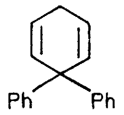
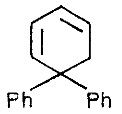
Formation and Rearrangement of 6,6-Diphenylbicyclo[3,1,0]hex-2-ene †

By **D. J. Atkinson, M. J. Perkins,*** and **P. Ward,** Department of Chemistry, King's College, Strand, London WC2R 2LS

The role of biradical intermediates in the addition of diphenylmethylene to cyclopentadiene is discussed. The adduct 6,6-diphenylbicyclohexene is oxidised to 6,6-diphenylfulvene by *N*-bromosuccinimide or t-butyl peroxybenzoate–copper. These results are reviewed in the context of cyclohexadienone photochemistry. With potassium t-pentoxide in t-pentyl alcohol the diphenylbicyclohexene is isomerised to a mixture of diphenylcyclohexadienes. With potassium t-butoxide in dimethyl sulphoxide, a mixture of benzhydrylcyclopentadienes is obtained.

ALTHOUGH the isomeric dienes (I) and (II) were obvious candidates for selection as precursors to the 6,6-diphenylcyclohexadienyl radical (V),[1] problems envisaged in their synthesis led to an initial investigation of the radical chemistry of 6,6-diphenylbicyclohexene (III). It was anticipated that this compound should be readily accessible by diphenylmethylene addition to cyclopentadiene, and that hydrogen abstraction from it might be attended by an allowed disrotatory opening of the cyclopentenyl ring in (IV) to give (V).


(I)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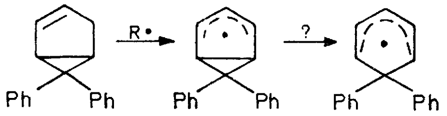

(III) (IV) (V)

The synthesis of (III) has now been effected independently by Zimmerman *et al.*,[2] in the course of their extensive investigations into cyclohexadienone photochemistry, using the reaction indicated above. As in our work, diphenylmethylene was generated by photolysis of diphenyldiazomethane, and its adduct with cyclopentadiene (III) was isolated as a colourless crystalline solid. It seems important to comment on the success of this synthesis, for with many olefins, *e.g.* cyclohexene, addition of diphenylmethylene leads predominantly, not to cyclopropanes, but to apparent insertion products.[3] This is rationalised in terms of a relatively ready intramolecular 1,4-hydrogen transfer in the initial adduct biradical ‡ which competes effectively with ring-closure [equation (1)]. Only in additions to molecules such as styrene,[4] where this path is not available, is there a good yield of the cyclopropane [equation (2)]. It was hoped that cyclopentadiene would fall into the second category, as the only plausible hydrogen transfer would involve a 1,2- or a 1,3-shift. The experiments were in good accord with this, for no C_{18} products other than (III) were identified [equation (3)]. The low yield of (III) (*ca.* 15%) is largely ascribable to the competing formation of products (*e.g.* tetraphenylethane) which must have arisen by processes in which the diphenylmethylene had not added to the diene. In contrast, addition of fluorenylidene [5] to cyclopentadiene gave the polycyclic hydrocarbon (VI) in much better yield (*ca.* 40%).

The initial attempts to effect hydrogen abstraction from (III), utilised t-butoxyl radicals generated by thermolysis of di-t-butyl peroxyoxalate. However, no products could be identified from these reactions.

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† A portion of this work has been communicated in preliminary form: D. J. Atkinson, M. J. Perkins, and P. Ward, *Chem. Comm.*, 1969, 1390.

‡ Diphenylmethylene adds to olefins as a biradical.[3]

[1] D. J. Atkinson, M. J. Perkins, and P. Ward, preceding paper.

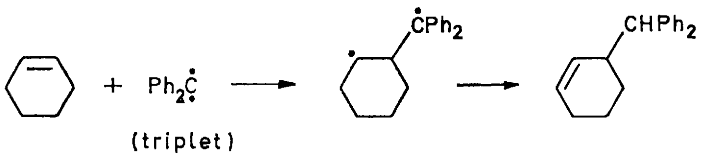
[2] H. E. Zimmerman, D. S. Crumrine, D. Döpp, and P. S. Huyffer, *J. Amer. Chem. Soc.*, 1969, **91**, 434.

[3] G. L. Closs and L. E. Closs, *Angew. Chem. Internat. Edn.*, 1962, **1**, 334.

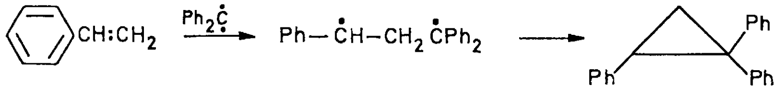
[4] B. S. Gorton, *J. Org. Chem.*, 1965, **30**, 648; see also H. Nozaki, M. Nakano, and K. Kondo, *Tetrahedron*, 1966, **22**, 477.

[5] *E.g.*, W. Kirmse, 'Carbene Chemistry,' Academic Press, New York and London, 1964, p. 250.

Subsequently reactions, either with *N*-bromosuccinimide (NBS), or with t-butyl peroxybenzoate in the presence of copper salts, were found to give 6,6-diphenylfulvene. Repetition of the experiments with di-t-butyl peroxyoxalate then revealed that diphenylfulvene was formed in this reaction also, though in trace quantities only. No additional products could be identified.



(1)



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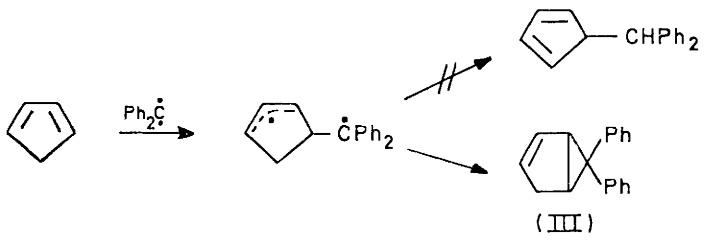

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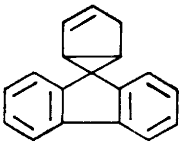
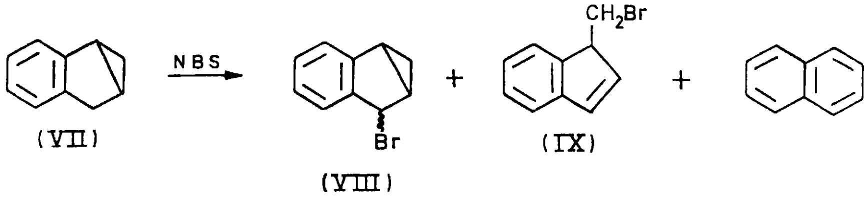
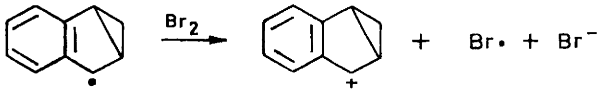


(VI)



A reasonable mechanism for the formation of diphenylfulvene involves scission of a perimetrical cyclopropane bond in the intermediate bicyclohexenyl radical (IV) to give a benzhydryl, rather than a cyclohexadienyl radical, but the possibility of prior oxidation to a bicyclohexenyl cation (by cupric copper, or by ionisation of an intermediate allylic bromide) cannot be excluded.* A somewhat similar ambiguity exists in the cyclisation reactions of aliphatic olefins promoted by peroxide–copper salt reagents, which were discovered by Breslow *et al.*[7] In the present reactions, however, a radical mechanism is strongly to be preferred by analogy with the results of Friedrich[8] concerning the NBS-bromination of cyclopropindene (VII). In that reaction a mixture of bromides (VIII) and (IX) were formed, together with a little naphthalene, all of which products were stable to the reaction conditions. Presumably a free-radical bicyclohexenyl → cyclohexadienyl rearrangement is responsible for the formation of the naphthalene, but the fact that ring-opening to give (IX) competes favourably with this suggests that scission of the perimetrical bond should be the exclusive mode of reaction when C-6 bears two phenyl substituents, as in the present work. The possibility remains, however, that oxidation of the bicyclohexenyl radical to a cation might proceed without the intervention of an allylic bromide, *e.g.*



(X)

* Thermal opening of a bicyclohexenyl cation to a cyclohexadienyl cation, forbidden by the rules of orbital symmetry conservation has nevertheless been observed, and has an activation energy of *ca.* 18 kcal mol^{-1}.[6]

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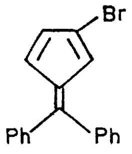
[6] R. F. Childs, M. Sakai, and S. Winstein, *J. Amer. Chem Soc.*, 1968, **90**, 7144; R. F. Childs and S. Winstein, *ibid.*, 1968 **90**, 7146.

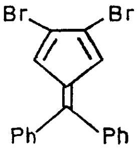
[7] R. Breslow, S. S. Olin, and J. T. Groves, *Tetrahedron Letters*, 1966, 4717; 1968, 1837.

[8] E. C. Friedrich, *J. Org. Chem.*, 1969, **34**, 528.

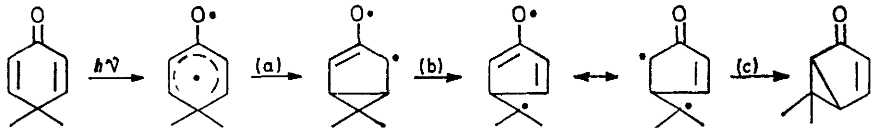
The reaction between (III) and NBS was investigated more closely, as t.l.c. on silver nitrate-impregnated silica gel revealed two coloured products additional to diphenylfulvene. These same compounds were produced in more substantial yield from the bromination of diphenylfulvene with NBS, and were identified as mono- and di-bromo-derivatives of diphenylfulvene, with the probable structures (XI) and (XII). Attempts to establish the substitution pattern in these products by spectroscopic examination of their Diels–Alder adducts with dienophiles were frustrated by the failure to effect any cycloaddition reactions with these compounds, despite the ready addition of similar dienophiles to diphenylfulvene itself.



(XI)



(XII)

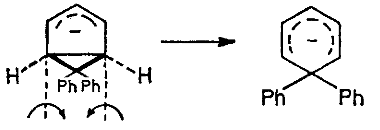


As in the preceding paper, the mechanism of the reactions discussed here appear to have a bearing on model photochemical systems. In particular, they provide ground-state analogies for the biradical mechanism suggested[9,10] for the 'Type A' photorearrangement of cross-conjugated cyclohexadienones to give bicyclohexenones, which is generalised in the annexed formulae. Step (a) is common to both this scheme and the alternative Zimmerman mechanism,[11] and in effect is the reverse of the electrocyclic ring opening of (X) which leads to naphthalene. Step (b) is akin to the ring-opening of the bicyclohexenyl radical, here believed to be a key process in the formation of diphenylfulvene, and step (c) is similar to the collapse of the biradical adduct of diphenylmethylene and cyclopentadiene.

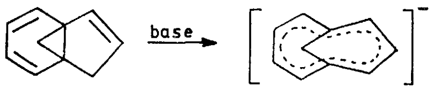
Whilst coloured intermediates have been detected in dienone photochemistry,[12] and have been assigned zwitterionic structures, and products have been characterised which are best rationalised as being derived from zwitterionic intermediates,[13] the conclusion that the Zimmerman mechanism is a unique path for the type A rearrangement of cyclohexadienones is, in the opinion of the present authors, still open to question (see also ref. 14).

Although the desired rearrangement of the diphenylbicyclohexenyl radical was not realised, the possibility existed that the corresponding carbanion might undergo a symmetry-allowed disrotatory ring-opening to a cyclohexadienyl structure [(XIII) ⟶ (XIV)]. This type of reaction is implicated in the formation of (XVI) from (XV) on treatment with strong base.[15] When the diphenylbicyclohexene (III) was dissolved in a boiling solution of potassium t-pentoxide in t-pentyl alcohol, it was slowly transformed into a mixture of the dienes (I) and (II), in which the former predominated (*ca.* 3 : 2, by n.m.r. integration).

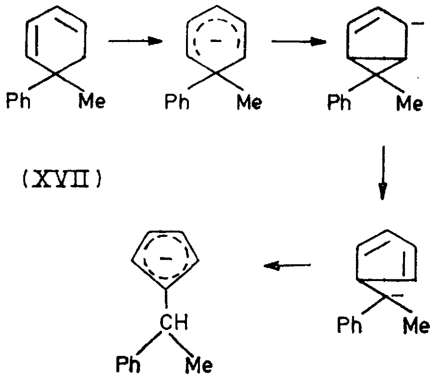
Calculated heats of formation of (I) and (III) are sufficiently close that the reverse isomerisation might occur at a detectable rate, and this is in accord with the recent report that 5-methyl-5-phenylcyclohexa-1,3-diene (XVII) slowly reacts with alkali-metal amides in liquid ammonia to give phenethylcyclopentadienide, presumably by the sequence shown.[16] We have now found that compound (III) is rapidly destroyed when it is dissolved at room temperature in Me$_2$SO containing



(XIII) (XIV)



(XV) (XVI)



(XVII)

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[9] B. Capon, M. J. Perkins, and C. W. Rees, 'Organic Reaction Mechanisms, 1967,' Interscience, London, 1968, p. 372.

[10] J. S. Swenton, E. Saurborn, R. Srinivasan, and F. I. Sonntag, *J. Amer. Chem. Soc.*, 1968, **90**, 2990.

[11] H. E. Zimmerman and J. S. Swenton, *J. Amer. Chem. Soc.*, 1967, **89**, 906, and related papers from Zimmerman's group.

[12] M. H. Fisch, *Chem. Comm.*, 1969, 1472.

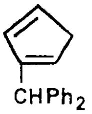
[13] D. I. Schuster and V. Y. Abratys, *Chem. Comm.*, 1969, 419.

[14] R. B. Woodward and R. Hoffmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 817.

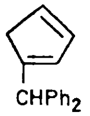
[15] W. Grimme, M. Kaufhold, V. Dettmeier, and E. Vogel, *Angew. Chem. Internat. Edn.*, 1966, **5**, 604; P. Radlick and W. Rosen, *J. Amer. Chem. Soc.*, 1966, **88**, 3461.

[16] S. W. Staley and J. P. Erdmann, *J. Amer. Chem. Soc.*, 1970 **92**, 3832.

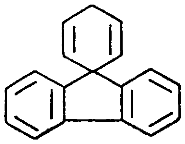
potassium t-butoxide, and that if the resulting solution is quenched into water a product is obtained whose n.m.r. spectrum is readily interpreted in terms of a mixture of the benzhydrylcyclopentadienes (XVIII) and (XIX). Curiously, however, when the dienes (I) or (II) are dissolved in the same medium, although rapid equilibration of the two isomers occurs, quenching into water does not reveal any detectable benzhydrylcyclopentadiene formation. Hence one is led to the conclusion that the base-catalysed opening of the cyclopropane ring in (III) is solvent-dependent. The mechanistic complexities of this and related base-catalysed isomerisation are currently under investigation.



(XVIII)



(XIX)



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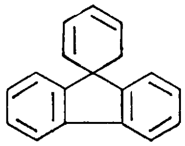

(XXI)

An attempt to prepare the dienes (XX) and (XXI) by base-catalysed isomerisation of (VI) was unsuccesful. Probably this is a consequence of the greater stability of fluorenyl carbanions when compared with diphenylmethyl, and therefore exclusive fission of the perimetrical cyclopropane bond following deprotonation of (VI), even in t-pentyl alcohol.

EXPERIMENTAL

6,6-*Diphenylbicyclohex*-2-*ene*.—This hydrocarbon was prepared essentially by the method subsequently reported by Zimmerman, Crumrine, Döpp, and Huyffer,[2] involving photolysis of diphenyldiazomethane in cyclopentadiene. The yield of needles, m.p. 80—80·5° (from ethanol), varied between 10 and 20%. Major by-products were benzophenone azine (*ca.* 20%) and tetraphenylethane (*ca.* 60%).

Fluorene-9-*spiro*-6-*bicyclo*[3,1,0]*hex*-2-*ene* (VI).—A solution of 9-diazofluorene[17] (23 g) in freshly distilled cyclopentadiene (225 ml) was deoxygenated and irradiated under nitrogen with a Hanovia medium-pressure 450 W mercury arc (Pyrex filter). The temperature of the solution was maintained at *ca.* 15° by means of a water cooling jacket. The progress of the reaction was monitored by t.l.c., and irradiation was discontinued when only a trace of diazo-compound remained (29 h). Cyclopentadiene and dicyclopentadiene were removed under reduced pressure, and the residual red oil was dissolved in a little chloroform. Addition of ethanol precipitated an orange powder (9·5 g) which, on treatment with a mixture of benzene and light petroleum (b.p. 60—80°) left a deeply coloured residue. The orange solution was boiled with decolourising carbon, the solvent was removed, and the residue was crystallised from ethanol–methylene chloride to give the *spiro-compound* (VI) as needles m.p. 160—161° (5·5 g) [Found: C, 93·4; H, 6·3%; *M* (mass spectrometry), 230. $C_{18}H_{14}$ requires C, 93·9; H, 6·1%; *M*, 230]; τ 2·0—3·1 (8H, m), 3·8—4·3 (2H, m), and 6·7—7·4 (4H, m).

Reaction of 6,6-*Diphenylbicyclohex*-2-*ene with* N-*Bromosuccinimide*.—A carbon tetrachloride solution (5 ml) of the hydrocarbon (140 mg), NBS (110 mg), and azobisisobutyronitrile (*ca.* 1 mg) was boiled under reflux for 14 h. The resulting deep red solution was filtered, and the solvent was then removed to leave a dark red oil. Examination of this oil by t.l.c., employing silica gel impregnated with silver nitrate, revealed three coloured products in addition to unchanged starting material. One of the coloured products had the same R_F value as authentic diphenylfulvene (prepared by condensation of benzophenone and cyclopentadiene in the presence of sodium ethoxide). The red oil was chromatographed on a silica-gel column impregnated with silver nitrate, which was eluted with a mixture of benzene (20%) and hexane (80%). Three major fractions were collected which on evaporation gave (*a*) 20 mg of deep red oil which deposited black crystals, m.p. 128—129° from ethanol; (*b*) 29 mg of red oil; (*c*) 79 mg of orange oil shown by g.l.c. to consist of diphenylfulvene (*ca.* 55%) and diphenylbicyclohexene (*ca.* 45%) by g.l.c. Further chromatography gave pure diphenylfulvene, m.p. alone and on admixture with authentic diphenylfulvene 81—82°. Fractions (*a*) and (*b*) were chromatographically indistinguishable from the products of the following experiment.

Reaction of 6,6-*Diphenylfulvene with* 1 *Equivalent of* N-*Bromosuccinimide*.—A carbon tetrachloride solution (14 ml) of diphenylfulvene[18] (230 mg, 10^{-3} mol), *N*-bromosuccinimide (178 mg, 10^{-3} mol) and azobisisobutyronitrile (*ca.* 2 mg) was boiled under reflux for 14 h. The resulting red-brown solution was filtered to remove succinimide, and chromatographed as above. Two major products corresponding to fractions (*a*) and (*b*) above were obtained, and separately rechromatographed. From the first, black crystals, m.p. 128—129° (32 mg) were isolated. Spectroscopic and analytical data were consistent with the formulation of this product as a symmetrical dibromodiphenylfulvene, probably 2,3-*dibromo*-6,6-*diphenylfulvene* (mass spectral peaks at *m*/*e* 386, 388, 390 in intensity ratio 1 : 2 : 1 respectively as expected for $C_{18}H_{12}Br_2$); τ 2·5—2·9 (10H, m), and 3·48 (2H, s).

The spectra of the second product, obtained as a red oil which could not be crystallised, were consistent with its formulation as a monobromo-6,6-diphenylfulvene, probably the 2-*bromo-derivative*; mass spectral peaks at *m*/*e* 308 and 310 in intensity ratio 1 : 1, as expected for $C_{18}H_{13}Br$; τ 2·5—3·0 (10H, m), 3·38 (1H, t, *J* 2 Hz), and 3·6—4·0 (2H, m).

The monobromo-derivative could not be induced to add to either maleic anhydride or tetracyanoethylene, despite the ready addition of diphenylfulvene itself to these dienophiles.

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[17] C. D. Nenitzescu and E. Solomonica, *Org. Synth.*, Coll. vol. II, 1943, 497.

[18] J. Thiele, *Ber.*, 1900, **33**, 666.

Reaction of Diphenylbicyclohexane with t-Butyl Peroxybenzoate in the Presence of Copper Ions.—The hydrocarbon (50 mg), t-butyl peroxybenzoate (60 mg), cuprous chloride (5 mg), and benzene (10 ml) were boiled under reflux for 24 h. The solution was cooled, a blue solid was removed, and the solvent was evaporated to leave an orange oil. Thin layer chromatography revealed the presence of a product with R_F identical with that of diphenylfulvene, together with a substantial amount of starting material. Preparative-layer chromatography gave an orange oil (12 mg) which did not crystallise, but whose u.v. spectrum in ethanol was indistinguishable from that of authentic diphenylfulvene.

Isomerisation of Diphenylbicyclohexene with Base.—(i) The diphenylbicyclohexene (0·5 g) was added to a boiling solution of potassium t-pentoxide in t-pentyl alcohol [prepared by dissolving potassium (2 g) in t-pentyl alcohol which had been dried over CaH_2 and fractionally distilled (50 ml)]. The reaction was followed by g.l.c. and was essentially complete after 118 h. The solvent was removed under reduced pressure, and the residue was extracted into pentane. The pentane solution was washed with water, dried ($MgSO_4$), and evaporated to leave a pale yellow oil (0·49 g). The n.m.r. spectrum of this oil showed it to be an essentially pure mixture of 5,5-diphenylcyclohexa-1,3-diene (37%) [1] and 3,3-*diphenylcyclohexa*-1,4-*diene* (63%). The latter hydrocarbon was isolated by treating the mixture (0·48 g) with maleic anhydride (0·12 g) in sulphur-free xylene in a sealed tube (N_2 atmosphere) at 145° for 2 h. The mixture was cooled and diluted with benzene, when a solid (203 mg, m.p. 190—191°) separated; this was identified as the maleic anhydride adduct of the conjugated diene.[1] Solvent was removed from the remaining solution, and the residual oil was chromatographed on a column of basic alumina. Elution with hexane gave a colourless oil which crystallised from ethanol as plates (192 mg, m.p. 35·5—36·5°) [Found: C, 93·3; H, 6·67%; *M* (mass spectrometry), 232. $C_{18}H_{16}$ requires C, 93·05; H, 6·95%; *M*, 232]; τ 2·82 (10H, s), 4·10 (4H, br s), and 7·35 (2H, br s).

(ii) A solution of the bicyclohexene (110 mg) in dry Me_2SO (distilled under reduced pressure from calcium hydride) (1·0 ml) was deoxygenated (N_2) in a vial which was then sealed by means of a screw-cap septum. The tube was warmed to 33° in a water-bath, and a solution of re-sublimed potassium t-butoxide (150 mg) in Me_2SO (2·0 ml) (prepared in a dry box under nitrogen, and contained in a similarly capped vial), also warmed to 33°, was transferred into it by means of a syringe. A green colour developed immediately. Portions (1 ml) of the green solution were removed by syringe 1 min, 10 min, and 30 min respectively after mixing, and each was quenched into water under nitrogen. The aqueous quenches were each extracted with pentane (20 ml), the extracts were washed thoroughly with water, dried ($MgSO_4$), and the pentane removed. The n.m.r. spectra of the residual oils showed *ca.* 30% of the bicyclohexene unchanged after 1 min, and none unchanged after 10 min. The residues from the 10 min and 30 min quenches were identical, and their spectra, by analogy with those of an equilibrium mixture of monomethylcyclopentadienes,[19] were entirely consistent with their identification as a mixture of the benzhydrylcyclopentadienes (XVIII) and (XIX), τ 2·87 (10H, s), 3·6—4·3 (3H, m), 4·94 (1H, br s), 7·12 (2H, m). An almost identical n.m.r. spectrum was recorded from a hydrocarbon product fraction obtained from the reaction of sodium cyclopentadienide and benzhydryl bromide.

Base-Catalysed Equilibration of Diphenylcyclohexadienes in Dimethyl Sulphoxide.—In an experiment similar to the above, 5,5-diphenylcyclohexa-1,3-diene (100 mg) in Me_2SO (1·0 ml) was treated with potassium butoxide (150 mg) in MeSO (2·0 ml) at 33° in the absence of oxygen. A green solution was again obtained. However, when this was quenched into water after 5 min, the hydrocarbon product, isolated as described above, was shown by n.m.r. to consist of a mixture of the starting diene (*ca.* 40%) and the isomeric 3,3-diphenylcyclohexa-1,4-diene (*ca.* 60%). No other products were detectable.

We are grateful to the S.R.C. for the award of Studentships to D. J. A. and P. W.

[1/1038 *Received, June* 22*nd*, 1971]

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[19] S. McLean and P. Haynes, *Tetrahedron*, 1965, **21**, 2313.