

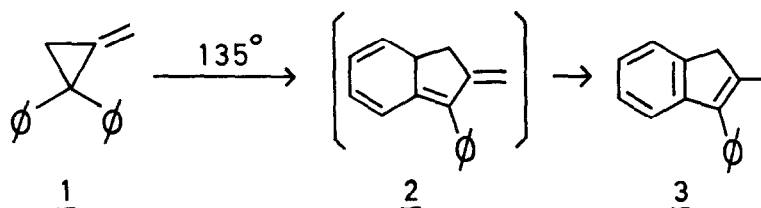
THERMAL REARRANGEMENTS OF 2,2-DIPHENYLMETHYLENECYCLOPROPANES TO INDENES¹

Maitland Jones, Jr.², Michael E. Hendrick³
Department of Chemistry
Princeton University
Princeton, New Jersey, 08540

John C. Gilbert, James R. Butler⁴
Department of Chemistry
University of Texas
Austin, Texas 78712

(Received in USA 15 January 1970; received in UK for publication 31 January 1970)

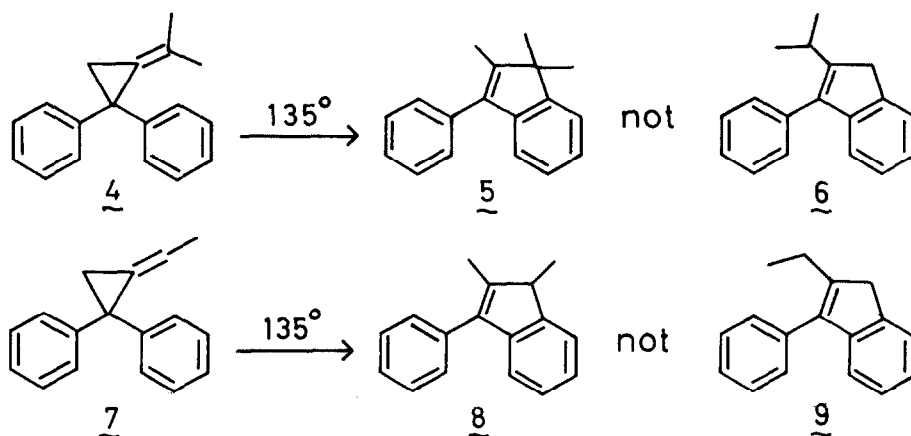
Notice has been twice taken of the thermal conversion of vinylmethylenecyclopropanes to methylenecyclopentenenes.^{5,6} We have come upon a close relative of this process in the thermal rearrangement of 2,2-diphenylmethylenecyclopropanes to indenenes. In our examples a final hydrogen shift masks the penultimate methylenecyclopentenenes.



2,2-Diphenylmethylenecyclopropane (1) was synthesized by the irradiation of diphenyldiazomethane in allene.⁷ Rearrangement of 1 to 2-methyl-3-phenylindene (3) could be accomplished either by gas-chromatography⁸ or by heating a degassed carbon tetrachloride solution. Indene 3 is known, as is the indene with the positions of the methyl and phenyl groups interchanged.⁹⁻¹¹ The distinction between the two rests both on a comparison of melting point and spectra¹² and an additional independent synthesis from 2-methyl-1-indanone. The structural course of the rearrangement is thus assured.

2,2-Diphenylmethylenecyclopropanes 4 and 7 which bear methyl groups on the exocyclic double bond also rearrange to indenenes and exhibit a remarkable specificity in so doing. Only indene having the added methyl groups at the 1-position is formed. Thus 4 gives only 5 and not 6, and 7 gives 8

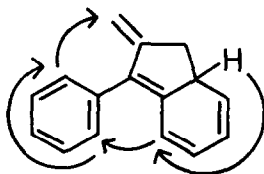
and not 9. Inspection of the nmr spectra fixes the methyl substitution at the 1 and 2 positions, and the ultraviolet spectra require that the phenyl group occupy the 3 position.¹³ As little as 1-2% of compounds 6 and 9 could easily have been detected. This specificity is not mirrored in the rearrangements studied by Shields and Billups,⁶ and may be associated with the apparent instability of 2,2-diphenyl-3-methylmethylenecyclopropane (10) relative to 7. Isomers 7 and 10 are related, at least formally, through a methylenecyclopropane rearrangement.^{16,17}



There is a surfeit of potential mechanisms for these changes, and we cannot yet make definitive distinctions between the alternatives. The intermediacy of 2 seems assured, although we have as yet been unable to trap it as a Diels-Alder adduct. The elusiveness of 2 might have been anticipated, as it is not expected to be a particularly reactive diene. Moreover, the gain in molecular stabilization associated with the formation of a new benzene ring probably serves as a thermodynamic driving force for the further conversion of 2 to 3. No such stabilization attends the analogous hydrogen shift in the simpler systems studied previously, and there it does not occur.⁶

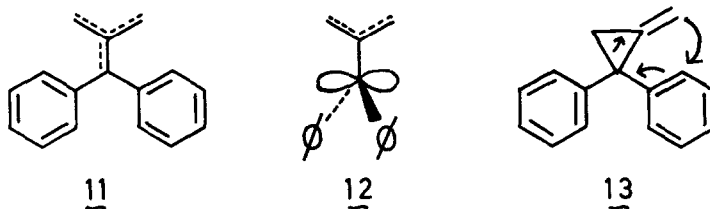
The hydrogen shift required to convert 2 to 3, although of the allowed 1,5 variety,¹⁸ is sterically difficult, and it is perhaps surprising that it occurs as rapidly as it does. We tentatively suggest that the hydrogen

shift may proceed not in a direct manner but rather via a conducted tour of four swoops, each a 1,5 shift. In this scheme the phenyl group provides a crucial link in the transportation of the migrating hydrogen to its goal.



Some support for this suggestion derives from the observation that 2-phenyl-methylenecyclopropane, which would give an intermediate tetraene lacking the phenyl ring necessary to consummate the tour, does not rearrange to an indene even when heated to 190° for one hour.

The detailed mechanism for the formation of 2 can proceed through a variety of intermediates, the most attractive of which are 11 and 12. Alternatively, a concerted process (13) resembling a Cope rearrangement is possible. Both 11 and 12 as well as the concerted reaction 13 are capable of explaining the



observed facts, including the specificity of the indene formation. Experiments designed to permit differentiation between the various mechanisms are in progress.

Acknowledgement. M. J., Jr. and M. E. H. are indebted to Professor Peter P. Gaspar and Messrs. Thomas M. Gorrie and Ronald H. Levin for enlightening conversations.

REFERENCES AND NOTES

- 1) We are pleased to thank the National Science Foundation for support, through Grant GP-7819, of the portion of this work performed at Princeton, and the Robert A. Welch Foundation for support of the work done at the University of Texas.
- 2) Alfred P. Sloan Research Fellow, 1967-9.
- 3) National Science Foundation Predoctoral Fellow, 1967-70.
- 4) N.D.E.A. Title IV Fellow, 1967-70.
- 5) T. C. Shields, W. E. Billups and A. R. Lepley, J.Amer.Chem.Soc., 90, 4749 (1968).
- 6) T. C. Shields and W. E. Billups, Chem. and Ind., 619 (1969).
- 7) New compounds were characterized by elemental analysis and examination of appropriate spectra.
- 8) Compound 1 can be isolated by gas-chromatography, but only under very specific conditions. A 1', 10% FFAP on 45/60 mesh Chromosorb P column operated at 120° with injector: 130°, detector: 130° and a flow rate of 100 ml/min He eluted unchanged 1, but all other columns tried gave only 3.
- 9) H. Christol, C.Martin and M.Mousseron, Bull.soc.chim.France, 1696(1960).
- 10) N.D.Heindel, S.McN.Lemke and W.A.Mosher, J.Org.Chem., 31, 2680(1966).
- 11) F. Mayer, A. Sieglitz and W. Ludwig, Ber., 54, 1397 (1921).
- 12) We thank Professor W. A. Mosher for providing the nmr spectrum of the alternate indene, 2-phenyl-3-methylindene.
- 13) 3, 263 nm;⁹ 5, 222,258 nm; 8, 220,260 nm; 1,1-diphenylethylene, 205,229, 250 nm;¹⁴ trans-stilbene, 297,309 nm;¹⁵ 2-phenyl-3-methylindene, 293 nm.⁹
- 14) UV Atlas of Organic Compounds, Vol. 1, Butterworths, Ltd., London, 1966.
- 15) R. N. Beale and E. M. F. Roe, J.Amer.Chem.Soc., 74, 2302 (1952).
- 16) J. P. Chesick, ibid., 85, 2720 (1963).
- 17) J. C. Gilbert, and J. R. Butler, ibid., 92, 0000 (1970).
- 18) R. B. Woodward and R. Hoffmann, J.Amer.Chem.Soc., 87, 2511 (1965).