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Reactions of Arylcyclohexadienyl Radicals: Rearrangement versus Fragmentation

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The genesis of 1-chloro-6-phenylcyclohexadienyl radicals and of 6,6-diphenylcyclohexadienyl radicals is described. The reactions of neither radical have given any evidence for intramolecular aryl migration. A major hightemperature reaction of the 6,6-diphenylcyclohexadienyl radical is fragmentation, giving phenyl radicals and biphenyl. Evidence for fragmentation of 6-phenylcyclohexadienyl radicals at ca. 200° has also been found.

An outstanding peculiarity of free-radical aromatic phenylation reactions is the fact that in phenylation of a given substrate PhX, the proportions of the resulting isomeric biphenyls, PhC₆H₄X, are almost independent both of the phenyl radical source, and of the experimental conditions. This is surprising because the isomeric intermediates in biaryl formation, *i.e.* the phenylcyclohexadienyl radicals (I), are often intermediates the small differences in isomer distribution which have, on occasion, been noted ³ in radical phenylation, might be attributed to an element of selectivity in the oxidation step.

Although several arguments based on literature data may be levelled against the foregoing hypothesis, few carry conviction. However, as will be discussed in more detail below, it is not easy to envisage a transition



also in the formation of other reaction products, e.g. dimers [equation (1)], and it is not easy to envisage circumstances under which the position and nature of X in (I) is without detectable influence on the competition between paths (a) and (b) [equation (1)] unless X is both extremely small, and lacking in perceptible polar character. Nevertheless, even in the case where X = But, it has been reported that drastic changes in the experimental conditions, which substantially affect the competition between paths (a) and (b), are without effect on the relative yields of the isomeric t-butylbiphenyls.¹

One possible explanation of these results might involve a relatively ready aryl migration in phenylcyclohexadienvl radicals [equation (2)].² If hydrogen abstraction



from the three isomeric radicals were assumed to show little dependence on the oxidising agent which converts them into biaryls, then the biaryl isomer distribution might reflect the equilibrium between these isomers, rather than the relative ease of attack on the three different hydrogen-bearing sites in PhX. Possibly

¹ R. T. Morrison, J. Cazes, N. Samkoff, and C. A. Howe, J. Amer. Chem. Soc., 1962, **84**, 4152. ² M. J. Perkins, Ann. Reports, 1968, **65**B, 181.

state of sufficiently low energy to allow rearrangement to occur to a significant extent in the normal life-span of phenylcyclohexadienyl radicals (ca. 10^{-2} — 10^{-4} s). On the other hand, examples of aryl migration to unstabilised radical centres (e.g. in the 2,2,2-triphenylethyl radical) are known which are very rapid indeed on this time scale.⁴ It was, therefore, considered that the possibility that any migration in any lcyclohexadienyl radicals might occur under any circumstances merited investigation.

Direct investigation of the isomerisation reactions (2) can be effected utilising a source of a phenylcyclohexadienyl radical with a specific substitution pattern. The production, from this, of more than one isomeric biphenyl would testify to the proposed isomerisation. The present paper describes some early experiments involving the 1-chloro-6-phenylcyclohexadienyl radical (II), and subsequent work on the 6,6-diphenylcyclohexadienyl radical (III).



Radical (II) was produced by pyrolysis of the transdihydrotritylbiphenyl derivative (IV). This was ob-

³ E.g., (a) D. I. Davies, D. H. Hey, and M. Tiecco, J. Chem. Soc., 1965, 7062; (b) H. J. M. Dou, G. Vernin, and J. Metzger, Tetrahedron Letters, 1968, 953.

⁴ D. J. Carlsson and K. U. Ingold, J. Amer. Chem. Soc., 1968, 90, 7047.

tained as a major product from the decomposition of chlorobenzene. No phenylazotriphenylmethane in isomers of (IV) (positional or geometric) were isolated though they may have been formed in minor amounts. The yield of (IV) (deduced to be trans from the magnitude⁵ of the homoallylic coupling between 1-H and 4-H) was greater than might have been anticipated by analogy with the yields of products from a similar reaction in benzene, and proved to have been formed almost entirely at the expense of o-chlorobiphenyl.



The chlorobiphenyl isomer distribution from this experiment is compared with those for other phenylation reactions in the Table.

Proportions of chlorobiphenyls formed by radical phenylation of chlorobenzene

Source of phenyl radical	% ortho	% meta	% para
(PhCO,), *	$62 \cdot 2$	24	13.8
$(PhCO_{2})_{2}^{*}$ †	54	25	21
PhN(NO)COCH ₃ ‡	64	21	15
PhN:NCPh ₃ §	33 ± 3	$40~\pm~3$	27 ± 3
			1

* Data from ref. 3a. † Data from Hey, Liang, and Perkins, Tetrahedron Letters, 1967, 1477. ‡ Data from Ito, Migita, Morikawa, and Simamura, Tetrahedron, 1965, **21**, 955. § This work. The proportion of ortho-isomer increases slightly as the reaction time is prolonged; this is presumably due to slow fragmentation of (II).

The above result is reminiscent of the formation of 2-phenyl-5-tritylpyridine (VI) at the expense of α phenylpyridine during the decomposition of phenylazotriphenylmethane in pyridine.⁶ Dehydrogenation of the initial coupling product (V) was probably effected by molecular oxygen, which had not been excluded from the reaction system. In support of this it has now been found that trans-1,4-dihydrotritylbiphenyl (VII)⁷ is readily dehydrogenated to 4-tritylbiphenyl



when heated at 105° in pyridine in the presence of oxygen. The fact that the coupling reaction diminishes the yield of α -phenylpyridine but not that of β -phenylpyridine remains unexplained. There is no obvious steric inhibition of coupling which might be an important factor in preventing the formation of (VIII) in the chlorobenzene reaction.

The isolation of (IV) and (VI) at the expense in each case of only one biaryl isomer constituted evidence against extensive rearrangement [equation (2)], even before pyrolysis of (IV) was investigated, for in these reactions (and in the phenylation of thiophen by phenylazotriphenylmethane reported recently⁸) the biaryl isomer distribution is substantially different from that normally encountered. However, these results do not preclude a relatively slow rearrangement; furthermore, as there is normally a high stationary-state concentration of trityl radicals during phenylazotriphenylmethane decompositions, the life-time of any counter radical is probably relatively short, and any competing unimolecular process in the counter radical such as fragmentation or rearrangement, may be masked.

Pyrolysis of (IV), under a variety of conditions, gave triphenylmethane and 2-chlorobiphenyl as the sole detectable products. Unfortunately, it is probable that, during this reaction also, there will be a high stationary-state concentration of trityl, and this view finds support from recent e.s.r. studies in the thiophen series.⁸ However, the failure to detect any 3- or 4chlorobiphenyl in these experiments suggests that rearrangement, if it can occur at all, must be very slow.

The possibility that the predominant decomposition path for (IV) might involve caged radical pairs, wherein the lifetime of the cyclohexadienyl species would be drastically curtailed, appears to be excluded by preliminary results of crossed thermolyses of mixtures of (IX) and (X), from which the triphenylmethane and chlorotriphenylmethane both contained ca. 50% of one deuterium atom.⁹ This is not unexpected, as



interaction of pairs of radicals as stable as trityl and phenylcyclohexadienyl might reasonably be expected to occur at a rate well below the encounter-controlled limit, and hence a significant cage component to the reaction would seem unlikely.

One positive outcome of the above experiments is the indication that anomalous isomer distribution in phenylation reactions employing phenylazotriphenylmethane may be quite general, although a recent Japanese report ¹⁰ indicates no anomalies in the product ratios from phenylation reactions employing phenylazotriphenylmethane; these include a reaction with chlorobenzene. Possibly any coupling products formed during that study were thermolysed to biaryl and triphenylmethane in the injection port of the gas chromatograph employed in the analyses, the overall result

⁵ L. J. Durham, J. Studebaker, and M. J. Perkins, Chem. Comm., 1965, 456; see also D. J. Atkinson and M. J. Perkins, Tetrahedron Letters, 1969, 2335.

 ⁶ R. Grashey and R. Huisgen, *Chem. Ber.*, 1959, 92, 2641.
 ⁷ D. H. Hey, M. J. Perkins, and G. H. Williams, *J. Chem.* Soc., 1965, 110.

⁸ C. M. Camaggi, R. Leardini, M. Tiecco, and A. Tundo, J. Chem. Soc. (B), 1969, 1251.

⁹ D. J. Atkinson and M. J. Perkins, unpublished observations. ¹⁰ M. Kobayashi, H. Minato, N. Watanabe, and N. Kobori, Bull. Chem. Soc. Japan, 1970, 43, 258.

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being an apparently normal biaryl distribution. A second point of interest is the observation that pyrolysis of (IV) gives only one chlorobiphenyl, even when the reaction medium is chlorobenzene. This not only excludes isomerisation, but also supports the generally accepted view that arylcyclohexadienyl radicals are, under normal reaction conditions, stable towards fragmentation. Fragmentation of (II) to phenyl abstraction from the isomeric 1,3-diene (XV) [obtained by dehydration of the allylic alcohol (XIV) over alumina poisoned with pyridine] proved unrewarding, probably as a result of competing radical addition to the diene system.

When hydrogen abstraction from (XIII) was effected by t-butoxyl radicals formed by thermolysis of di-tbutyl peroxyoxalate in oxygen-free benzene at 60°,



radicals and chlorobenzene would be expected to give all three chlorobiphenyls by phenylation of the chlorobenzene solvent. This result is in marked contrast to recent evidence for the occurrence of phenylcyclohexadienyl fragmentation under relatively mild conditions ¹¹ (see below).

At an early stage in the development of this work, we pointed out that an interesting cyclohexadienyl radical precursor, namely the dimer (XI), was already to hand in these laboratories. Pyrolysis of (XI) should give a pair of substituted cyclohexadienyl radicals (XII) which cannot disproportionate without prior rearrangement. Pyrolysis of (XI) and related compounds was investigated, and in each case rearranged products (phenanthridones) were obtained in good yield.¹² Early evidence that rearrangement involved aryl migration¹² (path c), although now reinterpreted in terms of exclusive nitrogen migration (path d),¹³ encouraged our pursuit of model systems, notably the 6,6-diphenylcyclohexadienyl radical (III). In this case, both crowding at C-6, and phenyl conjugation in the rearranged radical, might combine to facilitate an aryl shift. The system had the added attraction of a close resemblance to postulated intermediates in model photochemical studies in which diphenylcyclohexadiene structures have been irradiated, and where, in some instances, aryl migration has been observed.¹⁴

The 6,6-diphenylcyclohexadienyl radical was initially generated by hydrogen abstraction from 3,3-diphenylcyclohexa-1,4-diene (XIII).¹⁵ Attempted hydrogen

¹¹ M. Kobayashi, H. Minato, and N. Kobori, Bull. Chem. Soc. Japan, 1969, **42**, 2738. ¹² D. M. Collington, D. H. Hey, and C. W. Rees, J. Chem.

Soc. (C), 1968, 1026.
 ¹³ D. H. Hey, G. H. Jones, and M. J. Perkins, Chem. Comm.,

1970, 1438.

the major identifiable products were the dimer (XVI) (m.p. 198° dec., ca. 30%) and a small amount of the



less-soluble pentaene (XVII) (m.p. 283°). Traces (ca. 2%) of o-terphenyl were also produced, but the metaand para-isomers were apparently not formed.

o-Terphenyl was again among the products of a reaction in which di-t-butyl peroxide was allowed to



decompose in a chlorobenzene solution of the diene at ca. 130°. Additional minor products identified from this reaction included biphenyl and the isomeric monochlorobiphenyls (in proportions characteristic of homolytic phenylation of chlorobenzene), suggesting that (III) may be fragmenting to give phenyl radicals and biphenyl.

The dimer (XVI) seemed an ideal high-temperature source of (III), and its pyrolysis was therefore investigated. In 1,2,4-trichlorobenzene at 230° (sealed

¹⁴ (a) H. E. Zimmerman, R. C. Hahn, H. Morrison, and M. C. Wani, J. Amer. Chem. Soc., 1965, 87, 1939; (b) H. E. Zimmer-man, P. Hackett, D. F. Juers, and B. Schroeder, J. Amer. Chem. Soc., 1967, 89, 5973.
 ¹⁵ D. J. Atkinson, M. J. Perkins, and P. Ward, J. Chem. Soc.

(C), following paper.

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tube; N_2) the major products were benzene, biphenyl, and a new hydrocarbon (m.p. 98°) to which structure (XVIII) has been assigned, together with a trace of *o*-terphenyl, and a mixture of products tentatively



identified as trichlorobiphenyls resulting from phenylation of the solvent. Similar products were obtained from a reaction in chlorobenzene at 210° , except that the three monochlorobiphenyls were in this case identified among the products. Formation of the major products is summarised in the Scheme. It was subsequently found that (XVI) decomposes slowly at 130° , and is, therefore, probably an intermediate in the experiments involving hydrogen abstraction from the diene (XIII) at that temperature.



It was at first considered that the *o*-terphenyl might be the product of an inefficient rearrangement of the type sought, and which competes effectively with fragmentation at the temperatures employed in the hydrogenabstraction experiments. However, failure to obtain reproducible yields of this key product led to the conclusion that it is most probably formed by electrontransfer oxidation of (III) by adventitious oxygen, o-terphenyl in yields of ca. 50%: an even higher yield was obtained employing N-bromosuccinimide (NBS) as oxidant. (The participation of carbonium ions in reactions of olefins with NBS is discussed more fully in the accompanying paper.) Finally it was found that decomposition of (XVI) in carefully deoxygenated chlorobenzene, but in the presence of excess cupric acetate, again gave o-terphenyl, albeit in poor yield.

It has already been noted that the fragmentation of arylcyclohexadienyl radicals has generally been discounted, although loss of less-reactive fragments than aryl radicals from cyclohexadienyl radicals [equation (3)] is well known. Therefore the fragmentation found

$$\begin{array}{c} R^{1} \\ R^{2} \\ \end{array} \xrightarrow{(1)} R^{1} \\ R^{2} \\ \end{array} \begin{array}{c} R^{1} \\ R^{2} \\ \end{array}$$
(3)

for (III) is rather unusual. To investigate further the possibility of fragmentation in the simple phenylcyclohexadienyl radical (I; X = H), pyrolysis of the dimer (XIX) ¹⁶ was reinvestigated. In chlorobenzene at 170°, biphenyl and dihydrobiphenyl were formed in good yield, but at 210°, small amounts of the isomeric chlorobiphenyls were also obtained (*ca.* 10% of the C₁₂ products). It is reasonable to conclude that under the experimental conditions employed [*ca.* 0·15 mol (XIX) per l], loss of a phenyl radical from (I; X = H) is slow compared with disproportionation. The absence of a disproportionation path for (III), and crowding at C-6, are probably the main factors responsible for the more efficient fragmentation found for that radical.

It should be emphasised that these studies are far from exhaustive. The main objectives have been to define the types of reaction in which arylcyclohexadienyl radicals may participate. In some of the experiments there is undoubtedly competition between processes which are first order in cyclohexadienyl radical and others which are concentration dependent. Therefore product yields may be expected to show a marked dependence on precise experimental conditions. For example, the qualitative observation was made that the



followed by carbonium-ion rearrangement. *o*-Terphenyl could be almost completely eliminated from the reaction products by improved deoxygenation techniques, whereas hydrogen abstraction from the diene (XIII) in boiling benzene or chlorobenzene in the presence of cupric acetate as an added one-electron oxidant gave

¹⁶ D. F. DeTar, R. A. J. Long, J. Rendleman, J. Bradley, and P. Duncan, J. Amer. Chem. Soc., 1967, **89**, 4051.

degree of fragmentation observed during pyrolysis of (XVI) was highest in reactions employing the lowest initial concentration of (XVI), entirely in accordance with expectation. Details of individual experiments and product yields are given in the Experimental section. Despite these limitations, it seems justifiable to conclude (i) that if aryl migration can occur in arylcyclohexadienyl radicals it is slow with respect to

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fragmentation, and (ii) that the fragmentation of arylcyclohexadienyl radicals manifest in the reversibility of phenyl addition to aromatic substrates in Me_2SO at 20° is exceptional, and, if substantiated, may reflect a remarkable effect of that solvent on free radical behaviour. On the other hand, examples of reversibility Finally, we refer again to the structural similarity between the diphenylcyclohexadienyl radical and some model ketones and olefins whose photochemistry has been studied. Triplet excited states of enones, and singlet excited states of dienes, are commonly depicted as biradicals. In this biradical formulation, the excited



claimed (without comment) by Henderson, Lopresti, and Zweig,¹⁷ may be less exceptional because of the strain experienced in the arylcyclohexadienyl radicals in question.

Earlier in this paper it was mentioned that energetic considerations argued against aryl migration in arylcyclohexadienyl radicals. Indeed, *if* structure (XX) be regarded as a close approximation to the transition state for such a migration then an activation energy as high as 35 kcal mol⁻¹ can be estimated. It is interesting to point out that by cancelling the cyclohexadienyl components, this same activation energy might be predicted for the analogous cationic aryl migration (XXI) \longrightarrow (XXIII). This type of aryl shift is well known in, for example, dienol-benzene rearrangements, and has also been postulated in the present work. The fact that a cationic rearrangement can readily occur, therefore, suggests that (XXII)



may be an inadequate approximation to the transition state, and that significant non-classical electron distribution is important, as in Dewar's π -complex representation of a phenonium ion.¹⁸ states of the dienone (XXIV) ^{14a} and triene (XXVI) ^{14b} might be written as (XXV) (triplet) and (XXVII) (singlet) respectively, yet in both of these (very shortlived) species aryl migration occurs, and there is no evidence for fragmentation of the type now recorded for the related monoradical (III). This serves to emphasise the inadequacy of a simple biradical description of excited-state structures, although we hasten to add that in neither of the examples cited was a biradical formulation explicitly employed. Presumably a concerted di- π -methane mechanism ¹⁹ rather than a stepwise diradical mechanism affords an accurate interpretation of these reactions.

EXPERIMENTAL

Preparation of 2-Chloro-1,4-dihydro-4-tritylbiphenyl.-In a typical experiment, phenylazotriphenylmethane (2 g) was allowed to decompose in oxygen-free chlorobenzene (200 ml) at 80°, under an atmosphere of nitrogen for 24 h. The bulk of the solvent was then removed at 50° under reduced pressure to yield a yellow oil which, on treatment with a little cold ethanol, deposited a white solid (0.5 g; m.p.)164-166°). Crystallisation from methylene chloridelight petroleum (b.p. 40-60°) gave colourless 2-chlorotrans-1,4-dihydro-4-tritylbiphenyl, m.p. 166-167° (decomp.) (Found: C, 85.3; H, 5.8; Cl, 9.6%. C₃₁H₂₅Cl requires C, 85.9; H, 5.8; Cl, 9.3%) (the carbon figure was consistently slightly low). The n.m.r. spectrum (CDCl₃) showed a multiplet (20H) at ca. τ 3.9, a broad singlet and AB quartet (together 3H) at 4.2-4.6, and two broad doublets (2H) at 5.0 and 6.7 (J ca. 7.5 Hz).⁵ This spectrum is entirely consistent with the assigned structure.

The residual oily reaction product was chromatographed on a column of basic alumina which was eluted first with light petroleum (b.p. $60-80^{\circ}$) and then with light petroleum containing increasing proportions of benzene. The first product eluted (0.63 g) was a mixture of chlorobiphenyls contaminated with a little triphenylmethane (g.l.c.). This was followed by triphenylmethane (0.8 g, m.p. and mixed m.p. 93° after crystallisation from ethanol). Further elution gave a trace of tetraphenylmethane, followed by further chlorodihydrotritylbiphenyl (0.14 g). Traces of other products eluted from the column were not obtained crystalline, and were not identified. Examination of the chlorobiphenyl fraction by g.l.c. revealed an abnormally

¹⁷ W. A. Henderson, R. Lopresti, and A. Zweig, J. Amer. Chem. Soc., 1969, 91, 6049.
¹⁸ M. J. S. Dewar in 'Molecular Rearrangements,' P. de

¹⁶ M. J. S. Dewar in 'Molecular Rearrangements,' P. de Mayo, ed., Interscience, New York, 1963, p. 295.

¹⁹ E.g., H. E. Zimmerman and P. S. Mariano, J. Amer. Chem. Soc., 1969, **91**, 1718; see also K. Fukui, Accounts Chem. Res., 1971, **4**, 57.

low proportion of ortho-isomer (ca. 30%), and the experiment was therefore repeated, and the g.l.c. analysis carried out on the total reaction mixture. This confirmed the low yield of *ortho*-isomer (see Table in text). The analysis was performed at ca. 140° to avoid immediate pyrolysis of the chlorodihydrotritylbiphenyl on injection onto the column. (Slow decomposition on the g.l.c. column does not influence the analysis.)

Thermal Decomposition of 2-Chloro-1,4-dihydro-4-tritylbiphenyl.—In a typical experiment the dihydro-compound (100 mg) was dissolved in deoxygenated chlorobenzene (10 ml) and the solution was boiled under reflux in an atmosphere of nitrogen for 12 h. Examination of the products by g.l.c. revealed only two products identified as o-chlorobiphenyl (ca. 80%) and triphenylmethane (ca. 80%) by their retention characteristics on silicone gum rubber and Apiezon L columns. No m- or p-chlorobiphenyl could be detected (<0.5%). Similar results were obtained when the dihydro-compound was pyrolysed alone or in benzene (sealed tube).

Oxidation of trans-1,4-Dihydrotritylbiphenyl.-The dihydro-compound 7 (100 mg) was dissolved in dry pyridine (25 ml) and heated at 100° under reflux, with slow passage of oxygen through the stirred solution, for 15 h. After this time, examination by t.l.c. and g.l.c. (3% QF 1 on silanised Celite) showed the presence of one major product having retention characteristics identical with those of 4-tritylbiphenyl. Traces of biphenyl and triphenylmethane were also formed.

4.4-Diphenylcyclohex-2-enol.—Powdered sodium borohydride (0.3 g) was added to 4,4-diphenylcyclohex-2-enol 20 (3 g) in methylene chloride (25 ml) and methanol (2.5 ml), and the mixture was stirred at room temperature overnight. Water (25 ml) was added, and the organic layer was separated, washed again with water, and dried $(MgSO_4)$. Removal of solvent left a pale yellow solid which, after crystallisation from methylene chloride-light petroleum (b.p. 60-80°), had m.p. 100-102° (2.9 g). Spectroscopic and analytical data were consistent with the formulation of the product as 4,4-diphenylcyclohex-2-enol (Found: C, 86.2; H, 7.1%. $C_{18}H_{18}O$ requires C, 86.4; H, 7.25%).

5,5-Diphenylcyclohexa-1,3-diene .--- Finely powdered diphenylcyclohexenol (4 g) was shaken with a mixture of neutral alumina (8 g, activity 1) and pyridine ²¹ (16 drops), and the resulting mixture was then heated at 230° for 2 h (air condenser), cooled, and extracted into methylene chloride. The solvent was removed from the methylene chloride solution, and the residual oil was chromatographed on a column of basic alumina, which was eluted with benzene-light petroleum (b.p. $40-60^{\circ}$) (1:3) to give an oil (1.8 g). Distillation of this oil gave a major fraction, b.p. $118-123^{\circ}$ (0.2 mm) which gave colourless crystals from methanol, m.p. 55-57°. Spectroscopic and analytical data were consistent with the formulation of the product as 5,5-diphenylcyclohexa-1,3-diene (Found: C, 92.9; H, 7.0. Calc.f or C₁₈H₁₆: C, 93.0; H, 6.9%); τ 2.8 (10H, m), 3.8-3.95 (2H,m), 4.15 (2H, m), and 7.15 (2H, m); λ_{max} . (ethanol) 262 nm (z 3.42×10^3). In addition, the product gave benzophenone on oxidation with alkaline potassium permanganate, and with maleic anhydride it gave an

²⁰ H. E. Zimmerman and D. I. Schuster, J. Amer. Chem. Soc., 1962, 84, 4527.

²¹ E. von Rudloff, Canad. J. Chem., 1961, 39, 1860; E. J. Blanc and H. Pines, J. Org. Chem., 1968, 33, 2035.

adduct, m.p. 191° (from benzene) (Found: C, 80.4; H, 5.5. $C_{22}H_{18}O_3$ requires C, 80.0; H, 5.5%). The n.m.r. spectrum of this product was entirely consistent with its formulation as the expected 1:1 adduct. In some preparations, g.l.c. revealed o-terphenyl as a contaminant which was not removed by crystallisation (>10%).

Subsequent attempts to prepare the same diene by the method of Dauben et al.22 were unsuccessful. It was also shown that acid-catalysed dehydration of the cyclohexenol gave a complex mixture of products containing very low yields of the diene.

Preparative Scale Hydrogen Abstraction from 3,3-Diphenylcyclohexa-1,4-diene.-The diene (0.5 g) was dissolved in dry reagent grade benzene (5 ml), and the solution was deoxygenated (N_2) ; di-t-butyl peroxyoxalate ²³ (0.5 g)was then added. The mixture was maintained at room temperature overnight, under a nitrogen atmosphere, and then heated to 60° for 40 min. The solvent was removed under reduced pressure and ether (2 ml) added to the residual oil. A white solid (90 mg), m.p. 210-240° separated, which on treatment with a little cold benzene left an insoluble residue (ca. 10 mg) having m.p. 283-284°. The benzene solution was evaporated almost to dryness, and treated with a little ether to give needles, m.p. 196-197°. A further portion of the solid, m.p. 196-197° was obtained on concentration of the mother liquors of the total reaction mixture. The solid, m.p. 196-197° was identified as bi-(4,4-diphenylcyclohexa-3,5-dienyl) from spectroscopic and analytical data (Found: C, 93.1; H, 6·85. C₃₆H₃₀ requires C, 93·5; H, 6·5%); τ 2·68 (20H, m), 3.97 (8H, AB quartet, J ca. 12 Hz plus additional fine structure), and 6.90 (2H, br s). The solid m.p. 283-284° was similarly identified as bi-(4,4-diphenylcyclohexa-3,5dienylidene) [Found: C, 93.3; H, 6.35%; M, 460 (mass spectrometry). C₃₆H₂₈ requires C, 93·3; H, 6·1%; M, 460]; τ 2.74 (20H, brs), 3.05 (4H, d, J 10 Hz), and 3.82 (4H, d, J 10 Hz).

Small-scale Hydrogen Abstraction Experiments.—In the following experiments, and in the dimer pyrolyses described below, analyses were by g.l.c., normally on a 5% Carbowax 20 M/TPA on Chromasorb W column. However, identification of minor products was confirmed by re-examination on Apiezon L and/or silicone gum rubber columns. The biphenyl estimation was carried out with column and injection-block temperatures of ca. 150°. The diene and terphenyl assays employed an injection temperature of 230° and column temperature of 200°. It was also found that injection of the dimer (XVI) at 250°, and with the column temperature of 150°, gave a biphenyl peak the intensity of which could be used for semi-quantitative assay of (XVI) (after correction for biphenyl already present).

(i) The diene (5.3 mg), di-t-butyl peroxyoxalate (5.0 mg), and chlorobenzene (1.0 ml) were deoxygenated and then heated to 60° (N2 atmosphere) for 1 h. G.l.c. analysis then indicated the formation of traces of biphenyl and o-terphenyl (both <1%) and dimer (XVI) (ca. 2.2 mg) together with unchanged diene (0.73 mg).

(ii) The diene (5.9 mg) di-t-butyl peroxide (5 μ l) and chlorobenzene (0.1 ml) were deoxygenated, and heated to

²² W. G. Dauben, M. E. Lorber, N. D. Vietmeyer, R. H. Shapiro, J. H. Duncan, and K. Tomer, J. Amer. Chem. Soc., 1968, 90, 4762. ²³ P. D. Bartlett, E. P. Benzing, and R. E. Pincock, J. Amer.

Chem. Soc., 1960, 82, 1762.

 130° in a sealed tube (N₂ atmosphere) for 20 h. G.l.c. analysis revealed traces of *o*-terphenyl and unchanged diene (<1%), biphenyl (0.25 mg), and isomeric chlorobiphenyls (*ca.* 0.07 mg).

(iii) In an isolated experiment similar to (ii) but employing 1 ml of chlorobenzene, a 25% yield of *o*-terphenyl was obtained. Therefore an alternative procedure was adopted in which diene (6.3 mg) di-t-butyl peroxide (9.5 μ l) and chlorobenzene (1.0 ml) were deoxygenated and then boiled under reflux for 20 h (N₂ atmosphere). G.l.c. analysis then showed unchanged diene (1.8 mg), biphenyl (0.38 mg), and isomeric chlorobiphenyls (*ca.* 0.12 mg) together with a trace of *o*-terphenyl (<0.5%). A major product revealed by t.l.c. had chromatographic characteristics indistinguishable from those of the hydrocarbon (XVIII).

(iv) The effect of air on these reactions, suspected to be the cause of o-terphenyl formation in the sealed-tube experiment mentioned in (iii), was demonstrated by repetition of experiment (ii) without attempting to exclude air from the tube. An o-terphenyl yield of ca. 30% was obtained.

Preparative Pyrolysis of Bi-(4,4-diphenylcyclohexa-3,5dienyl). A solution of the hydrocarbon (150 mg) in 1,2,4trichlorobenzene (15 ml) was boiled under reflux for $l_{\frac{1}{2}}^{1}$ h in an atmosphere of nitrogen. The reaction was monitored by t.l.c., on which the initial hydrocarbon could not be detected after ca. 30 min. The solvent was removed and the residue was taken up in a little benzene-ether. A trace of insoluble material (2 mg, m.p. >300°) was removed, and the remaining solute, after removal of solvent, was chromatographed on a column of silica gel in a minimum of light petroleum. Elution with light petroleum (b.p. 60-80°) containing increasing proportions of benzene gave small quantities of oily products consisting of trichlorobenzene, biphenyl, and what was probably a mixture of trichlorobiphenyls, followed by a major fraction (63 mg), homogeneous to t.l.c., which eventually crystallised from benzene-ethanol as needles, m.p. 96-98°. Analytical and spectroscopic data were consistent with the formulation of this product as 3-(biphenyl-4-yl)-6,6-diphenylcyclohexa-1,4-diene [Found: C, 93.2; H, 6.43%; M, (mass spectrometry) 384. C30H34 requires C, 93.7; H, 6.3%; M, 384], τ 2·4—2·9 (19H, m), 4·04 (4H, AB quartet J 10 Hz, with additional fine structure), and 6.04 (1H, brs).

Small-scale Pyrolyses of Bi-(4,4-diphenylcyclohexa-3,5dienyl).—(i) The hydrocarbon (10 mg) and oxygen-free trichlorobenzene (100 μ l) were heated in a sealed tube for 1 h at 230°, and the products were analysed by g.l.c. These were found to include benzene (0.68 mg, 0.40 mol/mol), biphenyl (1.04 mg, 0.31 mol/mol) and a trace of o-terphenyl (ca. 0.1 mg, 0.02 mol/mol). Additional products were detected having retention characteristics expected for trichlorobiphenyls.

(ii) The hydrocarbon (6.5 mg) was pyrolysed in chlorobenzene (1 ml), using the same procedure as in (i). The products included biphenyl (1.78 mg, 0.82 mol/mole) and the isomeric chlorobiphenyls (1.8 mg, 0.68 mol/mol; o:m:p::56:27:17) as well as a trace of o-terphenyl (0.025 mg, 0.008 mol/mol) and diphenylcyclohexadiene (0.065 mg, 0.02 mol/mol).

(iii) The hydrocarbon (5.0 mg) and chlorobenzene (1 ml) were sealed in a tube from which no attempt had been made to exclude air. Pyrolysis, as before, gave products from which the diphenylcyclohexadienes were absent

(<0.002 mol/mol) but which contained *o*-terphenyl (0.1 mg, (0.04 mol/mol)).

(iv) The hydrocarbon (4.9 mg) and chlorobenzene (1.0 ml) were deoxygenated, and then boiled under reflux for 20 h $(N_2 \text{ atmosphere})$. After this time t.l.c. showed very little starting material remaining, and this was confirmed (<5%) by g.l.c. analysis employing a very high injection temperature shown in control experiments to cause pyrolysis of (XVI) and give biphenyl in amounts sufficiently reproducible to be employed as a semi-quantitative analytical method for estimating (XVI) (see above). The reaction products included biphenyl (0.4 mg; 0.25 mol/mol), chlorobiphenyls (0.12 mg, 0.08 mol/mol) and a trace of diphenylcyclohexadiene. There was no detectable formation of o-terphenyl in this experiment ($\ll 0.5\%$). T.l.c. on alumina and silica gel also showed a substantial yield of a product chromatographically indistinguishable from the hydrocarbon (XVIII).

(v) In an experiment similar to (iv), except that cupric acetate (4 mg) was added to the reaction mixture, the yields of biphenyls were diminished (biphenyl, 0.3 mg; chlorobiphenyls *ca.* 0.09 mg), diphenylcyclohexadienes were absent ($\ll 0.5\%$), but *o*-terphenyl was formed (0.3 mg, 0.12 mol/mol) T.l.c. again indicated the formation of (XVIII).

The above experiments are representative. With the exception of that of *o*-terphenyl, yields of products were reasonably reproducible, and the extent of fragmentation increased with decreasing initial concentration of dimer and increasing temperature.

In a control experiment 3,3-diphenylcyclohexa-1.4-diene (6.7 mg) in oxygen-free trichlorobenzene (100 l) was heated in a sealed tube at 230° for 22 h. After this time slight decomposition was evident from the formation of biphenyl (0.27 mg, 0.06 mol/mol) and benzene (0.03 mg, $0.01_{\rm 5}$ mol/mol).

Oxidation of 3,3-Diphenylcyclohexa-1,4-diene to o-Terphenyl.—(i) A solution of the diene (20.4 mg) in carbon tetrachloride (1 ml) was boiled under reflux with N-bromosuccinimide (20 mg), and a trace (ca. 0.5 mg) of azobisisobutyronitrile was added. After 1 h, during which evolution of HBr was detected, the solution was cooled, succinimide was removed, and the remaining products were examined by g.l.c. No diene remained, and o-terphenyl (14.4 mg, 71%) was the sole identifiable product.

(ii) A solution of the diene (4.5 mg), t-butyl peroxybenzoate (10 μ l) and cupric acetate (2 mg) in benzene (1 ml) was boiled under reflux for 14 h. Examination of the reaction mixture by g.l.c. then revealed the presence of unchanged starting material (0.35 mg) and o-terphenyl (1.9 mg, 46%).

(iii) The diene (4.9 mg), cupric acetate (1.2 mg), and di-t-butyl peroxide (10 μ I), in chlorobenzene (1.0 ml) were deoxygenated, and boiled under reflux for 20 h (N₂ atmosphere) to give unchanged diene (2.2 mg), o-terphenyl (0.7 mg, ca. 25%), biphenyl (0.16 mg) and the isomeric chlorobiphenyl (ca. 0.05 mg). T.1.c. examination showed the formation of a product with chromatographic characteristics indistinguishable from those of (XVIII).

Pyrolysis of Bi-(4-phenylcyclohexa-2,5-dienyl) (XIX).— (i) The hydrocarbon ¹⁶ (5.5 mg) in oxygen-free chlorobenzene (1 ml) was heated at 170° for 2 h in a sealed tube. Examination by g.l.c. revealed two major products formed in approximately equivalent proportions, which had retention characteristics of biphenyl and 1,4-dihydrobiphenyl ²⁴ (the possible presence of some 1,2-dihydrobiphenyl is not excluded by this result). A trace of *o*-chlorobiphenyl $(<1^{\circ}_{/o})$ was also detected.

(ii) Repetition of the above experiment at 210° gave, in addition to biphenyl and dihydrobiphenyl, a mixture of the isomeric chlorobiphenyls in proportions characteristic of homolytic phenylation of chlorobenzene (approximate proportions o:m:p:::60:25:15). The yield of o-chloro-

biphenyl was $\frac{1}{10}$ that of the yield of biphenyl. No chlorobiphenyls were formed when dihydrobiphenyl was heated in chlorobenzene at 210° for 2 h.

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²⁴ W. Hückel and R. Schwen, Ber., 1956, 89, 150.