Photosensitized Racemization of an Optically Active Allene[1]

By O. RODRIGUEZ and H. MORRISON*
(*Chemistry Department, Purdue University, Lafayette, Indiana* 47907)

Summary Toluene photosensitizes the racemization of optically active penta-2,3-diene through a triplet energy-transfer mechanism.

ALTHOUGH the photochemistry of olefins has been intensively investigated relatively little is known about the excited-state properties of allenes. In particular, though *cis–trans* isomerization of olefins in the triplet state (through photosensitization) is well known,[2] no comparable observations have yet been made for allenes. Such isomerization would only be observed by the use of an optically active substrate, and we herein report the first such example of allene photoracemization.

Optically active penta-2,3-diene, $[\alpha]_D^{25}$ + 16 to + 23° (hexane)† was prepared by asymmetric hydroboration[3] using (+)-α-pinene. Hexane solutions of allene (0·353M) and toluene (0·96M) were irradiated at room temperature in Vycor-shielded quartz tubes at 254 nm [ϵ_{254} (toluene) 175, ϵ_{254} (penta-2,3-diene) 0·52; >99·9% of the light is thus absorbed by the toluene] (see Table). There is clearly a rapid and essentially complete racemization of the allene.‡ Acetone and benzophenone likewise photosensitize the racemization, but in both of these cases, oxetans are also formed[4] (specific rotations were measured after isolation of the allene by g.l.c.).

TABLE

Photosensitized racemization of (+)-*penta*-3,3-*diene*[a]

Time of irradiation, t/min	$[\alpha]_D^{25}$/°
0	16·27
29	14·48
62	11·84
126	7·81
239	6·22
481	2·28
1056	1·59
1367	0·78

[a] Hexane solutions of allene (0·353M) and toluene (0·96M).

The most reasonable mechanism for the photoracemization by toluene§ is outlined in equations (1)—(5), where S,^{1}S and ^{3}S represent the sensitizer (toluene) in its ground and excited singlet and triplet states, PD and ^{3}PD are the

$$\mathrm{S} \xrightarrow{h\nu} {}^1\mathrm{S} \qquad (1)$$

$$^1\mathrm{S} \xrightarrow{\text{isc}} {}^3\mathrm{S} \qquad (2)$$

$$^3\mathrm{S} + \mathrm{PD} \longrightarrow \mathrm{S} + {}^3\mathrm{PD} \qquad (3)$$

$$^3\mathrm{PD} \longrightarrow (+)\text{-PD} \qquad (4)$$

$$^3\mathrm{PD} \longrightarrow (-)\text{-PD} \qquad (5)$$

penta-2,3-diene in its ground and excited triplet state, and isc is inter-system crossing. Thus, penta-2,3-diene does indeed efficiently quench toluene phosphorescence (77 K; isopentane glass) whereas quenching of toluene fluorescence (room temperature) is barely detectable. Because the allene antiplanar triplet is of relatively high energy (100—104 kcal mol^{-1}),[5] ^{3}PD must here represent the, as yet ill defined, planar triplet.[5,6] We have succeeded in attaining good Stern–Volmer quenching data in isopentane glasses[7,8] and find for toluene and penta-2,3-diene, a slope ($k_Q\tau$) of 425 ± 34 M^{-1} (least squares line with standard deviation); the data for *trans*-hex-2-ene and *cis*-penta-1,3-diene[7] are 588 ± 31 and 942 ± 106 M^{-1}, respectively. The reasonably easy toluene-sensitized isomerization suggests that the planar allene triplet has a triplet energy slightly above or less than the 83 kcal mol^{-1} of toluene; the phosphorescence quenching data for penta-2,3-diene compared to *trans*-hex-2-ene limit that triplet energy to one which is slightly higher than that for a simple olefin (*ca.* 80 kcal mol^{-1}),[2]¶ but probably still less than that of toluene.

We are grateful to the National Science Foundation and the Purdue Research Foundation for support of this research.

(*Received, March* 22*nd*, 1971; *Com.* 373.)

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† The predicted rotation of optically pure material is 174°, so that our best sample was *ca.* 12% optically pure; *cf.* J. H. Brewster, *J. Amer. Chem. Soc.*, 1959, **81**, 5475.

‡ G.l.c. analysis of the solutions demonstrated minimal loss of allene during the first 4 h; *ca.* 36% loss in allene was noted over the entire 23 h period. All specific rotations were calculated on the basis of the measured allene content of each tube.

§ Since we find that fluorene (E_t 68 kcal mol^{-1}) does *not* sensitize photoracemization whereas benzophenone (E_t 69 kcal mol^{-1}) does, the latter process presumably involves a triplet diradical adduct (*cf.* N. C. Yang, J. I. Cohen, and A. Shani, *J. Amer. Chem. Soc.*, 1968, **90**, 3264).

¶ Hammond and his co-workers[4b] have used the efficient addition of acetophenone to tetramethylallene as an indication that ^{3}PD > 74 kcal mol^{-1}.

[1] For previous paper in series "Organic Photochemistry," see: W. Ferree, jun., J. Grutzner, and H. Morrison, *J. Amer. Chem. Soc.*, in the press.

[2] For leading references, see H. Morrison, J. Pajak, and R. Peiffer, *J. Amer. Chem. Soc.*, in the press.

[3] W. L. Waters, W. S. Linn, and M. Caserio, *J. Amer. Chem. Soc.*, 1968, **90**, 6741.

[4] (a) D. R. Arnold and A. H. Glick, *Chem. Comm.*, 1966, **813**; (b) H. Gotthardt, R. Steinmetz, and G. S. Hammond, *J. Org. Chem.*, 1968, **33**, 2774. The latter workers report ϕ(disappearance) for tetramethylallene with acetophenone to be 0·59.

[5] (a) W. T. Borden, *J. Chem. Phys.*, 1966, **45**, 2512; (b) P. S. P. Wei, *Nuclear Sci. Abs.*, 1968, **22**, 11,193; (*Chem. Abs.*, 1968, **69**, 5272z).

[6] L. J. Schaad, L. A. Burnelle, and K. P. Dressler, *Theor. Chim. Acta* (*Berlin*), 1969, **15**, 91.

[7] P. Froehlich, to be published. Using a measured lifetime of 3·50 s for the toluene triplet state at 77 K [(toluene) = 1·4 × 10^{-3}M], the k_q derived from the penta-1,3-diene quenching data is 269M^{-1} s^{-1}, a factor of *ca.* 5 less than the calculated diffusion-controlled value. Very little quenching is observed in a (more viscous) ethanol glass.

[8] There are two reports of triplet quenching by an allene in the gas phase (*cf.* R. E. Rebbert and P. Ausloos, *J. Amer. Chem. Soc.* 1965, **87**, 5569; M. W. Schmidt and E. K. C. Lee, *ibid.*, 1970, **92**, 3579).