Concerning the Ring-opening of Substituted Cyclopropyl Radicals

By **Roger P. Corbally, M. John Perkins,*† and (in part) Arkadi P. Elnitski,** Department of Chemistry, King's College, Strand, London WCR 2LS, and Department of Chemistry, Chelsea College, Manresa Road, London SW3 6LX

The stereochemistry of the conversion of cyclopropyl radicals to allyl radicals is discussed. The rearrangement of 1,5-dimethyl-6-bicyclo[3.1.0]hexyl radicals to 1,3-dimethylcyclohex-2-enyl radicals affords a new example of disrotatory opening, and, taken in conjunction with the apparent failure of 2,2,3,3-tetramethylcyclopropyl radicals to rearrange under comparable conditions, is considered to exclude the possibility of any significant preference for conrotatory opening, in contrast to early predictions. An improved synthesis of *trans*-cyclo-octane is also reported.

UNTIL recently, rearrangement reactions of free radicals have afforded a rather limited field for the organic chemist. Although there are notable exceptions, the vast majority of examples fall into two or three clearly definable classes. These include (*a*) 1,2-shifts, where the migrating group, *e.g.* phenyl, vinyl, or halogen, has a low-lying orbital capable of accepting the unpaired electron, and (*b*) intramolecular analogues of well-established bimolecular reactions such as radical addition and atom transfer.[1]

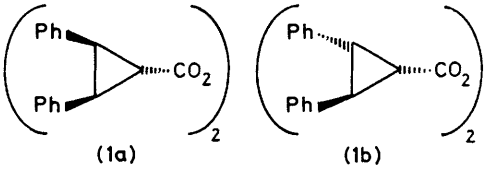
The short life-time of reactive radicals in solution prevents observation of many rearrangements where activation energies are $>$ *ca.* 15 kcal mol^{-1}. However, recent conflict between various theoretical predictions regarding pericyclic changes in free radicals has stimulated an interest in more elaborate radical rearrangements. To force such reactions to occur within the short lifetime of the radical, various devices have been adopted; *e.g.* a large exothermicity has been built into the rearrangement pathway, or high temperatures have been employed. The former technique is exemplified in the ring-opening reactions of suitably substituted cyclopropyl radicals, and an interesting case of the latter was the recent demonstration of conrotatory closure of a pentadienyl radical to a cyclopentenyl radical.[2]

A more elegant solution to the problem of radical lifetime has been the use of the adamantane matrix-isolation technique, in which radical rearrangements with significantly higher activation barriers can be observed directly by e.s.r. spectroscopy.[3]

Much of the theoretical effort on pericyclic reactions of free radicals has been concentrated upon the cyclopropyl→allyl transformation.[4] Here, early predictions that pericyclic radical reactions would be governed by the singly-occupied HOMO of the radical,[5] and hence follow the same course as predicted for the corresponding anion, were relatively easily tested by detailed MO calculations on the reaction pathway. These calculations showed considerable activation barriers for both disrotatory and conrotatory modes of ring opening, but, in contrast to the simplest ideas, they clearly favoured a disrotatory mode for the thermally activated reaction. The calculations, at various levels of sophistication, were for processes in which symmetry (either C_2 for conrotatory or σ_1 for disrotatory) was maintained along the reaction co-ordinate; an early qualitative suggestion by Bauld [6] that this was not the case found strong support in MINDO/3 calculations, the results of which suggested that the transition state was reached by rotation of only C-2 (or C-3) of the cyclopropyl radical, C-3 (or C-2) remaining substantially undisturbed.[7] Therefore whether a disrotatory or conrotatory path was followed must be determined after the transition state has been passed and no appreciable energetic discrimination between the two modes could be expected. The reliability of the MINDO/3 procedure for calculating reaction paths cannot yet be considered to have been established and therefore experimental evidence is still needed that will indicate which (if either) stereochemical course is preferred. This paper does not provide that evidence, but, we believe, it does add a little to our knowledge of the problem.

RESULTS AND DISCUSSION

Our early experiments depended on the literature reports that two phenyl substituents, at C-2 and C-3,[8] or both at C-2,[9,10] in a cyclopropyl radical provide sufficient stabilisation to the incipient allyl radical that ring-opening competes successfully with bimolecular decay or reaction with solvent.‡ In this respect our work was parallel with, but much less extensive than, that of Rüchardt and his co-workers,[12] and depended on



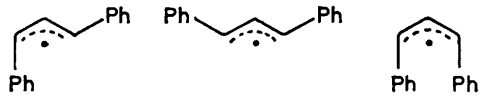
(1a) (1b)

an investigation of the products from *cis*- and *trans*-2,3-diphenylcyclopropyl radicals, generated from the symmetrical diacyl peroxides (1a and b). Although our results are inconclusive, neither supporting nor opposing the tentative conclusion that a disrotation is favoured,[12] they are mentioned here since they include one point of detail, apparently overlooked in ref. 12, which might possibly have contributed to the failure of our experi-

† *Present address:* Department of Chemistry, Chelsea College, Manresa Rd, London SW3 6LX.

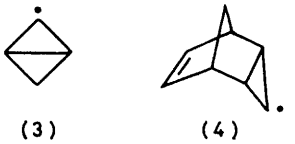
‡ The activation energy for opening of unsubstituted cyclopropyl radicals has been determined from gas-phase experiments to be *ca.* 19 kcal mol^{-1}.[11] In solution the reaction is not observed. Furthermore, a single phenyl substituent on C-2 provides insufficient driving force for the reaction to succeed under normal solution conditions.[9]

ment. Our approach depended on the formation of stereochemically distinct allyl radicals (2a and b) [and perhaps (2c)] from the two isomeric cyclopropyl radicals;

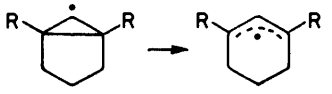


(2a) (2b) (2c)

it was hoped that there might be some memory of this stereochemistry in the main products of the reaction, namely the tetraphenylhexadiene dimers PhCH=CH–CHPh–CHPh–CH=CHPh. However, on decomposing both peroxides in benzene, similar proportions of the two diastereoisomeric *E*,*E*-dimers were found, with no evidence for *Z*-disubstituted olefin in the crude reaction product. But we also found that under the reaction conditions (boiling benzene) *these dimers slowly interconvert.* This equilibration may involve a facile Cope rearrangement,[13] or a dissociation–recombination mechanism. Whichever mechanism is operative, it seems probable that a similar process would more rapidly remove from the product any *Z*,*Z*- or *Z*,*E*-dimer which might result from kinetic-



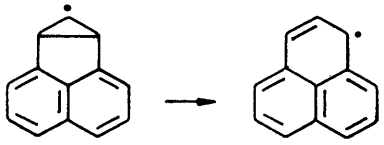
(3) (4)



(5) R = Ph (6) R = Ph
(7) R = Me (8) R = Me

ally controlled dimerisation of 1,3-diphenylallyl radicals. In experiments in which peroxide decomposition was allowed to proceed only to 25—40% completion, there was again no evidence (n.m.r.) for *cis*-disubstituted alkene in the crude product. It should of course be noted that these experiments depended on the assumption that the diphenylallyl radicals retain their configuration during their transitory life-times. Whilst this seems reasonable for simple allyl radicals,[14] its validity may be in doubt with strongly conjugating substituents.*

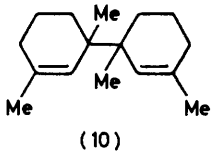
The only really satisfactory approach to determining the stereochemistry of electrocyclic scission of a cyclopropyl radical involves direct observation of the radicals by e.s.r., and conditions for this have yet to be discovered; however, a more restricted approach depends on the incorporation of cyclopropyl radicals into bicyclic or polycyclic ring systems where geometrical constraints permit only one of the alternative modes. Some evidence already exists which demonstrates the feasibility of the disrotatory path. Thus radicals (3),[15] (4),[16] (5),[17] and (9) [17,18] have been shown to rearrange when generated as reaction intermediates. The situation with (9) is less clear-cut, early indications that it would readily ring-open to perinaphthenyl [18] not having been substantiated.[17]



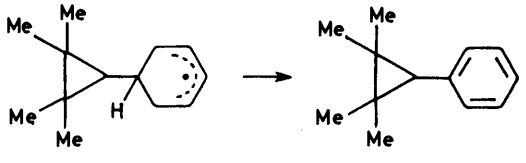
(9)

A considerable driving force for rearrangement of (3), and to a lesser extent for (4), must be relief of strain; furthermore, in (5) the bicyclic structure is more strained than the diphenylcyclopropyl radicals from (1a) or (1b), and the additional cyclopentane ring carbons provide further stabilisation for the product radical (6) than is present in the diphenylallyl radical (2).

We have synthesised a diacyl peroxide precursor to (7), and find that in boiling benzene this also decomposes to give a product (10) resulting from dimerisation of a monocyclic radical (8). Particularly significant here, however, was our failure to detect any rearrangement product from the related 2,2,3,3-tetramethylcyclopropyl radical, generated in a similar fashion. Instead, this gave low yields of two volatile products, (12) and its 1,4-dihydro-derivative, apparently resulting from attack of the unrearranged cyclopropyl radical on benzene,

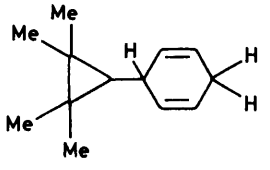


(10)



(11) (12)

+



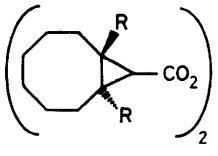
followed by disproportionation of the cyclohexadienyl adduct (11).

These two results permit a useful comparison to be made. Both reactions involve 2,2,3,3-tetra-alkylcyclo-

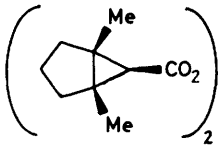
* Since this paper was written, a report of the isolation of *Z*,*Z*- and *Z*,*E*-dimers of diphenylallyl radicals formed at low temperatures has come to our attention. In that work it was concluded that the rotational energy barrier in the radical was small ($\leqslant 9$ kcal mol^{-1}); curiously, no mention was made of diastereoisomerism in the dimers, each of which was referred to as though it were a single compound (G. Boche and D. R. Schneider, *Angew. Chem. Internat. Edn.*, 1977, **16**, 869).

propyl radicals, but in (7) there is the additional ring strain of the bicyclohexane. Making appropriate allowance for the *cis*-methyl interactions, the strain difference between the two radicals is probably no more than 4 kcal mol^{-1}.[19] If this is the major factor which causes the two to behave differently when generated under comparable conditions, it appears to be possible to conclude that, for the general case, *either* disrotatory opening is marginally preferred, *or* the difference between the activation barriers for the two pathways must be very small indeed. Were there to be an appreciable preference for a conrotatory path, as one might be led to expect from the early discussion by Woodward and Hoffmann,[5] then it seems improbable that (6) would rearrange by a necessarily disrotatory path and the tetramethylcyclopropyl radical under similar conditions would not rearrange but instead react with solvent. However, even these simple conclusions must be qualified. If, as suggested by the MINDO/3 calculations, the disrotatory reaction follows an appreciably unsymmetrical pathway, the energy of the transition state might be raised for opening of (7) by conformational strain. The experimental result therefore argues against a highly unsymmetrical path.* On the other hand, for the *symmetrical* disrotatory pathway, two of the methyl groups of the tetramethylcyclopropyl radical will come together in the transition state and thus inhibit reaction by simple steric interference; indeed, it was once suggested that the tetramethylallyl radical adopts a twisted conformation, but the species under observation later proved to have been incorrectly identified.[20] Similar allyl radicals with a substituent on the central atom have now been shown to be non-planar,[21] but the central substituent is apparently essential for this.[22]

Establishing the feasibility of conrotatory opening of cyclopropyl radicals by a similar device requires construction of a suitably strained *trans*-bicyclo[*n*.1.0]alkyl radical precursor. 9-Ethoxycarbonyl-*trans*-bicyclo-[6.1.0]nonane was therefore prepared from *trans*-cyclo-octene,† and hydrolysed, and the resulting acid was converted to the diastereoisomeric peroxides (13) using hydrogen peroxide and dicyclohexylcarbodi-imide.[24]



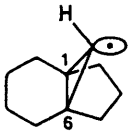
(13) R = H
(14) R = Me



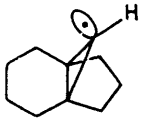
(15)

However, when this peroxide mixture was allowed to decompose in boiling benzene, the only identified products were the carboxylic acid, a compound considered to be 9-phenyl-*trans*-bicyclo[6.1.0]nonane, and the parent *trans*-bicyclononane. To extend this experimentation to a proper analogue (14) for the tetramethylcyclopropyl case would necessitate commencing with 1,2-dimethyl-*trans*-cyclo-octene. This is unknown, and has so far resisted our modest synthetic overtures.

Two other points are of interest. The precursor for the dimethylbicyclo[3.1.0]hexyl radical was obtained *via* ethoxycarbonylcarbene addition to 1,2-dimethyl-cyclopentene. This gave a mixture of *exo*- and *endo*-ethoxycarbonyl derivatives of dimethylbicyclohexane; these were separated by preparative gas–liquid chromatography, each was hydrolysed, and the acids were separately converted to peroxides. Whilst the *exo*-acid gave a crystalline peroxide (15) which could be handled without difficulty, the *endo*-acid gave an oily product, contaminated with starting acid, which decomposed



(16)



(17)

rapidly in warm benzene to give, after work-up, the acid as the only identified product. Further investigation of this unexpected behaviour seems warranted.

Finally, it is appropriate to relate our results to some observations made recently on [*x*.*y*.1]propellane-derived cyclopropyl radicals, *e.g.* (16).[25] Cyclopropyl radicals have attracted interest not only because of their rearrangement reactions, but also because of their high reactivity (evident in the aromatic substitution reactions noted here and elsewhere [26]) and their pyramidal configuration.[27] Radical (16) apparently prefers to adopt the configuration shown, rather than the epimeric form (17). It was suggested that this might be the result of a partial scission of the 1,6-bond,[25] and this clearly finds a close analogy in the actual scission of the 1,5-bond in (6), although no information on the preferred configuration of the radical centre in (6) is available. (The rapid decomposition of the *endo*-peroxide, which more probably involves a carboxy inversion reaction,[28] is *not* considered to be relevant to this.)

EXPERIMENTAL

Preparation of Diacyl Peroxides.—The general procedure adopted utilised the condensation of the appropriate carboxylic acid with hydrogen peroxide promoted by dicyclohexylcarbodi-imide in dry ether.[24] The cyclopropanecarboxylic acids were generally obtained by reaction of ethyl diazoacetate with olefin, catalysed by anhydrous copper sulphate.

(*i*) *Bis*-cis,trans-2,3-*diphenylcyclopropanecarbonyl peroxide.*[8] This was obtained, presumably as a mixture of diastereoisomers, as a colourless solid, m.p. 131—132 °C (decomp.) from CCl_4–MeOH (Found: C, 81.0; H, 5.5. Calc. for $C_{32}H_{26}O_4$: C, 81.0; H, 5.5%).

* This point can more forcibly be made for the rearrangements of (3) and (4), but here the strain factor is of course very much greater.

† Prepared by an established procedure [23] which was modified by inclusion of an antioxidant, and reproducibly gave *ca.* 95% yield of distilled *trans*-cyclo-octene (contaminated ⩽1% *cis*-isomer) based on (2-hydroxycyclo-oct-1-yl)diphenylphosphine oxide.

(*ii*) *Bis*-trans,trans-2,3-*diphenylcyclopropanecarbonyl peroxide*. This was similarly obtained as a colourless solid, m.p. 116—117 °C (decomp.).[12a]

(*iii*) *Bis*-2,2,3,3-*tetramethylcyclopropanecarbonyl peroxide*. This peroxide was similarly obtained from the corresponding acid [29] as colourless *crystals*, m.p. 98 °C (decomp.) (Found: C, 67.9; H, 9.4. $C_{16}H_{26}O_4$ requires C, 68.05; H, 9.3%); $\nu_{max.}$ 1 770 and 1 790 cm^{-1}; $\delta(CCl_4)$ 1.13 (2 H, d, CH), 1.23 (24 H, s, 8Me).

(*iv*) *Bis*-1,5-*dimethylbicyclo*[3.1.0]*hexane*-6-exo-*carbonyl peroxides*. (*a*) 1,2-Dimethylcyclopentene [30] (9.6 g), purified by preparative gas chromatography (30% SE30 or Chromosorb W), and anhydrous copper sulphate (1 g) were boiled together under reflux, and ethyl diazoacetate (16 g) was added during 40 min. The mixture was boiled for a further 1 h, and poured onto ice; the dried organic product was distilled through a short column, and the fraction of b.p. 78—90 °C (1 mmHg) was subjected to preparative gas chromatography (20% FFAP on Chromosorb W, 210 °C) to separate the stereoisomeric *ethyl* 1,5-*dimethylbicyclo*-[3.1.0]*hexane*-6-*carboxylates* from unidentified by-products. The required esters were then separated by preparative gas chromatography on a silicone oil column (30% SE30 on Chromosorb W, 190 °C) to give as colourless oils what were believed to be the *endo*-isomer, b.p. 203 °C (3.45 g, 19%) (Found: C, 72.3; H, 10.1%; *M*, 182. $C_{11}H_{18}O_2$ requires C, 72.5; H, 10.0%; *M*, 182.3); $\nu_{max.}$ 1 730 cm^{-1}; $\delta(CDCl_3)$ 1.12 (1 H, s), 1.17 (6 H, s, 2Me), 1.23 (3 H, t), 1.35—2.25 (6 H, m), and 4.08 (2 H, q), and the *exo*-isomer, b.p. 208 °C (4.0 g, 22%) (Found: C, 72.5; H, 9.8%; *M*, 182); $\nu_{max.}$ 1 730 cm^{-1}; $\delta(CDCl_3)$ 1.3 (6 H, s, 2Me), 1.25 (3 H, t), 1.47 (1 H, s), 1.5—2.1 (6 H, m), and 4.08 (2 H, q). The configurational assignment is based on the relative n.m.r. shifts of methyl and ring hydrogens on addition of a europium shift reagent. (*b*) Base hydrolysis gave the corresponding *carboxylic acids* as colourless solids: *endo*-isomer, m.p. 70 °C (Found: C, 70.3; H, 9.1%; *M*, 154. $C_9H_{14}O_2$ requires C, 70.1; H, 9.15%; *M*, 154.3); $\nu_{max.}$ 1 700 cm^{-1}; *exo*-isomer, m.p. 108 °C (Found: C, 70.4; H, 9.4%; *M*, 154); $\nu_{max.}$ 1 690 cm^{-1}. (*c*) The carboxylic acids were then condensed with hydrogen peroxide following the usual procedure.[24] The *exo*-acid gave the corresponding colourless *diacyl peroxide*, m.p. 105—107 °C (decomp.) in good yield (70%) (Found: C, 70.6; H, 8.5. $C_{18}H_{26}O_4$ requires C, 70.6; H, 8.55%); $\nu_{max.}$ 1 775 and 1 795 cm^{-1}. However, a similar reaction with the *endo*-acid gave, after removal of dicyclohexylurea and extraction of unreacted acid with 10% Na_2CO_3, a pale yellow oil which could not be induced to crystallise, which apparently contained further starting acid (i.r.), and which decomposed rapidly (see below).

(*v*) *Bis*-cis-*bicyclo*[6.1.0]*nonane*-9-*carbonyl peroxide*. Following essentially the procedure described under (*ivb*), *cis*-cyclo-octene was cyclopropanated using ethyl diazoacetate to give, after preparative gas chromatography (20% FFAP at 230 °C), a mixture of stereoisomeric products in the ratio 2.5 : 1 (lit.,[31] *exo* : *endo* ratio 2.1 : 1). The mixed esters were hydrolysed with base to give the mixed carboxylic acids, m.p. 110—114 °C (lit.,[32] 113.5—114.8 °C). After repeated crystallisation a sample with m.p. 112.5—113.5 °C was obtained. This was esterified (EtOH–H_2SO_4) to give a mixture of *exo*- and *endo*-bicyclononanecarboxylic acid ethyl esters (3 : 1), suggesting that the acids cannot be separated by crystallisation. The mixture of acids was condensed with hydrogen peroxide in the usual way to give a sharp-melting [111 °C (decomp.)] crystalline *peroxide* (20%), also apparently as a mixture of isomers (Found: C, 71.8; H, 9.1. $C_{20}H_{30}O_4$ requires C, 71.8; H, 9.0%); $\nu_{max.}$ 1 795 and 1 770 cm^{-1}; $\delta(CDCl_3)$ 0.5—2.5 (m, 12 CH_2 + 6 CH).

(*vi*) *Bis*-trans-*bicyclo*[6.1.0]*nonane*-9-*carbonyl peroxide*. (*a*) *trans*-Cyclo-octene was first prepared from *trans*-(2-hydroxycyclo-octyl)diphenylphosphine oxide by the following procedure, during which hydroquinone was added in small portions at each stage (total 1.0 g) to prevent free-radical polymerisation of the *trans*-cyclo-octene during its formation and extraction. Sodium hydride (12.0 g; 80% in oil), contained in a 2-litre 3-necked flask, fitted with a gas-tight stirrer, a dropping funnel with a side arm adapter for nitrogen gas lead, and a double adapter for a thermometer and reflux condenser plus calcium chloride tube, was washed twice with light petroleum (b.p. 40—60 °C) to remove the oil, and *trans*-(2-hydroxycyclo-octyl)diphenylphosphine oxide (90 g, 0.274 mol) in dry, distilled, dimethylformamide (1 100 ml) was added with stirring during 20 min under a nitrogen atmosphere. Stirring was continued at room temperature for a further 30 min when the flask was cooled in a bath of solid CO_2–acetone, and water (375 ml) was added dropwise during 20 min maintaining an internal reaction temperature of 0 ± 5 °C. The product was poured into ice–water (1 500 ml) which was then extracted with light petroleum (b.p. 40—60 °C, 2 × 500 ml). The petroleum extract was washed with water and dried (Na_2CO_3). Solvent was removed and the residual oil fractionated from a Vigreux flask to give *trans*-cyclo-octene (28.7 g, 95% yield) as a colourless liquid, b.p. 145 °C. This procedure reproducibly gave >90% yield of distilled *trans*-cyclo-octene contaminated with <1% *cis*-isomer (g.l.c.). (*b*) A mixture of *trans*-cyclo-octene (15 g), ethyl diazoacetate (16.7 g), and dry ether (50 ml) was refluxed for 2.5 h. After removing the ether, the residue was heated to 90 °C *in vacuo* to remove any cyclo-octene and diazoacetate. The remaining pyrazoline was dissolved in *o*-dichlorobenzene (100 ml) and the mixture refluxed for 86 h. Solvent was removed, and the residue distilled to give a colourless oil, b.p. 110—130 °C at 2 mmHg. From this was obtained ethyl *trans*-bicyclo[6.1.0]nonane-9-carboxylate (6.2 g, 23%) by preparative gas chromatography (20% FFAP on Chromosorb W at 210 °C), b.p. 96 °C at 1 mmHg (Found: C, 73.2; H, 10.3. $C_{12}H_{20}O_2$ requires C, 73.4; H, 10.3%); $\nu_{max.}$ 1 730 cm^{-1}; $\delta(CHCl_3)$ 0.5—2.4 (15 H, m, 6 CH_2 + 3 CH), 1.24 (3 H, t), and 4.11 (2 H, q). The product was contaminated with *ca.* 2% of the *exo-cis*-isomer, which was not cleanly removed by preparative gas chromatography. A second g.c. fraction (2 g) contained a roughly 1 : 1 mixture of the two isomers. (*c*) The ester was hydrolysed with base to give *trans*-bicyclo[6.1.0]nonane-9-carboxylic acid, m.p. 109—110 °C from light petroleum (b.p. 60—80 °C) (lit.,[33] m.p. 109—110 °C). (*d*) The acid was condensed with hydrogen peroxide in the usual way to give, after removal of dicyclohexylurea and unreacted acid, *bis*-(trans-*bicyclo*-[6.1.0]*nonane*-9-*carbonyl*) *peroxide* as a colourless viscous oil, $\nu_{max.}$ 1 795 and 1 770 cm^{-1}, which could not be induced to crystallise. Presumably both stereoisomers were present.

(*vii*) *Bis*-(1-*methylbicyclo*[3.1.0]*hexane*-exo-6-*carbonyl*) *peroxide*. This was prepared from 1-methylcyclopentene following the same procedure as that adopted for the dimethyl analogue [(*iv*) above]. The stereoisomeric ester intermediates were separated by preparative gas chromatography, and the predominant *exo*-isomer was hydrolysed to

the corresponding acid,[34] and condensed with hydrogen peroxide to give the desired *peroxide* as a colourless oil, $\nu_{max.}$ 1 765 and 1 785 cm^{-1}, which could not be induced to crystallise.

Thermolysis of Peroxides in Benzene.—For product investigation, each peroxide was added to boiling benzene, and the mixture boiled under reflux for 20 h. The reactions all employed the proportions 1 g peroxide to 100 ml benzene.

(*i*) *Bis*-cis,trans-2,3-*diphenylcyclopropanecarbonyl peroxide*. The products from this peroxide (1 g) were chromatographed on basic alumina, and hydrocarbon product eluted with benzene–light petroleum (b.p. 60—80 °C) (1 : 6). This comprised a 1 : 1 mixture (n.m.r.) of the two *E,E*-isomers of 1,3,4,6-tetraphenylhexa-1,5-diene (0.2 g, 25%). Crystallisation from light petroleum (b.p. 60—80 °C)–ethanol gave pure samples of the two isomers, one as colourless needles, m.p. 140—141 °C; $\nu_{max.}$ 850 cm^{-1}; $\delta(CCl_4)$ 3.8 (2 H, m), 6.15 (2 H, dd + 2 H dd), and 7.08 (10 H, s); and one as cubes, m.p. 140—141 °C; $\nu_{max.}$ 860 cm^{-1}; $\delta(CCl_4)$ 3.8 (2 H, m), 6.4 (4 H, m), and 7.05 (10 H, s).

(*ii*) *Bis*-trans,trans-2,3-*diphenylcyclopropanecarbonyl peroxide*. Work-up of the products as in (*i*) gave a 25% yield of the same product, again as a 1 : 1 mixture of stereoisomers.

(*iii*) *Bis*-2,2,3,3-*tetramethylcyclopropanecarbonyl peroxide*. The n.m.r. spectrum of the crude product from this peroxide (2.1 g) showed olefinic protons, but the pattern was not consistent with the formation of products derived from the tetramethylallyl radical. Instead they were suggestive of dihydrobenzene derivatives. Examination by gas chromatography (FFAP, 150 °C) indicated the presence of the following products, identified as indicated below: 2,2,3,3-tetramethylcyclopropanecarboxylic acid (250 mg, 12%); 2,2,3,3-*tetramethylcyclopropyl* 2,2,3,3-*tetramethylcyclopropane*-1-*carboxylate* (200 mg, 11%); 1-*phenyl*-2,2,3,3-*tetramethylcyclopropane* (50 mg, 2%); and traces of 1-(*cyclohexa*-2,5-*dienyl*)-2,2,3,3-*tetramethylcyclopropane* (*ca.* 0.5%) and an unidentified volatile product (*ca.* 0.5%). The low product balance may, in part, be due to the formation of dimers of cyclopropylcyclohexadienyl radicals, and products derived therefrom. The above ester was isolated by preparative gas chromatography as a colourless solid, m.p. 37—38 °C (Found: C, 75.7; H, 11.2. $C_{15}H_{26}O_2$ requires C, 75.6; H, 11.0%); $\nu_{max.}$ 1 760 cm^{-1}; $\delta(CCl_4)$ 0.93 (6 H, s), 1.07 (6 H, s), 1.1 (1 H, s), 1.17 (6 H, s), 1.21 (6 H, s), and 3.25 (1 H, s). A mixture of the phenyltetramethylcyclopropane and its dihydro-derivative was also isolated but could not be separated. The n.m.r. spectrum of this mixture included peaks attributable to the diene as follows: $\delta(CCl_4)$ 1.03 (6 H, s, 2Me), 1.08 (6 H, s, 2Me), 2.5—2.7 (3 H, m, CH_2 + CH), and 5.55 (4 H, m, vinyl). The mixture was oxidised by *o*-chloranil in hot benzene, in the presence of biphenyl as internal standard for g.l.c. analysis. The g.c. peak attributed to phenyltetramethylcyclopropane increased as the peak attributed to the diene disappeared. Chromatography of the total reaction product over basic alumina followed by gas chromatographic purification of the product gave phenyltetramethylcyclopropane identical with a sample prepared by ultra-violet irradiation of a solution of *trans*-stilbene oxide (3.8 g) and benzophenone (1 g) in tetramethylethylene (10 g) and cyclohexane (50 ml). The product (50 mg) from the photochemical reaction was isolated by preparative gas chromatography (first on 30% silicone oil SE 30 on Chromosorb W at 180 °C, and then on 20% FFAP on Chromosorb W at 170 °C) as a colourless oil, b.p. 213 °C (Found: C, 89.8; H, 10.5. $C_{13}H_{18}$ requires C, 89.6; H, 10.4%); $\delta(CCl_4)$ 0.93 (6 H, s), 1.25 (CH, s), 1.52 (1 H, s), and 7.08 (5 H, m)].

(*iv*) (*a*) *Bis*-1,5-*dimethylbicyclo*[3.1.0]*hexane*-6-exo-*carbonyl peroxide*. The product mixture from the peroxide (1 g) was washed with aqueous sodium hydroxide to remove carboxylic acid (0.12 g). The crude neutral product contained an olefin (n.m.r., δ 5.2), which was isolated by preparative gas chromatography (30% silicone oil SE 30 on Chromosorb W at 220 °C) as a colourless solid, m.p. 70—71.5 °C, and identified as bi-(1,3-dimethylcyclohex-2-en-1-yl) (10) (0.15 g, 21%) (Found: C, 87.9; H, 12.0. $C_{16}H_{26}$ requires C, 88.0; H, 12.0%); *m/e* 109 (base peak) $[\frac{1}{2}M]^+$; $\delta(CCl_4)$ 0.9 [6 H, s, 2Me (C-1)], 1.2—2.1 (12 H, m, $6CH_2$), 1.6 [6 H, s, 2Me (C-3)], and 5.2 (2 H, br s, vinyl).

(*b*) The only product isolated from the pyrolysis of the crude bis(dimethylbicyclohexane-*endo*-carbonyl) peroxide (1 g) was the corresponding carboxylic acid (0.5 g).

(*v*) *Bis*-cis-*bicyclo*[6.1.0]*nonane*-exo- *and* -endo-*carbonyl peroxides*. The product from the mixed peroxide (1 g) was free from carboxylic acid (0.1 g, 10%) by washing with aqueous Na_2CO_3. The neutral product contained an olefin (n.m.r.) apparently similar to the cyclohexadiene reported in (*iii*); it was therefore dissolved with *o*-chloranil (0.6 g) in CCl_4 (10 ml), and the mixture was refluxed for 15 min. Chromatography on basic alumina, followed by distillation under reduced pressure, gave a mixture of endo- and exo-9-*phenyl*-cis-*bicyclo*[6.1.0]*nonanes* as a colourless oil (0.5 g, 42%) (Found: C, 89.7; H, 10.2%; *M*, 200. $C_{15}H_{20}$ requires C, 89.9; H, 10.1%; *M*, 200.3); $\delta(CHCl_3)$ 0.0—2.4 (15 H, m, 6 CH_2 and 3 CH) and 7.1 (5 H, m).

(*vi*) *Bis*-trans-*bicyclo*[6.1.0]*nonanecarbonyl peroxide*. The product from decomposition of the peroxide (2.2 g) was freed from carboxylic acid (0.86 g, 39%) by washing with aqueous Na_2CO_3, and the neutral material, after n.m.r. examination, was heated as above with *o*-chloranil (1.3 g) in CCl_4 (50 ml). Chromatography of the product on a column of basic alumina coated with 20% w/w silver nitrate, beneath a column of basic alumina, and elution with light petroleum (b.p. 40—60 °C) gave, in the first fraction, a product which, after distillation and purification by preparative gas chromatography (SE30, 170 °C), was identified as *trans*-bicyclo[6.1.0]nonane (0.18 g, 11%), identical with a (g.c. purified) sample prepared by pyrolysis (360 °C) of the pyrazoline formed from diazomethane and *trans*-cyclo-octene. Further elution of the column gave a second product which was purified by distillation under reduced pressure, and identified as 9-*phenyl*-trans-*bicyclo*[6.1.0]*nonane* (0.55 g, 21%) (Found: C, 89.7; H, 10.5%; *M*, 200. $C_{15}H_{20}$ requires C, 89.9; H, 10.10; *M*, 200.3); $\delta(CDCl_3)$ 0.3—2.6 (15 H, m, 6 CH_2 + 3 CH) and 7.20 (5 H, s).

(*vi*) *Bis*-(1-*methylbicyclo*[3.1.0]*hexane*-6-*carbonyl*) *peroxide*. This peroxide (3 g) gave carboxylic acid (1.0 g, 33%), and a neutral product which from ^1H n.m.r. evidence and gas chromatography appeared to contain *endo*- and *exo*-1-methyl-6-phenylbicyclo[3.1.0]hexanes and the corresponding dihydro-derivatives. The mixture was not subjected to detailed examination.

Interconversion of Diastereoisomeric trans,trans-*Tetraphenylhexadienes*.—The diphenylcyclopropylcarbonyl peroxides were both found to have half lives of 1.5—2 h in boiling benzene at concentrations comparable to those em-

ployed in the preparative experiments (i.r.). Decomposition of each for *ca.* 1 h, and examination of the total product (n.m.r.), indicated that the two tetraphenylhexadiene isomers were formed in comparable amounts. However, when each tetraphenylhexadiene isomer (50 mg) was refluxed singly in benzene (10 ml) for 62 h, the following results were obtained; isomer 1 (needles) gave a 65 : 35 mixture of 1 and 2; isomer 2 (cubes) gave a 45 : 55 mixture of 1 and 2.

We are grateful to the S.R.C. for financial support, and to Dr. G. H. Whitham for details of the procedure for synthesis of *trans*-cyclo-octene. A. P. E. thanks the British Council for an Exchange Fellowship.

[8/540 *Received*, 22*nd March*, 1978]

REFERENCES

[1] J. W. Wilt, in ' Free Radicals,' vol. 1, ed. J. K. Kochi, Wiley, New York, 1973.
[2] R. E. Lehr, J. M. Wilson, J. W. Harder, and P. T. Cohenour, *J. Amer. Chem. Soc.*, 1976, **98**, 4867.
[3] *e.g.* R. Sustmann and D. Brandes, *Tetrahedron Letters*, 1976, 1791; R. Sustmann and F. Lübbe, *J. Amer. Chem. Soc.*, 1976, **98**, 6037.
[4] G. Szeimies and G. Boche, *Angew. Chem. Internat. Edn.*, 1971, **10**, 912; D. T. Clark and D. B. Adams, *Nature Phys. Sci.*, 1971, **233**, 121; L. Farnell and W. G. Richards, *J.C.S. Chem. Comm.*, 1973, 344; see also E. A. Halevi, J. Katriel, R. Pauncz, F. A. Matsen, and T. L. Welsher, *J. Amer. Chem. Soc.*, 1978, **100**, 359.
[5] R. B. Woodward and R. Hoffmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 781.
[6] N. L. Bauld, F. Farr, and C. S. Chang, *Tetrahedron Letters*, 2443; see also N. L. Bauld and J. Cessac, *J. Amer. Chem. Soc.*, 1977, **99**, 23.
[7] M. J. S. Dewar and S. Kirschner, *J. Amer. Chem. Soc.*, 1974, **96**, 5244; M. J. S. Dewar, *Chem. in Britain*, 1975, **11**, 97.
[8] J. C. Chen, *Tetrahedron Letters*, 1971, 3669.
[9] H. M. Walborsky and J. C. Chen, *J. Amer. Chem. Soc.*, 1970, **92**, 7573.
[10] J. W. Wilt, R. A. Dabek, and K. C. Welzel, *J. Org. Chem.*, 1972, **37**, 425.
[11] J. A. Kerr, A. Smith, and A. F. Trotman-Dickenson, *J. Chem. Soc.* (*A*), 1969, 1400.
[12] (*a*) S. Sustmann, C. Rüchardt, A. Bieberbach, and G. Boche, *Tetrahedron Letters*, 1972, 4759; S. Sustmann and C. Rüchardt, (*b*) *Tetrahedron Letters*, 1972, 4765; (*c*) *Chem. Ber.*, 1975, **108**, 3043.
[13] R. P. Lutz, S. Bernal, R. J. Boggio, R. O. Harris, and M. W. Nicholas, *J. Amer. Chem. Soc.*, 1971, **93**, 3985.
[14] J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, 1968, **90**, 7157.
[15] P. J. Krusic, J. P. Jenson, and J. K. Kochi, *J. Amer. Chem. Soc.*, 1969, **91**, 4566.
[16] R. Sustmann and R. W. Gellert, *Chem. Ber.*, 1976, **109**, 345.
[17] A. Barmetler, C. Rüchardt, R. Sustmann, S. Sustmann, and R. Verhuelsdonk, *Tetrahedron Letters*, 1974, 4392.
[18] G. Wittig, V. Rautenstrauch, and F. Wingler, *Tetrahedron Supplement*, 1965, **7**, 189.
[19] S. W. Benson, ' Thermochemical Kinetics,' Wiley, New York, 1968, p. 179.
[20] H. S. Chen, D. J. Edge, and J. K. Kochi, *J. Amer. Chem. Soc.*, 1973, **95**, 7036.
[21] W. H. Davis and J. K. Kochi, *Tetrahedron Letters*, 1976, 1761.
[22] H. Regenstein, W. Ahrens, and A. Berndt, *Tetrahedron*, 1975, **31**, 2837.
[23] A. J. Bridges and G. H. Whitham, *J.C.S. Chem. Comm.*, 1974, 142.
[24] F. D. Greene and J. Kazan, *J. Org. Chem.*, 1963, **28**, 2168.
[25] P. Warner and S.-L. Lu, *Tetrahedron Letters*, 1976, 4665.
[26] T. Shono and I. Nishiguchi, *Tetrahedron*, 1974, **30**, 2183.
[27] *e.g.* T. Kawamura, M. Tsumura, and T. Yonezawa, *J.C.S. Chem. Comm.*, 1977, 373; T. Kawamura, M. Tsumura, Y. Yokomichi, and T. Yonezawa, *J. Amer. Chem. Soc.*, 1977, 99, 8251, and reference therein.
[28] See *e.g.* R. Hiatt in ' Organic Peroxides ' ed. D. Swern, Wiley, New York, 1971, vol. II, p. 856.
[29] A. P. Mescheryakov and I. E. Dolgii, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1960, 931.
[30] M. van Rysselberge, *Bull. Soc. chim. belg.*, 1926, **35**, 311.
[31] W. R. Moser, *J. Amer. Chem. Soc.*, 1969, **91**, 1139.
[32] S. Akiyoshi and T. Matsudu, *J. Amer. Chem. Soc.*, 1955, **77**, 2476.
[33] W. R. Moore and R. D. Bach, *J. Amer. Chem. Soc.*, 1972, **94**, 3152.
[34] J. Meinwald, A. Lewis, and P. G. Gassman, *J. Amer. Chem. Soc.*, 1962, **84**, 982.