Thermal Rearrangements of Aryldimethylvinylidenecyclopropanes and Aryldimethylenecyclopropanes †

By **I. H. Sadler** * and **J. A. G. Stewart,** Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

1-Dimethylvinylidene-2-methyl-2-phenylcyclopropane (1a) undergoes thermal rearrangement in solution (130°) or in the vapour phase (350°) to give 2-isopropylidene-1-methylene-3-methyl-3-phenylcyclopropane (6a) exclusively.   A kinetic study in solution over the temperature range 120—155° yields values for the activation parameters of 30·4 kcal mol^{-1} for E_a, and −2·5 e.u. for $\Delta S^{\ddagger}$, which are shown to be consistent with the intermediacy of an orthogonal diradical.   Similar rearrangements are undergone by a series of six related dimethylvinylidene cyclopropanes.   Rearrangement of cis- and trans-1-dimethylvinylidene-2-methyl-3-phenylcyclopropanes (9) and (10) is kinetically controlled at 130° yielding mainly syn-1-ethylidene-2-isopropylidine-3-phenylcyclopropane (11); equilibration of the latter compound with the anti-isomer (12) became significant at 180°.   The relative rates of rearrangement of compounds (9) and (10) to products (11) and (12) are explained in terms of the interactions of the substituents bonded to the phenyl-substituted carbon atom and the substituents and the incipient half-filled p-orbital on the methyl-substituted carbon atom.   At higher temperatures (530°) the cyclopropanes (1a) and (6a) and 3,3-diphenyl-2-isopropylidene-1-methylenecyclopropane (6e) undergo further rearrangement to 1,2,3-trisubstituted indene derivatives.

THE thermal self interconversions of simple methylenecyclopropanes are of considerable current interest.[1,2] The available evidence, although not entirely conclusive, suggests that the rearrangements probably involve the formation of intermediate trimethylenemethane diradicals of the orthogonal type in preference to fully delocalised planar diradicals and that an alternative symmetry-allowed concerted process is unlikely.

The related allene derivatives, vinylidenecyclopropanes, have received somewhat less attention. The simpler alkyl derivatives rearrange in a manner analogous to the methylenecyclopropanes to give dimethylenecyclopropanes.[3] Some preliminary reports of the rearrangements of aryl derivatives have also appeared.[4-6] We now report a product study of the thermal rearrangements at various temperatures of a number of aryl dimethylvinylidenecyclopropanes, a detailed kinetic study of the rearrangement of one of these, and the rearrangement of the products at higher temperatures.

RESULTS AND DISCUSSION

The allenes (1a—e), (7a,b), (9), and (10) were obtained as 1 : 1 adducts of dimethylvinylidene carbene and the appropriate parent olefins. Optimum yields (>50%) of adducts were obtained using a twofold excess of 1-bromo-3-methylbuta-1,2-diene and potassium t-butoxide to generate the carbene with light petroleum as solvent. This bromo-diene was found to be superior, as has been reported elsewhere,[7] to the corresponding chloro-diene or 3-chloro-3-methylbut-1-yne[8] for adduct formation, and unlike these is readily obtained in excellent yield from ethynyldimethylmethanol. The use of an inert solvent rather than excess of olefin[8] allowed the cyclopropanes to be prepared from relatively small amounts of olefins. As expected the additions to cis- and trans-β-methylstyrene

proceeded stereospecifically. The structures of the allenes were confirmed by i.r. and ^{1}H n.m.r. spectroscopy and all the allenes were markedly susceptible to aerial oxidation and underwent polymerisation unless stored below 0°. The i.r. spectra of these compounds all show allenic absorption at slightly higher frequencies (2010—2030 cm^{-1}) than that normally observed (1960—1980 cm^{-1}) no doubt due to the additional strain imposed by the three-membered ring. Attempts to prepare adducts from cis- and trans-stilbene were unsuccessful, starting material only being recovered. The failure of these compounds to form cyclopropanes by this method suggests that the rates of the competing reactions of the carbene with t-butyl alcohol and t-butoxide ion are faster than the reactions with the olefins.

The dimethylvinylidenecyclopropanes (1a) and (1b) underwent complete and exclusive rearrangement to the 2-isopropylidenecyclopropanes (6a) and (6b) respectively in good yield when heated in xylene at 140° for 3 h. Prolonged heating resulted in some loss of product by polymerisation. However, excellent (>85%) yields of rearrangement products were obtained by a low-pressure vapour-phase pyrolysis technique in which the allenes were carried in a stream of nitrogen through a flow system at 350°. The rearrangement of the (p-tolyl)-vinylidenecyclopropane (1c) under similar conditions to give an analogous product (6c) demonstrated that the course of the rearrangement was unaltered by alkyl substitution in the para-position of the aromatic ring. Similarly the spiro-vinylidenecyclopropanes (7a,b) smoothly underwent rearrangement to form 2′-isopropylidene-3′-methyleneindane-1-spiro-1′-cyclopropane (8a) and the tetralin homologue (8b) respectively. The

[1] J. P. Chesick, J. Amer. Chem. Soc., 1963, **85**, 2720.
[2] W. von E. Doering and H. D. Roth, Tetrahedron, 1970, **26**, 2825; J. J. Gajewski, J. Amer. Chem. Soc., 1971, **93**, 4450, and the references contained therein.
[3] J. K. Crandall and D. R. Paulson, J. Amer. Chem. Soc., 1966, **88**, 4302; D. R. Paulson, J. K. Crandall, and C. A. Bunnell, J. Org. Chem., 1970, **35**, 3708.
[4] I. H. Sadler and J. A. G. Stewart, Chem. Comm., 1970, 1588.
[5] T. B. Patrick, E. C. Haynes, and W. J. Probst, Tetrahedron Letters, 1971, 432; J. Org. Chem., 1972, **37**, 1553.
[6] M. E. Hendrick, J. A. Hardie, and M. Jones, J. Org. Chem., 1971, **36**, 3061.
[7] S. R. Landor and P. F. Whiter, J. Chem. Soc., 1965, 5626.
[8] H. D. Hartzler, J. Amer. Chem. Soc., 1961, **83**, 4990.

methoxycyclopropane (1d) also readily formed the dimethylenecyclopropane (6d) which was particularly susceptible to polymerisation. The diphenylcyclopropane (1e) was particularly thermally labile and on vacuum distillation (110°/0·01 mm) underwent 80% rearrangement to diphenyldimethylenecyclopropane (6e).

methane diradical (3) in which the unpaired electrons occupy orbitals resembling those of resonance-stabilised allyl and benzyl radicals. Recombination by bond formation between carbon atoms C(2) and C(4) leads to the observed products (6). A fully planar structure for trimethylenemethane diradicals has been shown to be

a;	R = Me	Ar = Ph
b;	R = H	Ar = Ph
c;	R = Me	Ar = p-Me·C$_6$H$_4$
d;	R = MeO	Ar = Ph
e;	R = Ph	Ar = Ph
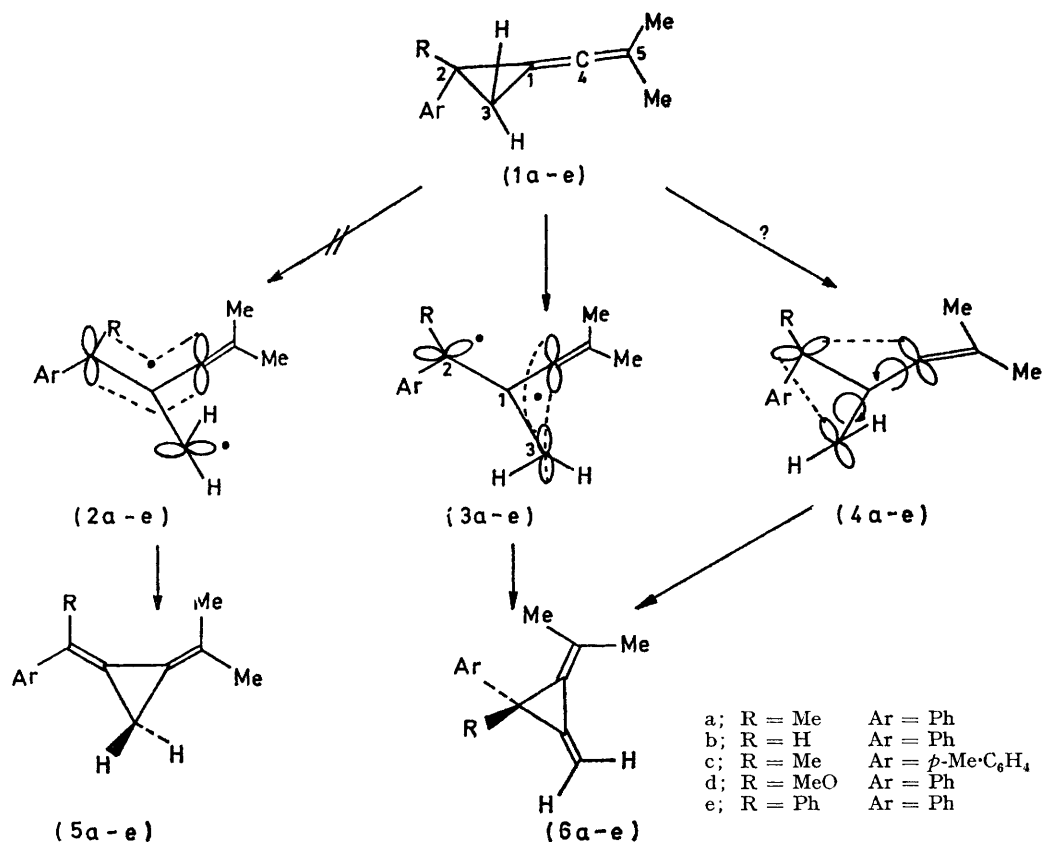
The dimethylene cyclopropanes show bands in their i.r. spectra characteristic of the terminal olefinic methylene group (880—910 cm^{-1}) and of strained exocyclic double-bonds (ca. 1800 cm^{-1}); the u.v. spectra are consistent with a conjugated diene system ($\lambda_{max.}$ 245—255 nm) and the structures are confirmed by the ^{1}H n.m.r. spectra. In no case was there any evidence for the formation of the isomeric benzylidenemethylenecyclopropanes (5a—e). Calculation of the heats of formation of the compounds (1a—e), (5a—e), (6a—e) using standard additivity data [9] indicate that the observed products (6a—e) are thermodynamically more stable than the corresponding reactants (1a—e) by ca. 2—3 kcal mol^{-1} but less stable than the isomeric benzylidenemethylenecyclopropanes (5a—e) by ca. 3—4 kcal mol^{-1}.

The rearrangement of vinylidenecyclopropanes resembles the methylenecyclopropane interconversion [1,2] and can be satisfactorily rationalised by a path which involves homolytic fission of the C(2)—C(3) bond of the cyclopropane ring to form an orthogonal trimethylene-

unlikely on theoretical grounds [10] and examination of stereomodels in the present case shows that coplanarity would result in severe steric interactions. The alternative diradical (2), is equivalent to a combination of a

a; n = 2
b; n = 3
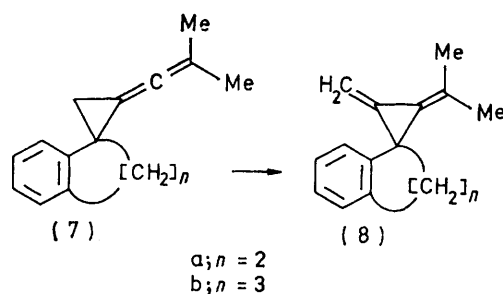
primary radical and a cinnamyl radical and would therefore be expected to be less stable than the diradical (3). Since only the diradical (2) can lead to the formation of the thermodynamically more stable isomeric benzylidenemethylenecyclopropanes (5), the absence of the latter is explained.

[9] S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, Chem. Rev., 1969, 69, 279.

[10] M. J. S. Dewar and J. S. Wasson, J. Amer. Chem. Soc., 1971, 93, 3081.

An alternative mechanism involves concerted ring-opening and bond formation *via* a symmetry-allowed $(\pi^2{}_s + \sigma^2{}_a)$ process. Such a process requires the simultaneous rotation of C(3) and C(4) to ensure adequate overlap of the associated orbitals with the orbital on the migrating atom C(2) in the transition state (4). However, any lowering in energy resulting from this additional electron delocalisation would be offset to some extent by an energy increase resulting from the reduced overlap in the lowest energy π-orbital of the C(1)–C(4)–C(3) system. Since the electron distribution in such a transition state is likely to resemble that of the diradical (3) the formation of the benzylidenemethylenecyclopropanes would also be unfavourable by this route. The greater ease of rearrangement of the diphenylcyclopropane (1e), which has also been noted elsewhere,[6] is also compatible with each mechanistic alternative, the two phenyl groups offering a higher degree of stabilisation to the intermediate diradical (3e) or rendering the transition state (4e) more accessible. Attempts to trap the diradical (3a) by carrying out the rearrangement of the allene (1a) in hexachlorobutadiene, 1,2-dichloroethylene, 2,3-dimethylbut-2-ene, or cumene in sealed tubes at 140° were unsuccessful, the cyclopropane (6a) being the only product. No bicumyl was detected using cumene as the solvent. Such negative results, however, do not exclude the formation of the diradical (3a) and suggest that if it is formed, the rate of ring closure is significantly faster than an alternative reaction.

The activation parameters were determined for the unimolecular rearrangement of the dimethylvinylidenecyclopropane (1a) in dilute solution (10^{-4}M) in decalin over the temperature range 120—155° by following the appearance of the diene absorption (246 nm) of the product (6a). First-order plots showed slight deviations from linearity after *ca.* 75% reaction suggesting that the product was slowly consumed by a non-first-order process. An alternative procedure in which the disappearance of the allene absorption (2010 cm^{-1}) of the reactant was followed, using a thousand-fold increase in initial concentration gave rate constants in good agreement with the high dilution method, thus verifying that the rearrangement was first order. Rate constants correlated well ($r = 0.9997$) with the Arrhenius equation which gave a value for the activation energy of 30·4 ($\pm$0·3) kcal mol^{-1}, and for log A of 12·82 corresponding to an entropy of activation, $\Delta S^{\ddagger}$ of -2.5 ($\pm$0·7) e.u. An assessment of the activation energy for a diradical process can be made [2] from that for the cleavage of a carbon–carbon bond in cyclopropane (64·2 kcal mol^{-1}), the incremental strain [9] due to an associated exocyclic methylene group (13·3 kcal mol^{-1}), and the resonance stabilisation energies [11] of benzyl and allyl radicals (13·5 and 10·8 kcal mol^{-1} respectively). Examination of molecular models of the reactant shows that the aromatic ring may readily adopt an orientation which allows the maximum overlap

[11] H. E. O'Neal and S. W. Benson, *Internat. J. Chem. Kinetics*, 1969, **1**, 221.
[12] H. M. Frey and R. Walsh, *Chem. Rev.*, 1969, **69**, 103.

of the π-system with the cyclopropane bond undergoing fission and therefore virtually full resonance assistance by the aryl group may be expected. The π-system of the exocyclic group is initially at right angles to the breaking bond and therefore the extent of its assistance will depend upon the orientation of the methylene group with respect to double bonds in transition state. The contribution due to the relief of additional strain will depend upon the degree of ring opening in the transition state. The above literature data suggest that the activation energy for a diradical process should therefore not be less than *ca.* 26 kcal mol^{-1}. The observed value of the activation energy (30·4 kcal mol^{-1}) is thus consistent with such a process in which there is significant participation by the aromatic ring and the exocyclic double-bond together with relief of much of the strain associated with the exocyclic double-bond, and suggests that the transition state to the diradical (3) bears rather more resemblance to the diradical than to the starting material. As in the methylenecyclopropane self-interconversion, it is not necessary to propose an additional element of concert to obtain a satisfactory estimate of the activation energy. Ring-opening reactions proceeding *via* acyclic transition states, in which free rotations are generated, are normally accompanied by a positive entropy of activation.[12] In the present situation only a single highly restricted rotation about C(1)–C(2) is produced and so a value of $\Delta S^{\ddagger}$ close to zero is expected. The slightly negative value, if significant may be attributed to the loss in rotation of the aryl group which must occur if the aryl-group is to participate as suggested above. It is noteworthy that the entropy of activation is slightly positive (*ca.* +3 e.u.) for the interconversion[1,2] of methylmethylenecyclopropane and ethylidenecyclopropane where obviously aryl participation cannot occur.
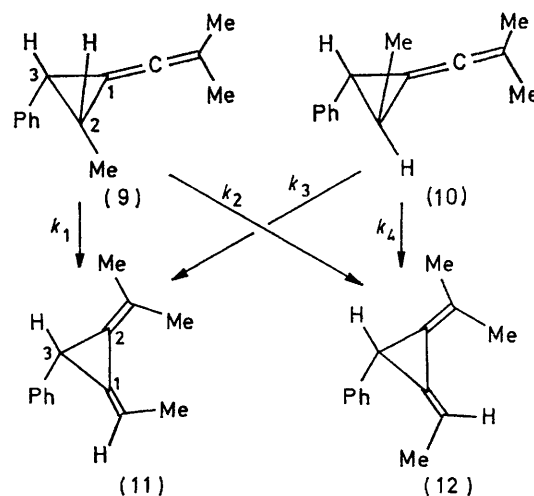
Both the *cis-* and *trans-*dimethylvinylidenecyclopropanes (9) and (10), rearrange in solution and the gas phase to yield mixtures of the *syn-* and *anti-*ethylidenecyclopropanes (11) and (12). The stereochemistry of each was assigned from its n.m.r. spectrum. It is to be expected that the olefinic proton of the *anti-*isomer (12)

will resonate downfield in the n.m.r. spectrum relative to that of the *syn*-isomer (11) since the former resides in the deshielding region of the neighbouring isopropylidene group. On this basis the *anti*-structure was allocated to that isomer showing olefinic absorption at τ 4·2, the *syn*-isomer showing olefinic absorption at τ 4·5. The proportions of the two thermolysis products were strongly dependent upon the reaction conditions employed. Rearrangement of the *cis*-isomer (9) in xylene solution at 130° was complete after 3 h and gave the *syn*- and *anti*-products in the ratio 87 : 13. Rearrangement of the *trans*-isomer (10) was complete after 2 h with a corresponding product ratio 98 : 2; during a further 1 h this ratio changed to 96 : 4 and reached 90 : 10 after a total reaction time of 10 h. Thus product isomerisation is not solely responsible for different product ratios obtained

competes effectively with rearrangement process. The equilibrium constant (2·34) for the interconversion process of (11) and (12) leads to a free-energy difference of 0·77 kcal mol⁻¹, which presumably arises from the interaction of the two methyl groups which is present only in the *syn*-isomer (11). Examination of stereo-models shows that this interaction is similar to that between the two methyl groups in *cis*-butene, where the interaction is *ca.* 1 kcal mol⁻¹.

The overall rates of rearrangement of the allenes (9) and (10) at 130° were found to be $5·63 \times 10^{-4}$ and $1·32 \times 10^{-3}$ s⁻¹ respectively. Taken with the *syn* : *anti* product ratios, these overall rates indicate that rates $(k_1—k_4)$ for the individual rearrangement of allenes (9) and (10) to cyclopropanes (11) and (12) are such that $k_3 \simeq 2·5\ k_1 \simeq 15\ k_2 \geqslant 50\ k_4$. This assessment is approximate in view
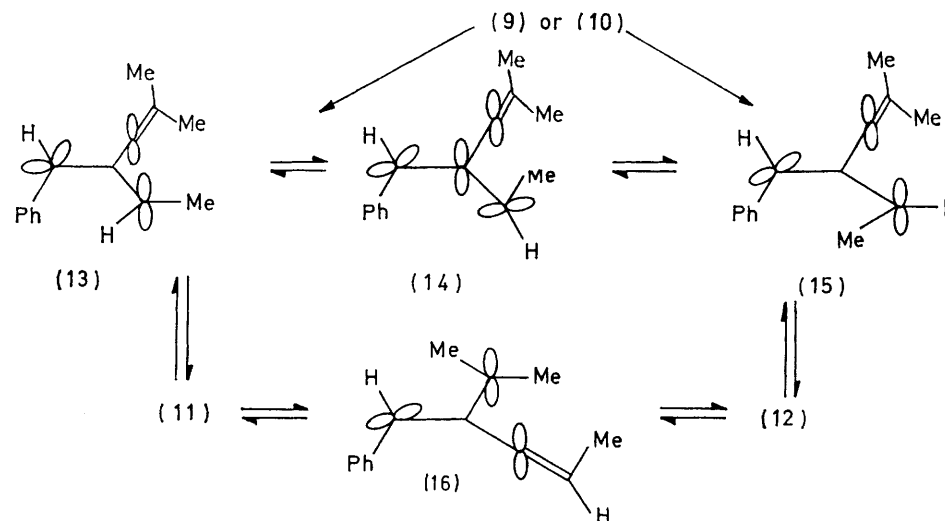
from the allenes (9) and (10). In a separate experiment the rearrangement of the *cis*-isomer was monitored by n.m.r. spectroscopy. The absence of signals due to the *trans*-isomer demonstrated that isomerisation, if any, of the starting material to the *trans*-form was not competitive with the rearrangement process. Passage of either of the allenes (9) or (10) or the product mixtures, or the pure products separately through a preparative v.p.c. column at 180° (1 h) gave mixtures of the *anti*- and *syn*-products in the ratio 7 : 3. The composition of these mixtures remained unchanged on recycling through the column, indicating that thermodynamic equilibrium had been attained. Prolonged heating (7—9 h) of each of the pure isomeric dimethylenecyclopropanes (11) and (12) at 130° by passage through the preparative v.p.c. column resulted in mixtures whose composition confirmed that at this temperature the interconversion process is slow compared with the vinylidenecyclopropane rearrangement reaction. These results indicate that at the lower temperature the rearrangement is kinetically controlled resulting in the predominance of the thermodynamically less-stable isomer (11). At the higher temperature thermodynamic equilibration of the isomers

of the small amount of product isomerisation which occurs during the rearrangement.

The higher rates of formation of the *syn*-product from both *cis*- and *trans*-isomers is consistent with the diradical mechanism described above. Rupture of the C(2)–C(3) bond in the allenes (9) and (10) is accompanied by the sterically more favourable rotation of the methyl group away from the migrating atom C(3) to give the diradical (13), which must lead to the *syn*-isomer. The alternative inward rotation of the methyl group which results in the diradical (15) and hence the *anti*-isomer, results in severe steric interaction between the methyl group and the substituents at the migrating carbon atom, C(3).

The relative rates also clearly demonstrate, as expected, that the allenes (9) and (10) pass through different transition states to the diradical (13), and also to the diradical (15). Initially unexpected are the observations that the *syn*-product (11) is formed faster from the *trans*-isomer (10) than from the *cis*-isomer (9), yet the reverse is true for the formation of the *anti*-product (12). This is in contrast to what would be expected on the basis of interaction between the substituents on C(2) and C(3) alone. These observations

may be rationalised in terms of an unfavourable interaction between the incipient half-filled p-orbital on C(3) and the substituents on C(2). Formation of the *syn*-product from the *trans*-isomer necessitates movement of the rotating orbital on C(3) away from the aromatic ring past the hydrogen atom on C(2), which would be expected to be more favourable than the formation of the *syn*-product from the *cis*-isomer which requires the rotating orbital to pass the more bulky aromatic ring. Such an effect would only be felt in the initial stages of bond breakage which no doubt accounts for its relatively small magnitude, compared with the dominant effect of the interaction of the substituents on the rates.

Two paths can be proposed for the interconversion of the *syn*- and *anti*-products (11) and (12). One involves breakage of the C(2)–C(3) bond in either product to form the appropriate diradical (13) or (15) followed by diradical isomerisation and ring closure. The two diradicals, however, are interconvertible only *via* a higher-energy bis-orthogonal diradical (14) in which allylic resonance stabilisation is lost. The alternative path requires breakage of the C(1)–C(3) bond in one product accompanied by rotation of C(1) to form a new orthogonal diradical (16) which by further rotation and ring closure yields the isomeric product. The possibility of the formation of the diradical (16) is reinforced by material presented later. Since the latter path does not involve the loss of resonance stabilisation which must occur in the former, the latter is considered to be the more likely isomerisation path; a full kinetic study however would be necessary before a clear distinction could be made.

The vapour-phase rearrangement of the dimethylvinylidenecyclopropane (1a) at 530° yielded a mixture of compounds containing three major components (90% of the total) (A), (B), and (C) in the ratio 20 : 14 : 9. The same product ratio was obtained from the isopropylidenecyclopropane (6a), and remained unaltered on recycling the product mixture through the flow system under the same conditions. The components were separated by preparative v.p.c. and their structures assigned from spectroscopic data and by the analogy of the reaction with the thermal conversion [13] of 1-methylene-2,2-diphenylcyclopropane to 2-methyl-3-phenylindene. Compound (A) was identified as 1-isopropenyl-2,3-dimethylindene (21), readily distinguishable from the other possible 1,2,3-trisubstituted indenes (19) and (22) by the appearance in the n.m.r. spectrum of the benzylic proton resonance as a broad singlet and isopropenyl methyl proton resonances, at high field (τ 8·93). Examination of stereomodels shows that the protons of this methyl group lie in the shielding region [14] above the plane of the aromatic ring and therefore resonate at a higher field than usual (τ 8·0—8·3). The structure of compounds (B) and (C) were identified as 3-isopropenyl-1,2-dimethylindene (22) and 2-isopropenyl-1,3-dimethylindene (19) respectively on the basis of the following

evidence. (1) The u.v. absorption maximum of (C) occurs at a higher wavelength and with a higher extinction coefficient than that of (B), consistent with linear
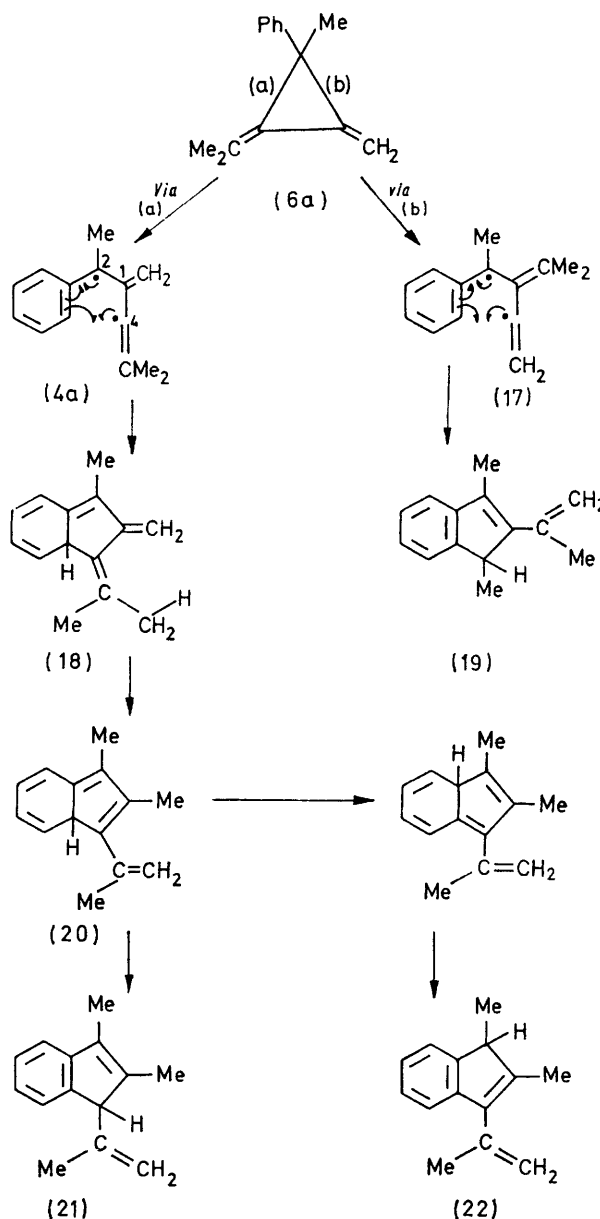
rather than cross conjugation. (2) The benzyl proton resonance and the lowest-field methyl proton resonance in (C) clearly show long-range coupling (2 Hz), confirmed by spin-decoupling experiments, indicative of homoallylic coupling.[15] The benzyl proton resonances in (B) appear at higher field than in (C) and are only very slightly broadened. Since the same ratio of product is obtained from both the allene (1a) and the dimethylenecyclopropane (6a) it appears that the latter is the precursor in both cases. The invariance of the isomer ratio

[13] M. Jones, M. E. Hendrick, J. C. Gilbert, and J. R. Butler, *Tetrahedron Letters*, 1970, 845; J. C. Gilbert and J. R. Butler, *J. Amer. Chem. Soc.*, 1970, **92**, 2168.

[14] C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, 1958, **29**, 1012.

[15] S. Sternhill, *Quart. Rev.*, 1960, **23**, 236.

upon recycling the products together with the observation that the composition does not reflect the relative thermodynamic stabilities of the products * as calculated from standard additivity data, indicates that each product is formed directly from the precursor and not by isomerisation of one of the other products. The failure of the products to undergo substituent migrations[16] is attributed to the relatively short time during which the molecules remain at 530° in the flow system.

The mechanism of the formation of the three indene derivatives appears to involve diradicals analogous to those proposed for the isomerisation of the *syn*- and *anti*-ethylidenecyclopropanes (11) and (12) discussed above. Breakage of bond (a) in the cyclopropane (6a) to give the diradical (4a), followed by ring closure between C(4) and the aromatic ring leads to the intermediate (18). A series of symmetry-allowed 1,5-suprafacial hydrogen-atom shifts leads to the indenes (21) and (22) *via* the intermediate (20). Of the two paths followed by intermediate (20), that to indene (21) is preferred since it results directly in aromatisation, no doubt accounting for the higher proportion of the indene (21) in the product mixture. The formation of the indene (19) is analogous to that of indene (21), if the initial step is breakage of bond (b) to give the diradical (17). The ring closure of the intermediate diradicals described here would require
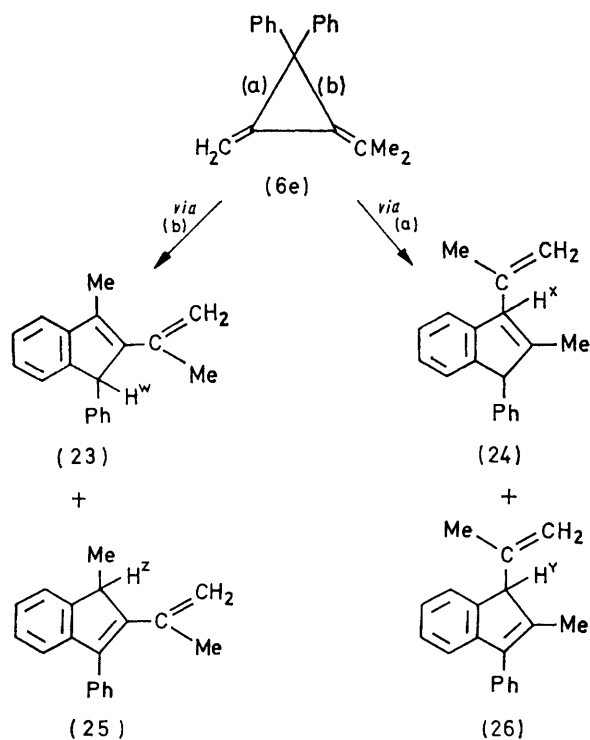
propylidenecyclopropane (6e) in the vapour phase at 530°. In this instance four major products (W), (X), (Y), and (Z) were formed in the ratio 9 : 21 : 28 : 12. Although not individually separated, these were identified by analogy with the above reaction and from the n.m.r. spectrum of the product mixture as the four possible isopropenyl methyl indenes, (23), (24), (26), and (25) respectively. Particularly significant were absorptions (see Figure 1) due to the benzylic protons (H_w—H_z),
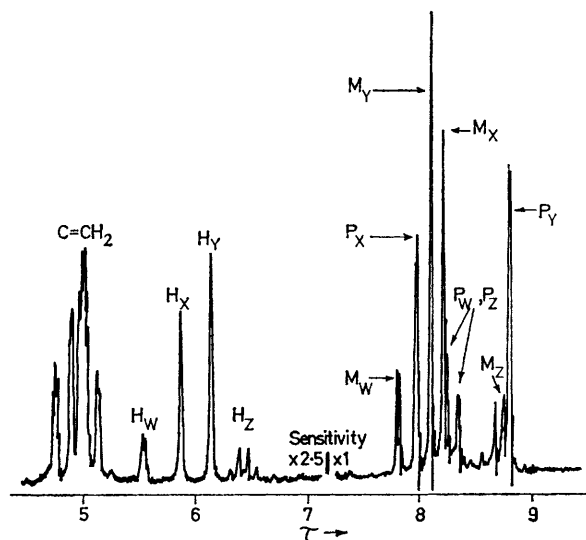

FIGURE 1   Part n.m.r. spectrum (100 MHz) of the mixture of isopropenylmethylphenylindenes (23)—(26)

whose integration ratio confirmed the v.p.c. analysis, the ring methyl protons (M_w—M_z), and the isopropenyl methyl protons (P_w—P_z). Component (Z) was distinguishable as 2-isopropenyl-1-methyl-3-phenylindene (25) by virtue of the benzylic resonance (τ 6·4) appearing as a quartet coupled to the doublet methyl resonance (τ 8·7). The remaining assignments were made on the following basis. (1) The benzylic resonance (H_w) occurring at lowest field shows clear long-range coupling (J 2 Hz) to the lowest-field methyl resonance (M_w); this was confirmed by spin-decoupling experiments. This is consistent only with the assignment of 2-isopropenyl-3-methyl-1-phenylindene (23) to component (W) and is analogous to the indene (22) above. (2) The relative intensities of the remaining benzylic resonance are much greater than the others and therefore arise from the same molecules (24) and (26) as the four intense methyl signals, two of which show a very small coupling[15] and arise from the isopropenyl methyl protons, the other two show no coupling and thus arise from the ring methyl protons. The relative intensities, confirmed by the integral spectrum (which is omitted for clarity), allow the grouping of the resonances of the (X) and (Y) as indicated in Figure 1. The high-field resonance (τ 8·8) arising from the isopropenyl group in (Y) indicates that this is 1-isopropenyl-2-methyl-3-phenylindene (26) and therefore (X) is 3-isopropenyl-2-methyl-1-phenylindene (24). The two

a relatively high activation energy since the aromatic π-electron system is destroyed, thus accounting for the high temperature necessary for the rearrangement.

A similar rearrangement is undergone by the iso-

* The calculated heats of formation of (19), (21), and (22) using standard additivity data are 33·8, 36·2, and 33·9 kcal mol⁻¹ respectively.

[18] L. L. Miller and R. F. Boyer, *J. Amer. Chem. Soc.*, 1971, **93**, 650.

remaining methyl resonances arise from the isopropenyl groups in the indenes (23) and (25).

The formation of the indenes (23)—(26) from the cyclopropane (6e) parallels the rearrangement of the cyclopropane (6a) to the indenes (19), (21), and (22). As in the last-named rearrangement the products (24) and (26) formed in highest yield arise from fission of the bond between the carbon atoms bearing the aromatic rings and the isopropylidene group. The isomer ratio for the pair of products (24) and (25) arising from path (a) is the same (1 : 1·33) as that for the pair of products (23) and (25) arising from path (b) and is close to that (1 : 1·43) for the corresponding pair of products (22) and (21) formed in the rearrangement of the cyclopropane (6a). This lends support to the mechanism proposed and also to the structural assignments.

EXPERIMENTAL

Spectroscopy.—Routine i.r. spectra were recorded on a Unicam SP 200 instrument; samples were examined as liquid films, Nujol mulls, or in solution in carbon disulphide. Routine u.v. spectra were recorded on a Unicam SP 800 instrument. Samples were examined in ethanol solution in 1-cm cells. For kinetic work either a Perkin-Elmer 237 i.r. spectrometer or a Unicam SP 500 u.v. spectrometer was used. Mass spectra and exact mass measurements were obtained on an A.E.I. M.S.902 double-focusing instrument. ^{1}H N.m.r. spectra were recorded on either a Perkin-Elmer R-10 60 MHz instrument at 33° or a Varian HA-100 100 MHz instrument at 28°; samples were examined as solutions (5—10%) in carbon tetrachloride (CCl$_4$). Chemical shifts (τ) were measured relative to tetramethylsilane (Me$_4$Si) used as an internal reference, taken to be 10 p.p.m.

Vapour Phase Chromatography.—Analytical work was carried out on a Griffin and George D6 chromatograph employing a gas-density balance detector thus rendering calibration unnecessary. Columns (2 m) containing either 5% neopentyl glycol succinate (NPGS) or 10% Apiezon L grease (APL) on silanised acid washed Chromosorb P, 80—100 mesh were used with nitrogen as carrier.

Preparative v.p.c. was carried out using either (*a*) a Wilkens Autoprep (Katharometer) chromatograph using 2 or 10 m columns packed with 10 or 30% silicone oil (S.E. 30) on Celite 545 respectively, with helium as carrier, or (*b*) a Pye series 105 (F.I.D.) chromatograph using a 14 ft column packed with either 10% Apiezon L grease (APL) on Chromosorb or 15% poly-m-phenyl ether (5 ring) (PPE) on Phaseprep W with nitrogen as carrier.

Materials.—Light petroleum (b.p. 30—40°) was distilled and stored over sodium wire. Unless otherwise stated all subsequent mention refers to this fraction.

Decalin (Koch–Light ' Puriss ') was washed with sulphuric acid (*d* 1·84) until the washings were colourless and then with water (×2); it was dried (K$_2$CO$_3$ + MgSO$_4$), refluxed (12 h) over sodium, and fractionated. The mixture of *cis*- and *trans*-isomers (b.p. 185—195°) was deoxygenated prior

to use by refluxing it under a stream of nitrogen (4 g) before being allowed to cool to room temperature in a stream of nitrogen.

Potassium t-butoxide was prepared by dissolving potassium (78 g) in anhydrous t-butyl alcohol (1·3 l) under nitrogen, refluxing the mixture for 15 h, and removing the excess of t-butyl alcohol under reduced pressure (15 mm) at 100°. The residual white solid (63% potassium t-butoxide by titration) was the 1 : 1 complex (Me$_3$COK–Me$_3$COH). Removal of the remaining t-butyl alcohol was found to be unnecessary for the present work. All subsequent mention of potassium t-butoxide refers to the 1 : 1 complex.

3-Chloro-3-methylbut-1-yne was prepared from ethynyldimethylmethanol essentially as described by Boisselle and Hennion.[1] The crude material was fractionally distilled from a small amount (0·5 g) of anhydrous potassium carbonate, to give 3-chloro-3-methylbut-1-yne (26%) b.p. 76—77° (lit.,[17] b.p. 76—77°), as a colourless liquid, pure by n.m.r. and v.p.c. which darkened with time. Further distillation of the residue afforded only dark fractions of increasing b.p. (78—100°). These were shown (v.p.c., i.r., n.m.r.) to contain the desired product together with increasing amounts of 1-chloro-3-methylbuta-1,2-diene together with several minor components.

1-Bromo-3-methylbuta-1,2-diene (72%; b.p. 70—71°/100 mm, lit.,[18] 53—54°/10 mm) was prepared from ethynyldimethylmethanol by a literature method.[18] The halide, pure by n.m.r. and v.p.c., darkened on exposure to air and light, and was stored under nitrogen at −15°.

The following olefins were dried (MgSO$_4$), fractionally distilled, and stored under nitrogen at −15°. All were shown to be pure (^{1}H n.m.r. and v.p.c.); b.p.s are given in parentheses: α-methylstyrene (57°/13 mm; lit.,[19] 55°/14 mm), *trans*-β-methylstyrene (76°/18 mm; lit.,[19] 74°/15 mm), 4,α-dimethylstyrene (69°/10 mm; lit.,[19] 76—78°/19 mm), styrene (53°/25 mm; lit.,[19] 48°/20 mm), 1,1-diphenylethylene (130°/12 mm; lit.,[19] 136°/13 mm), *cis*-stilbene (70°/0·01 mm; lit.,[19] 97°/1 mm).

1-Methyleneindane (70%; b.p. 87°/15 mm, lit.,[20] 38—39°/0·05 mm), and 1-methylenetetralin (78%; b.p. 105°/15 mm, lit.,[21] 103°/14 mm) were prepared by a modified Wittig reaction as described previously.[22]

α-Methoxystyrene was prepared by distillation of acetophenone dimethylacetal under reduced pressure from a small amount (*ca.* 0·1 g) of toluene-*p*-sulphonic acid. Redistillation gave α-methoxystyrene (89%; 98—100°/15 mm, lit.,[23] 79°/12 mm).

cis-β-Methylstyrene was obtained as follows. 1-Phenylpropyne was first prepared from styrene dibromide, *via* phenylacetylene, essentially as described [24] by Campbell and O'Connor. Fractional distillation of the crude product gave pure (v.p.c.) 1-phenylpropyne (67%; b.p. 75°/13 mm, lit.,[24] 76°/15 mm). A solution of 1-phenylpropyne (23·2 g, 0·2 mol) in cyclohexane (50 ml) was hydrogenated over freshly prepared Lindlar catalyst (1·5 g) partially poisoned with freshly distilled quinoline (3 ml). The product was fractionated to give *cis*-β-methylstyrene (78·5%, b.p. 62—62·5°/15 mm, lit.,[25] 69—69·5°/28 mm; 18·5 g), containing

[17] A. P. Boisselle and G. F. Hennion, *J. Org. Chem.*, 1961, **26**, 725.

[18] S. R. Landor, A. N. Patel, P. F. White, and P. M. Greaves, *J. Chem. Soc.* (*C*), 1966, 1223.

[19] I. Heilbron and H. M. Bunbury, ' Dictionary of Organic Compounds,' Eyre and Spottiswoode, London, 1965.

[20] A. T. Davidson and R. O. C. Norman, *J. Chem. Soc.*, 1964, 5404.

[21] G. Schroeter, *Ber.*, 1925, **58**, 713.

[22] I. H. Sadler, *J. Chem. Soc.* (*B*), 1969, 1024.

[23] J. I. G. Cadogan and I. H. Sadler, *J. Chem. Soc.* (*B*), 1966, 1191.

[24] K. N. Campbell and M. J. O'Connor, *J. Amer. Chem. Soc.*, **61**, 2897.

[25] C. M. Foltz and B. Witkop, *J. Amer. Chem. Soc.*, 1957, **79**, 201.

(v.p.c.) small quantities of the *trans*-isomer (3%) and 1-phenylpropane (2%).

Preparation of Isolation of the Dimethylvinylidenecyclopropanes.—The following general method was found to give maximum yields of the dimethylvinylidenecyclopropanes (allenes) (Table 1). A solution of 1-bromo-3-methylbuta-1,2-diene (5·9 g, 0·04 mol) in sodium-dried light petroleum (10 ml) was added dropwise during 0·5 h to a magnetically stirred slurry of potassium t-butoxide (9·3 g, 0·05 mol), the

arrangements of the allenes (0·25—1·00 g) were carried out either in solution, method (C), or in the gas phase using a flow system, method (D), or a preparative gas chromatograph, method (E).

(C) A 10% solution of the allene in xylene or toluene was heated (2—4 h) under a nitrogen atmosphere either in a sealed Pyrex tube or under reflux in a constant temperature bath (110—140°). The solvent was afterwards removed at 15 mm.

TABLE 1

Compound	Olefin *	Allene	Exact mass † of parent peak	Isolation technique	B.p. (°/mm)	Yield (%)
(1a)	α-Me-S	$C_{14}H_{16}$	184·12517 184·12519	A,B	68/0·4	70
(1b)	S	$C_{13}H_{14}$ ‡	170·10963 170·10955	B	60/0·3 (lit.,[8] 78/0·5)	68
(1c)	4α-Me_2S	$C_{15}H_{18}$	198·13986 198·14084	A	72/0·05	70
(1d)	α-MeO-S	$C_{14}H_{16}O$	200·11926 200·12011	A	66/0·05	50
(1e)	$Ph_2C_2H_2$	$C_{19}H_{18}$ ‡,§	246·14080 246·14084	B	112/0·01	70
(7a)	MI	$C_{15}H_{16}$	196·12447 196·12519	A	75/0·01	50
(7b)	MT	$C_{16}H_{18}$	210·14071 210·14084	A	79/0·01	50
(9)	c-β-Me-S	$C_{14}H_{16}$	184·12527 184·12519	A	72/0·3	50
(10)	t-β-Me-S	$C_{14}H_{16}$	184·12553 184·12519	A	74/0·3	55

* Abbreviations: S, styrene; MI, 1-methyleneindane; MT, 1-methylenetetralin; *c, cis*; *t, trans*. † Upper figures refer to Found and lower figures to Calculated values. ‡ Known compounds. § Underwent partial rearrangement on distillation.

olefin (0·02 mol), and sodium-dried light petroleum (15 ml) maintained at 0° under an atmosphere of nitrogen (essential). The deep red reaction mixture was stirred for a further 1 h, while warming to room temperature. Water (20 ml) was added to the mixture and the pH adjusted to *ca.* 5 with 10% aqueous hydrochloric acid while stirring vigorously. The organic layer was separated, washed with saturated aqueous sodium chloride (20 ml), and dried (K_2CO_3 + $MgSO_4$). Evaporation of the solvent followed by either (A) careful fractionation of the residue under reduced pressure or (B) careful removal of unchanged olefin under high vacuum at room temperature followed by chromatography of the residue on alumina (Spence type-H) with light petroleum as eluant, yielded the *allene* (50—70%) usually as a pale yellow liquid which appeared as a single peak on v.p.c. Repeated fractionation did not give colourless products. The use of ether as the reaction solvent or 3-chloro-3-methylbut-1-yne as the carbene precursor resulted in considerably lower yields of products (30—50%).

The molecular formulae of the allenes were confirmed by exact mass measurement of the parent ion (P+) in the mass spectrum; in nearly all cases significant (P + 16) and (P + 32) peaks were also apparent in freshly redistilled samples indicating very ready uptake of oxygen. In accordance with this it was usually not possible to obtain accurate elemental analyses. All the allenes showed a strong i.r. absorption at 2020 ± 10 cm⁻¹ (C=C=C stretch), and as expected none showed u.v. absorption maxima above 210 nm. The structures of the allenes were confirmed by their ¹H n.m.r. spectra (Table 2).

The allenes were reasonably stable at −15°, and samples stored in this manner had not deteriorated significantly during 6 months.

Thermal Rearrangements of the Allenes.—Thermal re-

(D) The allene was slowly distilled under reduced pressure (0·25 mm) from glass wool in a stream of nitrogen through a preheated Pyrex prolysis tube (115 mm × 7 mm i.d.) loosely packed with glass wool into an air-cooled receiver.

TABLE 2

¹H N.m.r. spectra of allenes

Compd.	τ Values
(1a)	2·91 (m, 5H, Ar-*H*), 8·22 (s, 6H, :C(CH_3)$_2$), 8·37 (s, 2H, 3-*H*), 8·42 (s, 3H, 2-CH_3)
(1b)	2·90 (m, 5H, Ar-*H*), 7·23 (d of d, *J* 5·1, 8·2 Hz, 1H, 2-*H*), 8·10 (d of d, *J* 6·8, 8·2 Hz, 1H, 3-*H*), 8·22 [s, 6H, :C(CH_3)$_2$], 8·56 (d of d, *J* 5·1, 6·8 Hz, 1H, 3-*H*)
(1c)	2·88, 3·07 (d, d, *J* 8·4 Hz, 4H, Ar-*H*), 7·75 (s, 3H, Ar-CH_3), 8·24 (s, 6H, :C(CH_3)$_2$), 8·4—8·5 (s, d, d, 5H, 2-CH_3 and 3-*H*)
(1d)	2·5—2·9 (m, 5H, Ar-*H*), 6·75 (s, 3H, −OCH_3), 7·88, 8·34 (d, d, *J* 8 Hz, 2H, 3-*H*)
(1e)	2·6—2·9 (m, 10H, Ar-*H*), 7·88 (s, 2H, 3-*H*), 8·23 [s, 6H, :C(CH_3)$_2$]
(7a)	2·9—3·4 (m, 4H, Ar-*H*), 7·00 (t, *J* 8 Hz, 2H, Ar-C*H*), 7·4—8·5 (complex m, 4H, cyclopentyl-*H* and cyclopropyl-*H*), 8·30 [s, 6H, :C(CH_3)$_2$]
(7b)	3·11 (m, 4H, Ar-*H*), 7·18 (m, 2H, Ar-C*H*), 7·8—8·4 broad m, 4H, cyclohexyl-*H*), 8·24 [s, 6H, :C(CH_3)$_2$], 8·4 (s, 2H, cyclopropyl-*H*)
(9)	2·88 (s, 5H, Ar-*H*), 7·03 (d, *J* 8·7 Hz, 1H, 3-*H*), 7·96 (d of d, *J* 6·8, 8·7 Hz, 1H, 2-*H*), 8·18, 8·26 (s, s, 6H, :C(CH_3)$_2$) 9·14 (d, *J* 6·8 Hz, 3H, 2-CH_3)
(10)	2·91 (s, 5H, Ar-*H*), 7·78 (d, *J* 4·2 Hz, 1H, 3-*H*), 8·2 (m, 1H, 2-*H*), 8·22 (s, 6H, :C(CH_3)$_2$), 8·63 (d, *J* 5·1 Hz, 3H, 2-CH_3)

The pyrolysis tube was maintained at a constant temperature (350—550°) by an electrically heated furnace controlled by a variable auto-transformer

(E) The allene (0·5 g) was diluted with an equal volume of pentane and the solution was passed in one portion along a

Wilkins chromatograph employing a 10 m column (30% SE 30).

Pertinent details are summarised in Table 3. Crude rearrangement products were examined by n.m.r. and i.r. spectroscopy and v.p.c. before purification or, in the case of

(30% S.E. 30, 180°) and the eluate collected after *ca.* 1·25 h. In all cases this contained 30% of the *syn*-product and 70% of the *anti*-product (by v.p.c., NPGS). Recycling of the mixture caused no change in the isomer ratio.

A sample of the *anti*-product was passed through a

TABLE 3

Allene	Rearrangement procedure	Products (ratio)	Yield (%)	B.p. (°/mm)	Exact mass † of parent peak	U.v. spectrum $\lambda_{max.}$ (nm)	$\varepsilon_{max.}$
(1a)	C, xylene, 140°, 3 h *	6a	68	59/0·4	184·12527 184·12519	246·0	18,600
(1a)	D, 350°/0·25 mm	6a	90				
(1b)	C, xylene, 140°, 3 h	6b	50	51/0·1	170·11028 170·10955		
(1b)	D, 350°/0·05 mm	6b	91				
(1c)	D, 350°/0·10 mm	6c	80	62/0·05	198·13993 198·14084	245·0	17,500
(1d)	C, toluene, 111°, 2 h	6d	60	65/0·1	200·11926 200·12011	254·5	16,800
(1e)	D, 350°/0·5 mm	6e	88	113/0·01	246·14116 246·14084		
(7a)	C, xylene, 140°, 2 h	8a	56	57/0·01	196·12459 196·12519	245	18,800
(7b)	C, xylene, 140°, 2 h	8b	74	66/0·01	210·14092 210·14084	243	16,800
(9)	C, xylene, 130°, 3 h *	11 : 12 (87 : 13)§	50	64/0·4	184·12499 ‡ 184·12519		
(9), (10)	D, 350°/0·25 mm	11 : 12 (33 : 67)§	90			(11) 249	17,600
(9), (10)	E, 180°, 1·25 h	11 : 12 (30 : 70)§	70			(12) 248	18,700
(10)	C, xylene, 130°, 2 h *	11 : 12 (98 : 2)§	75				
(10)	C, xylene, 130°, 3 h	11 : 12 (96 : 4)§	60				

* Minimum time required for complete disappearance of allene i.r. absorption at 2010 cm⁻¹. † Upper figures refer to Found and lower figures to Calculated values. ‡ Same value obtained for (11) and (12) determined separately. § Proportions determined by analytical v.p.c.

mixtures, separation into components. Each of the allenes (1a—e), and (7a,b) yielded only a single rearrangement product, shown by exact mass measurement of the parent ion to be isomeric with the adduct. The products, substituted *dimethylenecyclopropanes* (6a—e) and (8a,b) were purified by distillation under reduced pressure and all showed a strong i.r. absorption at 875 ± 5 cm⁻¹ (C=CH₂). Allenes (9) and (10) yielded mixtures of syn-1-*ethylidene-2-isopropylidene-3-phenylcyclopropane* (11) and its anti-*isomer* (12), pure samples of which were obtained by preparative v.p.c. employing a 10% SE 30 column. No *syn–anti* isomerisation (*vide infra*) occurred under these conditions. The structures of the dimethylenecyclopropanes were confirmed by their n.m.r. spectra (Table 4).

Investigation of Possible Isomerisation of the Allenes during Rearrangement.—Aliquots (*ca.* 1 ml) of a solution of *cis*-1-dimethylvinylidene-2-methyl-3-phenylcyclopropane (9) in AnalaR carbon tetrachloride (5 ml) were sealed in Pyrex tubes under nitrogen and placed in a thermostat at 130°. The tubes were removed at intervals (15 min) and the n.m.r. spectra of the contents recorded. Examination of the region between 7 and 8 showed peaks arising from the *cis*-adduct benzylic proton (τ 7·00) and the rearrangement products (11) and (12). No doublet was observed at τ 7·8 (*trans*-adduct benzylic proton), this particular region being free of peaks.

Isomerisation of syn- *and* anti-1-*Ethylidene-2-isopropylidene-3-phenylcyclopropane.*—Samples of the rearrangement products (130°) from the *trans*-adduct (*i.e.* a *syn* : *anti* ratio of 98 : 2), and from the *cis*-adduct (*i.e.* a *syn* : *anti* ratio of 87 : 13), a pure *anti*-product, and a pure *syn*-product were passed separately through a preparative chromatograph

preparative chromatograph (30% S.E. 30, 130°) and the eluate collected during *ca.* 3 h after *ca.* 7 h. This contained

TABLE 4

¹H N.m.r. spectra of dimethylenecyclopropanes

Compd.	τ Values
(6a)	2·7—3·0 (m, 5H, Ar-*H*), 4·74 and 4·88 (s, s, 2H, :C*H₂*), 8·09 and 8·16 [s, s, 6H, :C(C*H₃*)₂], 8·45 (s, 3H, 3-C*H₃*)
(6b)	2·9—3·0 (m, 5H, Ar-*H*), 4·67 and 4·86 (s, s, 2H, :C*H₂*), 7·14 (broad s, 1-H, 3-*H*), 8·02 and 8·15 [s, s, 6H, :C(C*H₃*)₂]
(6c)	2·9—3·1 (m, 4H, Ar-*H*), 4·75 and 4·87 (s, s, 2H, :C*H₂*), 7·76 (s, 3H, Ar-C*H₃*), 8·06 and 8·14 [s, s, 6H, :C(C*H₃*)₂], 8·47 (s, 3H, 3-C*H₃*)
(6d)	2·6—3·0 (m, 5H, Ar-*H*), 4·61 and 4·70 (broad ss, 2H, :C*H₂*) 6·75 (s, 3H, OC*H₃*), 8·00 and 8·10 [s, s, 6H, :C(C*H₃*)₂]
(6e)	2·7—3·0 (m, 10H, Ar-*H*), 4·63 and 4·74 (s, s, 2H, :C*H₂*), 8·06 [s, 6H, :C(C*H₃*)₂]
(8a)	2·9—3·5 (m, 4H, Ar-*H*), 4·75 and 4·96 (s, s, 2H, :C*H₂*), 6·98 (t, *J* 8 Hz, 2H, Ar-C-*H*), 7·80 (t, *J* 8 Hz, 2H, cyclopentyl-*H*), 8·04 and 8·24 [s, s, 6H, :(C*H₃*)₂]
(8b)	3·0—3·4 (m, 4H, Ar-*H*), 4·79 and 4·97 (s, s, 2H, :C*H₂*), 7·0—7·3 (broad m, 2H, Ar-C-*H*), 7·8—8·4 (broad m, 4H, cyclohexyl-*H*), 8·03 and 8·21 [s, s, 6H, :C(C*H₃*)₂]
(11)	2·98 (s, 5H, Ar-*H*), 4·50 (q, *J* 6·5 Hz, 1H, :C*H*), 7·22 (broad s, 1-H, 3-*H*) 7·93 [m, 6H, :C(C*H₃*)₂] 8·13 (d, *J* 6·5 Hz, 3H, :CHC*H₃*)
(12)	2·97 (s, 5H, Ar-*H*), 4·20 (q, *J* 6·0 Hz, 1H, :C*H*), 7·14 (broad s, 1H, 3-*H*), 8·0—8·3 [m, 9H, :CHC*H₃* and :C(C*H₃*)₂].

the *syn*- and *anti*-isomer in the ratio 1 : 9 respectively. A similar experiment with the *syn*-isomer gave rise to a *syn* : *anti* ratio of 1 : 1.

A solution of the *anti*-isomer (0·025 g) in xylene (0·5 ml) heated at 130° for 1 h showed no change in composition.

Thermal Rearrangement of 2-Isopropylidene-1-methylene-3-methyl-3-phenylcyclopropane (6a) *and 1-Dimethylvinylidene-2-methyl-2-phenylcyclopropane* (1a) *at 530°.*—The dimethylenecyclopropane (1 g) was passed through the flow system at 530° in a stream of nitrogen (0·01 mm). Examination (v.p.c., n.m.r.) of the crude product (0·9 g; 90%) showed three major components (90% of total) (A), (B), and (C) present in the ratio 20 : 14 : 9 together with several minor components. The mixture was distilled (b.p. 64—66°/0·05 mm) and pure samples of (A) and (B) were obtained from the Pye preparative chromatograph using a 10% APL column and of (C) using a 25% PPE column. On the former column (C) was eluted along with minor components and on the latter (B) eluted as a shoulder on (A). Insufficient quantities of the minor components were obtained for their identification.

An identical product mixture was obtained from the allene (1a) under the same conditions.

The n.m.r. and u.v. spectra allowed the following assignments. (A) 2,3-*Dimethyl-1-isopropenylindene* (21) [u.v. $\lambda_{max.}$ 261·5 nm, $\varepsilon_{max.}$ 10,740; n.m.r. τ 2·8—3·1 (m, 4H, Ar-*H*), 4·95 and 5·05 (s, s, 1H, 1H, C=C*H*$_2$), 6·28 (bs, 1H, Ar-C-*H*) 8·0 (s, 3H, 3-C*H*$_3$) 8·15 (s, 3H, 2-C*H*$_3$), 8·93 (s, 3H, isopropenyl C*H*$_3$); Found: *m/e* 184·12463]. (B) 1,2-*Dimethyl-3-isopropenylindene* (22) [u.v. $\lambda_{max.}$ 262 nm, $\varepsilon_{max.}$ 10,620; n.m.r. τ 2·7—3·1 (m, 4H, Ar-*H*), 4·80 and 5·12 (m, m, 1H, 1H, C=C*H*$_2$), 6·85 (q, *J* 8 Hz, 1H, Ar-C-*H*), 8·0 and 8·03 (s, s, 6H, 2-C*H*$_3$ and isopropenyl C*H*$_3$) 8·74 (d, *J* 8 Hz, 3H, 1-C*H*$_3$); Found: *m/e* 184·12519]. (C) 1,3-*Dimethyl-2-isopropenylindene* (19) [u.v. $\lambda_{max.}$ 276·5 nm, $\varepsilon_{max.}$ 14,030; n.m.r. τ 2·7—3·0 (m, 4H, Ar-*H*), 4·86 and 5·14 (bs, bs, 1H, 1H, C=C*H*$_2$), 6·47 (q of q, *J* 2 Hz, 7 Hz, 1H, Ar-C-*H*), 7·87 (d, *J* 2 Hz, 3H, isopropenyl-C*H*$_3$), 8·0 (d, *J* 2 Hz, 3H, 3-C*H*$_3$), 8·78 (d, *J* 7 Hz, 3H, 1-C*H*$_3$); Found: *m/e* 184·12519. Calc. for $C_{14}H_{16}$: 184·12519].

Thermal Rearrangement of 3,3-Diphenyl-2-isopropylidene-1-methylenecyclopropane (6e) *at 530°.*—The dimethylenecyclopropane (0·5 g) was passed through the flow system at 530°. Examination (v.p.c., n.m.r.) of the crude product (0·45 g; 86%) showed four major components (95% of total) (W), (X), (Y), and (Z) present in the ratio 9 : 21 : 28 : 12. The ^{1}H n.m.r. spectrum showed absorptions in the region τ 2·6—3·2 (m, 9H, aromatic), in addition to the olefinic (total integral 2H), benzylic (total integral 1H), and methyl absorptions (total integral 6H) illustrated in Figure 1, and allowed the following assignments: (W): 2-isopropenyl-3-methyl-1-phenylindene (23), (X): 3-isopropenyl-2-methyl-1-phenylindene (24), (Y): 1-isopropenyl-2-methyl-3-phenylindene (26), and (Z): 2-isopropenyl-1-methyl-3-phenylindene (25).

Kinetic Studies.—Rate constants for the thermal rearrangements of dimethylvinylidenecyclopropanes in solution were determined spectrophotometrically by following either the increase in intensity of the diene absorption maximum (u.v.) of the product, procedure (1), or the decrease in the intensity of the allene absorption maximum (i.r.) of the reactant, procedure (2). For a simple reaction: R $\xrightarrow{k}$ P the reactant concentration $[R_t]$ at any time, t, is given by

$$[R_t] = \frac{A_t - A_\infty}{\varepsilon_R - \varepsilon_P} = \frac{A_t - \varepsilon_P[R_0]}{\varepsilon_R - \varepsilon_P}$$

where, ε_R, ε_P represent the extinction coefficients at a given

wavelength of the reactant and product respectively, A_t, the optical density of the solution at time t, and $[R_0]$, the initial concentration of the reactant. For a first-order process, a plot of $\ln(A_t - \varepsilon_P[R_0])$ against t is linear with slope equal to the rate constants k.

Rearrangements were carried out under nitrogen in a Pyrex reaction thimble completely immersed in a thermostat ($\pm 0·2°$) as detailed below.

Procedure (1).—This was used to study the variation with temperature of the rate constant for the rearrangement of the allene (1a). A solution (*ca.* 10^{-4}M) of accurately known concentration of the reactant (*ca.* 0·1 mg) in purified decalin (50 ml) was introduced into the reaction thimble as rapidly as possible. Aliquots (2·5 ml) were then rapidly withdrawn by a syringe at suitable time intervals (1—8 min) and chilled by immersion in liquid nitrogen to quench the reaction. The aliquots were allowed to reach room temperature and the optical density, A_t, of each was determined at 246·0 nm, on
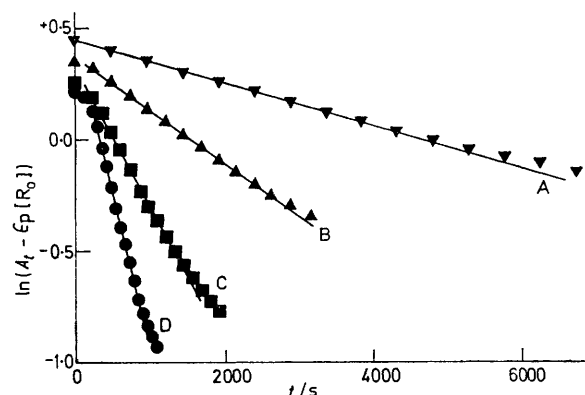

FIGURE 2 Typical plots of $\ln(A_t - \varepsilon_P[R_0])$ *vs.* time t for the rearrangement of the allene (1a). A at 122·5°, B at 132·5°, C at 142·5°, and D at 152·0°

a Unicam SP 500 spectrometer. The extinction coefficient of the product and reactant in decalin solution were also determined in triplicate at 246·0 nm: $\varepsilon_R = 4100 \pm 100$ and $\varepsilon_P = 15,500 \pm 200$. All weighings were carried out using a Cahn electrobalance.

Plots of $\ln(A_t - \varepsilon_P[R_0])$ *vs.* t were linear, up to at least 75% conversion after the sample had reached thermal equilibrium (2—4 min). The product was unstable to prolonged heating and this resulted in a deviation of the last few points. Visual estimation of the slope allowed this to be accommodated. Sample plots are illustrated in Figure 2. Rate constants were determined in triplicate (within 5%) in four temperature regions over the range 120—155°.

TABLE 5

Rate constants for the rearrangement of 1-dimethylvinylidene-2-methyl-2-phenylcyclopropane (1a)

$t/°C$	121·5	122·5	122·5	132·5	132·5	132·5
$10^4 K/s^{-1}$	0·965	0·959	0·997	2·73	2·64	2·65
$10^4[R°]/mol\ l^{-1}$	1·348	1·123	1·372	1·239	1·038	1·070
$t/°C$	142·5	142·5	142·5	152·0	152·0	152·5
$10^4 K/s^{-1}$	6·35	6·56	6·34	15·5	15·2	14·8
$10^4[R°]/mol\ l^{-1}$	1·217	1·120	1·206	1·079	1·100	1·081

The data in Table 5 yielded a linear Arrhenius plot (correlation coefficient $r = 0·9997$) described by the equation $\ln k = (29·52 \pm 0·32) - (15,310 \pm 130)/T$ which was obtained by use of a least-squares programme on an IBM

360/50 computer. This leads to an activation energy $E_a = 30 \cdot 4 \pm 0 \cdot 3$ kcal mol^{-1} and a correct formulation [12] of the absolute rate theory for unimolecular reactions leads to a value of $\Delta S^{\ddagger} = -2 \cdot 5 \pm 0 \cdot 7$ e.u.

Procedure (2).—This was used for the measurement of rate constants of the rearrangements of the allenes (1a), (9), and (10) at 132—133 °C. Aliquots (0·4 ml) were removed and quenched at 5 m intervals from 5% (*ca.* 3M) solution (10 ml) of the allene in decalin as in procedure (1). The transmittance, $(1/A_t)$, of each at the absorption maximum (2030 cm^{-1}) was measured at room temperature on a Perkin-Elmer 237E spectrometer. The pure product did not absorb at this wavelength (*i.e.* $\varepsilon_P = 0$) and therefore accurate measurement of the initial concentration of the reactant was not necessary. Plots of ln A_t against time were linear up to at least 85% conversion. The following values for the first-order rate constant k were obtained: allene (1a), $2 \cdot 83 \pm 0 \cdot 7 \times 10^{-4}$ s^{-1}; allene (9), $5 \cdot 63 \pm 0 \cdot 1 \times 10^{-4}$ s^{-1}; allene (10), $1 \cdot 32 \pm 0 \cdot 05 \times 10^{-3}$ s^{-1}.