Neither of the carbonyl-containing $C_3H_6O^{.+}$ ions, d or f, was observed as fragment ions in any of the compounds studied here. (By analogy to the formation of $CH_3CHO^{.+}$,[3] the formation of f from $HOC(CH_3)_2CH_2CH_2OH$ might be expected, but unfortunately this compound was not available to us.) Note, however, that at least five of the seven stable $C_3H_6O^{.+}$ isomers a–g should be common fragment ions, and the identification of their structures from CA spectra should thus be a valuable aid in elucidating the structures of complex molecules whose mass spectra contain an appreciable $C_3H_6O^{.+}$ peak.

Experimental Section

Measurements were made on a Hitachi RMU-7 double-focusing mass spectrometer in which the positions of ion source and electron multiplier were interchanged as described previously.[21] An ion accelerating potential of 3.9 kV, ionizing electrons of 100 μA and 70 eV (or lower where noted), and a sample reservoir and source temperature of 150° were used. Metastable ion spectra of the precursor ions selected by the magnetic field decomposing in the field-free drift region between the magnetic and electrostatic (ESA) analyzers are measured by scanning the ESA potential. The pressure in the field-free drift region between the magnet and ESA is then increased with helium until the precursor ion intensity is reduced to 35% of its original value, and the CA ion product abundances are determined in the same manner in a second ESA scan.[4] The data are the computer-averaged composites of at least 16 separate scans. The contributions from M1 products (corrected as described[4]) are subtracted from these values to obtain the CA spectrum.

Samples. Deuterated 3-chloro-1-propanol was prepared by exchange with D_2O in the spectrometer inlet system. All other compounds were obtained from commercial sources, checked for purity by mass spectrometry, and purified by gas chromatography where necessary.

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Carbanions. XVI. Reactions of 4-Chloro-1-p-biphenylylbutane with Alkali Metals. Formation of a Spiro Anion[1]

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Abstract: 4-Chloro-1-p-biphenylylbutane reacts with lithium in THF at −70° to give a mixture of 4-p-biphenylylbutyllithium and 8-phenylspiro[4.5]-6,8-decadienyllithium (7). With potassium, cesium, and Cs–K–Na alloy chiefly the spiro anion (7) and a little 1-p-biphenylylbutyl anion (6) are formed. Experiments with sodium and potassium, in which dioxane or tertiary alcohols were used as a proton source to "trap" intermediate anions, indicate that 4-p-biphenylylbutyl anion (5, M = K or Cs) is a precursor of 7. From labeling experiments no evidence was found for the spiro anion 7 reverting back to the open anion 5. The 4,4-diphenyl groups of 4-p-biphenylyl-4,4-diphenylbutyl anion facilitate both spiro cyclization and ring opening.

In a previous work,[2] it was shown that 4-chloro-1-p-biphenylyl-1,1-diphenylbutane reacts with potassium or cesium in tetrahydrofuran (THF) to give 4-p-biphenylyl-1,1-diphenylbutyl anion. Evidence was presented that this reaction proceeds according to Scheme I. Attempts, however, to detect the intermediate spiro anion 2 were unsuccessful

even from a reaction of Cs–K–Na with the chloride at −75° for some 2 min, whereupon only the rearranged anion 3 was present, according to the products of carbonation or protonation. Since the anion 3 is stabilized by the two phenyl groups on carbon-1 which serve to delocalize the negative charge, it was thought possible that if these phenyls were

Scheme I
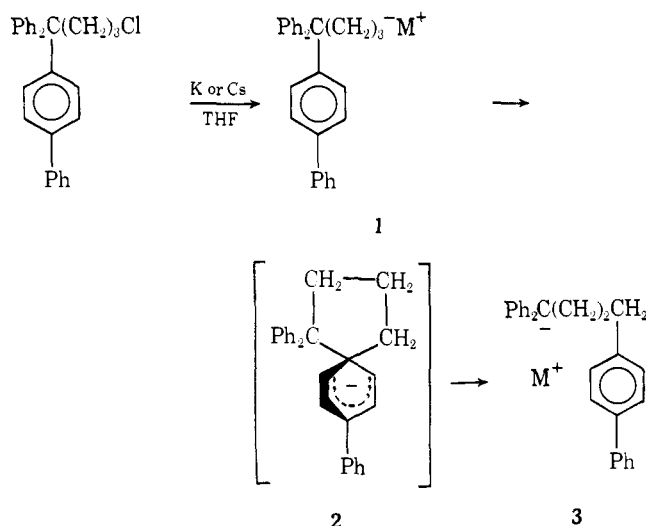
lacking in the spiro anion **2**, the resulting spiro anion might be stable. Accordingly a study of the reactions of 4-chloro-1-*p*-biphenylylbutane (**4**) with alkali metals was undertaken.

Results

4-Chloro-1-*p*-biphenylylbutane (**4h**) was allowed to react with alkali metals and the products of reaction were identified after protonation or carbonation to give the corresponding hydrocarbons or carboxylic acids as shown in Scheme II. From reaction of **4h** with lithium in THF at

Scheme II
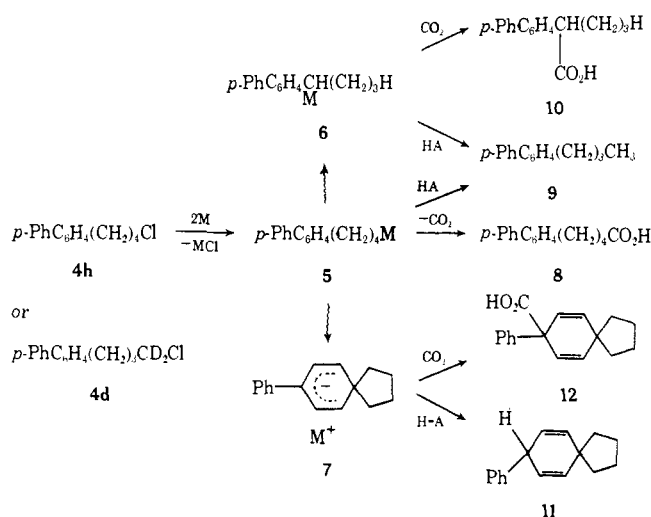
−70°, an organolithium reagent was obtained which upon carbonation gave a good yield of carboxylic acids which proved to be a mixture of 5-*p*-biphenylylpentanoic acid (**8**) and 8-phenylspiro[4.5]deca-6,9-diene-8-carboxylic acid (**12**) in a molar ratio of 63 to 37, respectively. Repetition of this run with 4-*p*-biphenylyl-1-chlorobutane-*1,1-d₂* (**4d**) gave a similar ratio of **8** to **12** with product **8** consisting entirely of 5-*p*-biphenylylpentanoic-*2,2-d₂* acid. This result indicates that the spiro anion **7** (Scheme II, $M^+ = Li^+$), which is doubtlessly the precursor of **12**, does not undergo ring opening to generate the organolithium compound **5** to any appreciable extent at −70°. In an effort to see if **5** will cyclize to **7**, the organolithium reagent prepared at −70° was held at −5° for 3 hr; however, because carbonation gave only a low yield of acid (essentially entirely **12**) and

much hydrocarbon and polymer, the result was indecisive. Since in other carbanion rearrangements organolithium reagents have been found to be much less reactive than potassium and cesium compounds,[2,3] we directed our attention to study of the latter.

Reaction of the chloride **4h** with finely divided potassium in THF at 65° for about 10 min before cooling and carbonation gave 22% yield of spiro acid **12**, 6% of 2-*p*-biphenylylpentanoic acid (**10**), and 9% of 1-*p*-biphenylylbutane (**9**) with the remainder primarily hydrocarbons and acids which were nonvolatile under conditions of gas chromatographic analysis. Repetition of this run with the labeled chloride **4d** but with decomposition by ice-water gave a 2:1 ratio of hydrocarbons **9** and 8-phenylspiro[4.5]deca-6,9-diene (**11**). Hydrocarbon **9** consisted of >99% of 1-*p*-biphenylylbutane-*4,4-d₂*; hence also under the present conditions no appreciable quantity of **9** is formed from the spiro anion **7**.

Reaction of the chloride **4h** with cesium in THF at 65° gave upon carbonation about the same low yield of spiro acid **12** and α metallation product **10** as with potassium; however, when the temperature of reaction was lowered to 35°, the yields of **12** and **10** rose to 59 and 10%, respectively. With Cs-K-Na alloy[4] in THF at −70°, the yield increased to at least 76% of **12** along with 4% of **10**. Attempts to characterize the spiro anion **7** by protonation rather than carbonation gave low yields (ca. 6%) of 8-phenylspiro-[4.5]deca-6,9-diene (**11**) under all the conditions tested; the chief material obtained from hydrolysis was nonvolatile under the conditions of GLC analysis and evidently resulted from ogliomerization processes involving the diene **11** or its conjugated isomer.
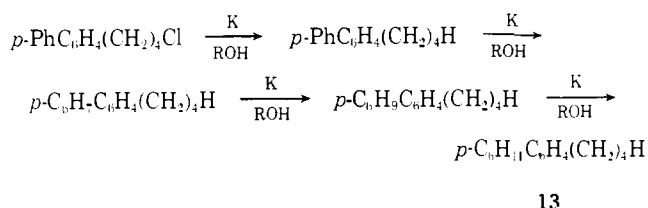
The spiro anion **7** from reaction of the chloride **4h** with Cs-K-Na alloy[5] at −70° was further characterized by its proton NMR spectrum at 40° in tetrahydrofuran-*d₈* as summarized in units of δ in **7a**. This carbanion has the
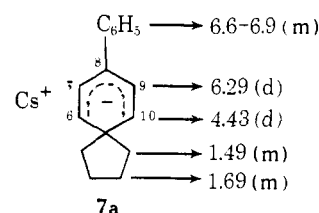
NMR spectrum expected for structure **7** by analogy with the spectrum[6] of 6,6-dimethylcyclohexadienyllithium in THF-hexane (δ 3.4 and 5.9 vs. δ 4.43 and 6.29, respectively, in **7a**) if it is considered that some of the negative charge of the spiro anion should reside on the phenyl substituent. The corresponding lithium compound was prepared[7] by reaction of *n*-butyllithium upon hydrocarbon **11** in THF-heptane and showed a similar spectrum except that the hydrogens of the cyclohexadienyl moiety absorbed at δ 4.24 and 6.48 rather than as shown in **7a**. This spectral difference might be attributed[8] to the lithium compound existing in large part as a loose (solvent separated) ion pair while the cesium compound likely exists more as a tight (contact) ion pair at 40°. In the tight ion pair the shielding of hydrogens at C-6 and C-10 appears to be decreased relative to that in the loose ion pair as has been observed previously;[8] however, the shielding at C-7 and C-9 appears to be proportionately increased such that the tight ion pair appears to have a somewhat more even distribution of charge than the loose ion pair.

In order to attempt to trap intermediates in the reaction of 4-chloro-1-*p*-biphenylylbutane (**4h**) with alkali metals, the reaction was run in the presence of various proton donors. Addition of a THF solution of **4h** containing excess *tert*-butyl alcohol to a large excess of potassium in THF at

reflux temperature gave a 90% yield of 1-(p-cyclohexyl-phenyl)butane (13) and 2% of 1-p-biphenylylbutane (9). Repetition of this experiment with 2 g-atoms of potassium per mol of 4h gave only 17% of 13 while the yield of 9 rose to 11% and 62% of the chloride remained unreacted. When the first experiment was repeated with 4d, the product 13 proved to be labeled predominantly as p-(C_6H_{11})-$C_6H_4CH_2CH_2CH_2CD_2H$ according to its NMR spectrum. Finally the reaction was repeated with 3 g-atoms of potassium per mole of 4h and with 3.4 mol of 3-ethyl-3-pentanol in place of excess tert-butyl alcohol; there resulted 27% of 13, 6% of spiro hydrocarbon 11, 9% of 1-p-biphenylylbutane (9), and about 25 and 9%, respectively, of dihydro and tetrahydro derivatives of 9. These results show that in the presence of excess potassium and proton donor, the reaction can be interrupted in high yield at a stage prior to appreciable cyclization. Furthermore, as the quantity of potassium and the activity of the protonating agent are decreased, a little spiro cyclization occurs but the products are predominantly 1-p-biphenylylbutane and its products of reduction. The main reduction sequence, therefore, appears to be

$$p\text{-PhC}_6\text{H}_4(\text{CH}_2)_4\text{Cl} \xrightarrow[\text{ROH}]{\text{K}} p\text{-PhC}_6\text{H}_4(\text{CH}_2)_4\text{H} \xrightarrow[\text{ROH}]{\text{K}}$$

$$p\text{-C}_6\text{H}_7\text{-C}_6\text{H}_4(\text{CH}_2)_4\text{H} \xrightarrow[\text{ROH}]{\text{K}} p\text{-C}_6\text{H}_9\text{C}_6\text{H}_4(\text{CH}_2)_4\text{H} \xrightarrow[\text{ROH}]{\text{K}}$$

$$p\text{-C}_6\text{H}_{11}\text{C}_6\text{H}_4(\text{CH}_2)_4\text{H}$$

13

This reaction constitutes another example of a general method[2] for the reduction of a 4-alkylbiphenyl to a 4-cyclohexyl-1-alkylbenzene.

Since dioxane has been found to protonate carbanions readily[2,9] but without the complications of appreciable direct reaction of dioxane with sodium or potassium or of Birch-like reductions of the p-biphenylyl group with these metals, reactions of 4-chloro-1-p-biphenylylbutane were studied in this solvent. The chief product with sodium after carbonation was 1-p-biphenylylbutane; this product from the labeled chloride 4d was >98% 1-p-biphenylylbutane-4,4-d_2 according to analysis by NMR and mass spectrometry. With potassium after carbonation the product was 18% of spiro hydrocarbon 11, 60% of 9, 1.7% of spiro acid 12, and 0.3% of 10; compound 9 from 4d was >89% 1-p-biphenylylbutane-4,4-d_2. In dioxane spiro cyclization obviously occurs more readily with potassium than with sodium.

Discussion

The experiments in which 4-chloro-1-p-biphenylylbutane was allowed to react with potassium in THF in the presence of tert-butyl alcohol or 3-ethyl-3-pentanol gave 1-p-biphenylylbutane (9) or products derived therefrom by further reduction. We believe that this result indicates that the chloride reacts with potassium to give the corresponding organopotassium compound 5 which is protonated by the alcohol to give 9 (see Scheme II). The alternative possibility that tert-butyl alcohol donates a hydrogen atom to an intermediate free radical derived from the chloride is most unlikely on the following basis. Alkyl radicals are very similar to hydrogen atoms in their rate of abstraction of hydrogen atoms from organic compounds and since hydrogen atoms abstract hydrogen from THF more than 150 times more readily than from tert-butyl alcohol,[10] the intermediate trapped by addition of tert-butyl alcohol in the present experiments must be the organopotassium compound 5 rather than the corresponding free radical. Since the rearrangement is blocked by tert-butyl alcohol and other proton donors, the forma-

tion of 5 precedes cyclization and likely cyclization takes place by way of 5.

While the organopotassium and -cesium compounds 5 cyclized rapidly under the conditions of the present experiments, the corresponding organolithium compound was comparatively stable at −70° as expected by analogy with other organolithium compounds which are capable of undergoing rearrangement.[2,3,11] Hence the fact that reaction of the chloride 4h with lithium metal at −70° gave a mixture of organolithium compound 5 along with the spiro anion 7 is taken to mean that 7 is formed not from 5 but from some precursor of 5. Similar observations have been made in related cases.[2,12]

An interesting observation in the present work is the slow rate of rearrangement (k_R) of 4-p-biphenylylbutylsodium (5) to 7 compared with the rate of protonation (k_H) of this organosodium compound by dioxane at 101°; the relative rate k_R/k_H is less than 0.02. In contrast for 4-p-biphenylylbutylpotassium under the same conditions the value of k_R/k_H is 0.33. While these relative rate ratios doubtlessly reflect the effect of the alkali metal cation on both the rate of protonation and the rate of spiro cyclization, we suggest that the larger effect is on the latter rate; large alkali metal cations evidently favor spiro-cyclic addition to aryl groups. Since such addition is postulated to be a key step in 1,4 rearrangement of the p-biphenylyl group (see Scheme I), it is agreeable to note that large cations have also been found to favor 1,4 rearrangement. In particular the ratio of the rate of 1,4 rearrangement of the p-biphenylyl group to the rate of protonation by solvent (k_R/k_H) for 4-p-biphenylyl-4,5-diphenylbutyl alkali compounds in dioxane at 101° is 0.08 for sodium and >80 for potassium.[2] While the trend in the ratios on going from sodium to potassium is similar for the two series, the ratios for a given alkali metal cation are larger for the 4-p-biphenylyl-4,4-diphenylbutyl alkali compounds than for the 4-p-biphenylylbutyl alkali compounds, e.g., >240-fold larger with K^+. This result implies that the additional two phenyl groups in 4-p-biphenylyl-4,4-diphenylbutyl as opposed to 4-p-biphenylbutyl alkali compounds accelerate the spiro cyclization reaction relative to protonation by the solvent. This acceleration can be understood in terms of delocalization of the negative charge in 2 (or the transition state leading to 2) by the phenyl groups as described by contributions from canonical structures such as 2a and 2b to the structure of 2. What the present work

2a   2b
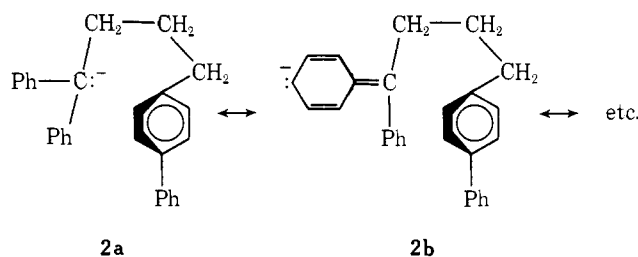
leaves unresolved is whether 2 is best described as an intermediate or a transition state from 1 to 3. In this regard it is of interest to note that while the conversion of 4-p-biphenylbutyl alkali compounds 5 to the spiro compound 7 is now well documented, no evidence was obtained for reversion of 7 back to 5. Evidently the two phenyl groups on C-1 of structure 2 greatly facilitate ring opening as well as ring closure.

In the present work some 5 to 10% of an anion 6, formed by an apparent 1,4 proton migration (see Scheme II), was observed during reactions of chloride 4h with potassium and cesium. While an intramolecular proton migration appears

to be an attractive route to **6**, the true mechanism of formation of **6** remains to be established.[13]

Fraenkel, Ho, Liang, and Yu[14] have recently described the synthesis of the spiro anion **14**. This stable spiro anion gave no evidence for ring opening to **15**; evidently the hetero nitrogen atom stabilizes **14** much as the phenyl substituent stabilizes **7**.

14

15
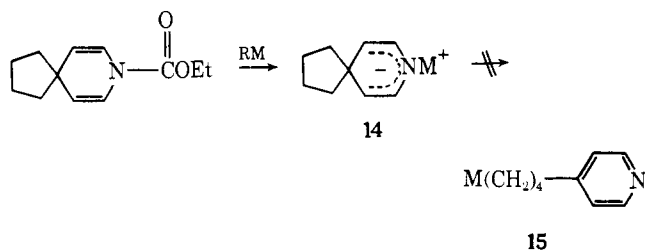
Since our work was begun[1] Julia and Malassiné[15] have reported a similar cyclization in the reactions of p-(4-halobutyl)benzoic acids with alkali metals in liquid ammonia. They found that the amount of spiro product decreased as halogen varied along the series Cl > Br > I and suggested the mechanism shown in Scheme III (Z = CO_2^-). This mechanism makes a subtle distinction between electronic isomers, the carbanion **e** (which alone is protonated to **f**) and the diradical anion **c** (which alone cyclizes to **d**). Our results can be made to accord with a modification of Scheme III (Z = Ph) if we postulate that for the 4-p-bi-

Scheme III
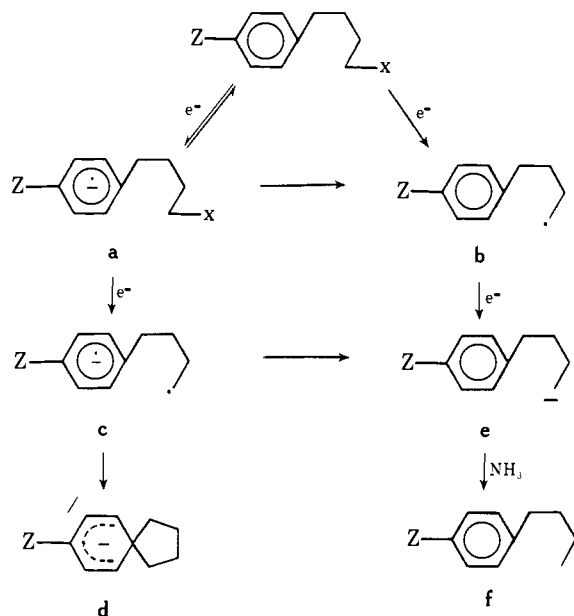
phenylylbutyl system the cyclization **c → d** occurs more slowly than the collapse of the diradical anion **c → e** (this might be true because in the biphenylyl system the charge on the radical anion is more highly delocalized than in the phenyl system; indeed lithium biphenylide in THF converts alkyl chlorides into alkyllithium compounds[2] in preference to alkylation of biphenyl). In liquid ammonia carbanions are very readily protonated (at a rate exceeding migration of phenyl in 2,2,2-triphenylethyl anion[16]) whereas in THF organoalkali compounds are much longer lived such that the cyclization **e → d** may now occur, especially where the para substituent is phenyl rather than carboxylate. Scheme III (Z = Ph) also contains the likely intermediate(s) which, unlike 4-p-biphenylylbutyllithium itself, cyclizes readily to give ultimately 8-phenylspiro[4.5]-6,8-decadienyllithium

(**7**) during reaction of lithium metal with 4-chloro-1-p-biphenylylbutane in THF; we would suggest that **b** and **e** (prior to firm bonding to lithium cation) are possibilities for such an intermediate.

Experimental Section[17]

1-p-Biphenylyl-1-butanone (mp 94–95°, lit.[18] 94°) was prepared by a procedure similar to that of Kaplan et al.[18] Reduction of 1-p-biphenylyl-1-butanone by a modified Wolff–Kishner process[19] in triethylene glycol gave 1-p-biphenylylbutane (**9**) (bp 140–141° (3 Torr), lit.[18] 140–141° (3 Torr)). 4-p-Biphenylylbutanoic acid (mp 116–118° from isooctane, lit.[20] 118°) was prepared from biphenyl in an overall yield of 43% by the procedure of Weizmann, Bergmann, and Bograchov.[20] Methyl 4-p-biphenylylbutanoate (bp 177° (0.2 Torr), lit.[21] bp 212–215° (3 Torr)) was prepared by esterification of the acid with methanol (H_2SO_4). 2-p-Biphenylylpentanenitrile (mp 82–83°, lit.[22] 83°) was prepared from p-biphenylylacetonitrile by a procedure similar to that of Cavallivi et al.;[22] hydrolysis of this nitrile gave 2-p-biphenylylpentanoic acid (**10**): mp 113–115° (lit.[22] 117°); NMR ($CDCl_3$) δ 0.94 (3 H, t, J = 6 Hz, CH_3), 1.36 (2 H, m, CH_2 at C-4), 1.96 (2 H, m, CH_2 at C-3), 3.63 (1 H, t, J = 7 Hz, CH at C-2), 7.3–7.7 (9 H, m, aromatic CH), 10.7 (1 H, broad s, CO_2H); mass spectrum m/e (rel intensity) 254 (65, M+), 211 (8), 209 (9), 167 (100). Alkali metals and solvents were of the grade and purity previously specified.[2]

4-p-Biphenylyl-1-butanol. A solution of 32.2 g (0.127 mol) of methyl 4-p-biphenylylbutanoate in 30 ml of tetrahydrofuran (THF) was added over a period of 45 min to a stirred suspension of excess (28 g, 0.74 mol) of lithium aluminum hydride in 300 ml of THF at reflux under an atmosphere of nitrogen. Stirring was continued at reflux for 5 hr. After careful decomposition with water and ice-cold hydrochloric acid, the reaction mixture was extracted with ether; the ether extract was washed with 5% $NaHCO_3$ solution and then water, dried over anhydrous $MgSO_4$, and filtered. After removal of solvent and recrystallization from CCl_4, there was obtained 28 g (98% yield) of colorless plates: mp 72.0–73.0°; NMR ($CDCl_3$) δ 1.5–1.8 (5 H, m, CH_2CH_2 and OH), 2.66 (2 H, t, J = 6.5 Hz, $ArCH_2$), 3.63 (2 H, t, J = 7 Hz, CH_2O), 7.1–7.7 (9 H, m, aromatic CH).

Anal. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 84.87; H, 8.07.

4-p-Biphenylyl-1-butanol-1,1-d₂. Addition of 34.0 g (0.127 mol) of methyl 4-p-biphenylyl-1-butanoate in 50 ml of THF over a period of 30 min to 6.3 g (0.15 mol) of lithium aluminum deuteride in 350 ml of THF stirred at reflux temperature gave, after stirring another 5 hr at reflux and the usual work-up, 29 g of product, mp 55–62°. One recrystallization from CCl_4 gave 23 g (80% yield) of plates: mp 72.0–73.0°; NMR ($CDCl_3$) δ 1.5–1.8 (4 H, m), 2.07 (1 H, s, OH), 2.63 (2 H, t, J = 6.5), 3.6 (no H detectable), 7.1–7.7 (9 H, m).

4-p-Biphenylyl-1-chlorobutane (4h). This compound was prepared from 4-p-biphenylyl-1-butanol with thionyl chloride in pyridine by the procedure previously reported[23] for 2-phenylethyl-1-14C chloride. The product after distillation in vacuo was obtained in 64% yield as colorless liquid: bp 175° (0.07 Torr); NMR ($CDCl_3$) δ 1.75 (4 H, m, CH_2CH_2), 2.63 (2 H, t, J = 7 Hz, $ArCH_2$), 3.48 (2 H, t, J = 7 Hz, CH_2Cl), 7.1–7.8 (9 H, m, aromatic CH).

Anal. Calcd for $C_{16}H_{17}Cl$: C, 78.51; H, 7.00; Cl, 14.49. Found: C, 78.49; H, 7.07; Cl, 14.37.

4-p-Biphenylyl-1-chlorobutane-1,1-d₂ (4d). This compound was prepared from 4-p-biphenylyl-1-butanol-1,1-d₂ by the procedure described above for the protium compound: NMR ($CDCl_3$) δ 1.70 (4 H, m), 2.57 (2 H, t, J = 7 Hz), 3.5 (no H detectable), 7.0–7.7 (9 H, m).

General Procedure for Alkali Metal Reactions. All reactions with alkali metals were run under a nitrogen atmosphere in a Morton high-speed stirring apparatus according to the procedure given previously.[2,4] For carbonation and protonation of organoalkali products the reaction mixtures were forced under nitrogen pressure through a glass–wool filter on the end of the siphon tube to remove as much unreacted alkali metal as possible. All reactions with cesium and Cs–K–Na alloy were run with the usual Morton apparatus enclosed in a glove box under an atmosphere of nitrogen to reduce fire hazards.

Reactions of 4-*p*-Biphenylyl-1-chlorobutane with Alkali Metals in Tetrahydrofuran. A. With Lithium. To 2.50 g (0.360 g-atom) of lithium wire cut into small pieces in 250 ml of tetrahydrofuran (THF) at $-10°$ were added 1.0 ml (0.016 mole) of methyl iodide and 5% of a solution of 4.85 g (0.0198 mol) of 4-*p*-biphenylyl-1-chlorobutane (**4h**). After 3 min of vigorous stirring a pink color appeared in the solution; after 7 min more of stirring the solution was cooled to $-70°$ and the remainder of the chloride was added dropwise over a period of 54 min. After 40 min more of stirring at $-70°$, the solution suddenly changed from a dark red to a dark green color (probably due to formation of a little radical anion) and was immediately forced onto crushed solid carbon dioxide (i.e., "carbonated"). The residual contents of the reaction flask were decomposed with methanol; analysis of the resultant neutral materials by gas–liquid partition chromatography[24] (GLC) at $200°$ indicated the presence of 68 area % of 1-*p*-biphenylylbutane (**9**) and 32% of 8-phenylspiro[4.5]deca-6,9-diene (**11**) at 0.65 times the retention time of **9**. The carbonated solution was allowed to stand overnight and then 100 ml of water was added. The THF was largely removed under partial vacuum, the aqueous residue was extracted with ether, and the ethereal solution was washed with water, dried over anhydrous $MgSO_4$, and filtered. Removal of ether gave 0.94 g of neutral product which contained only hydrocarbon **9**, according to GLC analysis of its volatile constituents. The aqueous phase after acidification and the usual isolation procedure by extraction with ether gave 3.14 g of crude acids which upon analysis as methyl esters by GLC[24] at $191°$ were found to contain 37 area % of **12** and 63% of **8** at 2.6 times the retention time of **12**. A 1.99-g portion of the crude acids was distilled (in a sublimation apparatus) at 50 μ and a bath temp of $168°$ to give 1.76 g of product, mp 100–105°. A 0.506-g portion of the distillate after two recrystallizations from CS_2 gave 0.21 g of **8** as platelets: mp 127–128°; uv$_{max}$ (95% EtOH) 253 nm (ϵ 16,100); NMR ($CDCl_3$) δ 1.70 (4 H, m, CH_2 at C-3 and C-4), 2.39 (2 H, t, $J = 6$ Hz, CH_2 at C-2), 2.68 (2 H, t, $J = 6$ Hz, CH_2 at C-5), 7.1–7.7 (9 H, m, aromatic CH), 10.93 (1 H, broad s, CO_2H); mass spectrum molecular ion at m/e 254.

Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.52; H, 7.12.

From the above evidence and its mode of synthesis, compound **8** is assigned the structure of 5-*p*-biphenylylpentanoic acid.

Removal of the solvent from the mother liquors which had yielded **8** gave a mixture of acids which was chromatographed on silica gel (70–325 mesh ASTM, E. Merck A.-G., Darmstadt, Germany, No. 7734) with elution by a 1:1 (by volume) mixture of *n*-hexane and benzene to give in early fractions 0.082 g of **8** and in later fractions 0.041 g of **12**. Compound **12** after recrystallization from *n*-heptane was obtained as colorless needles: mp 130–131°; uv$_{max}$ (95% EtOH) in nm (ϵ) 253 (241), 257 (248), 259 (293), 262 (283), 264 (242), 269 (210); NMR ($CDCl_3$) δ 1.5–1.9 (8 H, m, aliphatic CH), 5.93 (4 H, AB quartet, $\Delta\nu = \delta$ 0.10, $J = 11$ Hz, vinylic CH), 7.30 (5 H, broad s, aromatic CH), 11.4 (1 H, broad s, CO_2H); mass spectrum m/e (rel intensity) 254 (2, M⁺), 209 (82), 210 (37), 180 (20). 167 (100), 152 (14), 91 (12).

Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.03; H, 7.27.

From the above evidence and its mode of synthesis, compound **12** is assigned the structure of 8-phenylspiro[4.5]deca-6,9-diene-8-carboxylic acid.

The above reaction was repeated in detail but with reaction of 4-*p*-biphenylyl-1-chlorobutane-*1,1-d₂*(**4d**) (3.93 g, 0.0159 mol) and 1.55 g (0.223 g-atom) of lithium. After completion of the reaction at $-70°$, a small sample from the reaction mixture was decomposed with methanol and the remainder carbonated. Analysis of the products of methanolysis by GLC[24] indicated the presence of 25 area % of **11**, 65% of **9**, and 10% of an unknown at relative retention times of 0.65:1:1.48 respectively at $200°$. From the carbonation there was isolated 0.62 g of neutral product and 2.98 g of crude acids. Analysis of the acids as methyl esters by GLC gave 35 area % of **12** and 65% of **8** at 2.2 times the retention time of **12** at $230°$. A 1.16-g portion of the acid was recrystallized from CS_2 to give 0.32 g of purified acid: mp 127–128°; NMR ($CDCl_3$) δ 1.75 (4.1 H, m), 2.4 (no H in evidence), 2.72 (2.0 H, t, $J = 6$ Hz), 7.1–7.7 (8.9 H, m), 10.92 (1.0 H, broad s). From the spectral evidence this acid appears to be entirely 5-*p*-biphenylylpentanoic-*2,2-d₂* acid.

In another reaction of **4h** (2.53 g, 0.0104 mol) with lithium (1.45 g, 0.209 g-atom) run in the THF at $-70°$ as in the first run, as soon as the color of the reaction mixture changed to dark green, the solution was siphoned through a glass wool filter (to remove excess lithium metal) into a second flask under a nitrogen atmosphere. The solution was then allowed to stand at $-5 \pm 1°$ for 3 hr before carbonation of the red solution. The usual work-up gave 0.85 g of ether soluble neutral product, 0.05 g of acid, and 0.8 g of a white solid (mp ca. 110–140°) which was insoluble in ether or alkali and is therefore thought to be a polymeric hydrocarbon. According to analysis by GLC the acid was essentially pure compound **12** while the volatile neutral material contained 13 area % **11**, 66% 9, 3% **4h**, and 8 and 9% of two unknowns at 1.5 and 2.0 times the retention time of **9** at $200°$. Recrystallization of the acid from CS_2 gave **12**, mp 129–130°.

B. With Potassium. To 250 ml of THF was added 1.67 g (0.0427 g-atom) of potassium and the mixture was heated under reflux with vigorous stirring for 1 hr. To the finely divided potassium was added 4.99 g (0.0204 mol) of **4h** in 40 ml of THF over a period of 5 min. Vigorous stirring at reflux was continued for 5 more min and then the dark reddish brown solution was allowed to cool toward room temperature for 20 min before forcing it onto a large excess of solid carbon dioxide. The residue in the flask was decomposed with methanol. Analysis of the methanolysis product by GLC[24] at $200°$ indicated the presence of 28 area % of **11**, 55% of 9, and 17% of an unknown at 2.1 times the retention time of **9**. Solvent was removed from the carbonated mixture on a rotatory evaporator under vacuum, 200 ml of water was added (*Caution! Fire Hazard!*), and the solution was extracted with ether. The ethereal solution, after drying over anhydrous $MgSO_4$, yielded 1.36 g of oily neutral product; analysis of this product by GLC at $200°$ gave 74 area % of **9** and 26% of the unknown product of 2.1 times the retention time of **9**. This unknown is likely 4-*p*-biphenylyl-1-butene since its mass spectrum gave a molecular ion at m/e 208 as expected for $C_{16}H_{16}$. The aqueous phase after acidification with hydrochloric acid and extraction with ether yielded 2.70 g of crude acids. Analysis of the acids as methyl esters by GLC[24] revealed the presence of 76 area % of **12** and 24% of **10** at 1.5 times the retention time of **12** at $170°$. The identity of **10** as 2-*p*-biphenylylpentanoic acid was confirmed by comparison of its GLC retention time and mass spectrum with that of the authentic sample of this acid. A sample (1.0 g) of the crude acid was distilled in vacuo at a bath temperature of $150°$ at 0.6 Torr to give 0.62 g of a colorless viscous oil, which after one recrystallization from CCl_4 gave 0.32 g of crystals, mp 115–120°. One recrystallization of 0.10 g of this acid from *n*-pentane gave 0.07 g of crystals of mp 130–131° as expected for 8-phenylspiro[4.5]deca-6,9-diene-8-carboxylic acid. This acid was further characterized by its NMR and mass spectrum.

The first run was repeated with a THF solution of 3.19 g (0.0130 mol) of **4h** added to 1.12 g (0.0287 g-atom) of potassium over a period of 2 min before forcing it onto a large excess with stirring at reflux 3 min before cooling and carbonating. The usual work-up gave 1.09 g of neutral product and 1.76 g of crude acids. Quantitative GLC analysis[24] of the neutral material showed the presence of 0.25 g (9.0% yield) of **9**, 0.005 g (0.2% yield) of **11**, and 0.038 g of olefin; similar analysis of the acids as methyl esters gave 0.73 g (22% yield) of **12** and 0.18 g (5.5% yield) of **10**. Thus a considerable portion of both the acidic and neutral products were nonvolatile.

The first run was repeated in detail with 1.43 g (0.0366 g-atom) of potassium and 4.49 g (0.0183 mol) of **4d** except that, after the reaction mixture had been allowed to cool, the contents of the reaction flask were forced onto 250 ml of ice and water (the usual Morton apparatus was enclosed in a glove box under an atmosphere of nitrogen to prevent the hazard of fire during the hydrolysis). The usual isolation procedure gave 3.55 g of product which according to analysis by GLC contained 32 area % of **11**, 64% of 9, and 4% of olefin. The crude product was separated by chromatography on neutral alumina with cyclohexane as eluent; the first fraction contained 0.21 g of **11**, the second a mixture of **11** and 9, and the third 0.97 g of pure **9**. The isotopic distribution in **9** was determined from its mass spectrum which at m/e of 210–214 for the molecular ion corresponded to 97% d_2, 2% d_1, and 1.0% d_0 ($\pm$1%) components and at m/e 167–169 showed less than 1% d_2 component in the $C_{13}H_{11}^+$ ion fragment; accordingly the **9** isolated here was substantially pure 1-*p*-biphenylylbutane-*4,4-d₂* as was also demonstrated by its NMR spectrum ($CDCl_3$): δ 0.93 (0.9 H, t, $J = 5$ Hz,

CD$_2$H), 1.1–1.9 (4.0 H, m, CH$_2$CH$_2$), 2.57 (2.1 H, t, J = 7 Hz, ArCH$_2$), 7.0–7.6 (9 H, m, aromatic CH).

C. With Cesium. In a run at 65°, 3.34 g (0.0204 g-atom) of cesium was stirred vigorously in 250 ml of THF for 1 hr at reflux; then to this mixture was added dropwise a solution of 2.88 g (0.0118 mol) of **4h** in 25 ml of THF over a period of 3 min with stirring continued for 2 min more before cooling over a period of 10 min and then carbonation. The usual work-up following addition of methanol to decompose any unreacted cesium gave 0.86 g of neutral material which according to quantitative GLC analysis[24] contained 1.25 mg (0.059%, based on cesium) of **11**, 45 mg (2.1%) of **9**, and nonvolatile material. The yield of crude acids was 1.90 g, which according to quantitative GLC analysis contained 0.70 g (27%) of **12** and 0.124 g (4.8%) of **10**.

In a repetition of the first run, after stirring the THF at reflux with cesium (3.05 g, 0.029 g-atom) for 1 hr, the mixture was cooled to 35° before addition of 2.56 g (0.0105 mol) of **4h** in 25 ml of THF dropwise over a pe;riod of 3 min with stirring continued for 3 min more and cooling for 5 min before carbonation. The usual work-up gave 0.50 g of neutral product which, by quantitative GLC, contained 1.9 mg (0.09% yield based on **4h**) of **11**, 70 mg (3.2%) of **9**, and some 9 mg of an unknown, likely 4-p-biphenylyl-1-butene, of 2.1 times the retention time of **9** at 200°. The crude carboxylic acid amounted to 1.89 g and contained, according to quantitative GLC, 0.278 g (10.4%) of **10** and 1.58 g (59%) of **12**.

The previous runs at 35° were repeated with 5.85 g (0.0441 g-atom) of cesium and 5.33 g (0.0218 mol) of **4h**; after completion of the addition of the chloride and stirring for 3 more minutes, the dark green solution was cooled to −70° and 50 ml of methanol was added dropwise. The usual work-up gave 4.4 g of neutral product which according to quantitative GLC analysis[24] contained 0.25 g (5.4%) of **11**, 0.35 g (7.7%) of **9**, and no appreciable quantity of other products volatile under GLC conditions.

D. With Cs–K–Na Alloy. A mixture of 5.03 g (0.0378 g-atom) of cesium, 1.80 g (0.0460 g-atom) of potassium, 0.260 g (0.0113 g-atom) of sodium, and 250 ml of THF was stirred vigorously at reflux temperature for 1 hr. The solution was cooled to −70° with vigorous stirring continued while 1.033 g (0.00422 mol) of **4h** in 25 ml of THF was added dropwise over a period of 2 min. Stirring of the red solution was continued for 2 min more whereupon the solution turned green and was immediately carbonated. The usual work-up gave 0.023 g of neutral material and 1.02 g of crude acids. Analysis[24] of the neutral product by GLC indicated the presence of 94 area % of **9**, 4% of **11**, and 2% of an unknown; similar analysis of the acids as methyl esters gave 97 area % of **12** and 3% of **10**. The crude acid (0.83 g) was purified by chromatography on silica gel with elution by 95% (by vol) cyclohexane and 5% ether; the first component eluted, after recrystallization from a mixture of cyclohexane and heptane, consisted of 0.44 g of white needles of mp 130–131°. The spectral properties of the crystalline product were identical with those of other samples of **12**.

A second run was conducted just like the first with 4.62 g (0.0347 g-atom) of cesium, 1.80 g (0.0461 g-atom) of potassium, 0.200 g (0.0087 g-atom) of sodium, and 2.36 g (0.00964 mol) of **4h**. Carbonation and the usual work-up gave 0.28 g of neutral product which according to quantitative GLC contained 6.7 mg (0.33%) of **11**, 50 mg (2.5%) of **9**, and no appreciable additional volatile products under GLC conditions; in addition 2.02 g of acid was obtained which, according to quantitative GLC analysis of the methyl esters, consisted of 1.86 g (76%) of **12** and 0.109 g (4.5%) of **10**.

In a third run, conducted like the first run except as indicated, 5.43 g (0.0408 g-atom) of cesium, 1.94 g (0.0497 g-atom) of potassium, 0.281 g (0.0122 g-atom) of sodium, and 5.25 g (0.0214 mol) of **4h** were allowed to react at −70°. Three minutes following completion of the addition of **4h** to the alloy, the reaction mixture was forced into 200 ml of methanol chilled to −70°. The usual work-up gave 4.4 g of neutral product which according to analysis[24] by GLC contained 41 area % of **11**, 52% of **9**, and small quantities of two unknowns at 0.50 and 0.81 times the retention of **9** at 191°. The neutral product upon chromatography on neutral alumina with cyclohexane as eluent gave in a first fraction 0.20 g of **11** and in a subsequent fraction 0.21 g of **9**. Compound **11** had the following properties: NMR (CDCl$_3$) δ 1.5–1.8 (8 H, m, aliphatic CH), 3.92 (1 H, t, J = 1.5 Hz), 5.67 (4 H, ca. d, J = 1.5 Hz, vinyl-

ic CH), 7.25 (5 H, broad s, aromatic CH); mass spectrum m/e (rel intensity) 210 (63, M$^+$), 168 (44), 167 (100), 155 (38), 91 (37).

Anal. Calcd for C$_{16}$H$_{18}$: C, 91.37; H, 8.63. Found: C, 91.25; H, 8.69.

From its recorded properties and mode of synthesis compound **11** is assigned the structure of 8-phenylspiro[4.5]deca-6,9-diene.

Various attempts were made to improve the yield of **11** from protonation of the THF solution of the organoalkali compounds. Thus the previous reaction was repeated and an aliquot was protonated with methanol at −70°. The remainder was warmed to −35° and then 20 g of mercury was added over a period of 10 min with stirring; the dark green solution returned to a dark red color (because of destruction of radical anions of biphenyl nuclei). An aliquot of the solution at −35° was protonated by addition to excess ice-water and another aliquot by addition to excess methanol at room temperature. The remainder of the solution was cooled to −70°, an aliquot was decomposed by addition to methanol at −70°, and the remainder was carbonated. Analysis of the four protonated aliquots by quantitative GLC indicated that the absolute yield of hydrocarbon **11** was uniformly low (6 ± 1%) although the yield of carboxylic acid from the final carbonation was high, indicative of a yield of at least 65% of the spiro anion **7**.

E. With Potassium in the Presence of Proton Donors. A mixture of 4.23 g (0.108 g-atom) of potassium in 250 ml of THF was stirred at reflux for 1 hr. Stirring was stopped while a solution of 52.7 g (0.71 mol) of *tert*-butyl alcohol, 0.957 g (0.00391 mol) of **4h**, and 25 ml of THF was added at one time. Stirring was soon started again and continued for 5 min at reflux. The solution was allowed to cool for 10 min and then carbonated. The carbonated solution was concentrated on a rotatory evaporator to 30 ml, water was added, and the solution was extracted with ether. The ethereal extract gave 0.9 g of crude neutral product which by quantitative GLC analysis[24] contained some 2% of **9** and 90% of a compound of 0.58 times the retention time of **9** at 189°. The crude product was purified by chromatography on neutral alumina with cyclohexane as eluent; the first fraction contained 0.75 g of colorless oil: bp 100–110° (0.9 Torr) (lit.[25] 111.8° (1.5 Torr)); NMR (CDCl$_3$) δ 0.83 (3.0 H, t, J = 7 Hz, CH$_3$), 1.0–2.0 (13.9 H, m, aliphatic CH), 2.53 (3.0 H, m or ca. t, J = 7 Hz, benzylic CH), 7.05 (4 H, m, aromatic CH); mass spectrum m/e (rel intensity) 216 (100, M$^+$), 173 (71), 117 (61), 104 (40), 91 (60). On the basis of the data listed and its mode of synthesis, this compound is assigned the structure of 1-(p-cyclohexylphenyl)butane (**13**).

The first run was repeated but with addition of 1.24 g (0.0051 mol) of **4h** and 4.10 g (0.056 mol) of *tert*-butyl alcohol in 25 ml of THF to 0.444 g (0.0114 g-atom) of potassium in 250 ml of THF at reflux. Quantitative analysis of the product by GLC indicated the presence of 17 mol % of **13**, 11% of **9**, and 62% of unreacted **4h**.

The first run was repeated but with addition of 1.04 g (0.0042 mol) of **4d** and 52.8 g (0.71 mol) of *tert*-butyl alcohol to 4.25 g (0.109 g-atom) of potassium in 250 ml of THF at reflux. Distillation of the crude product in vacuo gave 0.82 g (90% yield) of colorless liquid, bp 110–115° (1.5 mm), which upon analysis by GLC showed only one peak at the retention time of 1-(p-cyclohexylphenyl)butane: NMR (neat) δ 0.91 (1.0 H), 1.0–2.0 (14 H), 2.54 (3.0 H), 7.03 (4.0 H). On the basis of the NMR spectrum, the product was 1-(p-byclohexylphenyl)butane-4,4-d_2. A repetition of this run with **4d** but with 14.9 g (0.201 mol) of *tert*-butyl alcohol gave a product of the same structure and isotopic composition according to analysis by GLC and NMR.

The first run was repeated with addition of 2.13 g (0.00870 mol) of **4h** and 3.54 g (0.0305 mol) of 3-ethyl-3-pentanol in 25 ml of THF to 1.06 g (0.0271 mol) of potassium in 250 ml of THF at reflux. Analysis of the product by GLC and mass spectrometry gave the following products listed as absolute percent yield, relative retention time at 166°, m/e of molecular ion, identity: 27, 0.60, 216, **13**; 6, 0.66, 210, **11**; 9, 0.77, 214, likely 4'-n-butyl-1,2,3,4-tetrahydrobiphenyl; 9, 1.00, 210, **9**; 25, 1.10, 212, likely, 4'-n-butyl-1,4-dihydrobiphenyl; and 9% unreacted **4h**.

Reaction of 4-p-Biphenylyl-1-chlorobutane with Alkali Metals in Dioxane. A. With Sodium. Purified dioxane (250 ml) was stirred at reflux in a Morton apparatus with potassium and then distilled into a second Morton flask immediately before use. To the dioxane was added 0.48 g (0.021 g-atom) of sodium and the mixture was stirred for one hour at reflux before a solution of 2.23 g (0.0091 mol) of **4h** in 25 ml of dioxane was added dropwise over a period of

5 min to the vigorously stirred, finely divided, molten sodium. The mixture was then stirred at reflux for 25 min and cooled to room temperature for 10 min before a 10-ml aliquot was decomposed with methanol and the remainder carbonated. The usual work-up of the carbonation mixture gave 1.69 g of neutral material and a negligible quantity of acids. Analysis of the product by GLC at 200° and mass spectrometry gave the following products listed as area percent yield (unless otherwise specified), relative retention time, m/e of molecular ion, identity: 1, 0.20, 168, likely p-methyl-biphenyl; 1, 0.43, 182, likely p-ethylbiphenyl; 1, 0.61, 206, unknown; 62% absolute yield, 1.00, 210, **9**; and 18% of unreacted **4h**. The product from methanolysis was indistinguishable from that of carbonation.

The first run was repeated with 0.34 g (0.0148 g-atom) of sodium and 1.45 g (0.0059 mol) of **4d**. There were isolated no carboxylic acids and 1.17 g of neutral product. The latter according to quantitative GLC analysis contained 58% of **9** and 26% of starting **4d**. The neutral product upon column chromatography on alumina with cyclohexane as eluent gave a first fraction of 0.53 g of **9**: NMR (CDCl₃) δ 0.92 (1.0 H, t, $J = 5$ Hz, CD₂H), 1.1–1.9 (4.0 H, m), 2.57 (2.1 H, t, $J = 7$ Hz, ArCH₂), 7.0–7.6 (9.0 H, m); mass spectrum m/e (rel intensity) 214 (1.6), 213 (17), 212 (88), 211 (1.2), 210 (0.2), 169 (1.8), 168 (17.1), 167 (100), 166 (4.6). These data show that **9** is essentially pure (>98%) 1-p-biphenylylbutane-4,4-d_2.

B. With Potassium. Purified dioxane (250 ml) was stirred vigorously at reflux for 1 hr with 0.309 g (0.0077 g-atom) of potassium. A solution of 0.824 g (0.00334 mol) of **4d** in 25 ml of dioxane was added dropwise over a period of 10 min. The light orange solution was stirred for another 20 min at reflux, cooled to room temperature for 15 min, and then carbonated. The usual work-up gave 0.73 g of neutral material and only a trace of acids. Quantitative analysis by GLC revealed the presence of 0.13 g (18% yield) of **11**, 0.43 g (60%) of **9**, and some 0.09 g of an unknown of 1.7 times the retention times of **9**. A sample of **9** was separated by GLC and subjected to mass spectral analysis; the analysis confirmed the identity of **9** but showed that it was accompanied by likely a dihydro derivative (m/e 214). Since this impurity complicates interpretation of the cleavage fragment at m/e 167–169, it may be concluded only that **9** is >89% 1-p-biphenylylbutane-4,4-d_2. In a similar run with **4h** an 88% yield of neutral hydrocarbon and an 8% yield of crude acids were obtained; the hydrocarbons were similar to those obtained from **4d** while the acids by quantitative GLC contained 1.7% (based on starting chloride) of **12** and 0.3% of **10**.

NMR Spectrum of Spiro Anion 7. A. From 11 with Butyllithium. A 5-ml reaction vial containing a magnetic stirring bar and 1 ml of tetrahydrofuran-d_8 (from Novell Chemical Co., Inc.) was flushed with nitrogen and sealed with a rubber septum before addition by means of a hypodermic syringe of 0.5 ml of 12% n-butyllithium in heptane. The solution was stirred for 5 min at room temp and then 0.025 ml of 8-phenylspiro[4.5]deca-6,9-diene was added via syringe. The solution immediately developed a red color. After the solution had been stirred for 5 min more, a 0.5-ml portion was transferred via syringe to a nitrogen-filled NMR tube which was then tightly sealed. The NMR spectrum, measured at 40° relative to the nearest weak THF peak which was taken as δ 3.75 relative to TMS, consisted of signals at δ 4.24 (2 H, d, $J = 9$ Hz), 6.48 (2 H, d, $J = 9$ Hz), 6.7–6.9 (5 H, m, aromatic CH); the signals due to aliphatic protons were obscured by components of the solvent.

B. From 4h with Cs–K–Na Alloy. A 3-ml reaction vial containing a glass-enclosed (NOT *Teflon!*) magnetic stirring bar and 1 ml of THF-d_8 was flushed with nitrogen and sealed with a rubber septum. Some 0.3 ml of Cs–K–Na alloy (of the composition described earlier) was added and the reaction mixture was stirred for 2 hr at room temperature. The mixture was cooled to −70° and 0.025 ml of **4h** was added via a syringe. The solution turned red and after 5 min of stirring it turned a dark green color. To this solution was

added via syringe some 0.3 ml of mercury. The solution was stirred for 3 min while cold and then was allowed to warm to room temperature with stirring. The final red solution was transferred with a syringe to a nitrogen-filled NMR tube which was then tightly sealed. The NMR spectrum, measured at 40° relative to solvent peak as previously described, consisted of signals at δ 1.49 (4 H, m, aliphatic CH), 1.69 (4 H, m, aliphatic CH), 4.43 (2 H, d, $J = 9.5$ Hz), 6.26 (2 H, d, $J = 9.5$ Hz), 6.6–6.9 (5 H, m).

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