diphenylcyclopropane do not occur *via* the lowest triplet state. No isotope effect was found when the efficiencies of addition of *n*-butylamine and *n*-butylamine-*N,N*- d_2 to *trans*-1,2-diphenylcyclopropane (**1**) were compared. Quantum yield studies of the addition of *n*-butylamine to **1** were carried out at various amine concentrations. A discussion of the reactive excited state of **1** and a reaction mechanism are presented.

Investigations carried out over the last several years by several groups,¹ most notably that of Griffin,^{1a–d} have revealed that *trans*-1,2-diphenylcyclopropane (**1**) is from the photochemical standpoint an exceedingly diverse molecule. This is illustrated in Scheme I which shows the paths taken by **1**, probably the most thoroughly studied of all arylcyclopropanes, when irradiated in methanol.^{1a,b}

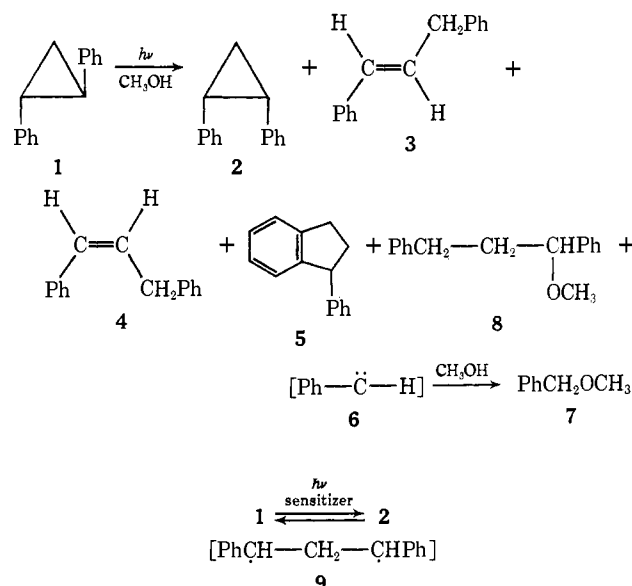
Thus, like stilbene, **1** undergoes *trans*–*cis* isomerization upon both direct^{1a,e} and triplet-sensitized^{1f,g} irradiation. In addition, however, the singlet excited state of **1** undergoes migration of hydrogen and of carbon to form **3**–**5**,^{1a,e} cleavage to give phenylcarbene **6**,^{1c,d,2,3} and addition of methanol to provide ether **8**.^{1b}

(1) (a) G. W. Griffin, J. Covell, R. C. Petterson, R. M. Dodson, and G. Klöse, *J. Amer. Chem. Soc.*, **87**, 1410 (1965); (b) C. S. Irving, R. C. Petterson, I. Sarkar, H. Kristinnson, C. S. Aaron, G. W. Griffin, and G. J. Boudreau, *ibid.*, **88**, 5675 (1966); (c) H. Kristinnson, K. N. Mehrotra, G. W. Griffin, R. C. Petterson, and C. S. Irving, *Chem. Ind. (London)*, 1562 (1966); (d) H. Dietrich, G. W. Griffin, and R. C. Petterson, *Tetrahedron Lett.*, 153 (1968); (e) E. W. Valyocsk and P. Sigal, *J. Org. Chem.*, **36**, 66 (1971); (f) G. S. Hammond, P. Wyatt, C. D. DeBoer, and N. J. Turro, *J. Amer. Chem. Soc.*, **86**, 2532 (1964); (g) C. D. DeBoer, Ph.D. Thesis, California Institute of Technology, 1966; (h) G. S. Hammond and R. S. Cole, *J. Amer. Chem. Soc.*, **87**, 3256 (1965); (i) S. L. Murov, R. S. Cole, and G. S. Hammond, *ibid.*, **90**, 2957 (1968); (j) R. S. Cole, Ph.D. Thesis, California Institute of Technology, 1968; (k) T. A. Matzke, Ph.D. Thesis, University of Texas at Austin, 1971.

(2) G. W. Griffin, *Angew. Chem., Int. Ed. Engl.*, **10**, 529 (1971).

(3) S. S. Hixson, *J. Amer. Chem. Soc.*, **95**, 6144 (1973).

Scheme I. Photolysis of *trans*-1,2-Diphenylcyclopropane in Methanol

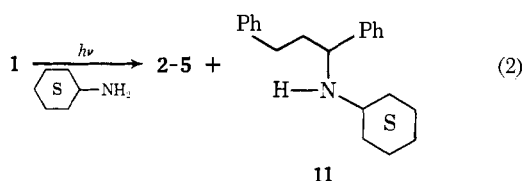
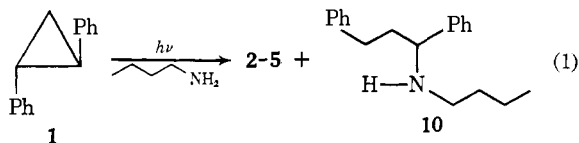


The formation of products **2**–**7** in the direct photolysis of **1** has been rationalized^{1a,e,2} as occurring *via* an intermediate diradical **9**, though the exact nature of **9** remains unclear.⁴

One of the most interesting of these observations was the formation of ether **8** and of similar solvent adducts when **1** (and other polyarylcyclopropanes) was irradiated in methanol and other hydroxylic solvents.^{1b} As pointed out by Griffin,^{1b} a 1,3-diradical species such as **9** does not rationalize this process as well as it does the formation of **2-6**, for one would expect attack of **9** on the C-H rather than the O-H bond of the alcohol. Rather, the reaction appeared to involve a polar species of some sort. This intriguing dichotomy in behavior of 1,2-diphenylcyclopropane (**1**) led us to our present investigations into the nature of the arylcyclopropane excited states involved in these polar additions. During our investigation we discovered that amines likewise add photochemically to arylcyclopropanes⁶ and, in fact, do so more efficiently than do alcohols. We present here our findings on this amine addition process.⁶ In a separate paper⁷ our work on the photochemical addition of hydroxylic solvents⁸ is detailed.

Results

Photochemical Addition of Primary and Secondary Amines to 1,2-Diphenylcyclopropane (1). Irradiation of solutions of **1** in primary and secondary amines with Corex-filtered light under nitrogen gave in addition to **2** and traces (gc) of **3-5**, which are the normal products obtained in a nonreactive medium, substantial yields of the products derived *via* addition of the N-H bond of the amine across the three-membered ring. Thus, photolysis of 1.00 g of **1** in 110 ml of the primary amine *n*-butylamine for 2 hr provided 57% of the adduct 1-(*N*-butylamino)-1,3-diphenylpropane (**10**) (eq 1). The structure of **10** (and other amine-derived products) was shown most definitively by its nmr spectrum which showed *inter alia* a triplet for the C-1 hydrogen at δ 3.55. Cyclohexylamine likewise added to provide 1-(*N*-cyclohexylamino)-1,3-diphenylpropane (**11**) (eq 2).



Irradiation of **1** in the secondary amine piperidine proceeded with similar high efficiency to give 1-(*N*-

(4) (a) It is interesting to note that if a singlet diradical **9** is indeed an intermediate in these photochemical transformations then it does not show the same behavior as the presumed singlet diradical intermediate in the thermal *cis-trans* isomerization of **1**. In the photochemical isomerization of **1** *trans-cis* isomerization predominates over olefin (**3** and **4**) formation by only a factor of *ca.* 2,¹⁶ whereas in the thermal isomerization only *cis-trans* isomerization and no olefin formation has been noted.^{16,k,5} (b) We have found³ that in at least one case of carbene elimination from a cyclopropane a long-lived diradical cannot be involved.

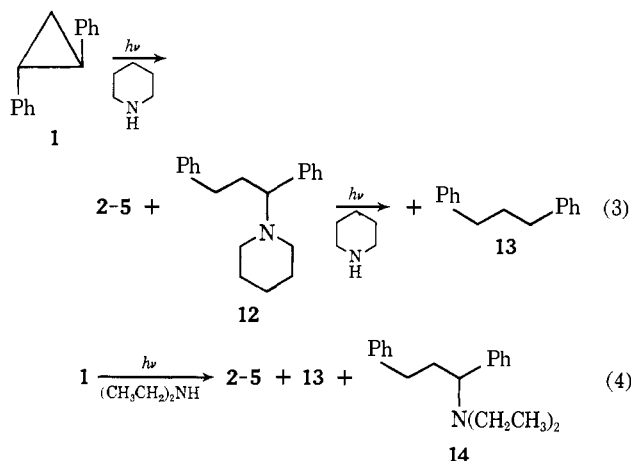
(5) (a) L. B. Rodewald and C. H. DePuy, *Tetrahedron Lett.*, 2951 (1964); (b) R. J. Crawford and T. R. Lynch, *Can. J. Chem.*, **46**, 1457 (1968).

(6) Part of this work has been communicated in preliminary form: S. S. Hixson, *J. Chem. Soc., Chem. Commun.*, 1170 (1972).

(7) S. S. Hixson and D. W. Garrett, *J. Amer. Chem. Soc.*, **96**, 4872 (1974).

(8) (a) S. S. Hixson, *J. Amer. Chem. Soc.*, **93**, 5293 (1971); (b) S. S. Hixson and D. W. Garrett, *ibid.*, **93**, 5294 (1971).

piperidino)-1,3-diphenylpropane (**12**) together with **2** and very small amounts of **3-5** (eq 3). However, in this case a substantial amount of the reduction product 1,3-diphenylpropane (**13**) was also produced. It was noted that the ratio of **13** to amine **12** increased as the photolysis proceeded. Moreover, separate irradiation of **12** in piperidine provided substantial amounts of **13**. Thus it appears likely that much of the **13** produced arises *via* secondary photolysis of **12**. Unfortunately we could not resolve **13** from the other photoproducts of **1** well enough on the gas chromatograph to determine whether it was a primary product of **1**. Diethylamine similarly added to **1** to give the expected tertiary amine **14** (eq 4).



Sensitization experiments presented a problem because of two factors: one, the known ability of amines to quench and react with excited states of ketones and aromatics, and, two, the slow rate of triplet energy transfer from suitable triplet sensitizers to **1**.¹⁸ These factors necessitated using high concentrations of both **1** and sensitizer. We found that irradiation of a benzene solution 1.00 *M* in **1** + **2**, 0.42 *M* in cyclohexylamine, and 0.01 *M* in xanthone at 350 nm resulted in net *trans* to *cis* isomerization of the cyclopropane but no detectable amounts of the amine adduct **11**. Similarly, irradiation of an acetophenone solution containing 1.05 *M* **1** + **2** and 0.42 *M* cyclohexylamine gave isomerization but no addition. We conclude that we have in these experiments generated the triplet state of diphenylcyclopropane as evidenced by the isomerization^{11,g} and that neither it nor a species formed from it is involved in the addition.⁹

Stereochemistry of Amine Addition. Photochemical

(9) (a) There is good evidence that with acetophenone, a relatively high energy triplet sensitizer ($E_t = 73.6$ kcal/mol),¹⁰ energy transfer to **1** occurs producing a triplet diradical free of sensitizer.^{16,k,11} With lower energy triplet sensitizers^{1k} (and with singlet sensitizers)^{11-k} a more complex process is apparently involved. Xanthone, having a triplet energy (74.2 kcal/mol)¹⁰ similar to that of acetophenone, presumably behaves like the latter. (b) The lowest triplet state of **1**, a "radical-like" state,^{11,12} apparently has an energy of *ca.* 53 kcal/mol¹² and thus should be readily obtained by acetophenone and xanthone sensitization. However, a higher non-"radical-like" triplet may be initially produced. (c) Our experiments indicate the triplet state of **1** derived by sensitization is not involved in the amine additions. There is always the possibility that addition occurs to a higher triplet state not produced by sensitization.

(10) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 298.

(11) C. Ouannès, R. Beugelmans, and G. Roussi, *J. Amer. Chem. Soc.*, **95**, 8472 (1973).

(12) R. S. Becker, L. Edwards, R. Bost, M. Elam, and G. W. Griffin, *J. Amer. Chem. Soc.*, **94**, 6584 (1972).

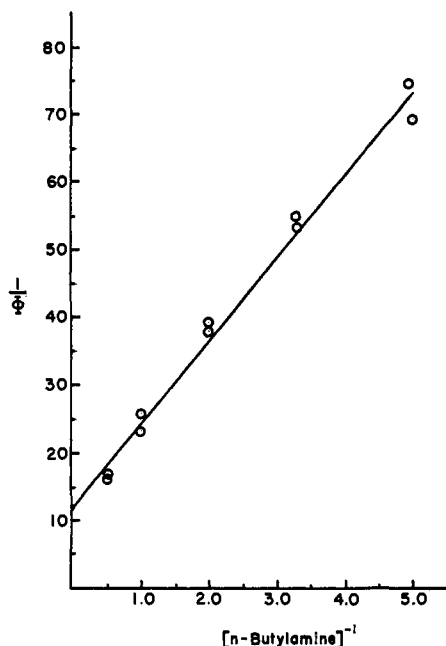
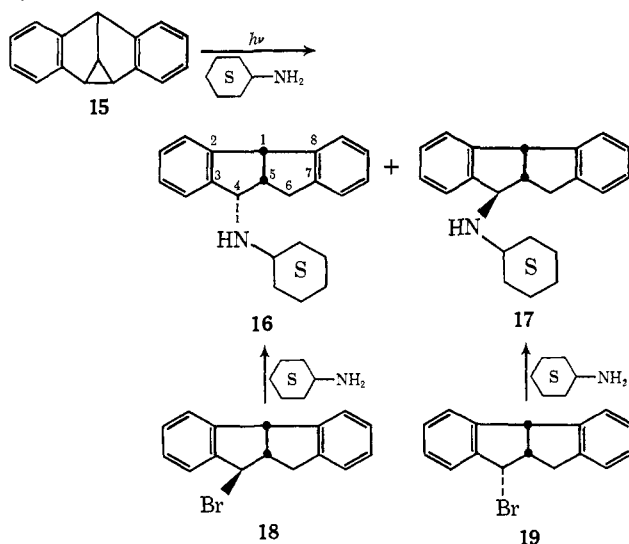


Figure 1. The dependence of the quantum yield for addition of *n*-butylamine to *trans*-1,2-diphenylcyclopropane on the concentration of *n*-butylamine.

Addition of Cyclohexylamine to Dibenzosemibullvalene.

The stereochemistry of the addition process was then examined by irradiating dibenzosemibullvalene (dibenzotricyclo[3.3.0.0^{2,8}]octadiene¹³ (**15**)) in cyclohexylamine. Dibenzosemibullvalene is a *cis*-diphenylcyclopropane which cannot undergo *cis*-*trans* isomerization; complications in determining the stereochemistry of addition which would result from the isomerization process are therefore avoided. Interestingly, as in the alcohol cases,^{7,8} the addition proceeded stereoselectively to give a 4:1 ratio of *syn* (**16**) to *anti* (**17**) amines (Scheme II). This isomer ratio is the same at 16 and 53% con-

Scheme II. Photolysis of Dibenzosemibullvalene in Cyclohexylamine



version of **15**. Thus, there was a pronounced preference for the formation of the more hindered *syn* isomer of the product.

(13) E. Ciganek, *J. Amer. Chem. Soc.*, **88**, 2882 (1966).

Products **16** and **17** were difficult to purify, and in the case of **17** we were unable to obtain an analytically pure sample of the compound itself or a derivative. However, the structures of **16** and **17** were readily proven by their nmr and mass spectra. The nmr spectra (see Experimental Section) allowed us to distinguish stereoisomers. The spectrum of **16** showed an overlapping pair of doublets appearing as a triplet centered at δ 4.49 due to the C-1 and C-4 hydrogens; $J_{1,5} = J_{4,5(\text{anti})} = 7.0$ Hz. The C-4 hydrogen of **17** appeared as a doublet at δ 4.10; $J_{4,5(\text{syn})} = 2.5$ Hz. These values for $J_{4,5}$ are typical for isomeric 4-substituted-dibenzobicyclo[3.3.0]octadienes and serve to define the stereochemistry at C-4; for it has been found that the *cis* coupling constant ($J_{4,5(\text{anti})}$) is invariably greater than the *trans* coupling constant ($J_{4,5(\text{syn})}$).^{7,8b,14} The most definitive proof of the structures of **16** and **17** was obtained by their independent syntheses by reaction of cyclohexylamine both with *anti*-4-bromodibenzobicyclo[3.3.0]octadiene (**18**)^{14a} to give **16** and with a mixture of *syn*- and *anti*-4-bromodibenzobicyclo[3.3.0]octadienes (**18** and **19**)^{14a} to produce **17** and **16** (Scheme II). Unfortunately, the nmr spectra of amines **16** and **17** did not allow for a determination of the stereochemistry of protonation in the photochemical addition.

Isotope Effect on the Addition of *n*-Butylamine to *trans*-1,2-Diphenylcyclopropane. As the reaction at some point involved a transfer of hydrogen from nitrogen to carbon, it was deemed of interest to determine whether there was an isotope effect on this process. Cyclohexane solutions of **1**, 1.0 *M* in *n*-butylamine or *n*-butylamine-*N,N*-*d*₂, were irradiated simultaneously in triplicate to low conversion on a merry-go-round apparatus with 254-nm light. Surprisingly, analysis of the reaction mixtures by gas chromatography revealed that identical amounts of amine **10** were formed in the deuterated and nondeuterated runs ($\phi_{\text{H}}/\phi_{\text{D}} = 0.99 \pm 0.04$). This was also true when runs were carried out with 0.5 *M* *n*-butylamine ($\phi_{\text{H}}/\phi_{\text{D}} = 0.99 \pm 0.03$). In short, we observed no isotope effect on the addition.

Quantum Yield Studies on the Addition of *n*-Butylamine to *trans*-1,2-Diphenylcyclopropane. Quantum yield studies on the addition of a representative primary amine,¹⁵ *n*-butylamine, to **1** at various amine concentrations were carried out both in cyclohexane and in acetonitrile. These data were obtained at very low conversions of **1** to its *cis* isomer **2** so that only addition to the former was being observed. The results are shown in Table I, and the cyclohexane data are plotted in Figure 1. Values for the slope (*S*) and intercept (*I*) of 12.3 mol l.⁻¹ and 12.1 were obtained, respectively. A plot of the acetonitrile data was not linear. However, it is important to note that the reaction is at all amine concentrations less efficient in acetonitrile than is cyclohexane.

Discussion

In discussing the mechanism for the photochemical addition of primary and secondary amines to 1,2-diphenylcyclopropane (**1**) we initially consider possible reaction pathways involving addition of the amines to

(14) (a) S. Cristol, W. Y. Lim, and A. R. Dahl, *J. Amer. Chem. Soc.*, **92**, 4014 (1970), and references therein; (b) S. J. Cristol and B. B. Jarvis, *ibid.*, **89**, 5885 (1967).

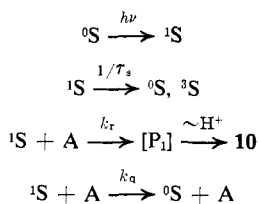
(15) The significant light absorption by secondary amines complicates similar studies with them.

Table I. Quantum Yield Studies of the Addition of *n*-Butylamine to *trans*-1,2-Diphenylcyclopropane

Amine concn, <i>M</i>	—Quantum yield of 10 ($\times 10^{-3}$)—	
	Cyclohexane	Acetonitrile
0.2	13.4, 14.4	1.75, 1.81
0.3	18.2, 18.8	2.21, 2.24
0.5	26.3, 25.6	2.97, 3.20
1.0	38.8, 42.7	4.54, 4.93
2.0	59.9, 62.1	7.19, 7.41

S 12.3 mol l.⁻¹
I 12.1

the lowest spectroscopic singlet ¹S of **1**, the sensitization data arguing strongly against the involvement of the lowest triplet ¹T.^{9c} Of these possibilities, pathways proceeding by way of initial protonation of ¹S by the amine or by a concerted addition of the N–H bond across the C–C bond appear very doubtful in light of the very low acidity of amines and the absence of an observable isotope effect on the addition. However, these objections do not pertain to a reaction involving nucleophilic attack of the amine on ¹S. To probe this latter possibility further we consider how the kinetic results fit with such a mechanism. Scheme III depicts

Scheme III

the minimal kinetic scheme for the process under consideration. In Scheme III, τ_s is the lifetime of ¹S diphenylcyclopropane, k_r is the second-order rate constant for reaction of the amine (A) with ¹S, k_q is the rate constant for quenching of ¹S by amine, and P₁ is a zwitterionic intermediate produced by attack of the amine on ¹S.

To obtain a value of k_r from our data using eq 5 one

$$\frac{1}{\Phi_{10}} = 1 + \frac{k_q}{k_r} + \frac{1}{k_r\tau_s[\text{A}]} \quad (5)$$

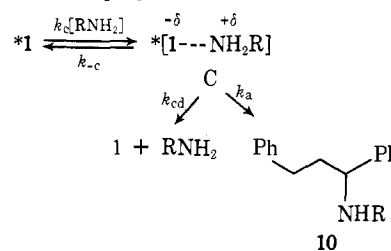
needs to know τ_s . Unfortunately, we have not been able to detect any fluorescence from **1** or from its *cis* isomer **2** at room temperature. This agrees with the work of Becker, *et al.*,¹² who also report the lack of fluorescence of **1** even at very low temperatures. (They do report weak fluorescence from *cis*-cyclopropane (**2**) at low temperature, however.) Thus we could not obtain a value for the lifetime of **1** nor any fluorescence quenching data. However, the ultraviolet spectrum of **1** is quite similar to that of toluene;¹² and if we assume that toluene and **1** have the same radiative lifetime (200 nsec)¹⁶ and conservatively estimate a maximum fluorescence quantum yield for **1**, $\Phi_f < 0.001$,¹⁷ we calculate a maximum lifetime τ_s for ¹S of **1** of 0.2 nsec. An allowance for possible exciton interaction¹² affects this figure only slightly, and we use 0.26 nsec as a very conservative upper limit for τ_s . Using this value for τ_s and the data in Table I, we calculate from eq 5 that $k_r = 3.1 \times 10^8$ l. mol⁻¹ sec⁻¹ and $k_q = 3.4 \times 10^9$ l. mol⁻¹

(16) I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, N. Y., 1971.

(17) This is a very conservative upper limit for Φ_f at the temperature of liquid nitrogen: R. Becker, private communication.

sec⁻¹ in cyclohexane. We include a separate quenching step in Scheme III to accommodate the fact that even at infinite amine concentration the quantum yield of adduct does not approach unity. If one attributes this inefficiency totally to the partitioning of an intermediate adduct, then $k_r = 3.8 \times 10^9$ l. mol⁻¹ sec⁻¹. These values of k_r which, it must be remembered, are minimum values based on a very conservative estimate for the upper limit of τ_s , are very fast. The rate of diffusion in cyclohexane is only *ca.* 7×10^9 sec⁻¹.¹⁸ Nucleophilic quenching of excited states at rates approaching that of diffusion has been reported by Whitten.¹⁹ However, here the interaction of the nucleophiles is with the π systems of excited states of molecules which are either positively charged or highly polar. In contrast, the present scheme involves a nucleophilic attack on a nonpolar molecule resulting in the cleavage of a carbon–carbon bond and is thus very different from the systems studied by Whitten. We feel uncomfortable with a mechanism which involves at a minimum such fast rates of attack. Moreover, the solvent effect (*i.e.*, the slower rate in acetonitrile relative to cyclohexane)²⁰ is the reverse of what it should be for a process in which charged species are being formed.

A more likely possibility for reaction of ¹S is a path proceeding *via* initial formation of a polarized complex (exciplex) between amine and cyclopropane (Scheme IV,

Scheme IV. Exciplex Formation between *n*-Butylamine and Excited Diphenylcyclopropane

***1** = ¹S) since such complex formation between amines and excited states of aromatic compounds is known to occur frequently at rates approaching or equal to the diffusion-controlled limit.²¹ Moreover, there is ample

(18) Calculated from the equation $k_{diff} = 8RT/3000\eta$: A. A. Lamola in "Energy Transfer and Organic Photochemistry," A. A. Lamola and N. J. Turro, Ed., Interscience, New York, N. Y., 1969, p 34; "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," API Project 44, Carnegie Press, Pittsburgh, Pa., 1953.

(19) M. T. McCall and D. G. Whitten, *J. Amer. Chem. Soc.*, **91**, 5681 (1969); D. G. Whitten, J. W. Happ, G. L. B. Carlson, and M. T. McCall, *ibid.*, **92**, 3499 (1970); J. W. Happ, M. T. McCall, and D. G. Whitten, *ibid.*, **93**, 5496 (1971).

(20) The best straight line through the acetonitrile data (Table I) gives $k_r = 4.1 \times 10^7$ l. mol⁻¹ sec⁻¹.

(21) Values of $K_q = k_c(k_a + k_{cd})/(k_{-c} + k_a + k_{cd})$ (Scheme IV) equal to the rate of diffusion are frequently observed for the reactions of excited aromatics with substituted anilines or in other cases where charge-transfer interaction between an excited aromatic and an amine is especially favorable due to a low ionization potential of the amine and a high electron affinity of the excited aromatic.²² Values of K_q for the interaction of alkyl amines, especially primary amines, with excited aromatics in cases where charge transfer is not set up to be especially favorable are generally somewhat slower than the rate of diffusion.^{22g-k}

(22) (a) H. Knibbe, D. Rehm, and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **72**, 257 (1968); (b) W. R. Ware and H. P. Richter, *J. Chem. Phys.*, **48**, 1595 (1968); (c) K. Koshihara, T. Kasuya, A. Inoue, and S. Nagakuru, *Chem. Phys. Lett.*, **9**, 469 (1971); (d) B. Stevens, *Advan. Photochem.*, **8**, 161 (1971); (e) R. J. McDonald and B. K. Seliger, *Aust. J. Chem.*, **24**, 1797 (1971); (f) B. K. Seliger and R. J. McDonald, *ibid.*, **25**, 897 (1972); (g) N. C. Yang and J. Libman, *J. Amer. Chem. Soc.*, **95**, 5783 (1973); (h) D. Schulte-Frohlinde and R. Pfefferkorn, *Ber., Bunsenges. Phys. Chem.*, **72**, 330 (1968); (i) K. Nakashima, N. Mataga, F. Ushio, and C. Yamanaka, *Z. Phys. Chem.*, **79**, 150 (1972); (j) N.

precedent for this reaction pathway in the photochemical addition of amines to other aromatic hydrocarbons.²³

In Scheme IV k_c is the rate constant for exciplex (C) formation from *1 and amine; k_a is the rate constant for formation of amine addition product 10 (probably by a series of steps) from C; and k_{cd} is the rate constant for decay of the exciplex to ground-state cyclopropane 1 and amine. Using eq 6 and the data in Table I, we

$$\frac{1}{\Phi_{10}} = 1 + \frac{k_{cd}}{k_a} + \frac{k_{-c} + k_a + k_{cd}}{\tau k_a k_c [A]} \quad (6)$$

calculate $K_q = k_c(k_a + k_{cd})/(k_{-c} + k_a + k_{cd}) \geq 3.7 \times 10^9 \text{ sec}^{-1}$, a value approaching the rate of diffusion.

However, in view of the very short lifetime of ¹S and the fact that K_q is *minimally* so large,²¹ we must consider the strong possibility that the reaction with amines occurs not with ¹S but with another state formed very rapidly from ¹S. It seems unlikely that this state is a ring-opened, planar zwitterionic species, for one would not then expect the preference for formation of the more hindered syn isomer in the addition of cyclohexylamine to dibenzosemibullvalene (15). The sensitization data argue against the involvement of the lowest triplet, though a higher triplet state remains a candidate.⁹ However, most interesting is the possible involvement of a second, lower energy singlet species. Indeed, the possibility of the intermediacy of such a species is strengthened by the fascinating recent paper of Becker and Griffin¹² describing spectroscopic studies on polyphenylcyclopropanes. In this paper,¹² Becker and Griffin report the observation of a long wavelength phosphorescence emanating from some of the cyclopropanes studied (including 1) which they ascribe to "radical-like" triplet states, *i.e.*, triplet states with a long, weakened three ring bond. In addition, Becker and Griffin provide convincing arguments for the formation of the corresponding "radical-like" singlets. It is these "radical-like" singlets—singlets with a long doubly benzylic bond—which may well be involved in the present reactions. Indeed, the authors themselves postulate that the radical-like states are important in the photochemical isomerizations and fragmentations of arylcyclopropanes.¹²

Moreover, on the theoretical side, calculations indicate that whereas the energy of the ground state of cyclopropane increases continuously as a carbon-carbon bond is stretched, that of the lowest excited state (singlet and triplet) decreases.²⁴ The energies of the two states thus approach each other at large bond distortions. In addition, as noted by Salem,²⁵ the lowest singlet of the trimethylene diradical, which the stretched excited singlet state of cyclopropane approaches, has considerable ionic character. Insofar as one can extrapolate these results to 1,2-diphenylcyclopropane (1), one expects that upon excitation of 1 to its singlet excited state relaxation would occur to an excited state

with a lengthened C-1-C-2 bond and that this state would be highly polarizable. Both polar and radical behavior are predicted for such a state, as observed. Additionally, considerable mixing of ground- and excited-state configurations should occur at such a geometry allowing for facile passage of excited-state to ground-state cyclopropane and accounting for some of the observed inefficiency in reaction of the diphenylcyclopropane singlet.²⁶

Both direct nucleophilic attack and exciplex mechanisms may be visualized for addition to this "radical-like" singlet. Unfortunately, with the limitations of the present system we cannot be certain of the involvement of such a state of 1 in the additions. With this in mind, we suggest an exciplex pathway as our preferred mechanism for reaction; this is outlined in Scheme IV where now *1 designates merely the reactive excited state of 1, not necessarily the initially obtained spectroscopic singlet ¹S and quite possibly a "radical-like" state instead.

With respect to Scheme IV, we point out that this mechanism, the details of which are necessarily somewhat vague, is similar in outline to that proposed by Yang^{22g} for the reactions of secondary amines with anthracene. Likewise, it bears a strong resemblance to that put forth by Bryce-Smith²³ for the addition of amines to photoexcited benzene, a reaction very similar to the present one. In the diphenylcyclopropane case, the absence of an observable isotope effect on the quantum yield of product formation in cyclohexane is a strong indication that transfer of the amino hydrogen is not involved in the rate-determining step of the addition. Such would be the case if (a) exciplex formation were rate-limiting, a reasonable possibility since exciplex formation between a primary amine and the excited cyclopropane should not be especially favorable, particularly in cyclohexane, or (b) the rate-determining step for conversion of a weakly bound exciplex to product did not involve hydrogen transfer, a possibility for such a step being carbon-nitrogen bond formation. In case (a), k_a could then represent a proton transfer step giving a neutral radical pair which combines to form product. The lower efficiency of reaction in acetonitrile is surprising. However, we point out that Yang found the photoaddition of diethylamine to anthracene, proceeding *via* an exciplex, was likewise less efficient in acetonitrile relative to a nonpolar solvent (benzene).^{22g} A solvent effect on partitioning of the exciplex was put forth to rationalize this result,^{22g} the conversion of the polar exciplex by proton transfer to a less polar product (a radical pair) being disfavored in the polar acetonitrile where, instead, complete electron transfer to give an ion pair was preferred. A similar solvent effect on exciplex partitioning could well be operating in the present case.²⁷

(26) The sum of the quantum yields for all processes observed upon direct irradiation of 1 is *ca.* 0.14.¹⁶ Furthermore, this low value is apparently not due to a high rate of intersystem crossing to a nonreactive triplet. Thus, the work of DeBoer¹⁸ suggests that the lowest triplet state of 1 dissociates to a biradical species such as 9 with unit efficiency.⁹ This biradical decays to *trans*- and *cis*-cyclopropanes (1 and 2) in a ratio of 1.86:1. If one assumes that all the *trans* to *cis* isomerization occurring upon direct irradiation of 1 ($\Phi = 0.089$) occurs *via* the triplet state, one calculates the triplet is formed with a quantum yield of 0.25. In this case the sum of the quantum yields of all the observed singlet state reactions plus the quantum yield of the triplet state formation equals only 0.30. Therefore, at a minimum the fate of 70% of the singlet states formed must be accounted for.

(27) We thank Professor N. C. Yang for a helpful discussion of the reaction mechanism.

Nakashima, N. Mataga, and C. Yamanaka, *Int. J. Chem. Kinet.*, **5**, 833 (1973); (k) A. Nakajima, *Bull. Chem. Soc. Jap.*, **42**, 3409 (1969).

(23) See, for example, ref 22g and also D. Bryce-Smith, M. T. Clarke, A. Gilbert, G. Klunklin, and C. Manning, *Chem. Commun.*, 916 (1971); M. Bellas, D. Bryce-Smith, and A. Gilbert, *ibid.*, 263, 862 (1967).

(24) (a) R. J. Buenker and S. D. Peyerimhoff, *J. Phys. Chem.*, **73**, 1299 (1969); (b) R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968); (c) A. K. Q. Siu, W. M. St. John, III, and E. F. Hayes, *ibid.*, **92**, 7249 (1970).

(25) L. Salem and C. Rowland, *Angew. Chem., Int. Ed. Engl.*, **11**, 92 (1972).

Experimental Section

General. Melting points were taken on a Mel-Temp apparatus and are corrected. Infrared spectra were recorded on a Beckman IR-10 spectrophotometer; nmr spectra were obtained with either a Varian A-60 or a Perkin-Elmer R12 A instrument using tetramethylsilane as an internal standard; mass spectra were run on an Hitachi-Perkin-Elmer RMU-6L mass spectrometer. All gas chromatography was carried out with a Perkin-Elmer Model 990 gas chromatograph equipped with a flame ionization detector. Peak areas were determined by the cut and weigh method; averages of at least three injections of each sample were used. Microanalyses were performed by the University of Massachusetts Micro-analytical Laboratory.

Cyclohexane (Spectral grade) was distilled from calcium hydride and stored over molecular sieves (3A). Cyclohexylamine was dried with calcium chloride and distilled under nitrogen from potassium hydroxide. Piperidine and *n*-butylamine were refluxed with and distilled from calcium hydride. Diethylamine was dried with potassium hydroxide and then refluxed with and distilled from the same. The amines were kept over molecular sieves prior to irradiation experiments.

Photolysis of 1,2-Diphenylcyclopropane (1) in *n*-Butylamine. A solution of 1.000 g (5.15 mmol) of 1,2-diphenylcyclopropane²⁸ in 110 ml of *n*-butylamine was irradiated at ambient temperature with Corex-filtered light from a Hanovia 450-W medium-pressure mercury arc for 2 hr. Nitrogen was bubbled through the solution both for 30 min prior to photolysis and throughout the irradiation. The solvent was then removed *in vacuo* and the residue chromatographed on a 2.0 × 40 cm deactivated silica gel (10% water) column packed in hexane. Elution with hexane provided 0.358 g (36%) of a mixture of *cis*- and *trans*-1,2-diphenylcyclopropanes plus a very small amount of the 1,3-diphenylpropenes. Elution with 15% ether-hexane provided 0.779 g (57%) of 1-(*n*-butylamino)-1,3-diphenylpropane. The spectral data were: nmr (CDCl₃) δ 0.84–2.67 (m, 14), 3.55 (t, 1, PhCHN), 7.12–7.23 (m, 10, arom); ir (neat) 3030, 2930, 2860, 1602, 1995, 1451, and 699 cm⁻¹.

Anal. Calcd for C₁₉H₂₅N: C, 85.34; H, 9.42; N, 5.24. Found: C, 85.15; H, 9.45; N, 5.02.

Photolysis of 1,2-Diphenylcyclopropane (1) in Piperidine. A solution of 1.002 g (5.15 mmol) of 1,2-diphenylcyclopropane²⁸ in piperidine was irradiated for 3.5 hr and chromatographed as above to give 0.557 g of a mixture of *cis*- and *trans*-1,2-diphenylcyclopropanes (36%) and 1,3-diphenylpropane (20%) plus 0.395 g (27%) of 1-piperidino-1,3-diphenylpropane:²⁹ nmr (CDCl₃) δ 1.02–2.90 (m, 14), 3.33 (dd, 1, PhCHN), 6.98–7.33 (m, 10, arom); ir (neat) 3070, 2940, 2860, 2800, 1605, 1496, 1452, 1105, and 700 cm⁻¹.

Photolysis of Dibenzotricyclo[3.3.0.0^{2,8}]octadiene (15) in Cyclohexylamine. A solution of 0.998 g (5.20 mmol) of dibenzotricyclo[3.3.0.0^{2,8}]octadiene¹³ in 110 ml of cyclohexylamine was irradiated as above for 20 min. The solvent was removed and the residue chromatographed on a 2.5 × 100 cm deactivated silica gel column packed in 5% ether-hexane. Elution with 5% ether-hexane provided 0.838 g (84%) of unreacted starting material. Elution with 8–10% ether-hexane provided 0.160 g (10%) of *syn*-4-cyclohexylaminodibenzobicyclo[3.3.0]octadiene. Elution with 30–50% ether-hexane afforded 0.037 g (2.3%) of *anti*-4-cyclohexylaminodibenzobicyclo[3.3.0]octadiene.

***syn*- and *anti*-4-Cyclohexylaminodibenzobicyclo[3.3.0]octadienes (16 and 17).** A solution of *anti*-4-bromodibenzobicyclo[3.3.0]octadiene^{14a} (prepared^{14a} from 0.200 g of dibenzotricyclo[3.3.0.0^{2,8}]octadiene) in 10 ml of benzene and 10 ml of cyclohexylamine was refluxed 24 hr. The solvent was removed and the residue chromatographed on a 2.5 × 50 cm deactivated silica gel column packed in 5% ether-hexane. Elution with 5% and then 8–10% ether-hexane provided 0.117 g of *syn*-4-cyclohexylaminodibenzobicyclo[3.3.0]octadiene: nmr δ 1.25–2.90 (m, 14), 3.29–3.80 (quintet, 1, C-5 H), 4.49 (overlapping pair of doublets appearing as a triplet, 2, C-1 and C-4 H's), 7.08–7.47 (m, 8, arom), $J_{1,5} = J_{4,5} = 7.0$ Hz. The C-6 *syn* and *anti* hydrogens have the same chemical shift (δ 2.82) and appear as a doublet; $J_{3,6(\text{syn})} = J_{3,6(\text{anti})} = 8.0$ Hz (decoupling experiments support these assignments); ir (neat) 3080, 3030, 2940, 2860, 1455 (br), 1135 (br), 740 (br); mass spectrum *m/e* (rel intensity) 304 (49), 303 (M⁺, 97), 260 (32), 232 (40), 220 (90), 210 (80), 209 (100), 208 (100), 207 (93), 206 (73), 178 (35), 130 (28), 115 (24), 98 (77), 91 (32). For analysis a solid acetyl derivative, mp 133°, was prepared by reaction with acetic anhydride.

(28) A *cis*-*trans* mixture was used.

(29) K. Thomae, British Patent 807,837 (1959); *Chem. Abstr.*, 53, 12308b (1959).

Anal. Calcd for C₂₄H₂₇NO: C, 83.44; H, 7.88; N, 4.05. Found: C, 83.15, H, 7.60; N, 3.84.

In a similar manner an approximately 1:2 mixture of *syn*- and *anti*-4-bromodibenzobicyclo[3.3.0]octadienes (prepared^{14a} from 0.305 g of dibenzotricyclo[3.3.0.0^{2,8}]octadiene) was converted to a mixture of 0.288 g of *syn*- and 0.108 g of *anti*-4-cyclohexylaminodibenzobicyclo[3.3.0]octadienes. The *syn* isomer was isolated as above; the *anti* isomer was eluted with 50% ether-Skelly and was purified further by rechromatography: nmr δ 1.18–3.48 (m, 14), 4.10 (d, 1, C-4 H), 4.70 (d (with addition peaks likely due to virtual coupling with the C-6 H's),³⁰ 1, C-1 H), 7.05–7.40 (m, 8, arom), $J_{1,5} = 2.5$ Hz; ir (neat) 3080, 3040, 2940, 2860, 1475, 1450, 1115, 740 cm⁻¹; mass spectrum *m/e* (rel intensity) 303 (M⁺, 100), 260 (17), 232 (42), 220 (93), 207 (87), 206 (100), 205 (100), 204 (90), 203 (77), 178 (50), 165 (20), 130 (31), 98 (77). We were unable to obtain a satisfactory analysis on this compound.

***n*-Butylamine-*N,N*-d₂.** A mixture of 65 g of distilled, dried *n*-butylamine and 200 g of deuterium oxide was stirred 18 hr at 50°. The amine was recovered by distillation and treated with an additional 100 g of deuterium oxide for 18 hr at 50°. The amine was distilled, dried over molecular sieves (3A), and redistilled carefully from molecular sieves. Analysis by the falling drop method gave 17.90 atom % excess deuterium corresponding to 98.5% exchange of hydrogen for deuterium (J. Nemeth, University of Illinois).

Isotope Effect Studies. Cyclohexane solutions, approximately 2.72 × 10⁻² M in *trans*-1,2-diphenylcyclopropane and 1.0 M in *n*-butylamine or *n*-butylamine-*N,N*-d₂, containing docosane as an internal standard were prepared. Portions of 6.5 ml were added to quartz irradiation vessels which were then stoppered with serum caps. Nitrogen was bubbled through each sample for 5 min *via* very thin syringe needles. The samples were irradiated in triplicate on a turntable apparatus for 0.5 hr at ambient temperature using 2537-Å light from a low-pressure mercury lamp. The samples were then concentrated to ca. 1 ml and analyzed by gas chromatography (10% SE-30, 190°) for 1-(*n*-butylamino)-1,3-diphenylpropane (10). Identical ($\Phi_H/\Phi_D = 0.99 \pm 0.04$) amounts of the amine product 10 were formed in the nondeuterated and deuterated runs. A similar experiment with 0.53 M amine gave the same result ($\Phi_H/\Phi_D = 0.99 \pm 0.03$).

Sensitized Irradiation of 1,2-Diphenylcyclopropane in the Presence of Cyclohexylamine. Three milliliters of a benzene solution containing 1.00 M 1,2-diphenylcyclopropane, 0.42 M cyclohexylamine and 0.1 M xanthone was placed in a Pyrex tube which was then stoppered with a serum cap. The solution was flushed with nitrogen (using syringe needles) for 15 min and then irradiated for 24 hr in a Rayonet photochemical reactor using the 350-nm lamps. Gc analysis (3% SE-52 on Varaport 30, 200°) showed no detectable amounts of 1-cyclohexylamino-1,3-diphenylpropane. A noticeable increase in the *cis*:*trans* ratio of the diphenylcyclopropanes had occurred.

An acetophenone (neat) solution (1 ml) containing 1.05 M 1,2-diphenylcyclopropane and 0.42 M cyclohexylamine was treated as above and irradiated similarly for 21 hr. Gc analysis once again indicated the absence of any detectable amount of 1-cyclohexylamino-1,3-diphenylpropane and the occurrence of net *trans*-*cis* isomerization.

Quantum Yield Studies. The Photochemical Addition of *n*-Butylamine to *trans*-1,2-Diphenylcyclopropane. Duplicate 6.5-ml samples containing 2.68 × 10⁻² M *trans*-1,2-diphenylcyclopropane, docosane (internal standard), and varying concentrations of *n*-butylamine in cyclohexane were prepared, irradiated, and analyzed as in the isotope effect experiment (*vide supra*). Similar experiments were carried out in acetonitrile solution; in these cases internal standard in cyclohexane solution was added after removal of the acetonitrile. Light intensity was determined by simultaneous irradiation of tubes containing potassium ferrioxalate solution.³¹ Optical density changes of each cyclopropane reaction solution as a result of photolysis were negligible.

Acknowledgment. I wish to express my thanks to Professors R. S. Becker, N. C. Yang, and C. P. Lillya for very helpful discussions, and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(30) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1969, p 147.

(31) C. A. Parker, *Proc. Roy. Soc., Ser. A*, 220, 104 (1953); C. G. Hatchard and C. A. Parker, *ibid.*, 235, 518 (1956).