Tetrahedron Letters No.33, pp. 2867-2870, 1969. Pergamon Press. Printed in Great Britain.

THE MECHANISM OF ALLENE DIMERIZATION: DIMERS OF 1-CHLORO-3-MESITYLALLENE

Oliver J. Muscio, Jr. and Thomas L. Jacobs
Department of Chemistry, University of California, Los Angeles, California 90024

(Received in USA 1 April 1969; received in UK for publication 16 June 1969)

1-Chloro-3-mesitylallene was examined as part of a study of the stereochemistry of allene dimerization. After 12 hours at 80° this allene gave a mixture of four dimers (I - IV; 30-45% yield) in the approximate ratio 6:7:1:3 respectively (determined by crystallization and column chromotography on Silica Gel). Higher products accounted for the remaining 70 to 55%. Photochemically-induced iodine-catalysed isomerization of I at 60° gave unisomerized I, III, and a new dimer, V, in the ratio 2:10:1; thermal iodine-catalyzed isomerization at 125° yielded a ratio of 4:11:1. Stereochemical assignments were based primarily on NMR spectra:

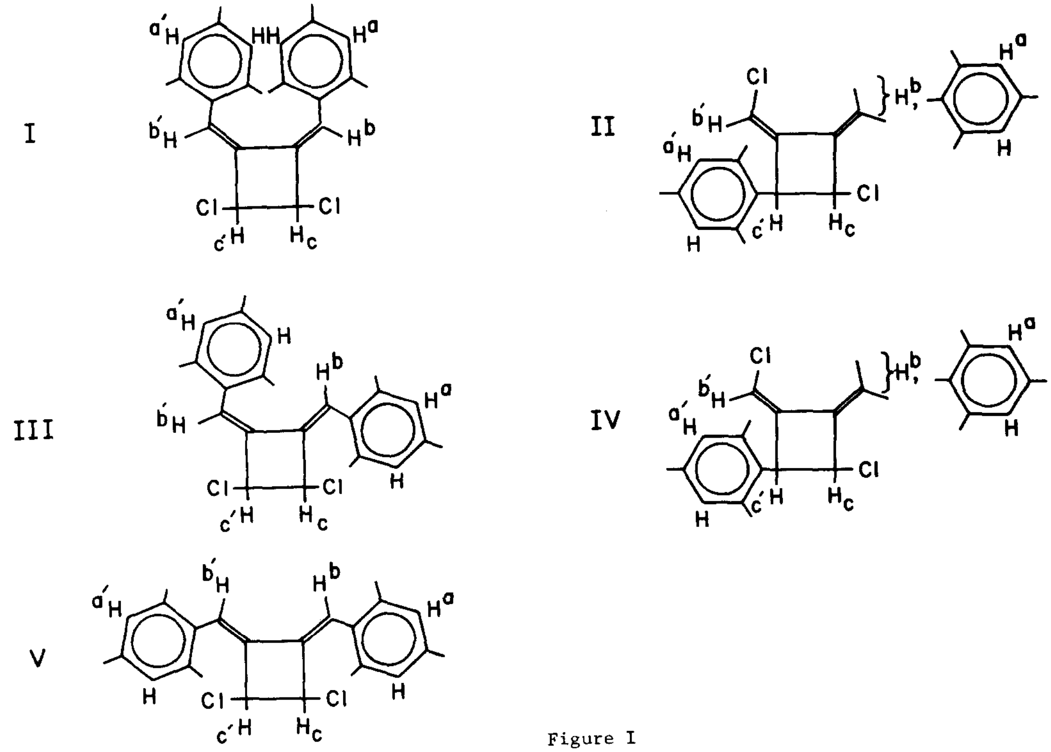


Figure I

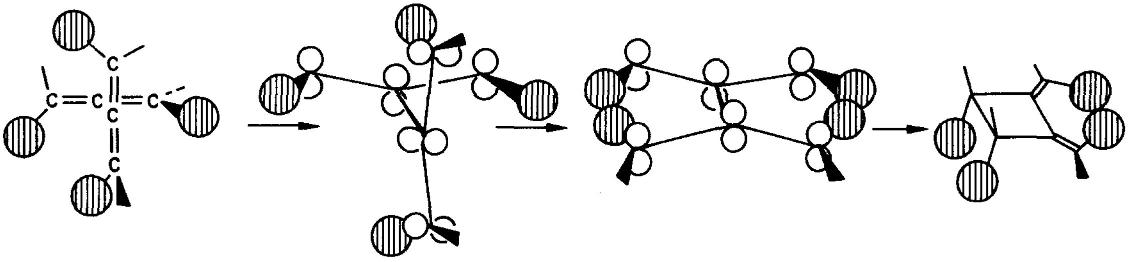
Table I Chemical Shifts of Dimers (τ)*

Dimer	a	a'	b	b'	c	c'	J_{bc}	$J_{bc'}$	$J_{cc'}$
I	3.70		3.43		5.08		1.2		
II	3.18	3.18	3.18	4.50	4.81	5.33	1.6	2.5	6.0
III	3.21	3.33	3.96	3.48	5.43	5.22	2.5	2.0	3.7
IV	3.20	3.27	3.38	4.48	5.08	5.32	1.9	3.3	6.0
V	3.12		3.12		5.32		1.5		
	*Determined in CCl_4 or $CDCl_3$ with TMS as internal reference.								

The geometry of I, III, and V is clear from the substantial shielding of the aryl protons (a) in I, and of the vinyl proton (b) in III, and the relative deshielding of the vinyl protons in V. The relative stereochemistry of II and IV is less obvious, but it is apparently the mesitylene that changes its orientation on the double bond, since the chlorovinyl proton chemical shift is the same in both dimers. This also implies that chlorine is directed inward in both, since an inward proton would be expected to be greatly affected by the change in orientation of the opposing aryl group. The relative chemical shifts of the (c) protons in II and IV compared to the trend in the I, III, and V series, and a slightly larger J_{bc} in IV compared to II (1) suggest that the vinyl mesitylene is inward in II and outward in IV, but this is not considered conclusive.

Comparison of the cyclobutyl proton chemical shifts in I, III, and V with that of the corresponding dimer of 1,1-diphenyl-3-chloroallene (τ 4.98), which is known (2) to have cis chlorines, suggests that these may be cis as well, as does the size of J_{cc} in II and IV.

Thus, the stereochemistries and product distribution of the dimers demonstrate a marked preference for putting at least one, or even both, of the two largest vinyl substituents into an inward orientation, in surprising contrast to the expected outward orientation, and the observed greater thermodynamic stability of III over I. It also appears that all of the dimers may have cis geometry at the cyclobutyl position, although this is less certain. We will show elsewhere, by means of additional examples from our laboratory and the literature that these directional tendencies appear to be general in allene dimerization, and shall attempt here to rationalize these results on the basis of a diradical mechanism, which we illustrate in Fig. II as proceeding through an orthogonal diradical VI, which flattens to a planar system VII as it closes to dimer. In fact, the diradical probably has neither geometry; it is sterically prohibited from the completely planar conformation, but gains electronic stability from any degree of planarity present, and probably has a skewed conformation. However, we find it convenient to discuss this species in terms of the two extremes, VI and VII.



VI

VII

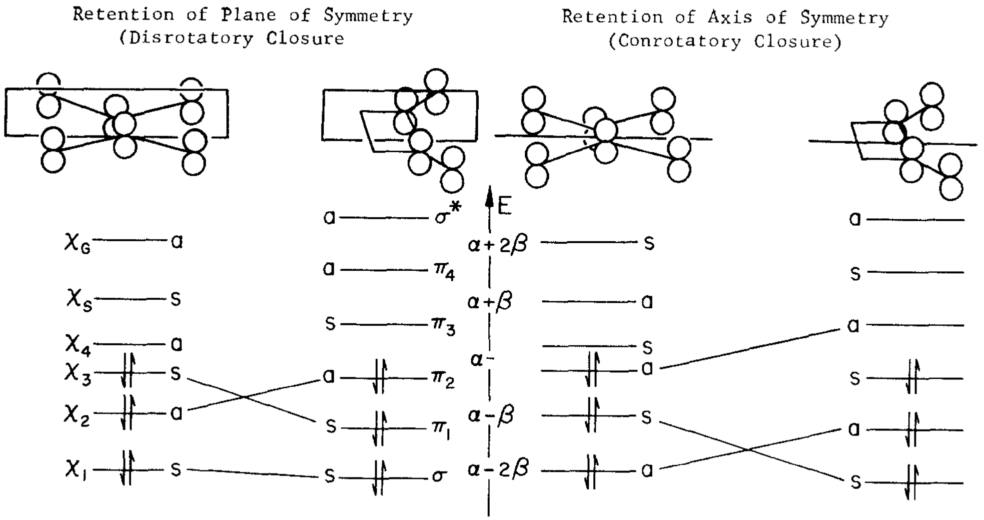
Figure II

Since formation of the diradical should be highly endothermic, and its closure highly exothermic, the transition states of these processes should closely resemble the diradical itself in both cases. Since initial approach to form the diradical, particularly, may resemble the orthogonal diradical (3), we use the orthogonal system as a model for that transition state, which, in the absence of equilibration of the diradical conformation, will determine the stereochemistry of the product upon closure. Such equilibration would necessitate rotation about an allylic bond with partial double-bond character, and is not considered likely in most systems.

Substituents on the end carbons have the choice of the inward position in the orthogonal system, represented by the balls in Fig. II, or the outward position. If a value of 1.7 Å, the half-thickness of benzene, is chosen for the Van der Waals diameter of the lobes of the opposing center p orbital, it appears that, in most cases, the inward position is actually the less crowded one, owing to 1,3-interaction of the outward substituents. Conformations of VI with some bulky substituents inward and some outward would be expected to be of intermediate stability. Ring closure of the diradical as in Fig. II then results in the preferred orientation placing the vinyl substituents in the inward positions of the dimer.

This ring closure step might occur in a disrotatory fashion as illustrated in Fig. II, giving *cis* dimers, or conrotatory, giving *trans*. We will show elsewhere (4) that the geometry is *cis* in every case where it has been reliably determined. This may be readily explained by correlation of the orbital symmetry of the planar diradical with that of the dimethylenecyclobutane system.

Zeroth order Huckel calculations indicate that the planar diradical should be a triplet with two degenerate non-bonding molecular orbitals, but consideration of non-bonded overlap removes the degeneracy of these two orbitals, suggesting the ground state should be a singlet. The results of the symmetry operations are presented in the correlation diagrams of Fig. III.


Retention of Plane of Symmetry (Disrotatory Closure

Retention of Axis of Symmetry (Conrotatory Closure)

Figure III

As can be seen, disrotatory closure with retention of the plane of symmetry is allowed, but conrotatory closure is not.

The combination of least steric crowding in the orthogonal diradical VI with formation of a 1,2-dimethylenecyclobutane by disrotatory closure accounts for the stereochemistry of allene dimerization to the limited extent it is known. However energy differences between the several relevant conformers of VI must often be small so it is not surprising that with a bulky group present as in 1-chloro-3-mesitylallene a mixture of dimers is obtained. Work is now in progress on a variety of substituted allenes to test the generality of the stereospecificity observed.

Acknowledgement: Contribution No. 2389 from the Department of Chemistry, UCLA. This research was supported by NSF Grants GP-5530 and GP-8489.

REFERENCES

(1) G. P. Newscroff and S. Sternhell, Tetrahedron Letters, 6117 (1968).
(2) P. D. Landor and S. R. Landor, J. Chem. Soc., 2707 (1963).
(3) J.D. Roberts and C. M. Sharts, Organic Reactions, 12, (1962).
(4) T. L. Jacobs, J. R. McClenon and O. J. Muscio Jr., paper in preparation.