

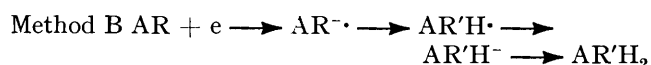
Reduction by Dissolving Metals. Part XX.¹ Some Biphenyl Derivatives

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Metal-ammonia reductions of biphenyl and of 2- and 4-methoxybiphenyl in the presence and in the absence of proton sources have been examined. Reaction probably proceeds, respectively, through one-electron and one-proton additions, and through two-electron and two successive proton additions. The differences in observed product ratios can be partly explained by the higher ratio of the conjugated diene (3) to the unconjugated diene (2) produced by protonation of the intermediate anion (1) with alcohols as compared with ammonium chloride.

REDUCTIONS of biphenyl by metal-ammonia solutions under various conditions yield various mixtures of products.² Recent work has illuminated the subject,³ but the theoretical basis is still unclear, and it would be useful to define the results of alteration of conditions in deciding experimental procedures.

Two procedures, involving different pathways, are (Method A) the reaction of at least 2 equiv. of metal in the absence of a proton source other than ammonia, and subsequent protonations of the dianion, and (Method B) simultaneous reaction of a metal and a more acidic proton source in ammonia. The first method almost certainly results in initial formation of the salt of a dianion, and the second, by analogy with similar reductions of monobenzenoid compounds,⁴ probably involves addition of one electron and protonation of the radical anion, followed by further reduction of the resulting radical. The products of the two processes may differ, since neither the first nor the second proton necessarily adds to the same positions in the molecule.

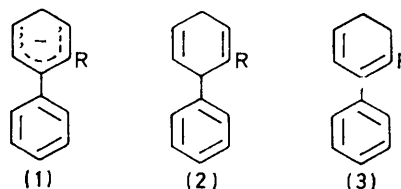


AR and AR' are aromatic compounds
(ARH⁻ and AR'H⁻, ARH₂ and AR'H₂ may or may not be identical)

A further difference in products can result from the fact that AR²⁻ and ARH⁻ (Method A) are protected by their charge from further electron addition; AR'H₂ as a neutral molecule formed in the presence of reducing agent can be further hydrogenated if its structure is suitable, for example if it contains conjugated double bonds.

The highly basic dianion AR²⁻ has already been shown³ to react with ammonia to produce the mono-anion (1), which is then not sufficiently basic to react further unless a more acidic proton source is added, such as an ammonium salt. The product is then exclusively 1,4-dihydrobiphenyl (2; R = H). The more basic charge is localised for reaction of the dianion in the 4-position. Protonation of the U-shaped mono-

anion,⁵ in accord with the original discussion on the kinetic protonation of such systems,⁶ occurs predominantly in the centre, to give (2; R = H) although



the conjugated isomer (3) is also a possible product if protonation occurs at the end of the charged system in (1). During work-up, any isomer (3) which is formed by protonation may be reducible in the presence of an excess of metal, if the reaction is competitive with hydrogen gas formation. This possibility can be avoided by removal of the metal by addition of sodium benzoate.

In the radical anion initially protonated in Method B, the charge should be principally localised at the 1- and 4-positions, because of the charge-stabilising nature of the phenyl group,⁷ and protonation at the less hindered 4-position, followed by electron addition to the radical, should give the same anion (1) as is produced by Method A. However, any isomer (3) produced should be reducible preferentially as compared with the aromatic biphenyl. The possibility exists also of a base-catalysed equilibration, during reduction, of (2) with (3) leading to further reduction. This last reaction was ruled out by showing that lithium t-butoxide in ammonia left 1,4-dihydrobiphenyl and its 2-methoxy-derivative unchanged during the time employed in Method B. Also, the further reduction of 1,4-dihydrobiphenyl and its 2-methoxy-derivative by Method B gave only non-aromatic tetrahydro-derivatives, probably the expected 1,2',4,5'- (see later), and less than 1% of phenylcyclohexane or phenylcyclohexene was detectable by g.l.c.; thus there is little if any further reduction of the initially hydrogenated ring.

That isomers of type (3) are readily reducible was further confirmed by using a mixture of 1,4- and 3,4-dihydro-2-methoxybiphenyl [Table 2, experiment (d)];

¹ Part XIX, A. J. Birch and K. P. Dastur, *Austral. J. Chem.*, 1973, **26**, 1363.

² P. J. Grisdale, T. H. Regan, J. C. Doty, J. Figueras, and J. L. R. Williams, *J. Org. Chem.*, 1968, **33**, 1116.

³ D. F. Lindon, C. N. Cortez, and R. G. Harvey, *J. Amer. Chem. Soc.*, 1972, **94**, 5406.

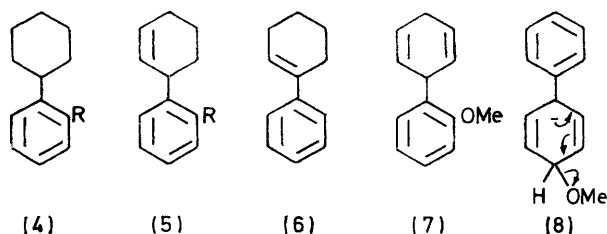
⁴ A. J. Birch and G. Subba Rao, *Adv. Org. Chem.*, 1972, **6**, 1.

⁵ R. B. Bates, R. H. Carnighan, and C. E. Staples, *J. Amer. Chem. Soc.*, 1963, **85**, 3032.

⁶ A. J. Birch, *Discuss. Faraday Soc.*, 1947, **2**, 246; *J. Chem. Soc.*, 1950, 1551; A. G. Catchpole, E. D. Hughes, and C. K. Ingold, *ibid.*, 1948, 8.

⁷ K. W. Bowers, in 'Radical Ions,' ed. E. T. Kaiser and L. Kevan, Interscience, New York, 1963, pp. 211, 232.

Method B preferentially removed the conjugated isomer, replacing it with phenylcyclohexane and 4-phenylcyclohexene.



The results of reducing biphenyl and 2-methoxybiphenyl by the two procedures with various metals

ion of the diene (3; R = OMe) (or its reduction products) as compared with (2; R = OMe). That reduction by Method A genuinely represents generation and reaction of (1; R = OMe) can be shown by quenching with methyl iodide to produce *ca.* 90% yield of the angular methylated derivative, readily hydrolysed to the expected $\beta\gamma$ -unsaturated ketone.

Before we consider the effects of conditions on the ratio of initial reduction in the occupied as compared with the unoccupied ring of 2-methoxybiphenyl, it is necessary to examine the origins of the hydrocarbon materials produced, notably by Method B.

If OMe is directly removed from 2-methoxybiphenyl the products should correspond to those obtainable

TABLE 1
Reductions of biphenyl

Method	Quenching agent or proton source	Li(g atom mol ⁻¹)	Products (%)					Conj./Unconj. (calc.)
			(4; R = H)	(5; R = H)	(2; R = H)	(6)	(3; R = H)	
(a)	A	NH ₄ Cl	2.2		100			0
(b)*	A	MeOH	2.24	13	5	57	1.5	22
(c)	B	Bu ^t OH	2.4	16.5	8	30.5	3	15

* Excess of metal was not destroyed before work-up.

TABLE 2
Reduction of 2-methoxybiphenyl by Method A

Quenching agent	Metal (g atom mol ⁻¹)	Product (%)						
		(4; R = H)	(5; R = H)	(2; R = H)	(3; R = H)	(2; R = OMe)	(3; R = OMe)	
(d)	NH ₄ Cl	Li, 2.53	3	3	7		81.5	5
(e)	NH ₄ Cl *	Li, 2.46	0.8	Trace	6.5		79	13.5
(f)	MeOH	Li, 2.55	4	3	4	2.5	55	26 †
(g)	MeOH *	Li, 2.52	0.8	Trace	3	2.6	64	29
(h)	H ₂ O *	Li, 2.43	0.7	Trace	3	3	67	22.5 ‡
(i)	MeOH	Ca, 1.59	1.5	0.5	44	12.5	34	2.5 §

* Excess of metal destroyed by sodium benzoate. † Also 6% 1-phenylcyclohexene. ‡ Also 3% starting material. § Also 1.5% biphenyl and 3.5% 1,4-dihydro-2'-methoxybiphenyl (7).

and proton sources, are shown in Tables 1, 2, and 4. Since the monoanion (1) can also be generated from dihydrobiphenyl by reaction with lithium amide in ammonia, the results of addition of protons from various sources in the absence of reducing metal are shown in Table 3.

In Table 1, experiment (a) confirms that with ammonium ion, 1,4-dihydrobiphenyl is the only observable product.³ With methanol as the quenching agent, experiment (b) shows that additionally either (3) or products likely to arise from its reduction by an excess of metal are formed in notable amounts. This is also true of Method B [experiment (c)].

Any reduction process involving protonation of an anion of type (1) by an alcohol, in contrast to ammonium chloride, is likely therefore to lead to a proportion of conjugated diene, which with Method B could be further reduced *in situ*. Table 3 confirms directly the effect expected on the basis of the results (above) of quenching the anion (1) in absence of any reducing metal. The expectation is also confirmed for 2-methoxybiphenyl (Table 2), in which case methanol or water generates a higher proportion than ammonium

from biphenyl under the same circumstances. The nature of the product does not indicate this as a major pathway, although (Table 2, Method A) up to 6%

TABLE 3
Products of quenching of the carbanion (1)

	LiNH ₂ (mol per mol)	Anion (1)	Quenching agent	Product ratio (3)/(2)
(j)	10.0	R = H	MeOH	0.7
(k)	13.0	R = H	Bu ^t OH	1.2
(l)	1.3	R = H	H ₂ O	0.4 §
(m)	20.0	R = OMe †	MeOH	0.5
(n)	11.0	R = OMe	MeOH	0.5
(o)	9.7	R = OMe *	Bu ^t OH	0.5
(p)	9.0	R = OMe *	NH ₄ Cl	0.17

* Results calculated from product obtained starting with material from experiment (d) (Table 2). † The pure (2; R = OMe) was used, separated by inverted dry column chromatography on silica gel. § Result supplied by Dr. B. Chauncy.

may be produced in this manner. By contrast, reductions of 2-methoxybiphenyl by calcium [experiment (i)] and of 4-methoxybiphenyl by Method A (see later) probably proceed through biphenyl.

The intermediate in loss of OMe is probably (3; R = OMe), which, on the basis of earlier work⁸ on the reduction of 1-methoxycyclohexa-1,2-dienes, is initially converted into (3; R = H). The products of reduction of the latter (phenylcyclohexane and 3-phenylcyclohexene) are produced in about the same ratio as those noted in Table 4, supporting this assumption. Therefore, we have assumed that the quantities of hydrocarbon products can be added to those of (2; R = OMe) and (3; R = OMe) to indicate the extent of initial reduction in the occupied ring (Table 4). Furthermore, the extent of demethoxylation can be combined with the extent of isolation of (3; R = OMe) to give the initial proportion of the latter produced by the particular protonation conditions. This assumption has been used to calculate the ratio of conjugated to unconjugated diene (Table 4) in the substituted

protonation of the biphenyl dianion does not occur and there seems little doubt that the nature of the reduced product obtained by Method A is determined by the relative rates of protonation at the 4- and 4'-positions. This has not yet been demonstrated for the radical anion process, so the possibility still exists that reversal of initial protonation may be a factor in deciding the extent of reduction of a given ring. There are no very obvious trends from the results which can be interpreted in this sense. The variations in proportions of lithium and t-butyl alcohol produce what are probably insignificant variations in products [experiments (q)–(s)]. The use of methanol directs reduction more to the unoccupied ring [experiments (v), (w), (s), and (t)]. The use of potassium instead of lithium has little effect on the ratios of reduction in each ring, but affects the nature of the products, giving a higher

TABLE 4
Reduction of 2-methoxybiphenyl by Method B

Material	Metal (mmol)	Metal (mg atom)	Proton source	Product (%) †						Recovered starting material	Calc. ratio conj./unconj. diene ‡ (i), (ii)	Calc. ratio subst./ unsubst. ring reduction
				(4; R = H)	(5; R = H)	(4; R = OMe)	(5; R = OMe)	(2; R = OMe)	(7)			
(q)	19.0	Li, 50.0	Bu ^t OH, 5 ml	12.5	4.3	9.1	12.5	37	22.5	27 §	0.95, 0.5	1.2
(r)	19.5	Li, 54.0	Bu ^t OH, 20 ml	14	4.5	11.5	7.6	37	25	28	0.78, 0.5	1.2
(s)	18.5	Li, 48.0	Bu ^t OH, 50 ml	17	5.5	14	6	32	25	20	0.8, 0.7	1.5
(t)	17.5	Li, 45.5	MeOH, 22 ml	11	3.5	11	8	32	33	36	0.6, 0.5	0.8
(u)	19.0	Li, 49.0	NH ₄ OAc, 10 g	2.5	2.5			53	36	61	0.09, 0	1.6
(v)	21.0	K, 54.5	Bu ^t OH, 50 ml	7.5	4.5	16	43	13	13	33	2.5, 0.3	1.5
(w)	18.0	K, 47.5	MeOH, 18 ml	14.5	4.5	12	11	33	25	40	0.9, 0.6	1.2
(x)	19.5	Ca, 26.0	Bu ^t OH, 50 ml	26.5	9.0	22	7	23.5	12	45	2.4, 1.5	1.1

* As % of total product. † Proportions in product other than recovered starting material. ‡ (i) In unsubstituted ring; (ii) in substituted ring. § The mixture also contains 2% 1-phenylcyclohexene as indicated by its g.l.c. retention time.

ring; that in the unsubstituted ring is calculated on the basis that formation of all tetra- or hexa-hydro-derivatives in that ring passes through the conjugated diene. Because of uncertainties of this kind and possible cumulative experimental errors, the ratios shown have a probable error of $\pm 10\%$ of the value shown. That conjugated diene is produced by alcohols rather than ammonium salts is clearly demonstrated, even in the case of Method B, by experiment (u), where virtually only the 1,4- and 1',4'-dihydro-derivatives were found.

The unusually large recovery of 2-methoxybiphenyl in this experiment is due to its insolubility and the rapidity of the competing hydrogen evolution.

2-Methoxybiphenyl is reduced by Method A (Table 2) largely in the substituted ring, whereas by Method B each ring is reduced to a similar extent. The substituent therefore seems to be more effective in concentrating the charge in an intermediate dianion for reaction at the 4-position in the substituted ring, than it is with the radical anion. The radical anion consumes reaction by protonation to a greater extent in the 4-position than in the 4'-position, with the exception of the reaction with lithium in methanol [experiment (t)]. Harvey³ has shown that reversal of

proportion of highly reduced compounds. This result could be due to effects of ion-pairing resulting in alterations of the ratio of conjugated to unconjugated diene in the protonation of the intermediate monoanion of type (1). It is deducible from the results that the protonation of the anion from the OMe-containing (1; R = OMe) ring gives less conjugated isomer than protonation of the similar anion in the other ring. The reason for this requires further investigation.

Table 3 shows that the isomer ratio varies little with the alcohol structure, but is considerably altered when ammonium chloride is used. This may be due to the ability of the ammonium ion to transfer a proton through the solvation shell, by rearrangements of hydrogen-bonding in the solvent, whereas attack by alcohols may be molecular. Virtually no steric hindrance would be expected in the first type of protonation. Although an alcohol such as methanol produces some ammonium ion initially, as reduction proceeds with accumulation of alkoxide, this must become vanishingly small. It can be deduced from the ratios of products in Table 1 that the ratio of unconjugated to initial conjugated diene is higher for methanol than for t-butyl alcohol,

⁸ A. J. Birch and G. Subba Rao, *Austral. J. Chem.*, 1970, **23**, 1641.

in protonation of the monoanion [experiments (a) and (b)]. This conclusion is borne out by Table 3 [experiments (j) and (k)] where the directly observed ratios are close to those calculated in Table 1. For no obvious reason, the nature of the alcohol seems to make little difference for 2-methoxybiphenyl (Tables 2 and 3) although the ratio is again strongly affected by ammonium ion [Table 3, experiment (p)]. The ratio here found also agrees with the effect of ammonium ion on reduction by Method B [Table 4, experiment (u)].

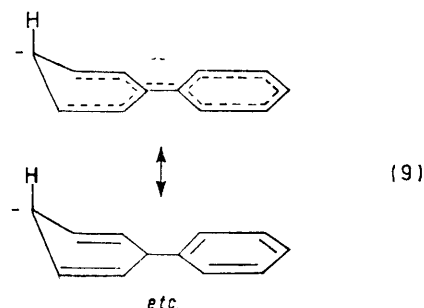
4-Methoxybiphenyl, as already noted, gives by Method A the products characteristic of biphenyl, with complete loss of OMe. By Method B, one series of hydrocarbon products also corresponds to reduction of biphenyl (see Experimental section), amounting to about a third of the compound reduced. The remaining material retains the OMe and corresponds to reduction in the unsubstituted ring [3-(4-methoxyphenyl)cyclohexa-1,4-diene (16%); 3-(4-methoxyphenylcyclohexene) (13%); and 4-methoxyphenylcyclohexane (3.5%)]. The ratios of the different degrees of hydrogenation are similar to those with biphenyl itself by Method B. The radical anion is probably protonated in either the 4'- or the 4-position, the anion (8) from reduction of the radical due to the latter process then expelling methoxide anion to give biphenyl. The dianion, in contrast, expels a methoxide anion entirely, but whether before or after protonation cannot be decided from the evidence available. Recovery of starting material in these reactions is due to low solubility of this substrate.

The much greater extent of removal of OMe from 2-methoxybiphenyl by calcium [experiments (q) and (x)] requires further exploration. The products could be largely derived from biphenyl. Removal of OMe may be assisted by ion-pairing with the doubly-charged calcium cation.

In the foregoing results above, little if any material formed by simultaneous reduction in both rings was observed. Further reductions of 1,4-dihydrobiphenyl and of the 2-methoxy-derivative were examined, using lithium-*t*-butyl alcohol. The products appear to be the expected 1,2,2',5'-tetrahydro-derivatives (see Experimental section). The reduction of the dihydrobiphenyl was noted to be very much slower than that of the biphenyl, as shown by the rate of disappearance of metal, and selective reduction of one ring is readily acceptable.

The electrons in the radical anions and dianions must be accommodated in aromatic antibonding orbitals. The dianions, as doubly charged antiaromatic systems, may be formed in only very low proportions in equilibria. However, the high basicity, in contrast to the weak basicity of the radical anions, would result in immediate abstraction of a proton from ammonia to give monoanions of type (1). No detectable con-

centration of dianion therefore need be present. The reason for protonations in the observed positions is not clear. Although radical anions probably largely maintain planarity,⁹ little is known about dianions, and the high basicity of the charged 4-carbon atom may be due to its virtual deconjugation from the remaining planar anion (9). Why OMe assists reaction in the occupied ring is not at present explicable; the possible factors involved include alterations of orbitals, the inductive effect of OMe, solvation, and ion-pairing. The lesser effect of the substituent with the radical



anion may be due to the lower energy level of the latter.

The results help to define the experimental conditions for a required structural objective; Method A is clearly that of choice in giving a much less complex and less reduced product, but the relative substituent specificities require study in a given case.

Before efficient analytical methods were available, a considerable amount of work was carried out in the reductions of biphenyl derivatives.¹⁰ Some later work¹¹ was carried out before a full appreciation of the factors involved had been made. We are greatly indebted to these workers, and some of the results will be published later.

Examination of Products.—The reduction products were analysed and separated by g.l.c. and although the detector was not calibrated for each compound individually, the probable error is not considered to be greater than $\pm 5\%$ of the estimated value. In similar runs the reproducibility was normally better than $\pm 5\%$ of the value. The products were isolated by preparative g.l.c. and characterised by spectra (i.r., u.v., n.m.r., and mass). Those in Table 4 were fully characterised only in experiment (q), the retention times being used for identification in experiments (r)—(x). In all other experiments the products were isolated on each occasion and the i.r. spectrum of each was compared with that of a fully characterised specimen. The spectral properties are in all cases consistent with the assigned structures (see Experimental section).

A few compounds merit more detailed discussion as follows.

3-Phenylcyclohexene. The position of the double bond (in the 2- and not the 3-position) was assigned on

⁹ C. S. Johnson and R. Chang, *J. Chem. Phys.*, 1964, **41**, 3272.

¹⁰ A. J. Ryan, M.Sc. Thesis, University of Sydney, 1956; S. Mejer (Wroclaw), work in the University of Manchester, 1960; G. Subba Rao, Ph.D. Thesis, University of Manchester, 1966.

¹¹ E. G. Hutchinson, Ph.D. Thesis, Australian National University, 1971; G. Subba Rao (Bangalore), work at the A.N.U., 1967—1970.

the ratios of the number of allylic (other than benzylic) protons to non-allylic methylene protons (2:4). The compound also has no styrenoid u.v. absorption. The structure of 3-(2-methoxyphenyl)cyclohexene was assigned on the basis of n.m.r. signals and u.v. absorption in the same way.

2-Phenylcyclohexa-1,3-diene. This diene is very unstable, but was characterised by M^+ 156 and absorption at 280 nm. It was converted into a crystalline adduct with maleic anhydride, the spectral properties of which are consistent with the expected structure, notably the styrenoid λ_{\max} 248 nm. (ϵ 15,000), which differentiates it from possible alternative structures, and the presence of a single olefinic proton resonance. The adduct cannot be formed from a 1,4-dihydrobiphenyl impurity, since this did not react with maleic anhydride under the experimental conditions.

1-Methoxy-2-phenylcyclohexa-1,3-diene (3; R = OMe) showed u.v. absorptions at 230 and 280 nm and was extremely unstable. For this reason and since the isomeric diene (2; R = OMe) is conjugated by, and reacts with, maleic anhydride, it was necessary to isolate (3; R = OMe) by preparative g.l.c. and to treat it immediately with maleic anhydride. That the product contains a bridgehead OMe, rather than the enol ether grouping to be expected from the isomeric 1-methoxy-6-phenylcyclohexa-1,3-diene, was demonstrated on several grounds. One was the similarity (with the expected difference due to OMe) of the spectra to those of the adduct with 2-phenylcyclohexa-1,3-diene (above). Another was the lack of generation of any ketonic product from the adduct by heating with aqueous *N*-hydrochloric acid, which indicates lack of presence of an enol ether function. Finally, the mixed product containing (3; R = OMe) and (2; R = OMe) gave only one (expected) ketone on acidic hydrolysis, which rules out the possible presence of 2-methoxy-3-phenylcyclohexa-1,3-diene, which would produce a different ketone.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. ^1H N.m.r. spectra were obtained on a Varian HA-100 spectrometer, i.r. spectra on a Perkin-Elmer 257 grating instrument, u.v. spectra on a Unicam SP 800 spectrophotometer, and mass spectra on either an A.E.I. MS-902 or an Atlas CH-7 instrument. Unless specified otherwise, i.r. spectra of liquids were measured for liquid films and of solids for Nujol mulls; solutions in ethanol were used for u.v. spectra. The reduction products were analysed on a Perkin-Elmer 881 gas chromatograph using a 5% Carbowax 20M column (6 ft \times 0.25 in; 80–100 mesh); retention times (t_R) reported were measured at 140° unless specified otherwise. The detector was not calibrated for each compound individually and the probable error is considered to be not greater than $\pm 5\%$ of the estimated value. In similar runs, the reproducibility was normally better than $\pm 5\%$ of the value. Preparative separations were effected on a 20% Carbowax column with a Varian Aerograph instrument.

Method A.—The alkali metal (about 2.5 equiv. per mol of aromatic substrate; see Tables 1 and 2) was added in small portions with stirring during about 2 min to a solution of biphenyl or its methoxy-derivative in tetrahydrofuran (15 ml per g of 2-methoxybiphenyl and 100 ml per g of biphenyl) and ammonia (75 ml per g of 2-methoxybiphenyl and 150 ml per g of biphenyl). Stirring was continued for a further 10–20 min, then the mixture was quenched with either solid ammonium chloride or an alcohol and brine was added. Ammonia was evaporated off and the residue was extracted with benzene. The extract was washed thrice with water and then brine and dried (Na_2SO_4). Removal of the solvent under suction gave the reduction products with virtually no loss of material.

Method B.—The alkali metal (about 2.5 equiv. per mol of substrate) was added with stirring during about 10 min to a solution of biphenyl or its methoxy-derivative in tetrahydrofuran and ammonia (same quantities of solvents as in Method A) in the presence of a proton source (Tables 1 and 4). Brine was added as soon as the mixture became colourless, which usually occurred rapidly. In the case of reduction of 2-methoxybiphenyl with calcium, the colour had not disappeared even after 30 min and was discharged with methanol. The reaction was worked up as in Method A.

Reduction of Biphenyl.—The products from the experiments mentioned in Table 1 were separated by preparative g.l.c. and characterised on the basis of their spectral data as follows.

Phenylcyclohexane (4; R = H), t_R 120 s; ν_{\max} 1601, 1493, 758, and 704 cm^{-1} ; δ 1.2–2.0 (10H, m, CH_2), 2.5 (1H), m, and 7.11 (5H, s), m/e 160 (M^+) (Found: C, 89.65; H, 10.4. Calc. for $\text{C}_{10}\text{H}_{16}$: C, 89.9; H, 10.1%).

3-Phenylcyclohexene (5; R = H), t_R 137 s; ν_{\max} 1650, 1600, 1492, 1450, 918, 900, 886, 795, 762, 730, 706, and 680 cm^{-1} ; δ (CCl_4) 1.49–1.9 (ca. 4H, m, $\text{C}-\text{CH}_2-\text{CH}_2-\text{C}$), 2.0–2.2br (2H, $=\text{C}-\text{CH}_2-\text{C}$), 3.35br (1H, s, CHAr), 5.76 (2H, m, $\text{CH}=\text{CH}$), and 7.16 (5H, s, ArH); m/e 158.109447 (Calc. for $\text{C}_{12}\text{H}_{14}$: 158.109545).

1-Phenylcyclohexene (6), t_R 245 s; λ_{\max} (cyclohexane) 247 nm (ϵ 6520); ν_{\max} 1640, 1600, 762, and 745 cm^{-1} ; m/e 158 (M^+), identified by the characteristic u.v. absorption due to the styrene chromophore at 247 nm.²

1,4-Dihydrobiphenyl (2; R = H), t_R 198 s; i.r. spectrum identical with that of an authentic specimen.³

3,4-Dihydrobiphenyl (3; R = H), t_R 302 s; λ_{\max} (cyclohexane) 230 (ϵ 9300) and 280 nm (3160); ν_{\max} 1670, 1640, 1600, 1275, and 1228 cm^{-1} ; m/e 156 (M^+). Owing to its instability, the compound could not be further characterised as such, but was isolated from the other products as an adduct with maleic anhydride. The mixture of products, obtained in experiment (b) (Table 1) (0.42 g) was added to a solution of maleic anhydride (0.082 g) in benzene (15 ml) and heated under reflux for 5 h under nitrogen. The solvent was removed and the residue triturated with pentane to give a solid (0.15 g). Crystallisation from ethyl acetate gave a sample of m.p. 126°. The adduct was characterised as 6-phenylbicyclo-[2.2.2]oct-5-ene-2,3-dicarboxylic anhydride on the basis of the following data: ν_{\max} 1870, 1840, 1770, 1635, 1595, 1570, and 960 cm^{-1} ; λ_{\max} 248 nm (ϵ 15,000); δ 1.2–1.9br (4H,

¹² E. L. Eliel, J. W. McCoy, and C. C. Price, *J. Org. Chem.*, 1957–1958, **22**, 1533; R. Y. Mixer and W. G. Young, *J. Amer. Chem. Soc.*, 1956, **78**, 3379.

q, $\text{CH}_2\cdot\text{CH}_2$), 3.06—3.45 (3H, m, C-4 bridgehead H and $\text{CO}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}$), 3.74br (1H, s, C-1 bridgehead H), 6.48 (1H, dd, J 6 and 3 Hz, $\text{C}=\text{CH}$), and 7.2—7.5 (5H, m, ArH); m/e 254 (M^+) (Found: C, 75.4; H, 5.5. $\text{C}_{16}\text{H}_{14}\text{O}_3$ requires C, 75.6; H, 5.55%).

Reactions of 1,4-Dihydrobiphenyl (2; R = H) with Bases. —(i) *Lithium amide*. Lithium amide was prepared in the usual way from a solution of lithium metal (see Table 3 for proportions of the reactants) in ammonia [25 ml per 100 mg of compound (2; R = H)] in the presence of catalytic amounts of iron(III) nitrate. 1,4-Dihydrobiphenyl in tetrahydrofuran [about 15 ml per 100 mg of (2; R = H)] was added with stirring to the amide solution and after 10 min the orange-coloured mixture was quenched with a protonating agent. The products (g.l.c.) were characterised by comparing their i.r. spectra with those of the authentic specimens and their compositions in experiments using various quenching agents are given in Table 3.

(ii) *Lithium *t*-butoxide*. This rearrangement was prepared in ammonia by adding *t*-butyl alcohol (5 ml) and a few mg of iron(III) nitrate to a solution of lithium in ammonia (50 ml) and stirring until the blue colour disappeared (about 30 min). 1,4-Dihydrobiphenyl (0.2185 g) in tetrahydrofuran (5 ml) was then added and the mixture was stirred for 15 min. Addition of brine and the usual work-up gave the pure unchanged 1,4-dihydro-compound.

Reduction of 1,4-Dihydrobiphenyl (2; R = H).—Reduction of 1,4-dihydrobiphenyl (0.7664 g) in ammonia (100 ml), tetrahydrofuran (50 ml), and *t*-butyl alcohol (5 ml) was carried out by Method B with lithium (0.073 g). The blue colour was discharged by adding methanol 5 min after the addition of lithium. The three products obtained after the usual work-up were separated by g.l.c. and characterised as follows: (a), t_R 290 (120°) (12%), v_{max} 1660, 1635, 962, 947, 792, 758, and 702 cm^{-1} (different from the spectra of 3- and 1-phenylcyclohexenes); m/e 158, not further characterised; (b) 1,2,4,5'-*tetrahydrobiphenyl*, t_R 375 s (120°) (75%), v_{max} 1685, 1645, 1630, 962, 950, and 806 cm^{-1} ; δ 2.3—3.0 (6H, m, $\text{CH}_2\cdot\text{C}=\text{C}$), 3.2—3.56 (1H, m, $\text{C}=\text{C}-\text{CH}=\text{C}=\text{C}$), and 5.4—6.0 (7H, m, $\text{HC}=\text{CH}$); m/e 158 (M^+); no u.v. absorption other than the end absorption at 222 nm (Found: C, 91.2; H, 9.2. $\text{C}_{12}\text{H}_{14}$ requires C, 91.1; H, 8.9%); (c) t_R 453 s (120°) (13%), unchanged reactant (2; R = H).

Reduction of 2-Methoxybiphenyl.—Reductions were carried out with the reagents and results indicated in Tables 2 and 4, by the foregoing methods. The products were separated by preparative g.l.c. and characterised by their spectral properties. Characterisation of the biphenyl hydrocarbons has already been discussed in connection with the reduction of biphenyl. Only the 2-methoxy-compounds are described here.

In the experiment (i), the product mixture also contained 3.5% of 1,4-dihydro-2'-methoxybiphenyl (7), which merged in g.l.c. with about 2.5% of 3,4-dihydrobiphenyl (3; R = OMe). The proportions were calculated by measuring the intensities in g.l.c. before and after hydrolysis of the product mixture with 2*N*-hydrochloric acid in methanol. The compound (7) was identified by comparing its i.r. spectrum with that of an authentic specimen.

2-Cyclohexylanisole (4; R = OMe), t_R 461 s; v_{max} 1600, 1585, 1493, 1240, and 756 cm^{-1} ; δ 1.2—2.0br (10H, m, 5CH_2), 2.96br (1H, CHAr), 3.82 (3H, s, OCH_3), and 6.7—7.25 (4H, m, ArH); λ_{max} 273.5 (ϵ 1976) and 280 nm (1900);

m/e 190 (M^+), i.r. spectrum identical with that of an authentic sample.

3-(2-Methoxyphenyl)cyclohexane (5; R = OMe), t_R 604 s; v_{max} 1680, 1648, 1600, 1585, 1493, 1243, 761, 748, 728, and 700 cm^{-1} ; δ (CDCl_3) 1.2—2.02 (*ca.* 4H, m, $\text{C}\cdot\text{CH}_2\cdot\text{C}$), 2.02—2.8 (*ca.* 2H, m, $=\text{C}\cdot\text{CH}_2\cdot\text{C}$), 5.77 (2H, m, $\text{CH}=\text{CH}$), and 6.75—7.3 (4H, m, ArH); λ_{max} 273 (ϵ 1974) and 279 nm (1880); m/e 188.120503. ($\text{C}_{13}\text{H}_{16}\text{O}$ requires M , 188.120109).

1,4-Dihydro-2-methoxybiphenyl (2; R = OMe), t_R 738 s; v_{max} 1685—1680, 1646, 1600, 1492, 1220, 780, 758, and 700—710 cm^{-1} ; δ (CCl_4) 2.86 (2H, m, $\text{C}=\text{C}\cdot\text{CH}_2\cdot\text{C}=\text{C}$), 3.39 (3H, s, OCH_3), 3.85 (1H, m, CH), 4.64 (1H, t, CHPh), 5.65br (2H, t, $\text{HC}=\text{CH}$), and 7.12 (5H, s, ArH); m/e 186 (parent ion) (Found: C, 83.7; H, 7.7. $\text{C}_{13}\text{H}_{14}\text{O}$ requires C, 83.8; H, 7.6%).

1,4-Dihydro-2'-methoxybiphenyl (7), t_R 920 s; v_{max} 1685, 1632, 1588, 1245, 760, 750, and 690 cm^{-1} ; δ 2.72br (2H, d, $\text{C}=\text{C}\cdot\text{CH}_2\cdot\text{C}=\text{C}$), 3.84 (3H, s, OCH_3), 4.2br (1H, q, ArCH), 5.76 (4H, unsym. t, $\text{CH}=\text{CH}$), and 6.78—7.3 (4H, m, ArH); λ_{max} 273 (ϵ 2183) and 280 nm (1995); m/e 186 (M^+) (Found: C, 83.5; H, 7.6. $\text{C}_{13}\text{H}_{14}\text{O}$ requires C, 83.8; H, 7.6%).

3,4-Dihydro-2-methoxybiphenyl (3; R = OMe), t_R 880 s; v_{max} (film) 1645, 1600, 1585, 1242, 1225, 750, and 705 cm^{-1} ; λ_{max} (cyclohexane) 230 (ϵ 28,800) and 280 nm (3200); m/e 186 (M^+). The compound, owing to its instability, was characterised as its adduct with maleic anhydride. The compound was isolated by g.l.c. in small batches which were immediately added to a solution of maleic anhydride in benzene. The combined mixture was heated under reflux for 3 h and left overnight. Solvent was evaporated off and the unchanged maleic anhydride was removed at 0.3 mmHg and 40°. The residue was washed with hexane and the adduct, m.p. 135—136°, crystallised from ethyl acetate-hexane. The hexane washings contained mainly 2-methoxybiphenyl and some polymeric material. The same adduct was obtained from the unconjugated isomer (2; R = OMe) and from (3; R = OMe) obtained by base-catalysed conjugation of the former. Since these isomers have different retention times, there is no doubt that the adduct above was derived from (3; R = OMe). Its structure (1-methoxy-6-phenylbicyclo[2.2.2]oct-5-ene-2,3-dicarboxylic anhydride) was established from the following physical data: v_{max} 1855, 1835, 1775, 1610w, 1246, 940, 915, and 770 cm^{-1} ; λ_{max} 241 nm (ϵ 10,300); δ 1.4—2.04br (4H, q, $\text{CH}_2\cdot\text{CH}_2$), 3.16—3.6 (m, $\text{CO}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}$ and bridgehead H) overlapping on 3.3 (s, OCH_3) (total 6H), 1.6 (d, J 6 Hz, $\text{C}=\text{CH}$), and 7.3 (5H, s, ArH); m/e 284 (M^+) (Found: C, 71.7; H, 5.8. $\text{C}_{17}\text{H}_{16}\text{O}_4$ requires C, 71.8; H, 5.7%). The compound does not behave as an enol ether, and consequently cannot be derived from the isomeric 2-methoxy-3-phenylcyclohexa-1,3-diene.

Examination of the products of hydrolysis further supports the structure (3; R = OMe). The mixture of the products (0.60 g), obtained by reducing 2-methoxybiphenyl by Method A with methanol as the quenching agent was hydrolysed with 2*N*-hydrochloric acid (5 ml) in methanol (50 ml) by heating the mixture under reflux for 40 min under nitrogen. Conventional work-up gave a mixture of products containing, however, only one $\alpha\beta$ -unsaturated ketone (70—80%) and minor proportions of unidentified non-ketonic products (g.l.c.; 70°). The 2-phenylcyclohex-2-enone crystallised from the product mixture on trituration with pentane and was recrystallised

from benzene and pentane; m.p. 92–93° (lit.¹³ 95–95.5°); t_R 680 s (170°); λ_{max} 227 (ϵ 4870) and 260 nm (4370); ν_{max} 1678, 1600, 762, and 702 cm^{-1} ; δ 2.0–2.32br (2H, q, $C=CH_2C$), 2.4–2.8 (4H, m, $=C\cdot CH_2\cdot C$), 7.18 (t, J 4.5 Hz, $HC=C$), and 7.43 (5H, s, ArH); m/e 172 (M^+). This compound would be expected from (2; R = OMe) and (3; R = OMe) but not from 2-methoxy-3-phenylcyclohexa-1,3-diene.

Reductive Methylation of 2-Methoxybiphenyl.—Reduction of 2-methoxybiphenyl (3.65 g) was carried out with lithium (0.3620 g) in ammonia (200 ml) and tetrahydrofuran (50 ml) by Method A and the reaction mixture was quenched rapidly with methyl iodide (12 ml); the dark colour disappeared immediately. Work-up in the usual way furnished a mixture of products which were separated by preparative g.l.c. The major product (90%), 2-methoxy-3-methyl-3-phenylcyclohexa-1,4-diene, had t_R 488 s; ν_{max} (film) 1685–1680, 1645, 1598, 1250, 1210, 760, 725, and 702 cm^{-1} , δ 1.62 (3H, s, CMe), 2.8–3.0br (2H, m, $C=C\cdot CH_2\cdot C=C$), 3.44 (3H, s, OCH_3), 4.75 (1H, t, $HC=C\cdot OCH_3$), 5.37–6.0 (2H, m, $CH=CH$), and 7.76 (5H, m, ArH); m/e 200 (M^+) (Found: C, 83.8; H, 7.8. $C_{14}H_{16}O$ requires C, 84.0; H, 8.05%).

A methanolic solution (50 ml) of the foregoing product mixture (1.0 g) was heated under reflux with 2N-hydrochloric acid (10 ml) for 40 min under nitrogen. Conventional work-up gave a mixture (0.955 g) from which the main component (about 90%) was separated by preparative g.l.c. and characterised as 2-methyl-2-phenylcyclohex-3-enone, t_R 691 s; ν_{max} 1712, 1600, 1580, and 895 cm^{-1} ; δ 1.51 (3H, s, Me), 2.12–2.64 (4H, m, $=C\cdot CH_2\cdot C=C$), 5.74–6.12 [2H, ABX, J_{AB} 10, J_{AX} 3 Hz, $-CH_2(X)-CH_A=CH_B-CPh$], and 7.08–7.48 (m, 5H, ArH) [the aromatic protons in this as in the enol ether (2; R = OMe) are non-equivalent, probably owing to the presence of the asymmetric tertiary carbon atom]; m/e 186 (M^+) (Found: C, 83.7; H, 7.5. $C_{13}H_{14}O$ requires C, 83.8; H, 7.6%). The minor compounds, t_R 227 (8%) and 795 s (2%), were not characterised.

Reaction of 1,4-Dihydro-2-methoxybiphenyl (2; R = OMe) with Base.—Lithium amide in ammonia (25 ml) was prepared from lithium (0.1145 g) and a solution of the product mixture obtained in experiment (f), Table 2 (0.336 g) in tetrahydrofuran (10 ml) was added to it. The mixture was stirred for 20 min. Following the addition of ammonium chloride, or methanol, or of *t*-butyl alcohol (in similar experiments), usual work-up gave a mixture of products whose composition is given in Table 3. The products were separated each time and their i.r. spectra compared with those of fully characteristic specimens. The pure 1,4-dihydro-compound (2; R = OMe) was separated (see later) and the anion was similarly generated and quenched with methanol. The results deduced from the pure material and the mixture agree and are shown in Table 3.

Reduction of 1,4-Dihydro-2-methoxybiphenyl (2; R = OMe).—Pure 1,4-dihydro-2-methoxybiphenyl was separated by inverted dry column chromatography of the mixture obtained in the experiment (d), Table 2, on silica gel. The column was developed by 1:3 benzene–hexane, in which the 3,4-dihydro-compound (3; R = OMe) moved faster than the 1,4-dihydro-compound (2; R = OMe). The latter (0.1383 g) in tetrahydrofuran (5 ml) was reduced by Method B by lithium (14.6 mg) in ammonia (25 ml) containing *t*-butyl alcohol (5 ml). Lithium was added

during 2 min and the mixture was stirred for 20 min. The blue colour was discharged with methanol (1 ml) and the product was worked up as usual to give a mixture consisting mainly of four compounds. These were separated by preparative g.l.c. at 155°; the main component was 1,2',4,5'-tetrahydro-2-methoxybiphenyl (61%), t_R 616 s; ν_{max} 1678–1690, 1645, 1215, 805–790, 765, and 695 cm^{-1} ; δ 2.3–3.2 (6H, m, $C=C\cdot CH_2\cdot C=C$), 3.52 (s, OMe) overlapping on 3.44 (m, $=C\cdot CH\cdot C=$) (total 4H), 4.73 (1H, unsym. t, $HC=C\cdot OCH_3$), and 5.3–6.0 [5H, m, $(CH=CH)_2$ and $C=CH$]; m/e 188 (M^+) (Found: C, 83.0; H, 8.2. $C_{13}H_{16}O$ requires C, 82.9; H, 8.6%).

The first two components of the mixture were not completely characterised; component (a), t_R 306 s (4.5%), showed ν_{max} (film) 1685–1680, 1645, 1215, 795, 765, and 735–725 cm^{-1} ; δ (CCl_4) 1.4–2.2br (m), 2.6–2.84br (m), 3.45 (s), 4.58 (t), and 5.42–5.6br (m) (integration was not possible owing to low concentration). The i.r. spectrum was different from that of 2-cyclohexyl-anisole. Component (b), t_R 426 s (13.5%) had ν_{max} 1682, 1645, 1215, and 795 cm^{-1} ; δ (CCl_4) 1.0–2.25 (m), 3.31 (s), 4.62 (t), and 5.2–6.0 (m); m/e 190 (M^+). The i.r. spectrum was different from that of cyclohexylanisole. The fourth component (20%) was unchanged 1,4-dihydro-compound (2; R = OMe). The mixture contained only traces (less than 1%) of phenylcyclohexane and 3-phenylcyclohexene as shown by g.l.c.

Selective Reduction of 3,4-Dihydro-2-methoxybiphenyl (3; R = OMe).—The mixture of reduction products obtained by Method B from 2-methoxybiphenyl using methanol as quencher [experiment (f), Table 2] (1.2 g) was reduced with lithium (0.0423 g) in ammonia (100 ml) and tetrahydrofuran (15 ml) containing *t*-butyl alcohol (5 ml) by Method B. The blue colour disappeared rapidly as the metal was added during 3 min. The usual work-up gave a product mixture containing the following five compounds [separated by preparative g.l.c. and compared (i.r.) with authentic specimens]: phenylcyclohexane (4; R = H) (25%); 3-phenylcyclohexene (5; R = H) (9%); 1,4-dihydrobiphenyl (2; R = H) (4%); 1,4-dihydro-2-methoxybiphenyl (2; R = OMe) (57%); and 3,4-dihydro-2-methoxybiphenyl (3; R = OMe) (5%). The composition of the starting mixture is shown in Table 2 and the product composition after further reduction, shown above, indicates that most of the conjugated diene ether (3; R = OMe) and the 1-phenylcyclohexene (6) and 3,4-dihydrobiphenyl (3; R = H) were selectively reduced to give increased amounts of phenylcyclohexane and 3-phenylcyclohexene.

The foregoing experiment was repeated with a mixture (120 mg) containing only the isomeric diene ethers (2; R = OMe) and (3; R = OMe) [derived from pure 1,4-dihydro-2-methoxybiphenyl (2; R = OMe) by quenching its monoanion with methanol; experiment (m), Table 3]. The product composition (analysed similarly) was: phenylcyclohexane (4; R = H) (14%); 3-phenylcyclohexene (5; R = H) (5.5%); 1,4-dihydro-2-methoxybiphenyl (2; R = OMe) (69%); 3,4-dihydro-2-methoxybiphenyl (3; R = OMe) (9.5%).

Reduction of 4-Methoxybiphenyl.—Method A. 4-Methoxybiphenyl (1.0 g) was reduced with lithium (0.0963 g) in tetrahydrofuran (45 ml) and ammonia (100 ml) by the general procedure. Ammonium chloride was used as the quenching agent. The product mixture was analysed

¹³ D. Ginsburg and R. Pappo, *J. Chem. Soc.*, 1951, 516.

and separated by g.l.c. (20% Carbowax, linear programme 150—210° in 2° steps). The chief components were 1,4-dihydrobiphenyl (46.5%) and biphenyl (18%), both characterised by comparison with authentic specimens; and the starting 4-methoxybiphenyl (30%).

Method B. 4-Methoxybiphenyl (1.0 g) was reduced by the general procedure with lithium (0.0958 g) in tetrahydrofuran (45 ml) and ammonia (100 ml). The products were analysed and separated on 20% Carbowax (linear programme 155—225° in 2° steps). The hydrocarbon products, phenylcyclohexane (4; R = H) (7.5%) t_R 103 s; 3-phenylcyclohexene (5; R = H) (2.5%) t_R 124 s; and 1,4-dihydrobiphenyl (2; R = H) (9.0%), t_R 184 s, were identified by comparing their i.r. spectra with those of authentic specimens. The presence of 1-phenylcyclohexene (6) (2.0%), t_R 234 s, and 3,4-dihydrobiphenyl (5; R = H) (0.5%), t_R 287 s, was indicated on the basis of retention times. The methoxy-derivatives were characterised on the basis of their spectral data: 4-methoxyphenylcyclohexane (13%), t_R 660 s; ν_{\max} 1610, 1580, 1510, 1250, and 828 cm^{-1} ; λ_{\max} (cyclohexane) 275.8 (ϵ 2385) and 277

nm (2300); δ 1.2—2.0 (10H, m, $[\text{CH}_2]_5$), 2.45br (1H, s, HCPH), 3.78 (3H, s, OCH_3), and 6.74—7.32 (4H, m, ArH); m/e 190 (M^+); m.p. 56—57° (lit.,¹⁴ 57—58°); 3-(4-methoxyphenyl)cyclohexene, t_R 776 s; ν_{\max} 1665, 1610, 1580, 1510, 1250, and 830 cm^{-1} ; λ_{\max} (cyclohexane) 278 (ϵ 1560) and 277.2 nm (1340); δ 1.2—2.0 (>4H, m, $\text{C}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}$), 2.0—2.24br (2H, m, $=\text{C}\cdot\text{CH}_2\cdot\text{C}$) 3.37br (1H, s, CHAr), 3.78 (3H, s, OCH_3), 5.6—6.0 (2H, m, $\text{CH}=\text{CH}$), and 6.7—7.3 (4H, m, ArH); m/e 188.119960 (M^+) ($\text{C}_{13}\text{H}_{16}\text{O}$ requires M , 188.12010); 3-(4-methoxyphenyl)cyclohexa-1,4-diene (16%) t_R 828 s; ν_{\max} (film) 1630—1640, 1610, 1580, 1250, 860, and 830 cm^{-1} ; λ_{\max} (cyclohexane) 276 (ϵ 2150) and 277 nm (1800); δ 2.6—2.84 (2H, unsym. d, $=\text{C}\cdot\text{CH}_2\cdot\text{C}$), 3.78 (s, OCH_3) overlapping on 3.6—4.04 (m, CHPh) (total 4H), 5.74 (4H, unsym. t, $[-\text{CH}=\text{CH}]_2$), and 6.7—7.3 (4H, m, ArH); m/e 186.104469 (M^+) ($\text{C}_{13}\text{H}_{10}\text{O}$ requires M , 186.104459); and unchanged starting material (45%).

[3/491 Received, 6th March, 1973]

¹⁴ V. Braun, *Annalen*, 1929, **472**, 56.