latter pK value was calculated from the observed rates of reactions of p-chlorobenzenediazonium ion in triethylamine and DABCO buffers. The value obtained in this experiment was in agreement with a similar experiment using p-methoxybenzenediazonium ion as reactant.

In the cases for which no data are reported in Table I, either the strong absorbance of solvent prevented us from following the reactions at the wavelengths of maximum absorption of reactants or products, or, in the case of p-nitrobenzenediazonium ion, there were complications which may be due to buffer reaction.

Carbanions. XII. *p*-Biphenylyl Migration in Reactions of 1-Chloro-2-*p*-biphenylylethane-*1,1*-d_2 with Alkali Metals[1]

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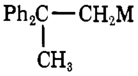
Contribution from the School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332. *Received December 12, 1971*

Abstract: The question of whether or not simple 2-arylethyl anions will undergo 1,2 migration of aryl is explored for the p-biphenylylethyl system. Reaction of 1-chloro-2-p-biphenylylethane-*1,1*-d_2 with excess lithium metal in tetrahydrofuran (THF) solution at −70° gave a good yield of 2-p-biphenylylethyllithium-*1,1*-d_2. On warming to 0° this organolithium reagent failed to undergo appreciable rearrangement as judged by the position of the deuterium label in the products of carbonation and protonation even though the conditions were so severe that most of the reagent had decomposed. In contrast, reaction of the same chloride with cesium or potassium metal in THF at reflux temperature gave an essentially 50/50 mixture of 1-p-biphenylylethane-*2,2*-d_2 and 1-p-biphenylylethane-*1,1*-d_2; in reaction of the chloride at −65° with Cs–K–Na alloy, scrambling of the label in the p-biphenylylethane was only partial. Repetition of the reaction with potassium in presence of a small amount of *tert*-butyl alcohol resulted in a greatly reduced amount of rearrangement in the product p-biphenylylethane. It is concluded that p-biphenylylethylcesium and potassium rearrange readily provided that protonation by solvent or solvent component does not intervene. The present work provides no evidence for participation of neighboring biphenylyl radical anions (or dianions) in a concerted reductive–rearrangement step.

While a 1,2 shift of a vinyl group in simple organometallic compounds is known, *e.g.*, rearrangement of allylcarbinylmagnesium halide,[2] corresponding 1,2 shifts of a phenyl or aryl group are known to occur only from a quaternary carbon having attached to it one or more additional phenyl or vinyl groups, *e.g.*, in 2,2,2-triphenylethyl,[3] 2,2-diphenylpropyl,[4] and 6-methyl-6-phenylcyclohexadienyl[5] alkali metal compounds, **1**, **2**, and **3**, respectively. The effects of the additional unsaturation in these substances are manifold. The extra unsaturation stabilizes the product of rearrangement and ensures that the product is more stable than (or as stable as) the reactant. It also accelerates the reaction by providing additional delocalization of electrons in the bridged transition state for rearrangement, as has been confirmed by molecular orbital calculations.[4] The unsaturated group along with the other groups present at the quaternary carbon of **1–3** probably produces some steric compression in these reactants which is likely reduced in the transition state for rearrangement (steric acceleration).[6] Finally the unsaturated groups help to stabilize the anion toward protonation by the solvent. The net effect of the additional unsaturation is evidently to increase the rate of rearrangement relative to the rate of destruction of the carbanion by solvent.

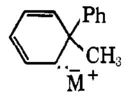
Ph_3CCH_2M

1



$Ph_2\underset{CH_3}{\underset{|}{C}}{-}CH_2M$

2



3

Cram and Dalton[7] have examined the question of aryl migration for reaction of alkali metal with four substrates in which additional unsaturation is absent in the organic moiety of interest. Reduction of 1,1-dideuterio-1-methoxy-2-(1-naphthyl)ethane and of 1,1-dideuterio-2-(1-naphthyl)ethyl methanesulfonate with potassium in 1,2-dimethoxyethane at 0° gave 1-ethylnaphthalene deuterated only in the methyl group; no detectable rearrangement (less than 5%) accompanied reduction. Reaction of *threo*-2-phenyl-3-pentyl methanesulfonate with potassium in 1,2-dimethoxyethane at 25° gave 94.5% of 2-phenylpentane and 5.5% of 3-phenylpentane (product of phenyl migration); reaction of *threo*-3-phenyl-2-pentyl methanesulfonate with sodium in liquid ammonia gave 75% of 3-phenylpentane and 3.1% of 2-phenylpentane. The most plausible mechanism for rearrangement was thought to be one-electron transfer from the alkali metal to the phenyl group, whose radical anion, as a powerful nucleophile, displaced the methanesulfonate group to give a phenyl-bridged radical. Further reaction with a second metal atom gave an organometallic compound which abstracted a proton from the solvent to give the observed

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[1] (a) Presented in part at the XXIIIrd International Congress of Pure and Applied Chemistry, Boston, Massachusetts, July, 1971. (b) Abstracted in large part from the Ph.D. thesis of Y.-M. Cheng, Georgia Institute of Technology, 1970.

[2] M. S. Silver, P. R. Shafer, J. E. Norlander, C. Rüchardt, and J. D. Roberts, *J. Amer. Chem. Soc.*, **82**, 2646 (1960); D. J. Patel, C. L. Hamilton, and J. D. Roberts, *ibid.*, **87**, 5144 (1965).

[3] (a) E. Grovenstein, Jr., *ibid.*, **79**, 4985 (1957); (b) H. E. Zimmerman and F. J. Smentowski, *ibid.*, **79**, 5455 (1957); (c) E. Grovenstein, Jr., and L. P. Williams, Jr., *ibid.*, **83**, 412 (1961).

[4] H. E. Zimmerman and A. Zweig, *ibid.*, **83**, 1196 (1961).

[5] S. W. Staley and J. P. Erdman, *ibid.*, **92**, 3832 (1970).

[6] E. Grovenstein, Jr., and L. P. Williams, Jr., *ibid.*, **83**, 2537 (1961).

[7] D. J. Cram and C. K. Dalton, *ibid.*, **85**, 1268 (1963).

reduction products. Evidently, reduction without rearrangement (the major reaction) involved either the aromatic ring or the sulfur of the sulfonate group as the electron transfer center.

In related work we have found[8] that 1-chloro-2-methyl-2-phenylpropane (neophyl chloride) reacts with lithium metal in tetrahydrofuran at −65° to give, according to the results of carbonation, 2-methyl-2-phenylpropyllithium (**4**) containing 6.4% of 1,1-dimethyl-2-phenylethyllithium (**5**) (product of 1,2-phenyl migration). Since warming the reaction mixture to 4° gave chiefly the corresponding hydrocarbons but failed to give additional products of phenyl migration, the results indicate that organolithium compound **4** does not rearrange to **5**. It was suggested that the observed rearrangement took place in an intermediate, presumably the neophyl radical, prior to formation of the organolithium reagent. Thus here and in the work of Cram and Dalton, rearrangements of radicals or radical anions and not rearrangements of organoalkali compounds (such as **1**, **2**, and **3**) evidently account for the small amount of phenyl migration observed.

It remains to be established, then, if aryl migration can be observed in a simple organoalkali compound lacking additional unsaturated groups at the center from which migration occurs. For a rearrangement of the type $ArCH_2CD_2M \rightleftarrows ArCD_2CH_2M$, the product of rearrangement is of the same stability as the reactant (barring isotope effects). This system where Ar is *p*-biphenylyl was selected for study in the present work because of the high migratory aptitude of the *p*-biphenylyl group observed in rearrangement of 2-*m*-biphenylyl-2,2-bis(*p*-biphenylyl)ethyllithium.[9]

Results

Reaction of 1-chloro-2-*p*-biphenylylethane with a large excess of lithium (1 RCl:15 Li) in tetrahydrofuran (THF) at −70° was found to give a satisfactory yield (~70%) of 2-*p*-biphenylylethyllithium,[10] as judged by the product of carbonation, provided that the reaction was terminated as soon as a green color appeared in the solution. Longer reaction times with lithium evidently led to formation of the radical anion of 2-biphenylylethyllithium (biphenyl radical anion[11] is reported to be blue in THF) and carbonation resulted in much nonvolatile, presumably polycarboxylic acid. Carbonation of 2-*p*-biphenylylethyllithium prepared from 1-chloro-2-*p*-biphenylylethane-*1,1*-d_2 at −70° led to an acid whose methyl ester on analysis by nmr showed the presence of methyl 3-*p*-biphenylylpropanoate-*2,2*-d_2 (**6**) containing at most only traces (2 ± 3%) of methyl 3-*p*-biphenylylpropanoate-*3,3*-d_2 (**7**). The reaction with lithium, therefore, gives essentially isotopically pure 2-*p*-biphenylylethyllithium-*1,1*-d_2.

When this lithium reagent was filtered to remove excess lithium metal and the solution warmed to 0° and held at this temperature for 3 hr before carbonation, there was obtained about equal amounts of *p*-biphenylylethane and 3-*p*-biphenylylpropanoic acid. Analysis of the methyl ester of the latter again showed the dominant presence of **6** containing only some 5 ± 4% of **7**. When the reaction time near 0° was extended to 9 hr, carbonation gave only some 8% of 3-*p*-biphenylylpropanoic acid, whose methyl ester analyzed for **6** containing some 7 ± 4% of **7**. The dominant neutral material from this run contained *p*-biphenylylethane whose analysis by nmr spectroscopy implied, on the assumption of a binary mixture of 1-*p*-biphenylylethane-*2,2*-d_2 (**8**) and 1-*p*-biphenylylethane-*1,1*-d_2 (**9**), that **8** containing 6 ± 4% of **9** was present; however, a more detailed mass spectral analysis showed that **8** was present along with 2% of **9** and 5% of 1-*p*-biphenylylethane-*2*-d_1 (**10**). Evidently the 2% protium impurity present (nmr analysis) at the 1 position of the starting chloride corresponds to 4 ± 2% of 1-chloro-2-*p*-biphenylylethane-*1*-d_1.

The conclusion from these studies is that 2-*p*-biphenylylethyllithium-*1,1*-d_2 undergoes little rearrangement according to eq 1, even though the reaction conditions

$$p\text{-}PhC_6H_4CH_2CD_2Li \rightleftarrows p\text{-}PhC_6H_4CD_2CH_2Li \qquad (1)$$

in THF were so severe that most of the lithium reagent decomposed. An attempt to catalyze this rearrangement, by carrying out the preparation and thermal decomposition of the organolithium reagent in THF containing some 4 molar equiv of *N,N,N′,N′*-tetramethylethylenediamine,[12] was no more successful than in absence of the amine.

Since organoalkali compounds of sodium and potassium have been found to rearrange more readily than the corresponding organolithium compounds,[3c,4] reactions of 1-chloro-2-*p*-biphenylylethane with cesium, potassium, and Cs–K–Na alloy[13] were next studied. A reaction in THF at −78°, in which 1-chloro-2-*p*-biphenylylethane was added over a period of 3 min to ten times the theoretical amount of Cs–K–Na alloy followed by stirring for 3 min before carbonation, gave only 1.3% yield of 3-*p*-biphenylylpropanoic acid and an equal yield of an isomeric acid, evidently 2-*p*-biphenylylpropanoic acid (glpc analysis of the methyl esters). The only volatile neutral product was *p*-biphenylylethane (8% yield). The remainder of the product was a complex mixture of acids and hydrocarbons of higher molecular weight. Reaction of the chloride with only a slight excess of the alloy at −65° over a period of some 40 min resulted in a negligible yield of 3-*p*-biphenylylpropanoic acid (0.3%) but an improved yield of *p*-biphenylylethane (*ca.* 30%). Evidently, excess cesium alloy adds to *p*-biphenylylethane to give, on carbonation, complex products.[14] The low yield of 3-*p*-biphenylylpropanoic acid in these runs may be attributed to the short lifetime of the 2-*p*-biphenylylethyl anion due to its reaction with THF (to give *p*-biphenylylethane) and with 1-chloro-2-*p*-biphenylylethane (to give products of Wurtz coupling and disproportionation). That some disproportionation occurred was evidenced by the

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[8] E. Grovenstein, Jr., and Y.-M. Cheng, *Chem. Commun.*, 101 (1970).

[9] E. Grovenstein, Jr., and G. Wentworth, *J. Amer. Chem. Soc.*, **89**, 2348 (1967).

[10] Curiously, preparation of the related 2-phenylethyllithium is not described in the open literature although a report of the catalytic activity of this compound has been made (U. S. Patent No. 3,069,407, 1962); we find that 2-phenylethyllithium can be made in the same yield and by the same method as reported here for 2-*p*-biphenylylethyllithium.

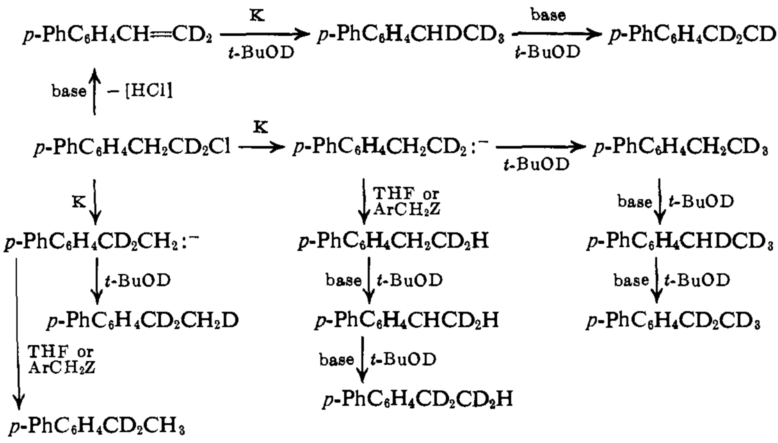
[11] P. Balk, G. J. Hoijtink, and J. W. H. Schreurs, *Recl. Trav. Chim. Pays-Bas*, 76, 813 (1957).

[12] *Cf.* G. G. Eberhardt and W. A. Butte, *J. Org. Chem.*, **29**, 2928 (1964).

[13] F. Tepper, J. King, and J. Greer, "The Alkali Metals, An International Symposium Held at Nottingham on 19–22nd July, 1966," The Chemical Society, London, 1967, p 25.

[14] *Cf.* E. Grovenstein, Jr., J. A. Beres, Y.-M. Cheng, and J. A. Pegolotti, *J. Org. Chem.*, 37, 1281 (1972).

Scheme I



appearance of *p*-biphenylylethene in a run in which effective excess of alloy was absent as judged by the presence of unreacted chloride in the final product.

Reaction of 1-chloro-2-*p*-biphenylylethane-*1,1*-d_2 with cesium alloy at −65° in THF gave *p*-biphenylylethane which, according to mass spectral analysis, consisted of 86% of **8**, 8% of **9**, 5% of **10**, and 1% of 1-*p*-biphenylylethane-*1*-d_1 (**11**); 9% of the product, therefore, appeared to result from 1,2 migration of *p*-biphenylyl. Repetition of this run with a larger excess of alloy gave *p*-biphenylylethane which, by nmr analysis, consisted of 78 ± 5% of **8** and 22 ± 5% of **9**. The disagreement in the percentage rearrangement in these runs is presumably due to the fact that under the present conditions the rate of protonation of 2-*p*-biphenylylethyl anion is only a little greater than the rate of rearrangement such that any factor which alters the rate of protonation (such as rate of addition and consumption of the chloride) can alter the percentage of rearrangement. The *p*-biphenylylethene formed in one of these runs was primarily 1-*p*-biphenylylethene-*2,2*-d_2 as expected for dominant β elimination upon the chloride.

Reaction of 1-chloro-2-biphenylylethane-*1,1*-d_2 with molten cesium in THF at reflux temperature gave, after carbonation, *p*-biphenylylethane (19% yield) containing 48 ± 5% of **8** and 52 ± 5% of **9**. The label was, therefore, effectively equilibrated at positions C-1 and C-2 of the ethane. This reaction gave an acidic product which after conversion to its methyl ester contained 6% yield of a volatile component whose nmr spectrum agreed with the structure of methyl 2-*p*-biphenylylpropanoate-*3,3*-d_2, containing no more than 10 ± 10% of methyl 2-*p*-biphenylylpropanoate-*2*-d_1.

A similar run with molten potassium in THF at reflux temperature gave 5% yield of 2-*p*-biphenylylpropanoic acid and 60% of *p*-biphenylylethane which, by mass spectral analysis (confirmed by nmr), contained 41% of **8**, 53% of **9**, and 3% each of **10** and **11**. The *p*-biphenylylethane, therefore, contained 56 ± 4% of the product of 1,2 migration of *p*-biphenylyl or essentially the same result as obtained with cesium metal at this temperature.

In order to see if rearrangement could be inhibited or retarded by a reactive proton donor, the reaction with potassium metal was repeated with addition of a solution of the chloride and *tert*-butyl alcohol to well-stirred, finely divided molten potassium in THF, at reflux temperature. The product consisted of a mixture of *p*-biphenylylethene and *p*-biphenylylethane; the latter contained 87% of **8**, 4% of **9**, 1% of **10**, 5% of **11**, and 3% of d_0 component. The appearance of 5% of the rearranged d_1 component **11** along with 4% of the rearranged d_2 component **9** suggests that considerable deuterium exchange occurred at the benzylic position of the *p*-biphenylylethane. On this basis, the d_0 component had its origin in the rearrangement product **9**. The present experiment, therefore, indicated that only 12 ± 3% rearrangement of *p*-biphenylyl occurred in presence of *tert*-butyl alcohol. This experiment does not directly prove that only 12% of a *p*-biphenylylethyl intermediate rearranged since it is unclear that all of the unrearranged *p*-biphenylylethane (**8** and **10**) came *via* such an intermediate. In particular *p*-biphenylylethane might have come by reduction of some of the *p*-biphenylylethene which is formed in the present reaction (*cf.* the reduction of styrene to ethylbenzene and polymers by sodium in liquid ammonia[15]). To test this postulate the experiment was repeated with use of $(CH_3)_3COD$ in place of ordinary *tert*-butyl alcohol. The product consisted of *p*-biphenylylethene, which was >90% *p*-biphenylylethene-*2,2*-d_2, and *p*-biphenylylethane which contained 17% d_2, 50% d_3, 30% d_4, and 3% d_5 components.

Discussion

Interpretation of the reduction of 1-chloro-2-*p*-biphenylylethane-*1,1*-d_2 by potassium in THF containing $(CH_3)_3COD$ requires consideration of the likely paths (Scheme I) leading to the variously labeled components. Since the *tert*-butyl alcohol used was labeled to the extent of 98.8 atom % deuterium in the hydroxyl group and since carbanions are not expected to show much isotopic discrimination upon protonation, we will neglect the minor source of protons in the *tert*-butyl alcohol. We further assume that only the 2-*p*-biphenylylethyl anion is reactive enough to remove protons from the solvent THF (or occasionally from the benzylic position of various aromatic species $ArCH_2Z$, such as the starting chloride). On this basis all d_2 and d_3 components in the *p*-biphenylylethane came from the 2-*p*-biphenylylethyl anion while d_4 and d_5 components could have come either by way of *p*-biphenylylethene or from 2-*p*-biphenylylethyl anion; therefore, at least 67% of the *p*-biphenylylethane came from protonation or deuteration of the 2-*p*-biphenylylethyl anion. Hence in conjunction with the similar experiment in presence of ordinary *tert*-butyl alcohol, less than 18% rearrange-

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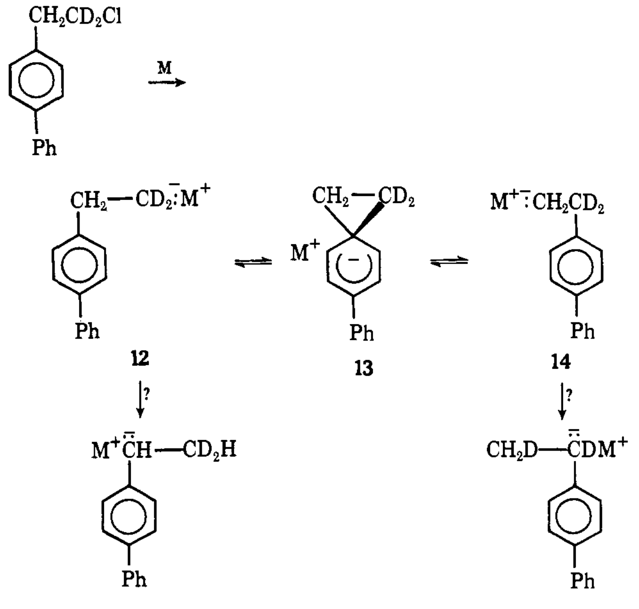
[15] C. B. Wooster and J. F. Ryan, *J. Amer. Chem. Soc.*, **56**, 1133 (1934).

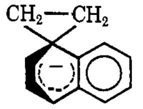
ment[16] occurred in the intermediate 2-*p*-biphenylylethyl anion (or its precursor) when the reaction with potassium in THF was run in presence of a little *tert*-butyl alcohol. Since the same reaction in absence of *tert*-butyl alcohol resulted in an essentially statistical distribution of the deuterium label in the *p*-biphenylylethane, *tert*-butyl alcohol is an effective trap for an intermediate leading to rearrangement.

Since 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,[17] the intermediate trapped by addition of small amounts of *tert*-butyl alcohol in our present experiments in the solvent THF cannot be the *p*-biphenylylethyl radical. On the other hand, the *p*-biphenylylethyl anion would be expected to react much more readily with *tert*-butyl alcohol than with THF because of the higher acidity of the alcohol than of the ether. Our present experiments imply that *p*-biphenylylethyl anion was trapped by *tert*-butyl alcohol before much 1,2 migration of *p*-biphenylyl occurred; therefore, most of the *p*-biphenylylethyl chloride must have been converted to *p*-biphenylylethyl anion prior to rearrangement. The simplest interpretation of the present results is that rearrangement also takes place largely or completely in the *p*-biphenylylethyl anion as has been suggested for related systems.[3,4]

In conclusion 2-*p*-biphenylylethylpotassium and cesium undergo ready 1,2 migration of the *p*-biphenylyl group in THF solution at 65° even though the product of rearrangement is no more stable than the starting anion. The rearrangement likely[9] occurs according to Scheme II. The failure of Cram and Dalton[7] to obtain appreciable rearrangement in the analogous 2-(1-naphthyl)ethyl system may be attributed to the more acidic solvent (1,2-dimethoxyethane) and lower temperature which they employed since, according to Hückel molecular orbital calculations,[18] spiro cyclization of a 1-naphthyl group (to give **15**) should be more favorable than of a 4-*p*-biphenylyl group by some 0.15 β unit.

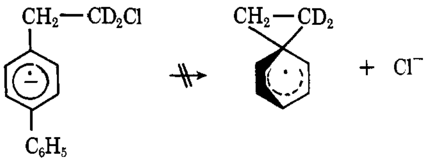
Scheme II





15

Since formation of 2-*p*-biphenylylethyl anion *preceded* appreciable rearrangement, we find no evidence in our work for participation of *p*-biphenylyl radical anion (or dianion) as a powerful nucleophile which displaced chloride to give directly the spiro radical (or anion **13**). Whether or not the *p*-biphenylyl radical anion acted as an "electron relay group"[7] in promoting the reductive cleavage of the carbon–chlorine bond cannot be ascertained in the present experiments. The failure to observe direct participation of neighboring biphenylyl radical anion in a concerted reductive rearrangement of the present chloride (eq 2) is in accord with the accepted mechanism[19] for the intermolecular reaction of naphthalene radical anion with alkyl halides where the first step gives naphthalene and a *free* alkyl radical rather than an alkylnaphthalene derivative (the latter is formed only in a subsequent step).



(2)

The formation of 2-*p*-biphenylylpropanoic-*3,3*-d_2 acid in the reactions of 1-chloro-2-*p*-biphenylylethane-*1,1*-d_2 with cesium and potassium, followed by carbonation, is indicative of formation of the 1-*p*-biphenylylethyl-*2,2*-d_2 anion. This anion could result from a 1,2-proton migration in 2-*p*-biphenylylethyl-*1,1*-d_2 anion (**12**). This interpretation would require that a large isotope effect existed in the rearrangement such that anion **12** underwent migration of a proton much faster than **14** (see Scheme II) underwent migration of a deuteron. Since 1,2 shifts of protons in simple carbanions are forbidden[4] according to the rules of orbital symmetry (in absence of a "determinative role" of the metal ion[20]), 1-*p*-biphenylylethyl-*2,2*-d_2 anion is likely formed by another route, namely proton removal from *p*-biphenylylethane by 2-*p*-biphenylylethyl anion or hydride cleavage from the same hydrocarbon by alkali metal. Evidently, a large isotope effect exists for such reaction of the hydrocarbon so that the unrearranged hydrocarbon **8** reacts more readily than the rearranged hydrocarbon **9**. On this basis the presence of somewhat more **9** than **8** in the final *p*-biphenylylethane from the reaction of 1-chloro-2-*p*-biphenylylethane-*1,1*-d_2 with cesium or

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(16) A similar upper limit to the amount of rearrangement is calculated if the nmr spectrum of the *p*-biphenylylethane from the experiment in $(CH_3)_3COD$ is used to estimate the percentage of rearrangement. For some more detailed arguments see ref 1b.

(17) W. A. Pryor and R. W. Henderson, *J. Amer. Chem. Soc.*, **92**, 7234 (1970); W. A. Pryor and J. P. Stanley, *ibid.*, **93**, 1412 (1971); W. A. Pryor, *Chem. Eng. News*, **49**, 42 (June 7, 1971).

(18) C. A. Coulson and A. Streitwieser, Jr., "Dictionary of π-Electron Calculations," W. H. Freeman, San Francisco, Calif., 1965, pp 37, 91, 204; A. Streitwieser, Jr., and J. I. Bauman, "Supplemental Tables of Molecular Orbital Calculations," Vol. I, Pergamon Press, New York, N. Y., 1965, p 94.

(19) For a recent review see N. L. Holy and J. D. Marcum, *Angew. Chem., Int. Ed. Engl.*, **10**, 115 (1971).

(20) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim/Bergstr., 1970, p 131.

potassium in THF at reflux temperature can now be explained.

In conclusion, 2-*p*-biphenylylethylcesium and potassium undergo rapid 1,2 migration of the *p*-biphenylyl group. In contrast 2-*p*-biphenylylethyllithium does not rearrange appreciably under any of the conditions tested. The failure of this lithium compound to rearrange under conditions effective for 2,2,2-triphenylethyllithium shows that the extra phenyl groups at the reaction center in the latter play an important role in accelerating the migration as previously supposed.[4,6] For the more reactive potassium and cesium compounds such activation is now found to be unnecessary for migration of *p*-biphenylyl; additional work is now required to see if the unsubstituted phenyl group will migrate in 2-phenylethylcesium or-potassium.

Experimental Section[21]

Proton nmr spectra were recorded on a Varian A-60 nmr spectrometer using tetramethylsilane as an internal standard. Gas liquid partition chromatography (glpc) was accomplished on a Perkin-Elmer Model 881 chromatograph employing a 12 ft × $^1/_8$ in. column packed with 5% silicone gum rubber (SE-30) on Chromosorb G which had been acid washed and treated with dimethyldichlorosilane. Mass spectra were run on a Varian M-66 mass spectrometer equipped with a gas chromatograph and entry port. *p*-Biphenylylacetic acid was prepared from 4-acetylbiphenyl according to the procedure of Schwenk and Papa.[22] *tert*-Butyl alcohol-*O-d* was from Merck Sharp and Dohme of Canada, Ltd., and was found (nmr analysis) to be 98.8 atom % deuterium. Cesium metal (99.9+%) was obtained from MSA Research Corp. in sealed glass ampoules. Lithium metal (0.05% Na max) was from Lithium Corp. of America. Lithium aluminum deuteride (99% D) was from Stohler Isotope Chemicals, Inc. Potassium was Baker reagent grade. Tetrahydrofuran (THF) was Baker reagent grade dried over sodium wire and distilled from $NaAlH_4$.

2-*p*-Biphenylylethanol. Addition of *p*-biphenylylacetic acid to a large excess of lithium aluminum hydride (3 $LiAlH_4$:1 RCO_2H) in tetrahydrofuran (THF) at reflux temperature, followed by stirring at reflux for 6 hr, gave an essentially quantitative yield of 2-*p*-biphenylylethanol, mp 95–96° (lit.[23] mp 93°); nmr ($CDCl_3$) τ 2.58 (9.0 H, m), 6.14 (2.0 H, t, J = 6.5 Hz), 7.14 (1.9 H, t, J = 6.5 Hz), 8.2 (1.0 H, s).

2-*p*-Biphenylylethanol-*1,1-d*$_2$. Methyl *p*-biphenylylacetate (mp 26–27°) was prepared by esterification of *p*-biphenylylacetic acid with methanol. Addition of 43.4 g (0.192 mol) of this ester in 200 ml of THF over a 40-min period to 9.56 g (0.228 mol) of lithium aluminum deuteride in 1.2 l. of THF at reflux temperature gave, after stirring another 5 hr at reflux and the usual work-up, 39 g of product, mp 93.5–96°. One recrystallization from CCl_4 gave 36.7 g (96.5% yield) of product, mp 95.5–96.3°; nmr ($CDCl_3$) τ 2.58 (9.0 H, m), 6.1 (<0.05 H), 7.18 (1.9 H, s), 7.75 (0.96 H, s).

1-Chloro-2-*p*-biphenylylethane. This compound was prepared from 2-*p*-biphenylylethanol with thionyl chloride in pyridine by the procedure previously reported[24] for 2-phenylethyl-*1*-^{14}C chloride. The crude oily product after recrystallization from pentane was obtained in 73% yield, mp 26–30°. Distillation in a sublimation apparatus at 95° (0.08 Torr) gave 69% overall yield of white crystals, mp 30–31.5°, which upon recrystallization from pentane had mp 30.7–31.5°; nmr (CCl_4) τ 2.64 (9.0 H, m), 6.35 (1.9 H, t, J = 7.5 Hz), 6.98 (1.9 H, t, J = 7.5 Hz).

Anal. Calcd for $C_{14}H_{13}Cl$: C, 77.59; H, 6.05. Found: C, 77.80; H, 6.11.

1-Chloro-2-*p*-biphenylylethane-*1,1-d*$_2$. This compound, mp 31–32°, was prepared from 2-*p*-biphenylylethanol-*1,1-d*$_2$ by the procedure described above for the protium compound; nmr (CCl_4) τ 2.67 (9.0 H, m), 6.38 (*ca.* 0.04 H), 7.01 (2.0 H, s). Another sample had nmr τ 6.38 (*ca.* 0.02 H), 7.01 (2.0 H); mass spectral analysis at m/e 217–221 gave 99% d_2 and 1 ± 1% d_1 components.

Bis(2-*p*-biphenylylethyl) Sulfite. This compound was prepared in several unsuccessful attempts[25] to obtain pure 1-chloro-2-*p*-biphenylylethane. To 4.96 g (0.025 mol) of 2-*p*-biphenylylethanol and 2.9 g of triethylamine in 100 ml of anhydrous ether cooled with stirring in an ice bath was added slowly 3.23 g (0.027 mol) of thionyl chloride at such a rate that the internal temperature did not exceed 8°. The mixture was then heated at reflux temperature for 3.5 hr before pouring onto crushed ice. Ether extraction yielded an oily product which upon crystallization from ethanol gave 0.16 g of a solid, mp 100–103°. Recrystallization from ethanol gave a product, mp 106–107°, whose analysis corresponds to that of the sulfite ester.

Anal. Calcd for $C_{28}H_{26}SO_3$: C,75.99; H, 5.92. Found: C, 75.65, 75.44; H, 5.78, 5.71.

In another reaction, thionyl chloride (6.65 g, 0.0559 mol) was added slowly to a mixture of 10.0 g (0.0506 mol) of 2-*p*-biphenylylethanol and 10.3 g (0.0557 mol) of tri-*n*-butylamine at ice bath temperature; the mixture was then heated at reflux for 3 hr. The usual work-up gave 10.6 g of product, mp 77–94°. Recrystallization from ethanol gave 1.0 g of crystals, mp 105–106°, which was doubtlessly again the sulfite ester.

General Procedure for Alkali Metal Reactions. For reactions with lithium and potassium, a three-necked, 500-ml Morton flask equipped with a high-speed Morton stirrer[26] was used. The flask was flame dried with a stream of dry nitrogen sweeping through the flask and then cooled to room temperature under an atmosphere of nitrogen which was maintained throughout all runs. The solvent was 250 ml of tetrahydrofuran (THF) which was freshly distilled from sodium aluminum hydride into the reaction flask. The same general procedure was used for reactions of cesium and cesium alloys; however, these reactions (to reduce fire hazards) were conducted inside a glove box filled with a nitrogen atmosphere using a four-necked, 500-ml Morton flask equipped with a shortened version of the Morton stirrer.

Reaction of 1-Chloro-2-*p*-biphenylylethane with Lithium. The reaction of 1-chloro-2-*p*-biphenylylethane (5.01 g, 0.0231 mol) with lithium (2.55 g, 0.367 g-atom, in small pieces as finely cut wire) was initiated at −10° by adding 1 ml of methyl iodide and *ca.* 4% of the halide (dissolved in 35 ml of THF) and stirring at −10 ± 5° for 1 hr. The final color of the solution after this period was green. The temperature was then lowered to −74° and the remainder of the halide was added dropwise over a period of 20 min. The first portion of halide added caused the appearance of a pink color, which deepended to brown at the end of addition. The solution was stirred at −73° for another 10 min, at which time a green color started to develop. The solution was immediately carbonated by forcing onto excess solid carbon dioxide. The next day 100 ml of water was added to decompose unreacted lithium. The THF was removed under partial vacuum on a rotating evaporator and the residue was extracted with ether to yield some 3 g of semisolid neutral material, which contained according to glpc analysis 0.41 g (9.7%) of *p*-biphenylylethane. The aqueous phase was acidified and extracted with ether to give 2.73 g (52% yield) of acid, mp 146–150.5°. This acid upon sublimation at 135° (0.06 Torr) gave 2.50 g of white crystals, mp 150–151.5°. A recrystallization from ethanol left the melting point unchanged.

Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.88; H, 6.04.

Reaction of the acid with excess diazomethane gave, after two sublimations *in vacuo* and recrystallization from methanol, the corresponding methyl ester, mp 57.5–58.3°; nmr (CCl_4) τ 2.66 (9 H, m), 6.43 (3 H, s, OCH_3), 7.11 (2 H, t, J = 6.5 Hz), 7.43 (2 H, t, J = 6.5 Hz). This nmr spectrum confirms the structure as the expected methyl 3-*p*-biphenylylpropanoate.

Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.12; H, 6.70.

The reaction of 1-chloro-2-*p*-biphenylethane was repeated under the conditions used previously except that after completion of the reaction the solution was filtered through a siphon tube packed at one end with glass wool to remove unreacted lithium metal. The solution was then stored at Dry Ice–acetone bath temperature and a portion carbonated after 1 hr and the remainder after 4 hr of storage. Since the ratio of crude acid (mp 148–150.5° in each fraction) to neutral material was essentially the same, 2-*p*-biphenyl-

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[21] Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

[22] E. Schwenk and D. Papa, *J. Org. Chem.*, **11**, 798 (1946).

[23] J. Colonge and P. Rochas, *Bull. Soc. Chim. Fr.*, 825 (1948).

[24] M. A. McMahon and S. C. Bunce, *J. Org. Chem.*, **29**, 1515 (1964).

[25] *Cf.* M. C. Caserio, W. H. Graham, and J. D. Roberts, *Tetrahedron*, **11**, 171 (1960).

[26] A. A. Morton and L. S. Redmon, *Ind. Eng. Chem.*, **40**, 1190 (1948).

ylethyllithium is evidently stable under the conditions of storage. In another run under the same conditions, the solution after filtration was allowed to warm to 0 ± 3° and was kept at this temperature for 1 hr before carbonation. There was isolated 2.0 g (38% yield) of acid of mp 145–150° (which with diazomethane gave methyl ester, mp 54.5–57°) and 2.8 g of semisolid neutral material. Analysis of the latter by glpc showed that *p*-biphenylylethane and *p*-biphenylylethene constituted 95.6 and 1.1%, respectively, of the volatile neutral material; however, quantitative glpc analysis indicated that the yields of these products based on starting chloride were only 24.4 and 0.28%, respectively; thus some 60% of the neutral material was nonvolatile under glpc conditions. Distillation of the neutral product (in a sublimation apparatus) three times *in vacuo* gave colorless crystals, mp 34–35.5° (lit.[27] mp of *p*-biphenylylethane: 32–34°); nmr (CCl_4) τ 2.81 (9 H, m), 7.47 (2 H, q, J = 7.5 Hz), 8.85 (3 H, t, J = 7.5 Hz).

In a reaction of 1-chloro-2-*p*-biphenylethane (4.89 g, 0.0226 mol) with lithium (1.24 g, 0.179 g-atom) which was run in the usual way at −70°, the solution was stirred for 1 hr after appearance of the green color before carbonation. The usual work-up yielded an acid, mp 128–146°, which was much less pure than usual and of which only some 60% could be sublimed at 130° (0.06 Torr). The volatile acid was 3-*p*-biphenylylpropanoic acid. Evidently prolonged reaction with excess lithium metal gives rise to an undesirable side reaction which leads to nonvolatile product.

Reaction of 1-Chloro-2-*p*-biphenylylethane-*1,1*-d_2 with Lithium. Five reactions of 1-chloro-2-*p*-biphenylylethane-*1,1*-d_2 with a 15:1 ratio of g-atoms of lithium to moles of halide were conducted at −70 ± 5° under the general conditions given above for the unlabeled chloride. The first of these was carbonated immediately upon appearance of the green coloration and yielded 69% of acid of mp 146–150°. A portion of the acid was converted to methyl ester with diazomethane and the ester sublimed *in vacuo* (91% of the ester was volatile) to give white crystals, mp 53–57.7°; nmr (CCl_4) τ 2.67 (9.0 H, m), 6.43 (3.1 H, s), 7.10 (1.9 H, s), 7.43 (*ca.* 0.04 H).

In the second run with 4.66 g (21.3 mmol) of the chloroethane, the solution was siphoned through a glass wool filter (to remove excess lithium) as soon as the green color began to appear and then was stored under nitrogen at 0 ± 3° for 170 min before carbonation. The usual work-up gave 2.2 g (46% yield) of acid, mp 137–146°, and 2.5 g of neutral material. The acid was converted to methyl ester and after sublimation *in vacuo* had mp 50.5–57°; nmr (CCl_4) τ 2.67 (9.0 H), 6.43 (3.1 H), 7.10 (1.8 H), 7.43 (*ca.* 0.09 H). The neutral material by glpc analysis was chiefly *p*-biphenylylethane (43% yield based on chloride).

In a third run with 5.0 g of the chloroethane, the reaction solution after filtration was allowed to stand at 1.0 ± 1° for 9 hr before carbonation. The usual work-up gave 0.91 g (18% yield) of crude acid. A portion (0.84 g) of the acid was esterified with diazomethane and distilled twice *in vacuo* to give 0.60 g (67% yield) of an ester, mp 54-57.5°. Analysis of this ester by glpc indicated that it consisted of 67% of methyl 3-*p*-biphenylylpropanoate and three unknown esters in relative yields (retention times relative to the propanoate) of 0.8 (0.68), 9 (0.76), and 23% (1.44). One recrystallization of the ester from pentane gave 0.22 g of white compound, mp 56.5–57.5°, which was pure methyl 3-*p*-biphenylylpropanoate according to glpc analysis; nmr (CCl_4) τ 2.67 (9.0 H), 6.43 (3.0 H), 7.1 (1.9 H), 7.43 (*ca.* 0.15 H). The crude neutral material (3.8 g) from this run contained 96% of *p*-biphenylylethane in the volatile portion by glpc analysis. A 3.3-g sample of this was distilled twice *in vacuo* to give 1.9 g of product, mp 32–33°; nmr (CCl_4) τ 2.81 (9.0 H, m), 7.47 (1.9 H, d, J = 8 Hz), 8.86 (1.1 H, t, J = 8 Hz). Mass spectral analysis at m/e 182–185 indicated that the *p*-biphenylylethane contained 95% d_2 and 5% d_1 component; the fragment (from methyl cleavage) at m/e 167–169 indicated that only some 2% of 1-*p*-biphenylylethane-*1,1*-d_2 was present and thus that the remainder consisted of 93% of the *2,2*-d_2 and 5% of the *2*-d_1 components. A repetition of this run (with 4.5 g of the chloroethane), but with the filtered solution allowed to stand at 2.5 ± 1° for 16.5 hr before carbonation, gave only some 0.04 g of volatile esters and a dominant neutral fraction. From the latter was isolated *p*-biphenylylethane whose distribution of deuterium was identical (nmr and mass spectral analysis) with that of the *p*-biphenylylethane isolated from the third run.

In a final run, 1-chloro-*2*-*p*-biphenylylethane-*1,1*-d_2 (2.01 g, 9.18 mmol) was allowed to react with excess lithium in the usual manner except that *N,N,N′,N′*-tetramethylethylenediamine (3.94 g, 34 mmol) was added simultaneously along with the chloride to the lithium. The reddish purple solution after filtration was allowed to stand at 4° for 1 hr before carbonation. The usual work-up gave 0.278 g (13% yield) of acids, mp 140–150°, and 1.7 g of crude neutral product. The acid fraction upon esterification with diazomethane and sublimation *in vacuo* gave 0.212 g of methyl ester, mp 52–55°. After recrystallization from pentane this sample had mp 56.3–57.0°; nmr (CCl_4) τ 2.67 (9.0 H), 6.41 (3.0 H), 7.10 (1.9 H, s), 7.43 (*ca.* 0.05 H). Analysis of the neutral material by glpc indicated that it contained 0.62 g (37% yield) of *p*-biphenylylethane. Distillation of the neutral material twice *in vacuo* gave 0.58 g of crystals, mp 28–31°. Recrystallization from pentane gave product of mp 31.5–33°; nmr (CCl_4) τ 2.81 (9.0 H), 7.47 (1.9 H, d), 8.86 (1.15 H, t).

Reaction of 1-Chloro-2-*p*-biphenylylethane with Cesium and Cs–K–Na Alloy. An alloy was prepared from 5.00 g of cesium, 1.67 g of potassuim, and 0.186 g of sodium; this same composition of alloy was used throughout the present work. A portion of this alloy (0.58 ml, 0.011 g-atom) was stirred in THF at reflux for 1 hr. The mixture was then cooled to −65 ± 3° and to the blue solution was added dropwise 1.02 g (4.71 mmol) of 1-chloro-2-*p*-biphenylylethane in 25 ml of THF over a period of 37 min with vigorous stirring continued for 5 min longer before carbonation of the reddish-brown solution. The usual work-up gave 0.38 g of acids and the remainder neutral material. Analysis of the corresponding methyl esters by glpc showed the presence of seven volatile components in an overall yield of only some 0.008 g, of which 0.003 g was methyl 3-*p*-biphenylylpropanoate. Similar analysis of the neutral fraction indicated the presence of 0.28 g (32% yield) of *p*-biphenylylethane as the only volatile constituent. The identification of *p*-biphenylylethane was confirmed by the nmr spectrum of the neutral fraction after distillation *in vacuo*. In similar runs but with a large excess of Cs–K–Na alloy for shorter reaction times, the yield of acids relative to neutral materials was increased; however, the methyl esters of the acids were again largely nonvolatile. The optimum yield of 3-*p*-biphenylylpropanoic acid (1.3%) was obtained in a run at −78° for 6 min.

Dropwise addition over a period of 20 min of a solution of 2.46 g (0.0114 mol) of 1-chloro-2-*p*-biphenylylethane in 25 ml of THF to 3.47 g (0.0261 g-atom) of cesium stirred vigorously in refluxing THF gave, after 5 min more of stirring, then cooling and carbonation, 1.4 g of acids, mp 118–320° dec, and a neutral material containing 0.37 g (18% yield) of *p*-biphenylylethane. The ethane constituted 95% of the volatile (glpc) neutral product.

Reaction of 1-Chloro-2-*p*-biphenylylethane-*1,1*-d_2 with Cesium and Cs–K–Na Alloy. Reaction of 1-chloro-2-*p*-biphenylylethane-*1,1*-d_2 (0.982 g, 4.49 mmol) with Cs–K–Na alloy (0.55 ml, 0.011 g-atom) at −65° was conducted as described for the unlabeled chloride. The usual work-up after carbonation gave 0.20 g of tarry acids and a dominant neutral fraction which, according to analysis by glpc, contained 0.23 g (28%) of *p*-biphenylylethane, 0.024 g (2.9%) of *p*-biphenylylethene, and 0.10 g (10%) of unreacted chloride. Two distillations *in vacuo* (60°, 0.08 Torr) gave 0.29 g of volatile neutral product. Mass spectral analysis (as previously described and semiquantitatively confirmed by glpc mass spectra) indicated[28] that the *p*-biphenylylethane contained 86% *2,2*-d_2, 8% *1,1*-d_2, 5% *2*-d_1, and 1% *1*-d_1 component. This analysis was semiquantitatively confirmed by an nmr spectrum, which also revealed that the *p*-biphenylylethene was primarily the *2,2*-d_2 compound.

In another run, 1.53 g (6.99 mmol) of 1-chloro-2-*p*-biphenylylethane-*1,1*-d_2 was added to 1.67 g (0.0215 g-atom) of Cs–K–Na alloy (thoroughly washed with pentane and then tetrahydrofuran to remove adhering hydrocarbons) over a 30 min period at −65° under the general conditions given for the unlabeled chloride. The usual work-up after carbonation gave 0.95 g of acids and 0.8 g of crude neutral product. Analysis of the neutral fraction by glpc indicated the presence of 0.32 g (25%) of *p*-biphenylylethane (contaminated by <1% of volatile impurity); distillation *in vacuo* gave 0.29 g of product, mp 29–32°. One recrystallization from pentane gave 0.11 g of white crystals of mp 33.0–33.6°; nmr (CCl_4) τ 2.81 (9.0 H, m), 7.48 (1.56 H, d), 8.85 (1.45 H, broad s). This nmr spectrum agrees with an isotopic composition of 78 ± 5% of *p*-biphenylylethane-*2,2*-d_2 and 22 ± 5% of *p*-biphenylylethane-*1,1*-d_2. Analysis

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(27) A. Rembaum, A. Eisenberg, R. Haack, and R. F. Landel, *J. Amer. Chem. Soc.*, **89**, 1062 (1967).

(28) The calculated values are based on the likely assumption that the *1,2*-d_2 compound is absent; since the maximum amount of the *1,2*-d_2 compound is equal to the percentage of *1*-d_1 compound listed, this assumption must in any event be very nearly correct.

of the acidic material (as methyl esters) showed that only some 15 mg of volatile (glpc) product was present (six components).

In a final run, 1-chloro-2-*p*-biphenylylethane-*2,2*-d_2 (2.89 g, 13.2 mmol) was added over a 30-min period to 4.08 g (0.0307 g-atom) of cesium in refluxing THF. The deep red solution was stirred for 5 min more before carbonation. The usual work-up gave 1.4 g of neutral material and 1.6 g of acids. The crude neutral material by glpc analysis contained 0.47 g (19% yield) of *p*-biphenylylethane and 0.12 g (5%) of *p*-biphenylylmethane. The neutral material upon distillation twice *in vacuo* yielded 0.51 g of semisolid volatile product. Recrystallization from pentane gave 0.21 g of white crystals of mp 29-31°; nmr (CCl_4) τ 2.79 (9.0 H, m), 7.47 (1.01 H, d), 8.86 (2.15 H, broad s). A mass spectral analysis showed that this *p*-biphenylylethane was >94% d_2. The crude acid on glpc analysis (of the methyl esters) was found to contain 0.19 g (6.0% yield) of an ester of 0.75 times the retention time of methyl 3-*p*-biphenylylpropanoate and a trace (*ca.* 5 mg) of ester at 0.66 times this retention time. The crude acid was converted to methyl ester and distilled three times at 80° (0.05 Torr) to give 0.15 g of volatile ester; nmr (CCl_4) τ 2.71 (9.0 H, m), 6.43 (0.9 H, d, J = 7 Hz), 6.52 (3.0 H, s), 8.62 (1.1 H, d, J = 7 Hz), 8.80 (0.63 H). On the presumption that the peak at τ 8.80 is from an impurity, the spectrum is essentially as expected for methyl 2-*p*-biphenylylpropanoate-*3,3*-d_2.

Reaction of 1-Chloro-2-*p*-biphenylylethane with Potassium. Potassium (0.478 g, 0.0123 g-atom) was stirred vigorously with THF at reflux temperature for 1 hr. A solution of 1-chloro-2-*p*-biphenylylethane (1.20 g, 5.53 mmol) in 25 ml of THF was then added dropwise to the finely divided potassium over a period of 8 min and stirring at reflux was continued for another 5 min before allowing the solution to cool (10 min) and carbonation. The usual work-up gave 0.39 g of acids and 1.2 g of crude neutral product. Distillation of the neutral product at 0.1 Torr and a bath temperature of 60° gave 0.56 g of *p*-biphenylylethane (identified by glpc and nmr). The acidic product was esterified with diazomethane. Analysis by glpc indicated that the crude ester contained 0.065 g (4.9% yield) of an ester of 0.75 times the retention time of methyl 3-*p*-biphenylylpropanoate and some 0.002 g of another ester of 0.66 times this retention time. Distillation of the crude ester (0.32 g) at 0.2 Torr gave 0.066 g of distillate; nmr (CCl_4) τ 2.71 (9.0 H, m), 6.44 (1.1 H, q), 6.52 (3.0 H, s), 8.62 (2.9 H, d), 8.7-9.4 (3.6 H, m). This spectrum is essentially that expected for methyl 2-*p*-biphenylylpropanoate, possibly containing a hydrocarbon impurity.

Reaction of 1-Chloro-2-*p*-biphenylylethane-*1,1*-d_2 with Potassium. Potassium (0.449 g, 0.0115 g-atom) was allowed to react with 1-chloro-2-*p*-biphenylylethane-*1,1*-d_2 (1.14 g, 5.20 mmol) in refluxing THF according to the procedure described for the unlabeled chloride. The usual work-up gave 0.34 g of acids and 1.1 g of neutral material. Distillation of the latter *in vacuo* gave 0.56 g (61% yield) of distillate. After redistillation and recrystallization from pentane, the product had mp 31.5–32.5°; nmr (CCl_4) τ 2.81 (9.0 H, m), 7.47 (0.93 H, d), 8.85 (2.04 H, broad s). Mass spectral analysis indicated[28] that this sample of *p*-biphenylylethane contained 53% *1,1*-d_2, 3% *1*-d_1, 3% *2*-d_1, and 41% *2,2*-d_2 component.

To a mixture of potassium (0.750 g, 0.0192 g-atom) and THF, which had been stirred at reflux for 1 hr, was added dropwise over a 15-min period a solution of 1.51 g (6.89 mmol) of 1-chloro-2-*p*-biphenylylethane-*1,1*-d_2 and 1.60 g (0.0213 mol) of *tert*-BuOD in 25 ml of THF. The solution was stirred at reflux for an additional 5 min and then carbonated. There was isolated 1.4 g of neutral product which according to quantitative glpc analysis contained 0.30 g (23% yield) of *p*-biphenylylethane, 0.40 g (32%) of *p*-biphenylylethene, and *ca.* 0.06 g of an unknown of 0.74 times the retention time of *p*-biphenylylethane. Distillation *in vacuo* gave a first fraction which was enriched in *p*-biphenylylethane. Recrystallization of this from pentane gave a third batch of crystals (mp 65–92°) which according to glpc analysis contained 51.6% of *p*-biphenylylethane and 48.4% of *p*-biphenylylethene; nmr (CCl_4) τ 2.81 (9.0 H), 3.42 (0.48 H), 7.47 (0.71 H), 8.85 (0.14 H). The nmr spectrum agrees with a mixture containing 48% of *p*-biphenylylethene-*2,2*-d_2 (<5%, if any, of *p*-biphenylylethene-*1*-d_1) and 52% of *p*-biphenylylethane which contains 1.4 ± 0.1 α and 0.26 ± 0.02 β hydrogens. Mass spectrometric analysis indicated that the *p*-biphenylylethene was at least 97% d_2 and less than 3% d_1; the *p*-biphenylylethane was 17% d_2, 50% d_3, 30% d_4, and 3% d_5.

The previous reaction with potassium was repeated in exactly the same manner but with ordinary *tert*-butyl alcohol; since after the addition of about two-thirds of the chloride-alcohol solution the potassium had all reacted, this addition was terminated and the reaction was completed as previously. There was isolated 0.89 g of neutral product which according to glpc analysis contained a 63 to 37 molar ratio of *p*-biphenylylethene to *p*-biphenylylethane. Analysis by a mass spectrometer attached to a glpc column indicated[28] that the *p*-biphenylylethane contained some 87% *2,2*-d_2, 4% *1,1*-d_2, 5% *1*-d_1, 1% *2*-d_1, and 3% d_0 components (probable accuracy, ±1% for minor components).

Test of Thermal Stability of 1-Chloro-2-*p*-biphenylylethane-*1,1*-d_2. The chloride in THF solution was added dropwise over a period of 11 min to refluxing THF in the usual apparatus and under the usual conditions for alkali metal reactions. The solution was then stirred at reflux for 5 min. After removal of solvent and sublimation (both *in vacuo*), chloride of unchanged nmr spectrum was recovered quantitatively.

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