bp 88–90° (0.5 mm), which furnished a crystalline hydrochloride, mp 171–174°. The hydrochloride had rotations of $[\alpha]^{23}\text{D}$ +1.62° and $[\alpha]^{23}_{300}$ +10.8° (*c* 0.283, chloroform).[32] The infrared spectra of the free base and its hydrochloride were identical with those of authentic III and its hydrochloride.

Calculation of Asymmetric Induction.—The cyclohexenol sample, $[\alpha]\text{D}$ −5.88° (neat), used for the phenylurethan rearrangement is calculated to have $[\alpha]^{24}\text{D}$ −5.66° (*c* 5.54, chloroform), by comparing the rotation of its phenylurethan with that reported by Denney.[20] If no racemization occurred in the preparation and displacement of the allylic dichlorobenzoate, a sequence in which alcohol of $[\alpha]\text{D}$ −15.2° gave amine of $[\alpha]_{300}$ +10.8°, alcohol of $[\alpha]\text{D}$ −5.66° should have given amine of $[\alpha]_{300}$ +4.02° if asymmetric induction were quantitative. The experimental amine rotation of $[\alpha]_{300}$ +2.6° corresponds to 65% asymmetric induction.

Registry No.—(*S*)-(−)-Δ^2-Cyclohexenol, 6426-24-2; II, 15619-41-7; III, 15619-43-9; III hydrochloride, 15619-44-0; N,N′-diphenyl-N-(Δ^2-cyclohexenyl) urea, 15717-36-9; (*S*)-(−)-Δ^2-cyclohexenol dichlorobenzoate, 15717-37-0; VI, 6246-96-4; VII, 15645-60-0; VII *p*-nitrobenzoyl derivative, 15717-39-2; VIII, 15645-61-1; XI, 15645-62-2; 1,2-dianilinopropane, 15717-40-5; XII, 15645-63-3; XIII, 15645-64-4; XIV, 15717-41-6.

Phenylcyclohexadienes

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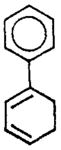
A detailed examination of the published methods for the reduction of biphenyl, *via* the alkali metal adducts, has shown that the phenylcyclohexadienes **3** and **4** may be formed depending on the conditions employed. The more reduced compounds, phenylcyclohexene and phenylcyclohexane, may also be produced. Dienes **1** and **2** can be prepared by the elimination of certain groups from the substituted 1-phenylcyclohexenes (**6**). Dienes **1–4** were isolated by glpc and the structures assigned on the basis of ultraviolet, mass, and nuclear magnetic resonance spectroscopic measurements.

During a study of the photochemistry of sodium tetraphenylborate[1] we isolated a compound the analytical data for which indicated that it was one of the phenylcyclohexadienes **1–5** and probably **2**.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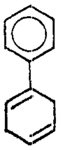
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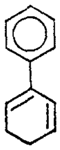
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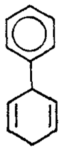
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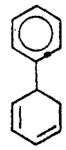
5

In the last 40 years, reports of compounds **1–4** have appeared but conclusive evidence for the structural assignments has been lacking. Although calculations predict **4** as the product resulting from the addition of alkali metals to biphenyl,[2] the Russian workers,[3] on the basis of spectral evidence, have reported **2** as the product. Their report was claimed as a correction of the earlier work of Schlenk and Bergmann[4] on the addition of lithium to biphenyl. These authors, on the basis of chemical evidence, assigned the structure **4** to the diene which they obtained. In 1939, Hückel and Bretschneider[5] studied the reaction between sodium and biphenyl in liquid ammonia at −70°. The adduct was decomposed with methanol and the diene **3** was claimed as the product on the basis of chemical evidence. In 1956, a further study was conducted[6] and, under conditions that the authors state are not appreciably different from those used previously, a diene was isolated to which the structure **4** was assigned. In this latter reaction the adduct was decomposed with ammonium chloride after a much shorter reaction time More recently, this preparation has been repeated by DeTar and Long[7] to provide an authentic sample of **4** to compare with the product obtained by the thermal decomposition of benzoyl peroxide in benzene. In an unrelated study,[8] isomer **1** has been reported to be formed by the dehydration of 3-phenyl-2-cyclohexen-1-ol over alumina at 350°. It was pointed out, however, that rearrangement under these conditions was possible.

Our unknown diene (A) had *m/e* 156, mp 89°, $\lambda_{\max}$ 249 mμ (ε 9300), which suggested a phenylcyclohexadiene type **2**. However, the Russian workers[3] claim **2** as a liquid with $\lambda_{\max}$ 250 mμ (ε 12,000). In addition the melting point and ultraviolet spectrum of the unknown compared favorably with the physical data reported for **1**—mp 85°, $\lambda_{\max}$ 248 mμ (ε 9000).[8] We have therefore repeated the earlier preparations of these dienes. In view of the contradictions mentioned earlier, we have isolated *all* the products from the diene syntheses by preparative glpc and examined each peak by mass and ultraviolet spectrometry. Peaks with *m/e* values of 156 were then examined by high-resolution mass spectrometry and elemental analyses were carried out on the more stable compounds. The homogeneity of each diene was tested on a second glpc column. Assignments were made on the basis of the spectroscopic data and in some cases deuterium tagging facilitated the interpretation. By avoiding chemical methods, we hoped to eliminate the possibilities of isomerization and oxidation to biphenyl.

For the reduction of biphenyl, the method of Egerov, *et al.*,[3] yielded phenylcyclohexane, a phenylcyclohexadiene (B), and 1-phenylcyclohexene; the method of Hückel and Bretschneider[5] yielded a similar mixture, together with another phenylcyclohexadiene (C), and the method of Hückel and Schwen[6] yielded the phenylcyclohexadiene (B). Biphenyl was recovered in each

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(1) J. L. R. Williams, J. C. Doty, P. J. Grisdale, T. H. Regan, and D. G. Borden, *Chem. Commun.*, 109 (1967); *J. Amer. Chem. Soc.*, **89**, 5153 (1967).

(2) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 425.

(3) Iv. P. Egorov, E. P. Kaplan, Z. I. Letina, V. A. Shliapochnikov, and A. D. Petrov, *J. Gen. Chem. USSR*, **28**, 3284 (1958).

(4) W. Schlenk and E. Bergmann, *Ann.*, **463**, 92 (1928).

(5) W. Hückel and H. Bretschneider, *ibid.*, **540**, 173 (1939).

(6) W. Hückel and R. Schwen, *Chem. Ber.*, **89**, 150 (1956).

(7) D. F. DeTar and R. A. J. Long, *J. Amer. Chem. Soc.*, **80**, 4742 (1958).

(8) G. F. Woods, N. C. Bolgiano, and D. E. Duggan, *ibid.*, **77**, 1800 (1955).

preparation. The ultraviolet spectrum of **4** is reported to be similar to that of toluene[7] and indeed the diene (B) isolated from the above reactions had such a spectrum (Table I).

TABLE I
ULTRAVIOLET SPECTRA OF THE PHENYLCYCLOHEXADIENES AND RELATED COMPOUNDS IN CYCLOHEXANE

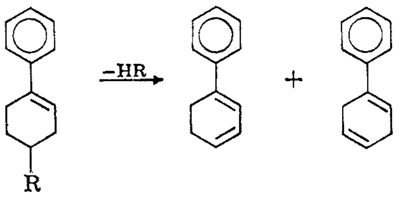
Compd		λ_{max}, mμ(ϵ)	Comments
1	1-Phenyl-1,3-cyclohexadiene	303 (13,800)	Broad band
2	1-Phenyl-1,4-cyclohexadiene	249 (9,300)	Broad band
3	2-Phenyl-1,3-cyclohexadiene	276 (8,140[a])	Broad band
4	3-Phenyl-1,4-cyclohexadiene	262 (465)	Peaks at 242, 249, 256, 269 mμ
7	1,3-Diphenyl-1,3-cyclohexadiene[b]	314 (11,250)[c]	Broad band

[a] This diene is very sensitive to air; this ϵ value may be low. [b] See ref 10. [c] This diene had mp 93–95° (lit.[10] mp 98–99°). Our sample had some *m*-terphenyl as impurity; this ϵ value is low.

The nmr spectrum of B showed protons in the ratios of 1 benzylic, 2 allylic, 4 olefinic, to 5 aromatic, so that the structure must be either **4** or **5**. Initially, we chose **5** since the sum of the two benzylic allylic coupling constants was 18 Hz, suggesting a vicinal relationship. However, the absence of absorption in the ultraviolet characteristic of a 1,3-diene contradicted this and a report in the literature suggested that coupling constants across five bonds in 1,4-cyclohexadienes may be unusually large.[9] Reduction of 4,4′-dideuteriobiphenyl by the Hückel–Bretschneider method[5] provided a sample of B-d_2. The nmr spectrum of this sample had only one allylic proton whose signal was now a skewed *doublet* of multiplets (peak separation 9 Hz). Compound B was therefore unequivocably assigned the structure **4**.

The nmr spectrum of C-d_2, isolated from the same reduction, showed three olefinic protons but only three allylic protons. This enabled us to assign the structure **3** to diene C.

Our failure to isolate a sample of **2** by the Russian method[3] prompted us to attempt to prepare a sample by elimination reactions on various substituted cyclohexene derivatives of type **6**.



6 **1** **2**

a, R = Cl
b, R = $OCOCH_3$
c, R = $OCOC_6H_5$
d, R = $OCSSCH_3$

We had anticipated that such a reaction would produce **1** as the major product and **2** as the minor product. This would be particularly convenient since **1** had been described as a solid, mp 85°.[8] We examined the elimination of hydrogen chloride from **6a**, when attempts to pyrolyze the esters **6b** and **6c** failed to yield dienes. Under rather drastic basic conditions this dehydrohalogenation reaction furnished a mixture of two dienes in poor yield. The fact that a similar mixture was obtained by the pyrolysis of the xanthate ester **6d** led us to assume that no unexpected rearrangements had taken place. The minor product had mp 89° after isolation by preparative glpc and was assigned the structure **2** on the basis of its ultraviolet spectrum, λ_{max} 250 mμ (*cf.* phenylcyclohexene, 250 mμ). It was identical in every respect with the unknown (A). The major product had mp 39° after preparative glpc and was assigned the structure **1** by a process of elimination and because it showed extended ultraviolet absorption (λ_{max} 303 mμ). The nmr spectra (Figure 1) support all these assignments and show the expected ratios of various protons. The methylene absorption of compound **2** falls in a multiplet centered at δ 2.90, at a significantly lower field than **1** or **3**, in keeping with the assignment of the methylenes as diallylic. The olefinic protons fall in two distinct groups: a 1 H multiplet at δ 5.98 and a 2 H multiplet at δ 5.72. The chemical-shift difference between the methylene protons of **1** and **3** on the one hand and **2** on the other is consistent with that found for 1,3-cyclohexadiene (δ 2.1) and 1,4-cyclohexadiene (δ 2.6). The chemical shifts of the methylene protons of **1** and **3** are also in agreement with the shift we have measured for the known compound, 1,3-diphenyl-1,3-cyclohexadiene[10] (δ 2.50). Attempts to repeat the work of Woods, Bolgiano, and Duggan[8] on the dehydration of 3-phenyl-2-cyclohexen-1-ol have failed and only biphenyl has been obtained. As judged by physical constants, the product which Woods and coworkers isolated corresponds to our structure **2**.

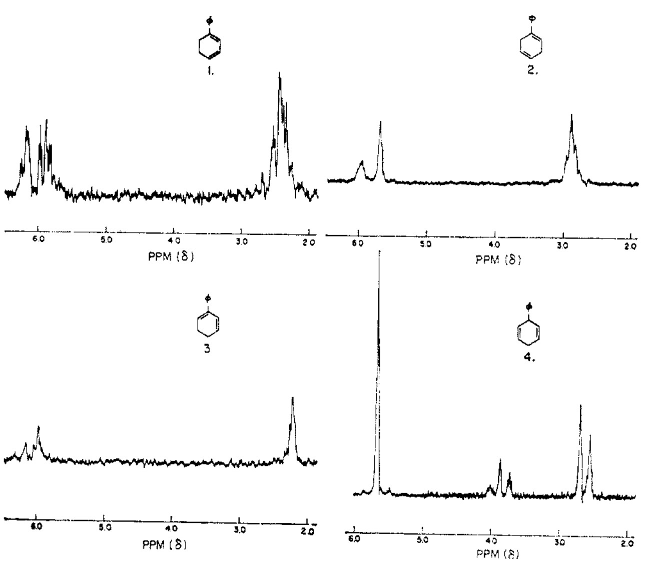


Figure 1.—Portions of the nmr spectra of compounds **1–4** in CCl_4.

The work reported here illustrates the fact that in most cases (the work of Hückel and Schwen[6] excepted) the alkali metal reduction of biphenyl leads to a complex mixture of products. This complexity has no doubt contributed to the incorrect assignments in the early work. The most characteristic physical properties of the dienes **1–4** are their ultraviolet spectra. These data are listed for reference in Table I.

The present assignments are in accord with the ultraviolet spectral data recorded for the open-chain analogs of **1** and **3**. 1-Phenylbutadiene absorbs at

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(9) L. J. Durham, J. Studebaker, and M. J. Perkins, *Chem. Commun.*, 456 (1965).

(10) G. F. Woods, and I. W. Tucker, *J. Amer. Chem. Soc.*, **70**, 2174 (1948).

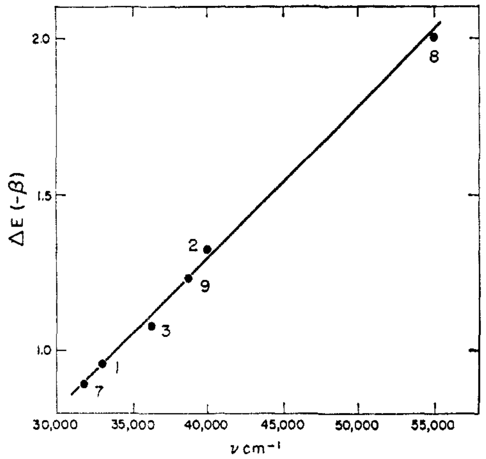

Figure 2.—Calculated transition energies (ΔE) *vs.* observed values (ν) for the compounds indicated.

longer wavelength (279 mμ) than does the 2 isomer (241 mμ).[11]

The transition energies calculated in terms of β by the HMO method[2] for the conjugated dienes correlate well with the experimental values. A plot of such a correlation is shown in Figure 2. 1,3-Diphenyl-1,3-cyclohexadiene (**7**) was prepared according to the method of Woods and Tucker.[10] Cyclohexene (**8**) and 1,3-cyclohexadiene (**9**) are included for reference. An excellent correlation is obtained, which may however be fortuitous, because of the assumptions inherent in the HMO method and our assumption that the interplanar angle between the phenyls and the diene ring can be ignored.

Owing to the limited availability of these dienes, we have made no attempt to study their chemistry, although their sensitivity to oxygen has been observed. The order toward oxidation in air is **3** > **1** > **4** > **2**. Diene **3** decomposes on exposure overnight to air at room temperature, whereas **2** is stable for prolonged periods at room temperature.

Experimental Section

The various spectra were determined on Cary Model 15 (uv), Perkin-Elmer Infracord (ir), and Varian A-60 (nmr) instruments. Tetramethylsilane was used as an internal standard for the nmr measurements. Mass spectra were determined with a 60° sector-type instrument. High-resolution mass spectra were determined with a CEC 21-110B instrument. Both mass spectrometric instruments were equipped with heated inlet systems.[12]

4-Chloro-1-phenylcyclohexene (6a).—4-Chlorocyclohexanone[13] (26 g, 0.2 mol) in dry ether (50 ml) was treated at room temperature, with stirring, with phenylmagnesium bromide solution (0.22 mol). When an oily precipitate appeared, dry benzene (50 ml) was added and the addition of the Grignard solution completed. The resulting solution was stirred for 30 min at room temperature, poured into crushed ice, and acidified with dilute hydrochloric acid. The organic layer was separated and the aqueous layer extracted with ether (100 ml). The combined extracts were dried and evaporated. The pale yellow oily residue showed a strong OH band in the infrared spectrum at 3300 cm^{-1}. This crude 1-phenylcyclohexanol was dehydrated by heating it under reflux in aqueous oxalic acid (200 ml, 15%) for 2 hr. Extraction of the crude product with chloroform and subsequent evaporation of the chloroform extract yielded a pale yellow liquid. It was fractionated through a 6-in. column packed with glass helices to yield the desired cyclohexene derivative (**6a**): 12.6 g (33%); bp 102–105° (0.2 mm); $n^{25}\text{D}$ 1.5765. The nmr spectrum shows $\delta^{\text{acetone-}d_6}$ 1.8–2.8 (doublet of multiplets, 6 H), 4.1–4.5 (multiplet 1 H), 5.85–6.1 (multiplet 1 H), 7.1–7.5 (multiplet 5 H).

Anal. Calcd for $C_{12}H_{13}Cl$: C, 74.8; H, 6.8; Cl, 18.4. Found: C, 74.7; H, 6.8; Cl, 18.5.

4-Benzoyloxy-1-phenylcyclohexene (6c).—4-Benzoyloxycyclohexanone[14] (150 g, 0.69 mol) was treated with phenylmagnesium bromide in exactly the same manner as that described for 4-chlorocyclohexanone, to yield the crude cyclohexanol derivative (190 g). This oily solid was dehydrated by heating it with 15% oxalic acid solution under reflux for 40 hr to yield the oily solid, crude cyclohexene derivative (**6c**). A 25-g portion of this material was triturated with petroleum ether (bp 66–75°) and the solid residue crystallized from ethanol–water to yield white needles of 4-benzoyloxy-1-phenylcyclohexene, 4.25 g (18%), mp 114–116°. The nmr spectrum showed δ^{CDCl_3} 1.8–2.8 (doublet of multiplets, 6 H), 5.1–5.6 (multiplet, 1 H), 5.8–6.2 (multiplet, 1 H), 7.1–7.6 (multiplet, 8 H), 7.9–8.2 (multiplet, 2 H).

Anal. Calcd for $C_{19}H_{18}O_2$: C, 82.0; H, 6.5. Found: C, 82.0; H, 6.5.

4-Phenyl-3-cyclohexen-1-ol.—Crude 4-benzoyloxy-1-phenylcyclohexene (100 g) in ethanol (300 ml) and water (150 ml) was treated with 40% sodium hydroxide solution (35 ml) and the solution heated under reflux for 1 hr. This solution was then evaporated to near-dryness and the residue extracted with chloroform. The chloroform extract was washed with water, dried, and evaporated to give a pale yellow solid, which was crystallized from petroleum ether (bp 65–75°) as colorless needles, 23 g (36% based on the benzoyloxycyclohexanone), mp 82–84°. The nmr spectrum showed δ^{CDCl_3} 1.5–2.8 (doublet of multiplets, plus a signal at δ 2.47, exchangeable H with D_2O, total 7 H), 2.7–4.2 (multiplet 1 H), 5.8–6.1 (multiplet, 1 H), 7.1–7.5 (multiplet, 5 H).

Anal. Calcd for $C_{12}H_{14}O$: C, 82.8; H, 8.0. Found: C, 82.9; H, 8.0.

The acetate (**6b**) had bp 105–110° (0.3 mm), $n^{25}\text{D}$ 1.5488.

Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.7; H, 7.4. Found: C, 77.4; H, 7.6.

S-Methylxanthate Ester of 4-Phenyl-3-cyclohexen-1-ol (6d).—4-Phenyl-3-cyclohexen-1-ol (5 g, 0.028 mol) in dry ether (100 ml) was converted into the lithium salt by the addition of phenyllithium (16 ml, 1.8 *M* solution). Dry carbon disulfide (3.5 g) was then added and after 1.5 hr the solution was treated with methyl iodide (10 g) and stirred overnight. The mixture was filtered. The filtrate was washed with water, dried, and evaporated at room temperature to yield the crude xanthate ester as a yellow oil, 5.0 g (76%). An analytical sample purified by chromatography with benzene–hexane on alumina was obtained as a yellow oil. The nmr spectrum showed δ^{CCl_4} 1.9–2.8 (triplet of multiplets, 9 H), 5.6–6.1 (doublet of multiplets, 2 H), 7.1–7.4 (multiplet, 5 H).

Anal. Calcd for $C_{14}H_{16}OS_2$: C, 63.6; H, 6.1; S, 24.2. Found: C, 63.9; H, 6.3; S, 24.0.

Chromatographic Analysis of the Phenylcyclohexadienes (1–4).—The two techniques which were employed for the analysis, separation, and isolation of the dienes (**1–4**) produced in the present experiments are described in the following section. Method A, an F & M Model 720 gas chromatograph, equipped with a $^1/_4$ in. × 8 ft long column, packed with 20% SE 30 on Anakrom ABS at 110°, was used. The detector and injector temperatures were 300°. A helium flow of 150 ml/min was used. Method B, an Aerograph Model A90-P gas chromatograph, equipped with a $^1/_4$ in. × 10 ft long column, packed with 25% Carbowax 20M on dimethyldichlorosilane-treated Chromosorb W, was used. The column was maintained at 200°. The helium flow was 60 ml/min. The detector and injector temperatures were 230°.

Under these conditions, the adjusted retention times given in Table II were obtained.

1-Phenyl-1,3-cyclohexadiene (1) and 1-Phenyl-1,4-cyclohexadiene (2). A. From Xanthate Ester (6d).—The crude xanthate ester **6d** was injected into the heated inlet of a gas chromatograph and the resulting pyrolysis products were analyzed under conditions of method A. The composition of the mixture

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[11] I. N. Nazarov, Yu. A. Titov, and A. I. Kuznetsova, *Izvest. Akad. Nauk SSSR*, 1270 (1959).

[12] The system is described by V. J. Caldecourt, *Anal. Chem.*, **27**, 1670 (1955), but was constructed of glass.

[13] R. Grewe, W. Lorenzen, and L. Vining, *Chem. Ber.*, **87**, 793 (1954).

[14] E. R. H. Jones and F. Sondheimer, *J. Chem. Soc.*, 615 (1949).

TABLE II

Compound	Retention time, min Method A	Retention time, min Method B
Phenylcyclohexane	16.0	8.5
3-Phenyl-1,4-cyclohexadiene (4)	16.0	11.4
1-Phenylcyclohexene	25.3	13.4
2-Phenyl-1,3-cyclohexadiene (3)	21.5	15.8
Biphenyl	21.0	20.1
1-Phenyl-1,3-cyclohexadiene (1)	25.3	18.1
1-Phenyl-1,4-cyclohexadiene (2)	28.4	20.1

was analyzed as 80 ± 2% 1-phenyl-1,3-cyclohexadiene (**1**) and 20 ± 2% 1-phenyl-1,4-cyclohexadiene (**2**). In some runs, only traces of biphenyl were formed; in others, as much as 20% was observed. The use of lower injection port and detector temperatures (230°) had no effect on this ratio. Compound **1** melted at 38–39°. Since **1** reacted rapidly with oxygen, routine elemental analyses of several samples gave consistently low C and H values. The high-resolution mass spectrum of a freshly isolated sample indicated a parent ion peak at *m/e* 156.0929 (duplicate measurements). $C_{12}H_{12}$ requires 156.0939. Diene **2** melted at 89–90°.

Anal. Calcd for $C_{12}H_{12}$: C, 92.3; H, 7.7. Found: C, 91.9; H, 8.0.

B. **From the Chloro Compound (6a).**—A mixture of 4-chloro-1-phenylcyclohexene (1.0 g) and potassium *t*-butoxide (1.0 g) in *t*-butyl alcohol (50 ml) was heated under reflux for 16 hr. The solution was then poured into cold water and the solid which was isolated by filtration and dried weighed 0.2 g and melted at 40–52°. Glpc analysis (method A) indicated a mixture of biphenyl (3%), 1-phenyl-1,3-cyclohexadiene (80%), and 1-phenyl-1,4-cyclohexadiene (17%).

Alkali Metal Reduction of Biphenyl. A. Sodium in Liquid Ammonia.—Biphenyl was reduced with sodium in liquid ammonia according to the method of Hückel and Bretschneider.[5] The crude product was chilled overnight to remove some unchanged biphenyl. The liquid portion of the chilled product was analyzed by glpc (method B). In addition to unreacted biphenyl, there was obtained phenylcyclohexane, 21%; 3-phenyl-1,4-cyclohexadiene, **4**, 52%; 1-phenylcyclohexene, 20%; and 2-phenyl-1,3-cyclohexadiene, **3**, 6%. In a second run, traces of a $C_{12}H_{16}$ isomer (mass spectrum *m/e* 160) were eluted after 8.1 min. Diene **3** was extremely sensitive to air, but a freshly isolated sample had a parent ion peak at *m/e* 156.0939 in its high-resolution mass spectrum. $C_{12}H_{12}$ requires *m/e* 156.0939. Diene **4** had $n^{25}D$ 1.5595.

Anal. Calcd for $C_{12}H_{12}$: C, 92.3; H, 7.7. Found: C, 92.6; H, 8.0.

B. **Sodium in Liquid Ammonia.**—Reduction of biphenyl according to the method of Hückel and Schwen[6] and treatment as just described yielded 3-phenyl-1,4-cyclohexadiene (**4**) in addition to recovered biphenyl. No other dienes or reduced products were observed.

C. **Lithium in Ether.**—Reduction of biphenyl with lithium in ether according to the method of Egorov, *et al.*,[3] and treatment as described yielded, in addition to unreacted biphenyl, phenylcyclohexane, 19%; 3-phenyl-1,4-cyclohexadiene, **4**, 72%; and 1-phenylcyclohexene, 9%. No diene **3** was detected.

Phenylcyclohexadienes 3-d_2 and 4-d_2.—4,4′-Dideuteriobiphenyl, prepared by treatment of the corresponding dilithio derivative[15] with D_2O, was reduced as under A to yield the dideuterio compounds corresponding to the hydrogen analogs described earlier.

Registry No.—**1**, 15619-32-6; **2**, 13703-52-1; **3**, 15619-34-8; **4**, 4794-05-2; **6a**, 15619-36-0; **6b**, 15619-37-1; **6c**, 15619-38-2; **6d**, 15619-39-3; **7**, 10345-94-5; 4-phenyl-3-cyclohexen-1-ol, 15619-51-9.

Acknowledgment.—The authors would like to thank Messrs. G. P. Happ and D. P. Maier for determining the mass spectra.

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[15] H. Gilman, W. Langham, and F. W. Moore, *J. Amer. Chem. Soc.*, **62**, 2327 (1940).

Preparation of Mixed Organotin Chlorides by the Redistribution Reaction[1a]

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Under appropriate reaction conditions, organotin dichlorides with two different alkyl or aryl groups can be prepared in good yields by redistribution between organotin trichlorides and tetraalkyltins or trialkyltin chlorides. Some of these organotin dichlorides have been converted into trialkyltin chlorides with three different alkyl groups by alkylation with tetraalkyltins. The following organotin dichlorides have been prepared: butylmethyl, isobutylmethyl, methylphenyl, ethylphenyl, propylphenyl, butylethyl, and butylpropyl. In addition, butylethylmethyl, butylmethylvinyl, butylethylvinyl, and butyldimethyltin chlorides have been prepared.

Organotin halides with two or more different alkyl or aryl groups are usually prepared by alkylation of an organotin halide with Grignard reagent, followed by cleavage of one of the alkyl groups with a halide,[2] *e.g.*, eq 1 and 2.

In many cases special care has to be taken in the cleavage step in order to avoid a mixture of organotin halides (*e.g.*, in eq 2 RR'_2SnX and $R_2R'SnX$). This proved to be extremely difficult, especially when R and R′ are very similar, for example ethyl and butyl. The preparation of organotin dihalides of the type $RR'SnX_2$ or monohalides of the type $RR'R''SnX$ is even more difficult. In order to prepare the latter, a series of alkylations and cleavage reactions has to be carried out.[2] The stepwise addition of different groups by Grignard reagents in most cases is impossible.[2]

$$R_2SnCl_2 \xrightarrow{2R'MgX} R_2R'_2Sn \qquad (1)$$

$$R_2R'_2Sn \xrightarrow{X_2} RR'_2SnX \qquad (2)$$
$$(X = Cl, Br, I)$$

A more convenient synthesis of these halides seemed to be desirable and would be a prerequisite in the investigation of asymmetric organotin compounds.

The most frequently applied method for the preparation of organotin halides is the redistribution reaction, first investigated by Kocheshkov.[3,4]

Recently it was observed that these reactions (eq 3–5)

$$3R_4Sn + SnX_4 \longrightarrow 4R_3SnX \qquad (3)$$

$$R_4Sn + SnX_4 \longrightarrow 2R_2SnX_2 \qquad (4)$$

$$R_4Sn + 3SnX_4 \longrightarrow 4RSnX_3 \qquad (5)$$

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[2] For a review, see R. K. Ingham, S. D. Rosenberg, and H. Gilman, *Chem. Rev.*, **60**, 459 (1960).

[3] K. A. Kocheshkov, *Ber.*, **62**, 996 (1929).

[4] K. A. Kocheshkov, *ibid.*, **66**, 1661 (1933).