Tetrahedron Letters No.3, pp. 203-206, 1970. Pergamon Press. Printed in Great Britain.

TRANSFORMATION OF LINEAR 1, 3-DIENES TO CYCLOPROPENES ON PHOTOSENSITIZATION

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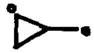
(Received in USA 7 November 1969; received in UK for publication 17 December 1969)

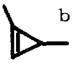
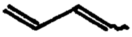
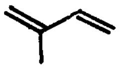
It had been suggested that many of the photochemical reactions of 1, 3-dienes in general, and 1, 3-butadiene in particular, can be rationalized in terms of a diradical intermediate with a cyclopropane structure:  (I).[1] One reaction path that may be available to I is the formation of a cyclopropene by a hydrogen migration, but only a single instance of such a reaction had hitherto been described, and that too as a minor process. We report here evidence to show that such a reaction is of general importance for several linear 1, 3-dienes in a mercury $^3P_1$ system, at pressures from 100 to 300 torr. In a flow system, some of these reactions (e. g. isoprene to a mixture of dimethylcyclopropenes) have synthetic value as they can be scaled up to give alkylcyclopropenes on a gram scale.

In Table I, the reaction conditions and the major products are listed for the 1, 3-dienes that were investigated. A few additional comments are pertinent. In the case of 1, 3-butadiene, no evidence for the formation of 1-methylcyclopropene or 2-butyne was obtained. From cis-1, 3-pentadiene, relative to the rate of cyclization to 1, 3-dimethylcyclopropene, the stereoisomerization was 25- to 50-fold faster. In the 1, 3-hexadiene system (a mixture of cis- and trans-), the rapid process was an isomerization to a mixture of 2, 4-hexadienes. Two cyclopropenes were formed at a slower rate. One of these was the known[2] 1-ethyl-3-methylcyclopropene, while the other was identified to be 1-methyl-3-ethylcyclopropene from the following data[3]: Mol. Wt. by mass spectrometry: 82; infrared spectrum: 1775 (C=C), 1375 (CH_3), 990, 935, and 699 cm^{-1}; n. m. r. spectrum 6. 55 δ -1H (broad), 2. 09 δ -3H (slightly broadened); complex pattern form 1. 4 to 0. 9 δ -3H; 0. 78 δ -3H (triplet, J = 5Hz). From isoprene, there was no evidence for the formation of 1, 2-dimethylcyclopropene.

TABLE I

Mercury ($^3P_1$) Sensitized Isomerization of Linear 1, 3-Dienes

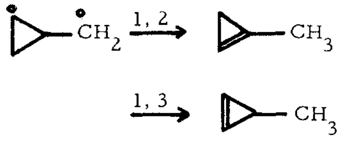
Room temp. ; 25 w. hot cathode germicidal lamp; cell volu. 1-5 liter

Reactant	Press Torr	Conv. %	Cyclopropene	Yield Per Cent	Other Products (Yield)[a] (Excluding condensed material)
	194	8	 [b]	30	1-butyne (15) + 1, 2-butadiene (?)
 CH$_3$	200	8	 [b]	20	two minor products
 C$_2$H$_5$	100	65	 	5	 (33) +  (26) +  (13) + other minor products
	300	10	 [b]  [b]	20	none
	10	60	-do- -do-	3	 (24), 2-pentyne (30), 3-methyl-1-butyne (30) + one unidentified product

a. Yields were calculated at conversions indicated in column 3

b. Identified by comparison of spectroscopic data with those of G. L. Closs, L. E. Closs and W. A. Boll, J. Am. Chem. Soc. 85, 3796 (1963); G. L. Closs, Adv. Alicyclic Chem. 1, 74 (1966)

It is evident that a general photoisomerization reaction takes place in all of these systems to yield cyclopropene derivatives. The reaction can follow two pathways from the initially formed diradical, one of which corresponds to a 1, 2-migration of a hydrogen atom and the



second, a 1, 3-migration. Since mixtures of the two products have not been observed, we shall discard the third possibility that a net 1, 3-migration occurs via two successive 1, 2-shifts. In the 1, 3-butadiene and isoprene systems, the cyclopropenes that were identified can originate only in a 1, 3-hydrogen migration. In 1, 3-pentadiene, the two paths are indistinguishable. The case of 1, 3-hexadiene is complicated by the incidental and fast photoisomerization to 2, 4-hexadienes. If the former gave rise to 1-ethyl-3-methylcyclopropene and the latter to the 1-methyl-3-ethylcyclopropene, both reactions can be explained by 1, 3-migrations. Reliable data on the kinetics of the formation of these products was difficult to obtain in the present system. Studies on the vapor phase, mercury sensitized reactions of 2, 4-hexadienes are being undertaken to help clarify this system[4]. The failure of cis-1, 3-pentadiene and 1, 3-hexadiene to yield any ethyl and propylcyclopropene respectively should also be noted.

Quantitative studies were carried out on isoprene since complications due to stereochemical choice of pathways in the formation of the diradical do not exist in this case. The plots for the formation of each of the two cyclopropenes as a function of time were satisfactorily linear and passed through the origin, which showed the photoisomerization of isoprene to these products was a primary reaction. The Stern-Volmer plot for 3, 3-dimethylcyclopropene with isoprene as the quencher was linear from 200 to 80 torr, but showed a minimum at ~ 70 torr[5]. At 10. 3 torr, the yield of the cyclopropenes had decreased to a fourth of the maximum value. At the same time, three new products were formed which were identified to be 3-methylbutyne-1, 2-pentyne, and 2-methylmethylene cyclopropane (infrared: 1753, 893 cm^{-1}; n. m. r. : 5. 25 δ -2H, multiplet; ~ 1. 1 δ -6H complex). These compounds can be explained as products of the thermal decomposition of the two dimethylcyclopropenes, which, in turn, suggests that initially, these compounds are formed in a vibrationally "hot" state. It is obvious that in earlier studies[6] on the photochemistry of 1, 3-butadiene, the formation of a cyclopropene had not been observed because these studies were generally carried out at pressures less than 50 torr. Self-quenching of the excited diene molecules undoubtedly occurs and would account for the diminution in the quantum yields for the cyclopropenes at high pressure.

In the present work (in contrast to work done in solution) the triplets of the 1, 3-dienes have been produced with as much total energy (112 Kcal/mole) as the singlet states, which undergo isomerization to cyclobutenes either in solution or in the gas phase. Hence, the failure to observe any cyclobutene in these systems is of more than passing interest[7]. It reinforces our suggestion[8] that the closure of a 1, 3-diene in an electronically excited state does not occur in the low vibrational levels of the triplet state of the diene presumably because the product (the cyclobutene) has no excited state accessible to it in terms of energy.

References

1. R. Srinivasan, Pure and Applied Chemistry (in press).
2. R. Srinivasan, Journal of the American Chemical Society 90, 4498 (1968).
3. Infrared spectra were recorded in CCl_4 solution. NMR spectra in CCl_4 with TMS or benzene as internal reference.
4. It has been shown[2] that in solution, 2, 4-hexadiene gives 1-ethyl-3-methylcyclopropene on direct irradiation.
5. A similar plot was obtained for the formation of 1, 3-dimethylcyclopropene.
6. For a review, see R. Srinivasan, Advances in Photochemistry 4, 113 (1966).
7. Since the highly-strained cyclopropenes were isolated without any difficulty, the failure to detect the cyclobutenes cannot be attributed to the thermal lability of these compounds.
8. R. Srinivasan, Journal of the American Chemical Society 91, (in press) (1969).