Thermal Rearrangements in the Tetra-arylcyclopropene Series

By MERLE A. BATTISTE*, BRIAN HALTON, and ROBERT H. GRUBBS

(Department of Chemistry, University of Florida, Gainesville, Florida 32601)

THE literature provides many examples of thermal rearrangements of small-ring compounds to yield systems involving less bond-angle strain.[1] In the arylcyclopropene series these involve, in many cases, fairly complex pathways, and only formalized mechanisms have been suggested.[1,2] Tetra-aryl-cyclopropenes have the advantage of no labile hydrogen atom, exhibit moderate thermal stability, and would be expected to yield only primary products from ring cleavage. We now report that 3-aryl-1,2,3-triphenylcyclopropenes (I) readily available by action of the appropriate aryl Grignard reagent on triphenylcyclopropenyl bromide, re-arrange, either in a melt above 200° or in solution at somewhat lower temperatures, to 1,2,3-triaryl-indenes. The rearrangement also proceeds under acidic conditions at considerably lower tempera-ture.[3]

Molten tetraphenylcyclopropene (Ia)[4] rearranged at 235—240° in almost quantitative yield to 1,2,3-triphenylindene (IIa)§ The rearrangement exhib-ited first-order kinetics in diphenyl ether (88%)–quinoline (12%) (See Table), but was sensitive to traces of acid and oxygen.†

† Analysis was by n.m.r. integration, at 120°, of the increasing 1-indenyl proton (τ 4·93) against the aliphatic protons of fluorene (τ 6·28) used as an internal standard. The average of 12 integrations was taken for each point. Erratic kinetic behaviour was observed for tubes sealed at pressures greater than 10^{-4} mm. Hg, and with less than 12% quino-line in the solvent mixture. Since (IIa), as well as most triarylindenes, fluoresces strongly in the visible the rearrange-ment can also be conveniently followed by fluorimetry.

Triphenylindene formation from (Ia) under thermal conditions can be formally written in three ways: (i) a homolytic cleavage of a ring carbon–carbon single bond giving rise to a diradical intermediate; (ii) a heterolytic cleavage yielding ionic intermediates; and (iii) a concerted process. The

SCHEME
R = (a) Ph; (b)
p-anisyl; (c) mesityl
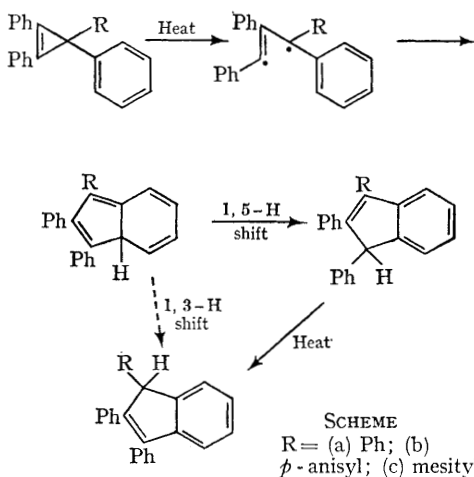
diradical route is shown in the Scheme. Aromatization of the intermediate isoindene (III) affords indene (II) by a thermally favoured 1,5-hydrogen shift,[6] but (IV) may also arise by a series of 1,5-hydrogen shifts, before or after aromatization or directly by a less favoured 1,3(1,7)-hydrogen shift. A similar set of indene products would result from ring opening followed by ring closure on to the 3-aryl substituent. Preliminary investigations with 3-p-anisyl-1,2,3-triphenylcyclopropene (Ib),‡ support this product scheme. Two major indene components, contaminated with isomeric impurities, are obtained from the thermal rearrangement of (Ib) at 200°.

With the ortho-positions of the aryl group of (I) formally blocked towards further substitution, the product distribution on rearrangement should be greatly simplified. Thus, heating 3-mesityl-1,2,3-triphenylcyclopropene (Ic) at 190—200° for 2 hr. afforded two cleanly separable indene products, m.p. 179—181° and 131—132°, in about equal amounts. The higher-melting product [λ_{max} (CHCl$_3$) 330 (sh), 315 (sh), 307, and 240 mμ; n.m.r., complex multiplet at τ 2·84 (17H), sharp singlet at 4·73 (1H), doublet centred at 7·65 (6H), and sharp singlet at 8·12 (3H)] has been identified as 3-mesityl-1,2-diphenylindene (IIc). The nonequivalence of the ortho-methyl groups of the pendant

mesityl ring in (IIc) is attributed to restricted rotation of this group. The lower-melting isomer [λ_{max} (CHCl$_3$) 297·5 and 240 mμ; n.m.r., complex multiplet at τ 2·80 (17H) with sharp singlets at 7·74 (3H), 8·10 (3H), and 8·30 (3H)], at first suspected to be the 1-mesitylindene (IVc), is now tentatively assigned the 1,4,6-trimethyl-1,2,3-triphenylindene structure (V) on the basis of the highly non-equivalent nature of the methyl groups in the n.m.r. spectrum, the stability to base under aerobic conditions, and the mode of formation involving a 1,5-methyl shift from isoindene intermediate (VI).

(V)   (VI)
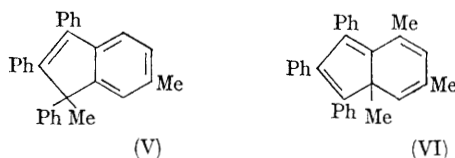
The formation of (V) on thermal rearrangement of (Ic) is taken as evidence for the diradical nature of the rearrangement, despite the fact that we have not, as yet, been able to trap the intermediate by conventional means. Thermal rearrangement of (Ia) in cumene gave almost quantitative yields of (IIa) with no evidence of bicumyl formation. Similar trapping attempts with methyl acetylene-dicarboxylate were unsuccessful.

The above arylcyclopropene–indene rearrangements are analogous to the better studied vinyl-cyclopropane rearrangements,[1] but to our knowledge there is no report in the literature of corresponding indane formation from arylcyclopropanes. For the purpose of comparison, cis-1,1,2,3-tetraphenylcyclopropane (VII) was synthesized in 78% yield by di-imide reduction[4,7] of (Ia). Heating (VII) in diphenyl ether at 200° for 3 hr. resulted in quantitative rearrangement to the trans-isomer (VII).[8] No olefin or indane products were detected even at higher temperatures. The first-order rate parameters for the isomerization (Table) were determined by the n.m.r. technique, integrating the respective singlets for the cis- and trans-cyclopropyl protons.

From the Table it is seen that the isomerization
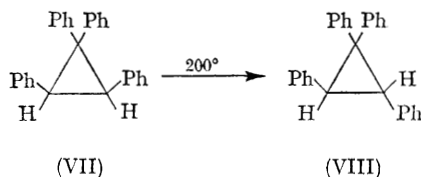
(VII)   (VIII)

‡ Satisfactory analytical data were obtained for all new compounds reported.

TABLE

Kinetic parameters in diphenyl ether

Isomerization	$T(°c)$[b]	$10^5 k$ (sec.$^{-1}$)	E_a (kcal./mole)	log A
(I) → (II)[a]	176·7	0·450 ± 0·035	40 ± 1	14·0 ± 0·5
	205·1	5·76 ± 0·28		
(VII → (VIII)	176·6	4·93 ± 0·08	38·4 ± 0·2	14·3 ± 0·1
	155·5	0·602 ± 0·009		

[a] solvent contains 12% (by wt.) of quinoline; [b] ± 0·2°.

of (VII) proceeds at a rate approximately ten times that for the rearrangement of (Ia) to (IIa). While this rate difference is small, it is significant that opening of the cyclopropane ring is occurring faster than that for the more highly strained cyclopropene. This result must have some bearing on the nature and stability of the intermediates involved, and argues against a concerted process. In terms of the radical mechanism, however, homolytic cleavage of (VII) would lead to a more stable diradical than that obtained from (Ia), accounting for the observed kinetic data and lack of indane formation from the arylcyclopropane.

[1] R. Breslow in "Molecular Rearrangements", Part I, ed. P. de Mayo, Interscience, New York, 1963, pp. 236—261.

[2] R. Breslow and P. Dowd, *J. Amer. Chem. Soc.*, 1963, **85**, 2729; R. Breslow, P. Gal, H. W. Chang, and L. J. Altman, *ibid.*, 1965, **87**, 5139.

[3] M. A. Battiste and R. B. Grubbs, in preparation.

[4] M. A. Battiste, *Tetrahedron Letters*, 1964, 3795.

[5] E. P. Kohler, *Amer. Chem. J.*, 1908, **40**, 217.

[6] W. R. Roth, *Tetrahedron Letters*, 1964, 1009.

[7] R. S. Dewey and E. E. van Tamelen, *J. Amer. Chem. Soc.*, 1961, **83**, 3729; E. W. Garbisch, jun., S. M. Schildcrout, D. B. Patterson, and C. M. Sprecher, *ibid.*, 1965, **87**, 2932.

[8] An independent synthesis of (VIII) by photocyclization of the 1,3,3,3- and 1,1,3,3-tetraphenylpropenes has been previously reported by G. W. Griffin, A. F. Marcantonio, H. Kristinsson, R. C. Petterson, and C. S. Irving, *Tetrahedron Letters*, 1965, 2951. These authors also observed the thermal isomerization of (VII) to (VIII), and we are indebted to them for a complete interchange of compounds and structural data.