axial and equatorial position.
(15) The principal ground state interactions due to X can be specified. When X is CH_3, there are CH_3-H and Cl-H parallel (1,3) interactions.[11] However, if the CH_2X group is rotated to another gauche conformation, then although one of these is removed, a much stronger CH_3-CH_3 parallel (1,3) interaction is introduced.
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Carbanions. XIV. 1,4 Migration of the *p*-Biphenylyl Group in Reactions of 4-Chloro-1-*p*-biphenylyl-1,1-diphenylbutane with Alkali Metals[1]

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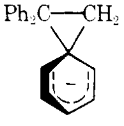
Abstract: 4-Chloro-1-*p*-biphenylyl-1,1-diphenylbutane reacts with potassium, cesium, and Cs-K-Na alloy in tetrahydrofuran (THF) to give 4-*p*-biphenylyl-1,1-diphenylbutyl anion as deduced from the nmr spectrum of the anion and products of carbonation and protonation. When the reaction with potassium is run in the presence of a small quantity of a sufficiently reactive proton donor such as *tert*-butyl alcohol, the product is 1-*p*-biphenylyl-1,1-diphenylbutane or products derived from the latter by subsequent reduction of the *p*-biphenylyl group. With sodium in refluxing dioxane the chloride gives 1-*p*-biphenylyl-1,1-diphenylbutane containing only some 7% of the rearranged hydrocarbon 4-*p*-biphenylyl-1,1-diphenylbutane; with potassium or cesium in the same solvent chiefly the rearranged hydrocarbon is obtained. From these results it is concluded that the chloride reacts with sodium, potassium, and cesium to give 4-*p*-biphenylyl-4,4-diphenylbutyl alkali metal compound which is either rapidly protonated or undergoes 1,4 migration of *p*-biphenylyl to give the more stable 4-*p*-biphenylyl-1,1-diphenylbutyl anion. Reaction of the chloride with excess lithium in THF at −75° gave 4-*p*-biphenylyl-4,4-diphenylbutyllithium (**4**) containing up to 47% of 4-*p*-biphenylyl-1,1-diphenylbutyllithium (**5**). Attempts to induce thermal rearrangement of the lithium compound **4** to **5** resulted primarily in protonation of **4**. Addition of the chloride to excess lithium biphenylide in THF at −75° gave **4** containing a little **5**; the percentage of **5** decreased as the concentration of lithium biphenylide increased. It is concluded that reaction of lithium biphenylide, and likely of lithium metal, with the chloride initially gives 4-*p*-biphenylyl-4,4-diphenylbutyl radical which either rearranges to 4-*p*-biphenylyl-1,1-diphenylbutyl radical or is reduced to the lithium compound **4**. The lithium compound **4** is readily rearranged to 4-*p*-biphenylyl-1,1-diphenylbutyl anion by potassium *tert*-butoxide in THF at −75°. The ease of 1,4 migration of *p*-biphenylyl in 4-*p*-biphenylyl-4,4-diphenylbutyl alkali metal compounds increases along the series: Li ≪ Na ≪ K or Cs; 1,4 migration is much less facile than analogous 1,2 migration of *p*-biphenylyl in carbanions.

Previous investigations[2] have shown that 1,2 migrations of aryl groups occur readily in organoalkali compounds in ethereal solvents. These rearrangements are believed[2d,3] to proceed by way of cyclic transition states or intermediates such as **1** from the 2,2,2-triphenylethyl anion. It might be expected that analogous 1,4 migrations of aryl would occur in carbanions, for example, by way of **2** from 4,4,4-triphenylbutyl anion. In fact, reaction of 4-chloro-1,1,1-triphenylbutane with alkali metals under a variety of conditions gave[4] only minor amounts of products of 1,4 migration of phenyl, and the reactions seemed too complex for study of the mechanism of the observed migration. In the present work reactions of 4-chloro-1-*p*-biphenylyl-1,1-diphenylbutane with alkali metals have been studied in hope of avoiding the difficulties encountered in the simpler system, thanks to the expected superior migratory aptitude[5] of *p*-biphenylyl over phenyl in anionic rearrangements. In addition it was thought conceivable that the intermediate **3** might prove stable enough under mild conditions to be detectable by spectroscopic means or by "trapping" experiments.



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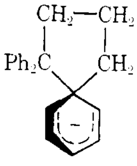

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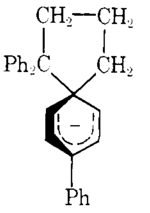

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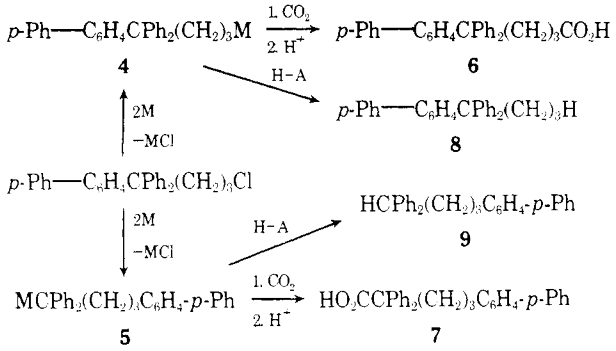
Results and Discussion

4-Chloro-1-*p*-biphenylyl-1,1-diphenylbutane 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 I. From reaction with molten potassium in tetrahydrofuran (THF) at 65°, carbonation gave in the acidic fraction only 5-*p*-biphenylyl-2,2-diphenylpentanoic acid (**7**), while methanolysis gave 4-*p*-biphenylyl-1,1-diphenylbutane (**9**) containing some 1.4% of 1-*p*-biphenylyl-1,1-diphenylbutane (**8**). Similar reaction with cesium metal at 65° gave **7** as the only acid from carbonation and a 98:2

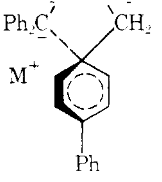
Scheme I



ratio of hydrocarbons **9** and **8** from methanolysis. These results imply that the rearranged organoalkali compound **5** is the major product of these reactions.

In order to attempt to identify likely precursors of **5** such as the unrearranged organoalkali compound **4** or the halfway rearranged spirocyclic anion **3**, the reaction of 4-chloro-1-*p*-biphenylyl-1,1-diphenylbutane was run with the minimum melting alloy[4] of cesium, sodium, and potassium in THF at −75°. The products of carbonation and hydrolysis, even after a reaction time of only 2 min, again proved to be primarily **7** and **9**, derived from the rearranged organoalkali compound **5**.

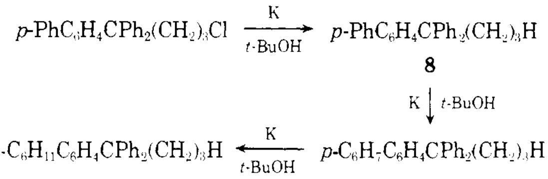
The structure of the dark red carbanion from reaction of 4-chloro-1-*p*-biphenylyl-1,1-diphenylbutane with Cs–K–Na alloy was further confirmed by its nmr spectrum in THF which had absorption by the protons of the *p*-biphenyl group at δ 7.17, much like the absorption reported[2f] (δ 7.19) for the aromatic protons in *p*-biphenylylethane, while the aromatic protons of the diphenylmethyl anion moiety absorbed as a doublet at δ 6.93 (ortho hydrogens), a triplet at δ 6.70 (meta hydrogens), and a triplet at δ 5.84 (para hydrogens). The latter absorptions are similar to those reported[6] for triphenylmethyllithium (δ 7.31 (d, ortho H), 6.52 (t, meta H), 5.96 (t, para H)) and diphenylmethyllithium (δ 6.52 (ortho and meta H) and 5.65 (para H)) in THF and are very different from those[1b] of 9-phenylspiro[4.5]deca-6,9-dienyl anion. The nmr spectrum of the present dark red anion is therefore fully in agreement with structure **5**. The failure to observe products of carbonation and protonation which retain the carbon skeleton of the spiro anion **3** is accordingly due to the absence of this carbon skeleton in the products, not to an artifact in the chemical reactions of the anion. Any nonclassical interaction of the diphenylmethyl anionic center of **5** with the biphenylyl group as implied by the dashed line in structure **11** must be small or nonexistent.



11

In further experiments to attempt to trap intermediates in the reaction of 4-chloro-1-*p*-biphenylyl-1,1-diphenylbutane with alkali metals, the reaction was run in the presence of various proton donors as given in Table I. The reactions with potassium in THF at reflux temperature are listed according to the expected order of proton donating ability of the proton source. With no added proton donor or in the presence of *n*-butylamine, the hydrocarbon produced (after addition of methanol) is predominantly the rearranged hydrocarbon **9**. In the presence of triethylcarbinol, increased amounts of the nonrearranged hydrocarbon **8** are produced. In the presence of the still more reactive proton donor *tert*-butyl alcohol, only products of nonrearranged carbon skeleton are produced.

The reduction of the chloride in THF in the presence of alcohols is complicated by reduction of the biphenyl group to dihydro and hexahydro (cyclohexyl) derivatives. Analysis of the reaction mixture in the experiment with *tert*-butyl alcohol showed that the yield of hydrocarbon **8** reached a maximum of 18% after the third incremental addition of potassium and *tert*-butyl alcohol but that this product largely disappeared with continued reduction with excess potassium. The final product, after eight incremental additions of potassium and *tert*-butyl alcohol, consisted of 3% of **8**, 90% of 1-*p*-cyclohexylphenyl-1,1-diphenylbutane, and 6% of a dihydro derivative of **8** of likely structure, 1-*p*-(1,4-dihydrophenyl)phenyl-1,1-diphenylbutane. The reduction sequence, therefore, appears to be as follows.



Phenylcyclohexane has been reported[7] as a minor product of alcoholysis of the biphenyl adducts of lithium and sodium. The present procedure appears to have synthetic merit as a general method for the reduction of a 4-alkylbiphenyl to a 4-cyclohexyl-1-alkylbenzene.

In refluxing dioxane 2-chloro-1,1,1-triphenylethane reacts[2a] readily with sodium to give the rearrangement product, 1,1,2-triphenylethylsodium. Accordingly these same conditions have been applied to the reaction of 4-chloro-1-*p*-biphenylyl-1,1-diphenylbutane with sodium. Since in a preliminary reaction only the unrearranged hydrocarbon **8**, but no carboxylic acid, was obtained on carbonation, the reaction was repeated (see Table I) with dioxane which was treated with *n*-butyl chloride and excess sodium just before the addition of 4-chloro-1-*p*-biphenylyl-1,1-diphenylbutane, in order that the *n*-butylsodium formed might scavenge any impurities in the dioxane. This pretreatment resulted in the formation of some 8% of the rearranged hydrocarbon **9** along with 92% of **8**. Another run in which the dioxane was stirred vigorously and finally distilled from molten potassium before pretreatment with *n*-butyl chloride gave about the same ratio of **9** to **8** in the final product. The high yield of nonrearranged hydrocarbon **8** in these reactions suggests that dioxane is functioning as a proton donor[8] to an intermediate carbanion much as *tert*-butyl alcohol functioned in the previous reactions with potassium in THF; however, the reactions with sodium in dioxane are not complicated by reduction of the biphenylyl group.

In contrast to the reaction with sodium, reaction of 4-chloro-1-*p*-biphenylyl-1,1-diphenylbutane with potassium in dioxane gave, after carbonation, primarily the rearranged hydrocarbon **9**, containing none of the nonrearranged hydrocarbon **8**, and only a trace (0.4%) of the rearranged carboxylic acid **7**. Evidently organopotassium compound **5** is nearly completely protonated by dioxane at 101° in less than 20 min to give hydrocarbon **9**. By way of comparison 1,1,2-triphenylethylsodium is somewhat less than half protonated by dioxane at 101° in some 45 min.[2a] With the present chloride, rearrangement occurs much more readily with potassium than with sodium.

In order to examine further the effect upon the product composition of varying the alkali metal, reaction with cesium was studied (Table I). Because of the ready cleavage of dioxane by cesium metal (*cf.* the slow cleavage of dioxane

Table I. Products from Reaction of 4-Chloro-1-*p*-biphenylyl-1,1-diphenylbutane (RCl) with Alkali Metals in the Presence of Various Proton Donors

RCl,			Proton donor added		Products,[a] %[b]				
mmol	Metal (mg-atom)	Temp, °C	A–H	(mmol)	**9**	**9** + 6H	**8**	**8** + 2H	**8** + 6H
			In Tetrahydrofuran						
2.6	K (7.1)	65	None		98	0	1.4	0	0[c,d]
2.7	K (5.8)	65	*n*-$BuNH_2$	(12.5)	95	0	4.5	0	0[c]
2.3	K (7.1)	65	$(CH_3CH_2)_3COH$	(6.8)	43	7	5.5	0	7[e]
0.72	K (5.8)	65	CH_3COCH_3	(9.5)	0	0	3.3	0	5.4[e]
2.54	K (5.9)	65	$(CH_3)_3COH$	(14.2)	0	0	4.0	1.8	11[e]
	K[f] (3 × 6.5)	65	$(CH_3)_3COH$	(3 × 6.2)	0	0	14.6	5.0	65[e]
			In Dioxane						
4.6[g]	Na (120)	101	None		8	0	92	0	0
5.3[g]	Na (99)	101	None		5.3	0	86	0	0[h]
5.1[g]	K (123)	101	None		77[i]	0	0	0	0
2.5	Cs (38)	40	None		89	1.3	3.6	0	0[e,j]
2.5	Cs (38)	30[k]	None		14	82	0	0	3.6

[a] Excess methanol (or ethanol) was added to all analytical samples at the conclusion of the reaction. The products are: **9,** 4-*p*-biphenylyl-1,1-diphenylbutane; **9** + 6H, 4-*p*-cyclohexylphenyl-1,1-diphenylbutane; **8,** 1-*p*-biphenylyl-1,1-diphenylbutane; **8** + 2H, likely structure, 1-*p*-(1,4-dihydrophenyl)phenyl-1,1-diphenylbutane; **8** + 6H, 1-*p*-cyclohexylphenyl-1,1-diphenylbutane. [b] The area per cent yield of volatile products are listed; see footnote.[45] [c] Also 0.15% of *p*-biphenylyldiphenylmethane (**10**) was observed. [d] Also 0.8% of an unknown of 0.52 times the retention time of **10** was observed. [e] The remainder was unreacted chloride. [f] The reaction mixture from the first reaction in the presence of *tert*-butyl alcohol was treated with three successive portions of potassium and *tert*-butyl alcohol to give the final product shown. [g] *n*-Butyl chloride was added prior to addition of RCl. [h] The other products were 6% of **10** and 2% of unknown of 1.2 times the retention time of **10.** [i] This product was obtained in the neutral fraction from carbonation; for the other products see the Experimental Section. [j] The absolute mole per cent yield of products was 3.3% of **8,** 1.2% of **9** + 6H, 81% of **9,** and 6.6% of unreacted RCl. [k] The temperature rose to 37° after addition of RCl.

by Na–K alloy at 101° to give ethylene and alkali metal salt of ethylene glycol[8]), the reaction had to be studied at temperatures of 30–40°. At 40° where the excess of cesium was destroyed by cleavage of dioxane, the products were chiefly the rearranged hydrocarbon **9** and some 3% yield of unrearranged hydrocarbon **8.** In a run initiated at 30° with excess of cesium present the product was about the same mixture of **8** and **9** but this time reduced to their hexahydro(*p*-cyclohexylphenyl) derivatives. This reaction illustrates the superior reducing power toward benzenoid rings of cesium[4] over sodium and potassium and the use of dioxane as a proton source in Birch-like[9] reductions.

Since 1,2 migrations of aryl groups have been observed in rearrangements of many organolithium compounds,[2,3] frequently upon warming THF solutions of such lithium compounds to 0°, corresponding 1,4 migration of *p*-biphenylyl has been sought in reactions of 4-chloro-1-*p*-biphenylyl-1,1-diphenylbutane with lithium. Reaction of this chloride with a 15:1 ratio of gram atoms of lithium to moles of chloride at −70 to −75° gave in four runs upon hydrolysis a 75:25 mixture (±6%) of nonrearranged **8** to rearranged **9** hydrocarbons or upon carbonation a similar ratio of acids **6**:**7.** Attempts to induce further rearrangement by storing the organolithium reagent at −11° for 8 hr gave only a 2% (if any) increase in the amount of rearrangement as judged by the products of protonation or, after storage at 0° for 4 hr, a 4% increase in rearrangement. Since most of the organolithium reagent, according to the results of carbonation, was protonated by solvent after such long periods of storage, attempts to induce appreciable thermal rearrangement of 4-*p*-biphenylyl-4,4-diphenylbutyllithium (**4**) are deemed to be impractical. To be sure, the organolithium reagent which better survived such thermal treatment was the more stable rearranged organolithium compound **5.**

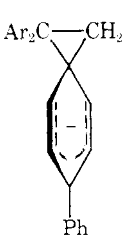
In these runs a large excess of lithium metal over halide was used in the preparation of the organolithium compound in order to give a high yield of lithium reagent in a few hours at the low temperatures of the present preparations. When the ratio of gram atoms of lithium metal to moles of chloride was increased to about 80:1, the product in four runs after methanolysis consisted of a 53:47 (± 1%) ratio of nonrearranged **8** to rearranged **9** hydrocarbons. The increase in extent of rearrangement with increase in the ratio of lithium metal to halide is notable and proved to be reproducible under our conditions. Also the very large amount of rearrangement observed during preparation of the organolithium reagent from the present chloride appears to be without precedent. It has been previously reported[10] that 6.4% of the rearranged product 1,1-dimethyl-2-phenylethyllithium is present in the 2-methyl-2-phenylpropyllithium prepared from the reaction of neophyl chloride with lithium metal in THF at −70°. Since 4-*p*-biphenylyl-4,4-diphenylbutyllithium (**4**), once prepared, undergoes little if any rearrangement upon warming to 0° for several hours, it is clear that the large amount of 4-*p*-biphenylyl-1,1-diphenylbutyllithium (**5**) produced during preparation of **4** at −70 to −75° cannot result from rearrangement of the organolithium compound **4.** A similar conclusion applies to the rearranged product from reaction of neophyl chloride with lithium.

In an attempt to gain further insight into the reaction of lithium metal with 4-chloro-1-*p*-biphenylyl-1,1-diphenylbutane, we have studied the reaction of the chloride with lithium biphenylide. Addition of the chloride to an excess of 0.03 *M* lithium biphenylide in THF at −75° upon methanolysis a 92:8 ratio of hydrocarbons **8**:**9** or upon carbonation a similar ratio of acids **6**:**7.** The yield of **6** based upon starting chloride was 63%. Other experiments showed that if the initial concentration of lithium biphenylide was higher (0.24 *M*) the ratio of hydrocarbons **8**:**9** from methanolysis was 98:2 while if the concentration was lower (0.011 *M*) this ratio was 88:12. In a similar reaction of neophyl chloride with lithium biphenylide, carbonation of the product gave a 99:1 ratio of 3-methyl-3-phenylbutanoic acid to 2,2-dimethyl-3-phenylpropanoic acid or a 76% yield of the former acid based on the amount of starting neophyl chloride (or a 92% conversion based upon the neophyl chloride consumed). Under appropriate conditions, therefore, *lithium biphenylide can react with organic chlorides,* which are prone to give lithium reagents of rearranged structure with lithium metal, *to give organolithium compounds of unrearranged structure in high yields.* The synthetic utility of lithium biphenylide for the preparation of organolithium compounds from organic chlorides seems not to have been previously noted, though Eisch[11] reported a 70% yield phenyllithium from reaction of fluorobenzene with reportedly a 2:1 adduct of lithium with biphenyl in THF at −10°. Other synthetically useful reactions of alkali metal adducts of aromatic hydrocarbons have been reported by Bank and coworkers.[12]

Having demonstrated that 4-*p*-biphenylyl-4,4-diphenylbutyllithium does not undergo any appreciable thermal rearrangement in THF by itself, we next sought reaction conditions which might facilitate such rearrangement. The report[13] that organopotassium compounds can sometimes be synthesized by the reaction of potassium alkoxides with organolithium compounds in hydrocarbon solvents, or that very reactive adducts[13,14] of organolithium compounds with potassium alkoxides are formed, encouraged us to look for catalysis of the rearrangement of 4-*p*-biphenylyl-4,4-diphenylbutyllithium by potassium *tert*-butoxide in tetrahydrofuran. Addition at −75° of a THF solution of about two formula weights of potassium *tert*-butoxide to a preparation of 4-*p*-biphenylyl-4,4-diphenylbutyllithium containing one formula weight of organic and inorganic lithium compounds resulted in an immediate intensification of color. Carbonation after 6 min gave an acidic product containing the rearranged acid **7** (49% yield) but none of the nonrearranged acid **6.** Whereas the initial organolithium reagent on methanolysis gave 63:37 ratio of nonrearranged **8** to rearranged **9** hydrocarbons, after addition of potassium *tert*-butoxide this ratio became 32:68. From these results it is evident that potassium *tert*-butoxide has brought about a ready rearrangement of 4-*p*-biphenylyl-4,4-diphenylbutyllithium (**4**) to rearranged organoalkali compound **5.**

Conclusions

Reaction of 4-chloro-1-*p*-biphenylyl-1,1-diphenylbutane with potassium, cesium, or Cs–K–Na alloy tetrahydrofuran results in a very facile 1,4 migration of *p*-biphenylyl with no evident 1,4 migration of phenyl. This highly selective 1,4 migration of *p*-biphenylyl is similar to the reported[3b] exclusive (>98.6 ± 0.4%) 1,2 migration of *p*-biphenylyl as opposed to *m*-biphenylyl in 2-*m*-biphenylyl-2,2-bis(*p*-biphenylyl)ethyllithium. The product of the present rearrangement is 4-*p*-biphenylyl-1,1-diphenylbutyl anion (**5**) as deduced both from its products of protonation and carbonation. Since the 1,2 migration of *p*-biphenylyl in 2-*m*-biphenylyl-2,2-bis(*p*-biphenylyl)ethyllithium is believed to occur in an anion by way of a spirocyclic transition state or intermediate **12,** it is attractive to postulate a similar intermediate, **3,** for the present 1,4 migration of *p*-biphenylyl. The formation of such an intermediate would be in agreement with the observed greater migratory aptitude of *p*-biphenylyl over phenyl since in **3,** unlike in the intermediate **13** for migration of phenyl, the *p*-phenyl group should provide significant stabilization by further delocalizing the charge on the anion. The analogy of 1,4 to 1,2 migrations of aryl groups in anions is weakened by the observation in the present work that 4-*p*-biphenylyl-4,4-diphenylbutyllithium does *not* undergo appreciable rearrangement under thermal conditions which suffice for effecting related 1,2 rearrangements of organolithium compounds.



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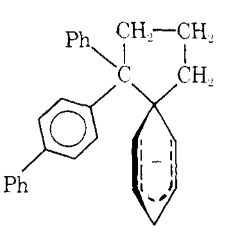

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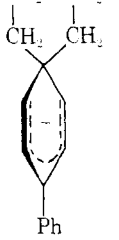

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An alternative explanation for the rearrangement observed during reaction of potassium, cesium, or Cs–K–Na with 4-chloro-1-*p*-biphenylyl-1,1-diphenylbutane is that the rearrangement occurs in an intermediate free radical. Indeed hitherto unknown cases[15] of 1,4 and 1,5 migrations[16] of aryl groups in free radicals have been reported since the present work was initiated. In order to establish whether or not formation of organoalkali compound **4** precedes rearrangement, 4-chloro-1-*p*-biphenylyl-1,1-diphenylbutane was allowed to react with potassium in THF in the presence of various proton donors, the results (Table I) show that the amount of rearrangement in the hydrocarbon products decreased as the expected effective acidity of the proton donor increased. In particular, in the presence of *tert*-butyl alcohol all of the products are of unrearranged carbon skeleton. 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 the present experiments must be the organopotassium compound **4** rather than the corresponding free radical.

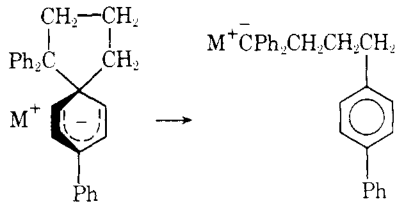
Since, therefore, formation of the organopotassium compound precedes rearrangement, we believe that the rearrangement with potassium and likely also that with sodium, cesium, and Cs–K–Na alloy takes place in the ionic organoalkali compound **4** (see Scheme II). The inability in the present work to detect the presence of the supposed spirocyclic intermediate **3** even at −75° must be attributed to a very facile ring opening of **3** to give **5.** This interpretation has been confirmed by reaction[1b,18] of cesium or potassium with 4-chloro-1-*p*-biphenylylbutane in THF to give the stable spiro anion **14.**

Scheme II

$p\text{-PhC}_6\text{H}_4\text{CPh}_2(\text{CH}_2)_3{}^-\text{M}^+ \longrightarrow$

4

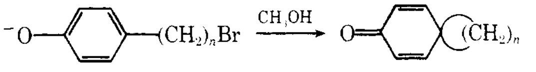
$\text{M}^+ = \text{Na}^+, \text{K}^+, \text{Cs}^+$



3 **5**

An interesting observation in the present work is the slow rate of rearrangement (k_R) of 4-*p*-biphenylyl-4,4-diphenylbutylsodium (**4**) compared to the rate of protonation (k_H) of this organosodium compound by dioxane at 101°; the relative rate k_R/k_H equals about 0.08. In contrast the corresponding relative rate[2a] k_R/k_H for 2,2,2-triphenylethylsodium in dioxane is 4.5. In this comparison the former organosodium compound undergoes 1,4 migration of *p*-biphenylyl while the latter compound undergoes 1,2 migration of phenyl. Since 2-*m*-biphenylyl-2,2-bis(*p*-biphenylyl)ethyllithium[3b] at 0° undergoes 1,2 migration of *p*-biphenylyl to the extent of at least 98.6 ± 0.4%, the *p*-biphenylyl group undergoes 1,2 migration more than 35 times (after statistical correction) more readily than the *m*-biphenylyl; a similar or greater ratio should apply to the relative rate of migration of *p*-biphenylyl *vs.* phenyl. From such considerations it is estimated that the relative rate of *p*-biphenylyl migration to protonation (k_R/k_H) for 2-*p*-biphenylyl-2,2-

diphenylethylsodium is greater than 157 in dioxane at 101°. If k_H for 2-p-biphenylyl-2,2-ethylsodium is the same as k_H for 4-p-biphenylyl-4,4-diphenylbutylsodium within a factor of two, then it is estimated that the rate of 1,2 migration of p-biphenylyl in the former compound exceeds the rate of 1,4 migration of p-biphenylyl in the latter by more than 1000-fold. By way of comparison it has been estimated[19] that 2-p-hydroxyphenylethyl bromide in the form of its anion (**15**, n = 2) undergoes cyclization to **16** some 1100 times more readily than the anion (**15**, n = 4) of 4-p-hydroxyphenylbutyl bromide. In the case of cyclization of ω-aminoalkyl chlorides, bromides, and nitrates, however, the five-membered heterocycle is formed 10^2 to 10^4 times more rapidly than the three-membered heterocylic amine.[19a,20] The factors relating to the ease of formation of various ring sizes have frequently been discussed but are not generally well understood.[19,20] For the present rearrangements of carbanions, it seems likely that the rearrangement has an early transition state (*cf.* the Hammond[21] postulate for reactive intermediates) and therefore that the strain in formation of the three-membered ring is not well-developed in the transition state and thus that the "proximity" [22] of aryl to carbanionic center governs the relative ease of cyclization.

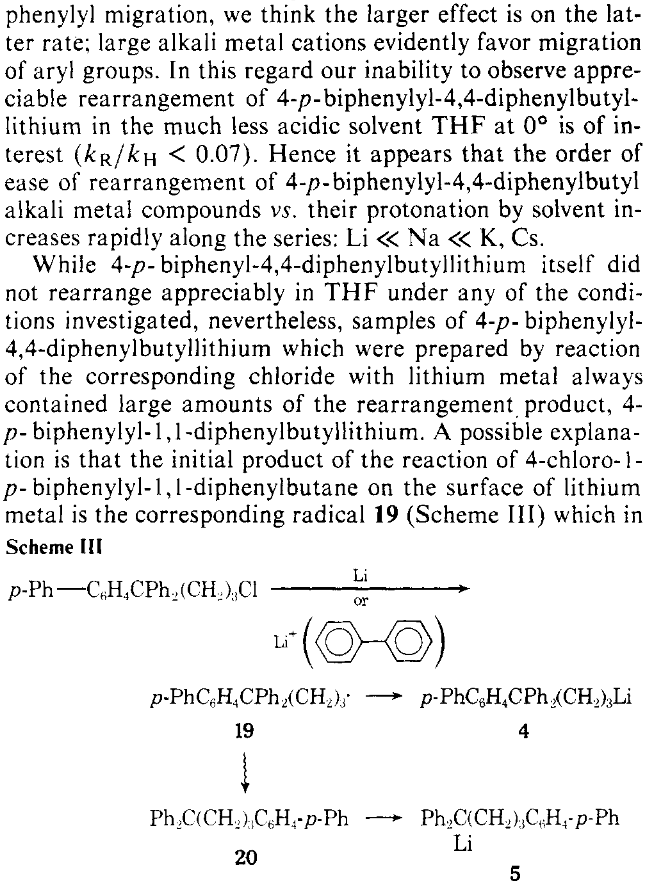


15 **16**

Another interesting observation in the present work (see Table I) is that the rate of rearrangement of 4-p-biphenylyl-4,4-diphenylbutyl alkali compound relative to the rate of protonation of the unrearranged organoalkali compound by dioxane, k_R/k_H, is much larger for potassium (>80) than for sodium (0.08) at 101°. Also the value for cesium (25) at 40° is near that of potassium. While these relative rate ratios doubtlessly reflect the effect of the alkali metal cation on both the rate of protonation and the rate of p-biphenylyl migration, we think the larger effect is on the latter rate; large alkali metal cations evidently favor migration of aryl groups. In this regard our inability to observe appreciable rearrangement of 4-p-biphenylyl-4,4-diphenylbutyllithium in the much less acidic solvent THF at 0° is of interest ($k_R/k_H < 0.07$). Hence it appears that the order of ease of rearrangement of 4-p-biphenylyl-4,4-diphenylbutyl alkali metal compounds *vs.* their protonation by solvent increases rapidly along the series: Li ≪ Na ≪ K, Cs.

While 4-p-biphenyl-4,4-diphenylbutyllithium itself did not rearrange appreciably in THF under any of the conditions investigated, nevertheless, samples of 4-p-biphenylyl-4,4-diphenylbutyllithium which were prepared by reaction of the corresponding chloride with lithium metal always contained large amounts of the rearrangement product, 4-p-biphenylyl-1,1-diphenylbutyllithium. A possible explanation is that the initial product of the reaction of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane on the surface of lithium metal is the corresponding radical **19** (Scheme III) which in part is free enough from the metal surface to undergo 1,4 migration of p-biphenylyl. Reduction of the radicals **19** and **20** with lithium then gives the observed products. Related 1,4-migrations of aryl groups in free radicals are known[15,16] and analogous explanations have been advanced to explain the 1,2 migration of phenyl during reduction of neophyl chloride with magnesium[23] and lithium[10] or at a cathode.[24] Similar mechanisms have also been proposed to account for racemization during the corresponding reactions of 1-halogeno-1-methyl-2,2-diphenylpropane.[25] While the proposed mechanism appears reasonable, it does not readily explain why the percentage of rearrangement increases with increase in the ratio of lithium metal to chloride. Perhaps only on certain portions of the surface of the lithium metal are the radicals free enough to rearrange and that the quantity of such surfaces increases with the amount of lithium metal used. Alternatively other mechanisms could be proposed; thus the rearrangement might be induced by traces of impurities in the lithium metal.

Scheme III



As a test for the plausibility of the mechanism of Scheme III for reduction by lithium metal, reduction of 4-chloro-1-p-biphenylyl-1,1-diphenylbutane by lithium biphenylide in THF has been studied. This alkali metal adduct of biphenyl like other such alkali metal adducts of aromatic hydrocarbons[26] should function as a one-electron-transfer reagent and, therefore, upon reaction with the chloride afford the radical **19**. The subsequent fate of **19** should depend upon the concentration of lithium biphenylide in the immediate surroundings. We find that as the initial concentration of the lithium biphenylide to which the chloride is added varied from 0.011 to 0.24 M the percentage rearrangement decreased from 12 to 2%. This observation is in agreement with Scheme III which requires that as the concentration of lithium biphenylide increases the amount of rearrangement of **19** to **20** should decrease because of competitive reduction of **19** to the corresponding organolithium compound **4**. Evidently in the present experiments lithium biphenylide is a more effective "trap" for the intermediate radical **19** than is lithium metal; consequently *lithium biphenylide is preferable to lithium metal* for the preparation of 4-p-biphenylyl-4,4-diphenylbutyllithium from the corresponding chloride.[27]

Whereas 4-p-biphenylyl-4,4-diphenylbutyllithium itself does not undergo appreciable thermal rearrangement in THF under conditions sufficiently vigorous to destroy most of the lithium reagent by extraction of protons from the solvent, addition of potassium *tert*-butoxide to the reagent brings about very ready rearrangement at −75°. This result is most readily explained if the corresponding organopotassium compound[13] is formed since, as we have demonstrated above, the organopotassium compound rearranges much more readily than the organolithium compound. The present example appears to be the first report of the use of a potassium alkoxide to induce the rearrangement of an organolithium compound; subsequent work[28] has demonstrated that sodium, potassium, and cesium, but *not* lithium *tert*-butoxides greatly accelerate the rearrangement of suitable[2,3,4] organolithium compounds.

Experimental Section[29]

Proton nmr spectra were recorded on a Varian A-60 nmr spectrometer using tetramethylsilane as an internal standard unless otherwise specified. Mass spectra were run upon either a Varian M-66 or a Hitachi (Perkin-Elmer) RMU-7L mass spectrometer; exact mass determinations were made with the latter instrument.

p-Biphenylyldiphenylchloromethane was prepared by the procedure of Lichtin and Glazer.[30] p-Biphenylyldiphenylmethane (**10**), mp 110-112° (lit.[31] mp 111°) was prepared in 23% yield (based on p-bromodiphenyl) by coupling[32] p-biphenylylmagnesium bromide with benzhydryl bromide in ether-benzene solution; 1,1,2,2-tetraphenylethane was formed as a by-product. Cesium metal (99.9+%) was obtained from MSA Research Corporation in sealed glass ampoules. Dioxane was Fisher Scientific Co. certified ACS grade and was purified by treatment with hydrochloric acid and then sodium according to a published procedure.[33] Lithium metal (0.05% Na max) was from Lithium Corporation of America. Methyl 4-*p*-biphenylylbutanoate[34] (bp 177° at 0.2 Torr; lit[35] bp 212-215° at 3 Torr) was prepared by esterification of 4-*p*-biphenylylbutanoic acid[36] with methanol. Potassium and sodium were Baker reagent grade. Tetrahydrofuran (THF) was Baker reagent grade dried over sodium wire and then distilled from sodium aluminum hydride immediately before use.

Neophyl chloride was prepared by the procedure of Whitmore and coworkers.[37,38] 2,2-Dimethyl-3-phenylpropanoic acid (mp 57.0-58°, reported[39] mp 57°) was prepared[38] in 10% yield by carbonation of the Grignard reagent from 2-benzyl-2-chloropropane; this acid upon 50/50 admixture with 3-methyl-3-phenylbutanoic acid melted below room temperature. 3-Methyl-3-phenylbutanoic acid (mp 56-58°, reported[40] 57.5-58.5°) was prepared by oxidation of 4-methyl-4-phenyl-2-pentanone[40] with potassium hypochlorite according to a general procedure.[38,41]

4-Chloro-1-*p*-biphenylyl-1,1-diphenylbutane. *p*-Biphenylyldiphenylmethylsodium was prepared from 112 g (0.315 mol) of *p*-biphenylyldiphenylchloromethane with powdered sodium amalgam (13.3 g of Na, 546 g of Hg) in 1 l. of anhydrous ether according to the general procedure used for preparation of triphenylmethylsodium.[42] One-fifth of the *p*-biphenylyldiphenylmethylsodium was removed for synthesis of 1-*p*-biphenylyl-1,1-diphenylbutane (see below) and the remainder was siphoned from the mercury at room temperature into 500 ml of 1-bromo-3-chloropropane under a nitrogen atmosphere. The solution, after standing overnight, was filtered through a sintered glass funnel and the filtrate was concentrated *in vacuo* to a yellow viscous oil. The oil was dissolved in petroleum ether (bp 30-60°) and the solution was stored at refrigerator temperature for 2 days. An oily material was deposited. The solution was separated from the oil by decantation; the solution was evaporated to dryness *in vacuo* and the residue was recrystallized successively from *n*-heptane and then acetone. Colorless crystals (47 g, 47% yield), mp 97.5-100°, were obtained. The analytical sample after recrystallization from acetone, ethanol, and finally *n*-heptane had mp 99.3-100.2° and nmr (CCl_4) δ 7.25 (19 H, m), 3.32 (2 H, t, J = 6.0 Hz), 2.72 (2 H, t, J = 8.0 Hz), and 1.58 (2 H, m).

Anal. Calcd for $C_{28}H_{25}Cl$: C, 84.72; H, 6.35; Cl, 8.93. Found: C, 84.90; H, 6.36; Cl, 8.95.

1-*p*-Biphenylyl-1,1-diphenylbutane (**8**). *p*-Biphenylyldiphenylmethylsodium (as prepared in the previous section) was siphoned at room temperature into 100 ml of 1-bromopropane under an atmosphere of nitrogen. The reaction mixture was worked up and recrystallized in the manner given for 4-chloro-1-*p*-biphenylyl-1,1-diphenylbutane. There was isolated some 9.3 g (41% yield) of product of mp 92.5-94°. The analytical sample after recrystallization from ethanol and twice from *n*-hexane consisted of white crystals of mp 94.7-95.3° and nmr (CCl_4) δ 7.23 (19 H, m), 2.52 (2 H, t, J = 6 Hz), and 0.96 (5 H, broad m).

Anal. Calcd for $C_{28}H_{26}$: C, 92.77; H, 7.23. Found: C, 92.87; H, 7.04.

5-*p*-Biphenylyl-5,5-diphenylpentanoic Acid (**6**). 4-Chloro-1-*p*-biphenylyl-1,1-diphenylbutane (4.35 g, 11.0 mmol), sodium cyanide (0.951 g, 19.4 mmol), and sodium iodide (1.86 g, 12.4 mmol) were placed in 300 ml of dimethyl sulfoxide and stirred with a magnetic stirrer in a stoppered flask at room temperature for 10 days.[43] The mixture was poured into 300 ml of water and the resinlike white product (4.0 g, 94% yield) was separated by filtration and washed with water. Attempts to purify this hard resin (crude 5-*p*-biphenylyl-5,5-diphenylpentanenitrile) by recrystallization from common solvents were unsuccessful. The crude nitrile (3.15 g, 8.1 mmol) was dissolved in 80 ml of ethylene glycol containing 1.31 g of potassium hydroxide and the solution was heated at reflux for 6 hr. The usual work-up gave 3.13 g (95% yield) of crude acid, mp 97-115°. A portion (0.98 g) of this acid was recrystallized twice from glacial acetic acid and once from *n*-hexane to give 0.41 of white crystals: mp 121.5-122.5°; nmr (CCl_4) δ 11.8 (1 H, s), 7.26 (19 H, m), 2.63 (2 H, *t*, J = 7.5 Hz), 2.28 (2 H, t, J = 6.5 Hz), 1.46 (2 H, m).

Anal. Calcd for $C_{29}H_{26}O_2$: C, 85.68; H, 6.45. Found: C, 85.73; H, 6.81.

4-*p*-Biphenylyl-1,1-diphenyl-1-butanol. Phenylmagnesium bromide[44] was prepared from 39.6 g (0.252 mol) of bromobenzene in 140 ml of anhydrous ether. To this solution was added dropwise with stirring 16.0 g (0.063 mol) of methyl 4-*p*-biphenylylbutanoate in 50 ml of ether. The mixture was decomposed by addition of a saturated solution of ammonium chloride in water and extracted four times with ether. The ethereal extract, after drying over anhydrous $MgSO_4$ and removal of ether, yielded a product which after recrystallization from *n*-heptane amounted to 18.8 g (79% yield based on methyl ester) of white crystals, mp 101-103°. One recrystallization from petroleum ether (bp 30-60°) afforded white needles, mp 103.5-104.2°.

Anal. Calcd for $C_{28}H_{26}O$: C, 88.84; H, 6.92. Found: C, 88.78; H, 6.98.

1-Methoxy-4-*p*-biphenylyl-1,1-diphenylbutane. To 6.99 g (18.5 mmol) of 4-*p*-biphenylyl-1,1-diphenyl-1-butanol in 200 ml of anhydrous methanol was added 0.6 ml of concentrated sulfuric acid. A precipitate rapidly formed and after 20 min of stirring at room temperature was separated by filtration. The crystals were washed with methanol and recrystallized from anhydrous methanol to yield 6.68 g (92%) of white crystals, mp 134-136°. The analytical sample after two additional crystallizations from methanol had mp 137.2-138.0° and nmr (CCl_4) δ 7.23 (19 H, m), 2.94 (3 H, s), 2.57 (2 H, t, J = 7.5 Hz), 2.28 (2 H, t, J = 7.5 Hz), and 1.44 (2 H, quintet, J = 7.5 Hz).

Anal. Calcd for $C_{29}H_{28}O$: C, 88.72; H, 7.20. Found: C, 88.76; H, 7.42.

5-*p*-Biphenylyl-2,2-diphenylpentanoic Acid (**7**). A solution of 6.68 g (17.0 mmol) of 1-methoxy-4-*p*-biphenylyl-1,1-diphenylbutane in 35 ml of tetrahydrofuran (THF) was added dropwise over a period of 30 min to 1.52 g (0.0390 g-atom) of potassium metal stirred vigorously in 250 ml of THF at reflux temperature, according to a general procedure[2f] for alkali metal reactions. Stirring of the deep black-red solution was continued for 1 hr at reflux temperature. The reaction solution was cooled to room temperature and then about three-fourths of the solution was forced onto crushed solid carbon dioxide and to the remainder in the reaction flask was added excess methanol. The usual work-up of the carbonated mixture gave 4.2 g of crude acid and 1.3 g of neutral material. Recrystallization of the acid from glacial acetic acid and then from *n*-hexane-acetic acid gave 2.6 g of white crystals of mp 191.4-191.8° which were identical in melting point, mixture melting point, and nmr spectrum with the acid isolated from carbonation of the reaction mixture from 4-chloro-1-*p*-biphenylyl-1,1-diphenylbutane with potassium metal in boiling THF (see subsequent description).

4-*p*-Biphenylyl-1,1-diphenylbutane (**9**). The methanolic solution, from decomposition of 4-*p*-biphenylyl-1,1-diphenylbutylpotassium with methanol in the previous preparation, yielded 1.9 g of crude hydrocarbon which was combined with the 1.3 g of neutral material obtained from carbonation of the same organopotassium compound. The combined product upon recrystallization from ethanol yielded 2.3 g of crystals of mp 78-82°. Two further recrystallizations from ethanol and one from methanol yielded white crystals of mp 81.5-82.3° and nmr (CCl_4) δ 7.18 (19 H, m), 3.88 (1 H, t, J = 7.5 Hz), 2.65 (2 H, t, J = 7.5 Hz), and 1.86 (4 H, broad m).

Anal. Calcd for $C_{28}H_{26}$: C, 92.76; H, 7.24. Found: C, 92.74; H, 7.14.

This hydrocarbon was identical in melting point, mixture melting point, and in spectral characteristics (ir and nmr) with the hydrocarbon isolated from methanol decomposition of the carbanion from reaction of 4-chloro-1-*p*-biphenylyl-1,1-diphenylbutane with potassium in boiling THF.

General Procedure for Alkali Metal Reactions. All reactions were run in a Morton high-speed stirring apparatus according to the procedure given previously.[2f,4] In particular all reactions with cesium and cesium alloys were conducted in a glove box under an atmosphere of nitrogen to reduce fire hazards. Also for carbonation and protonation of organoalkali products the reaction mixtures were forced under nitrogen pressure through a stainless-steel fine-mesh screen (on one end of the siphon tube) in order to remove as much unreacted alkali metal as possible.

Reactions of 4-Chloro-1-*p*-biphenylyl-1,1-diphenylbutane in Tetrahydrofuran. A. With Potassium. To vigorously stirred, finely divided potassium (0.99 g, 0.0253 g-atom) in 130 ml of THF at reflux temperature was added dropwise, over a period of 10 min, 4.13 g, 0.0104 mol) of 4-chloro-1-*p*-biphenylyl-1,1-diphenylbutane in 30 ml of THF. A red color instantaneously appeared upon addition of the chloride and the color rapidly deepened to black-red. The solution was allowed to cool for 8 min and then forced onto excess solid carbon dioxide. Methanol was added to the residual contents of the flask and the mixture heated at reflux for a few minutes to decompose traces of potassium. Gas-liquid partition chromatography[45] (glpc) at 254° of the methanolysis product gave the following products, listed as area per cent (relative retention time, identity): 6 (0.51), 4 (1.00, *p*-biphenylyldiphenylmethane,[46] **10**), 1.0 (1.54, **8**), 82 (2.12, **9**), 7 (2.78). The carbonation mixture was cautiously treated with water (fire hazard; use nitrogen atmosphere), concentrated *in vacuo* on a steam bath to remove THF, and extracted well with ether. The ethereal extracts were combined and extracted with 1 *N* sodium hydroxide. The ethereal layer, after drying over anhydrous $MgSO_4$, yielded 1.2 g of neutral material. The combined alkaline layers were strongly acidified with hydrochloric acid and extracted with ether. From the ethereal extract, after drying over anhydrous $MgSO_4$ and removal of ether, was isolated 3.4 g of carboxylic acid. Analysis of the neutral material by glpc at 254° gave the products, listed as area per cent (relative retention time, identity): 4 (0.51), 1.5 (1.00, **10**), 4.6 (1.54, **8**), 90 (2.12, **9**). Analysis of a small portion of the isolated carboxylic acid by glpc[45] of its methyl ester (from reaction with diazomethane) at 254° showed the presence of only one ester at a retention time (22.9 min) shorter than that of an authentic sample of methyl 5-*p*-biphenylyl-5,5-diphenylpentanoate (25.0 min). Recrystallization of a 2.0-g portion of the crude acid two times from glacial acetic acid and then from *n*-hexane gave 1.4 g of white crystals of mp 191.5–192.0° and nmr (CCl_4) δ 7.25 (19 H, m), 2.50 (4 H, m), and 1.45 (2 H, m).

Anal. Calcd for $C_{29}H_{26}O_2$: C, 85.68; H, 6.45. Found: C, 85.56; H, 6.71.

This carboxylic acid was identical with the sample of 5-*p*-biphenylyl-2,2-diphenylpentanoic acid (**7**) prepared from 1-methoxy-4-*p*-biphenylyl-1,1-diphenylbutane (see previous description).

In a second run under similar conditions with 1.04 g (0.00261 mol) of 4-chloro-1-*p*-biphenylyl-1,1-diphenylbutane and 0.28 g (0.0071 g-atom) of potassium, the THF solution of the dark red carbanion after cooling to room temperature was decomposed by dropwise addition of 30 ml of methanol with stirring over a period of 5 min. Solvents were removed *in vacuo*, water was added to the residue, and the mixture was extracted well with ether. The ethereal extract, after drying over anhydrous $MgSO_4$, yielded 1.1 g of crude oil. Analysis (area per cent yields) by glpc[45] showed that the product consisted of 0.1% of **10**, 1.4% of **8**, and 98% of **9**. Recrystallization of the crude hydrocarbon once from *n*-heptane and twice from 95% ethanol and subsequent sublimation *in vacuo* (0.3 mm, bath temperature 135°) gave 0.15 g of white solid of mp 80–81°. Further recrystallization raised the mp to 81.2–82.0°. This product was identical with the sample of 4-*p*-biphenylyl-1,1-diphenylbutane (**9**) obtained from 1-methoxy-4-*p*-biphenylyl-1,1-diphenylbutane (see previous description).

B. With Cesium. To vigorously stirred, finely divided cesium (2.21 g, 0.0166 g-atom) in 150 ml of THF at reflux temperature was added dropwise over a period of 2 min 3.00 g (7.57 mmol) of 4-chloro-1-*p*-biphenylyl-1,1-diphenylbutane in 20 ml of THF. Stirring of the black-red solution was continued for 2 more min before the mixture was forced onto solid carbon dioxide. To the residual contents of the flask was added excess methanol; glpc analysis of the methanolysis product showed 2.5% of **8** and 97.5% of **9** (area per cent yields[45]). The usual work-up of the carbonated mixture gave 2.6 g of solid acid and 0.40 g of neutral material. Analysis of the methyl ester of the acid by glpc showed only one peak identical in retention time with that of authentic methyl ester of **7** and different in retention time from the methyl ester of **6**; similar analysis of the neutral material gave 4.4 area % of **8**, 93% of **9**, and 2.5% of an unknown at 0.38 times the retention time of **8** at 257°. A portion of the acid after recrystallization from glacial acetic acid and *n*-hexane consisted of white crystals of mp 190.2–191.2° which were identical in melting point, mixture melting point, and nmr spectrum to authentic **7**.

C. With Cs–K–Na Alloy. A mixture of 10.6 g (0.0795 g-atom) of cesium, 3.63 g (0.0928 g-atom) of potassium, and 0.562 g (0.0244 g-atom) of sodium in 250 ml of THF was stirred vigorously at reflux for 1 hr. After cooling down to −75° in a Dry Ice-acetone bath, the solution was stirred vigorously for 30 min and then a solution of 2.1 g (5.3 mmol) of 4-chloro-1-*p*-biphenylyl-1,1-diphenylbutane in 20 ml of THF was added over a period of 30 sec. Upon addition of the first drops of chloride the solution instantly developed a deep red color. The mixture was stirred for 1 min longer until the solution suddenly developed a deep green color. About one third of the reaction mixture was quickly forced into water (hydrocarbon I) and the remainder was forced onto crushed solid carbon dioxide. Methanol was added to the carbonated mixture while Dry Ice was still present to decompose any Cs–K–Na alloy. The usual work-up gave 0.50 g of neutral product (hydrocarbon II) and 0.94 g of acids. Reaction of a portion of the acids with diazomethane and analysis of the methyl esters by glpc at 260° gave 95.4 area % of **7**, no **8**, and 4.6% of an unknown (likely methyl *p*-biphenylyldiphenylacetate) at 0.49 times the retention time of the methyl ester of **7**. One recrystallization of 0.62 g of the acid from glacial acetic acid gave 0.47 g of white crystals of mp 187–189°; further recrystallization from glacial acetic acid and then pentane gave 0.33 g of crystals of mp 190.0–191.2°, which were identical in melting point, mixture melting point, and nmr spectrum to authentic **7**. Hydrocarbon **I** (0.61 g) on glpc analysis at 260° gave the following products, listed as area per cent (relative retention time, identity): 2 (0.82, unknown 1), 4.4 (1.00, **10**), 2 (1.21, unknown 2), 15 (1.74, unknown 3), 76 (2.21, **9**); hydrocarbon II similarly contained the products 0.7 (0.82, unknown 1), 17 (1.00, **10**), 3 (1.21, unknown 2), 3.4 (1.74, unknown 3), and 76 (2.21, **9**). Treatment of a carbon disulfide solution of hydrocarbon I with 1 g of 5% Pd-C catalyst, removal of carbon disulfide *in vacuo*, heating the residue at 125° for 20 hr under an atmosphere of nitrogen, solution in hot acetone, and filtration to remove catalyst gave a product containing greatly decreased amounts of unknowns 1, 2, and 3. Repetition of this dehydrogenation procedure with fresh catalyst for 20 hr and then again for 32 hr gave a final hydrocarbon mixture which on glpc analysis contained the following products, listed as area per cent (relative retention time, identity): 8.7 (1.00, **10**), 2.8 (1.53, **8**), 3.2 (1.74, unknown **3**), 85 (2.21, **9**). From these results it is concluded that the neutral products from this run with a large excess of Cs–K–Na alloy are complicated by a Birch-like reduction of the aromatic rings (likely the *p*-biphenylyl group).

In a small scale run for nmr spectral measurements, 0.5 ml (0.73 g) of Cs–K–Na alloy, of the same composition as used previously, and 2 ml of THF were added to a small vial in a glove box filled with nitrogen. 4-Chloro-1-*p*-biphenylyl-1,1-diphenylbutane (0.192 g, 0.485 mmol) was added in one portion and then the vial was tightly stoppered with a rubber septum. The solution was cooled to −75° and then the solution was stirred for 10 min with a magnetic stirrer equipped with a glass-enclosed magnet. The color of the solution turned deep red and finally black. To the solution was added through the septum with the aid of a hypodermic syringe 3 ml of mercury (to remove excess alkali metal and radical anions) over a period of 20 min with continued stirring and cooling with a Dry Ice-acetone bath. The solution was allowed to warm with stirring up to room temperature and slowly turned back to a deep red color. The amalgam was allowed to settle and some of the solution was added to a nitrogen-filled nmr tube which was then tightly sealed. Another portion of the dark red solution was decomposed with ethanol; glpc analysis[45] of the ethanolysate revealed the presence of 87 area % of rearranged hydrocarbon **9**, 8% of **8**, and 2% of **10**. The red solution had nmr absorption (at 40°) at δ 7.17 (11.7 H, m), 6.80 (7.8 H, m), and 5.84 (2.0 H, t, J = 6.5 Hz). The complex multiplet centered at δ 6.80 seems to consist of a doublet at δ 6.93 (4 H, J = 9 Hz) overlapped by a triplet at δ 6.70 (4 H, J = 7.5 Hz). These nmr absorptions were measured relative to the peaks of solvent THF which were subsequently measured relative to internal TMS. By taking the hydrogens at δ 6.70 as standard of reference and on the basis that this triplet must correspond to the two para hydrogens of the diphenylmethyl portion of anion **5** while the absorption near δ 7.17 corresponds to the nine hydrogens of the *p*-biphenylyl group of **5** as well as the aromatic protons of hydrocarbons such as **8** and **10**, it may be estimated from the nmr spectrum that the yield of 4-*p*-biphenylyl-1,1-diphenylbutyl anion **5** is 87%, in reasonable agreement with expectations based on the glpc analysis of the products of ethanolysis.

D. With Potassium in Presence of Proton Donors. These reactions (see Table I) were run in the usual Morton high-speed stirring apparatus in 120–150 ml of THF. The THF was vigorously stirred at reflux with the potassium metal for 30–60 min (to remove any reactive proton donors from the solvent) and then a solution of the 4-chloro-1-*p*-biphenylyl-1,1-diphenylbutane and the proton source in 15–30 ml of THF was added rapidly at one time without stirring. Rapid stirring near reflux temperature was then resumed until reaction appeared to be complete (0.5–15 min). Before analysis the analytical samples were always decomposed by addition of excess methanol. Only in the case of *n*-butylamine was the reaction mixture a deep red color (as expected for the organopotassium compound **5**) before addition of methanol.

For the reaction of 4-chloro-1-*p*-biphenylyl-1,1-diphenylbutane (1.01 g, 2.54 mmol) in the presence of 14.2 mmol of *tert*-butyl alcohol, since 5.94 mg-atoms of potassium gave only some 17% reaction of the chloride according to glpc analysis of a 5-ml aliquot, the reaction mixture was treated with three separate additional increments of potassium and *tert*-butyl alcohol with vigorous stirring at reflux for some 5 min after each addition. Excess methanol was added to the reaction flask and the crude product was isolated in the usual fashion. Since it still contained some unreacted chloride (*ca.* 15%), the entire reduction procedure in THF was repeated with four incremental additions of potassium and *tert*-butyl alcohol, essentially with the quantities of reagents given in Table I for the first reduction procedure. The usual work-up gave a viscous oil which, according to glpc analysis[45] at 262°, contained the following products, listed as area per cent (relative retention time, identity): 90 (0.79, 1-*p*-cyclohexylphenyl-1,1-diphenylbutane), 3.4 (1.00, **8**), 5.8 (1.09, 1-*p*-(1,4-dihydrophenyl)phenyl-1,1-diphenylbutane), 1.0 (1.37, unknown). To a carbon disulfide solution of the crude reaction product was added 1.1 g of 5% Pd–C catalyst, the solvent was removed *in vacuo*, and the mixture was heated *in vacuo* for 5 hr on a steam bath. The product was dissolved in THF and the solution was filtered to remove catalyst. Since glpc analysis indicated that dehydrogenation had started but was incomplete, the dehydrogenation was repeated with 1.4 g of 5% Pd–C catalyst at 135° for 5 hr under a nitrogen atmosphere. After removal of catalyst, analysis of the product by glpc gave a composition (retention time) of 90% 1-*p*-cyclohexylphenyl-1,1-diphenylbutane (0.79), 6.8% **8** (1.00), 2.4% 1-*p*-(1,4-dihydrophenyl)phenyl-1,1-diphenylbutane (1.09), and 0.5% of the unknown (1.37). This dehydrogenation process is interpreted to mean that the major product from the reduction with potassium was a compound not readily dehydrogenated. This result is in agreement with final assignment of the structure of 1-*p*-cyclohexylphenyl-1,1-diphenylbutane to this compound. In contrast the product of relative retention time of 1.09 is evidently dehydrogenated to 1-*p*-biphenylyl-1,1-diphenylbutane (**8**) and, therefore, in view of the structural assignment (see below) of the major product of the reaction with potassium and in light of the structure[7c] of the major hydrocarbon from alkali metal reduction of biphenyl, we assign this hydrocarbon the tentative structure of 1-*p*-(1,4-dihydrophenyl)phenyl-1,1-diphenylbutane. The crude reaction product was distilled *in vacuo* at a bath temperature of 130° and 0.264 g of the oily yellow product was chromatographed on a 1.5 × 15 cm column packed with alumina with elution by cyclohexane. The first fraction contained 0.237 g of colorless viscous material which after distillation at 20 μ (bath 135°) gave 0.12 g of white crystals. After recrystallization from 95% ethanol the product had mp 100.6–102.0°: λ_{max} (EtOH) 260 nm (ϵ 952); nmr (CCl_4) δ 7.10 (14.0 H, m), 2.48 (2.1 H, t, J = 7 Hz), 2.2 (0.9 H, broad m), 2.0–1.0 (12.2 H, complex m), 0.91 (2.9 H, *ca.* t) (ratio of aromatic to all other hydrogens, 14.0:18.1); mass spectrum *m/e* (rel intensity, assignment), 368 (2.5, $C_{28}H_{32}^+$), 325 (100, $C_{25}H_{25}^+$), 167 (24, $C_{13}H_{11}^+$), 165 (30, $C_{13}H_9^+$), 43 (36, $C_3H_7^+$), 41 (23, $C_3H_5^+$). The structure of 1-*p*-cyclohexylphenyl-1,1-diphenylbutane is accordingly assigned this compound.

Anal. Calcd for $C_{28}H_{32}$: C, 91.24; H, 8.76. Found: C, 91.02; H, 8.99.

Reactions of 4-Chloro-1-*p*-biphenylyl-1,1-diphenylbutane in Dioxane. A. With Sodium. Purified dioxane (150 ml) was stirred vigorously for 1 hour at reflux with 0.442 g (19.2 mg-atoms) of sodium and then 5% of a solution of 4-chloro-1-*p*-biphenylyl-1,1-diphenylbutane (3.0 g, 7.6 mmol) in 30 ml of dioxane was added. Since no appreciable color change was observed after 20 min of vigorous stirring, 0.23 g (1.6 mmol) of methyl iodide and 0.21 g (0.72 mmol) of 2-chloro-1,1,1-triphenylethane[2a] in dioxane were added. The reaction mixture developed the violet color of Wurtz sodium halide but no red color attributable to a carbanion was observed throughout the reaction. The remainder of the chloride solution was added dropwise over a period of 20 min, the mixture was stirred vigorously at reflux for an additional 30 min, and then the reaction mixture was forced onto solid carbon dioxide. The usual work-up gave 3.3 g of neutral material but no carboxylic acid. Analysis[45] of the neutral material at 254° by glpc revealed the presence of 96 area % of **8**, no **9**, and 4% unreacted chloride.

The first run was repeated but with stirring with 2.77 g (0.120 g-atom) of sodium for 1 hr at reflux before addition of 3.34 g (0.0361 mol) of *n*-butyl chloride in 20 ml of dioxane over a period of 15 min. Addition of 1.83 g (0.00461 mol) of 4-chloro-1-*p*-biphenylyl-1,1-diphenylbutane in 15 ml of dioxane, and completion of the reaction as previously, gave 1.80 g of neutral material and no carboxylic acids. Analysis by glpc of this neutral material and the product from treatment of the residual contents of the reaction flask with ethanol gave the same results (see Table I). Fractional crystallization of the neutral material from *n*-heptane gave 1.1 g of crystals of mp 88–93°; two more recrystallizations from heptane and one recrystallization from ethanol gave 0.24 g of crystals, mp 94.2–95.0°, which were identical in melting point, mixture melting point, and nmr spectrum with the sample of **8** prepared from *p*-biphenylyldiphenylmethylsodium and 1-bromopropane.

In a final run, 400 ml of purified dioxane was stirred for 1 hr at reflux temperature with 3 g of potassium under a nitrogen atmosphere in the usual Morton high-speed stirring apparatus. This further purified dioxane (250 ml) was then directly distilled into a second apparatus containing 2.28 g (0.099 g-atom) of sodium. The mixture was stirred vigorously at reflux temperature for 1 hr and then 3.29 g (0.0356 mol) of *n*-butyl chloride in 20 ml of dioxane (further purified as described above from potassium) was added dropwise over a period of 15 min. Next 2.10 g (0.0053 mol) of 4-chloro-1-*p*-biphenylyl-1,1-diphenylbutane in 20 ml of dioxane (further purified as described from potassium) was added over a period of 15 min with stirring at reflux continued for an additional hour before addition of a 10-ml aliquot to excess methanol and carbonation of the remainder. The usual work-up gave 1.8 g of neutral material from carbonation and negligible acids (~0.03 g), none of which were volatile as methyl esters under usual glpc conditions. The neutral materials from carbonation and methanolysis were identical within experimental error according to analysis by glpc (see Table I).

B. With Potassium. Purified dioxane (150 ml) was vigorously stirred with potassium (4.79 g, 0.123 g-atom) at reflux temperature for 30 min. A solution of 2.87 g (0.031 mol) of *n*-butyl chloride in 20 ml of dioxane was added dropwise over a period of 15 min. Next a solution of 2.02 g (0.00509 mol) of 4-chloro-1-*p*-biphenylyl-1,1-diphenylbutane in 20 ml of dioxane was added dropwise to the vigorously stirred solution over a period of 20 min. About half way through this addition a reddish brown color appeared in the solution and the color deepened to black-red at the end of the addition. The reaction mixture was stirred an additional 1 min before cooling to room temperature and carbonation. The usual work-up gave 1.45 g of neutral product and 0.57 g of crude acids. Analysis[45] of the neutral product by glpc at 300° gave the following products listed as area per cent yield (relative retention time, identity): 1 (0.45), 3 (0.52), 3 (0.71), 2 (0.87), 1.6 (1.00, **10**), 77 (1.94, **9**), and 11 (2.90), with no hydrocarbon **8** found. A quantitative glpc analysis revealed that the absolute yield of **9** was, in fact, 75% by weight of the crude neutral product. The neutral product obtained from ethanolysis of a small portion of the original reaction mixture had the same area ratio of the two major components as in the product from carbonation. Analysis of the acidic products, determined as methyl esters by glpc at 300°, gave the products, listed as previously, 5 (0.73), 6 (0.92), 8 (1.00, **7**), 39 (1.29), 10 (1.63), as well as five compounds of shorter retention time than those listed. Since the absolute yield of **7** was only 8.7 mg or 1.5% by weight of the crude acids, the crude acid obviously consisted of a complex mixture of cleavage products as well as materials of higher molecular weight than **7**.

C. With Cesium. Purified dioxane (250 ml per run) was distilled from potassium. In the run at 40° upon addition of cesium metal to the dioxane, gas evolution was observed and after stirring for 30 sec the solution was quite cloudy (much cleavage of dioxane by cesium). Upon addition of 4-chloro-1-*p*-biphenylyl-1,1-diphenylbutane (all in one portion in 20 ml of dioxane) the solution developed an instantaneous red color which rapidly disappeared. The solution was stirred for 30 sec before carbonation and treatment of the residual contents of the flask with ethanol. The usual work-up gave only neutral materials and no carboxylic acids; the products of carbonation were identical with those of ethanolysis (see Table I). The nmr spectrum of the crude product was that expected for hydrocarbon **9** with minor impurities.

A second run with 0.974 g (2.46 mmol) of 4-chloro-1-*p*-biphenylyl-1,1-diphenylbutane was initiated at a lower temperature in order to decrease the amount of reaction of cesium (5.1 g) with dioxane; however, after addition of the chloride the temperature rose to 37° within 1 min and developed a brown-pink color. After stirring for 5 min, a 5-ml aliquot was decomposed with methanol (see Table I). An additional 5.2 g (39 mg-atoms) of cesium was added and the solution was stirred vigorously for 10 min (deep red color) before carbonation. The usual work-up gave 0.62 g of neutral material and 0.27 g of acids. A quantitative glpc analysis of the methyl esters of the acid fraction gave only a 0.13% yield (based on starting chloride) of **7** and comparably small amounts of four unknown acids which had volatile methyl esters at 264°. Analysis of the neutral fraction by glpc under the same conditions gave the following products, listed as area per cent yield (relative retention time, identity): 3 (1.00, A), 32 (1.3, B), 1.2 (3.0, C), 54 (4.3, D), 9.7 (5.3, **9**). These products after separation by glpc were analyzed by mass spectrometry. Compound A had mass spectrum *m/e* (rel intensity, assignment) 250 (23, $C_{19}H_{22}^+$), 249 (100, $C_{19}H_{21}^+$), 167 (22, $C_{13}H_{11}^+$), 165 (25, $C_{13}H_9^+$), 91 (44, $C_7H_7^+$), 83 (8, $C_6H_{11}^+$), and 81 (8, $C_6H_9^+$); in accord with this spectrum and other general evidence this compound is assigned the tentative structure of *p*-cyclohexyldiphenylmethane. Compound B (12% absolute yield) had mass spectrum 292 (38, $C_{22}H_{28}^+$), 210 (18, $C_{16}H_{18}^+$), 201 (3, $C_{15}H_{21}^+$), 173 (31, $C_{13}H_{17}^+$), 159 (40, $C_{12}H_{15}^+$), 133 (6, $C_{10}H_{13}^+$), 131 (56, $C_{10}H_{11}^+$), 117 (41, $C_9H_9^+$), and 91 (100, $C_7H_7^+$); the exact mass was 292.2204 (calcd for $C_{22}H_{28}$: 292.2191); hence compound B is assigned the tentative structure of 4-*p*-cyclohexylphenyl-1-phenylbutane. Compound C (0.3% absolute yield) had a mass spectrum identical with that of 1-*p*-cyclohexylphenyl-1,1-diphenylbutane isolated from the reaction of 4-chloro-1-*p*-biphenylyl-1,1-diphenylbutane with potassium in THF containing *tert*-butyl alcohol. Compound D (16% absolute yield) had mass spectrum, 368 (36, $C_{28}H_{32}^+$), 201 (3, $C_{15}H_{21}^+$), 193 (16, $C_{15}H_{13}^+$), 186 (14, $C_{14}H_{18}^+$), 180 (19, $C_{14}H_{12}^+$), 173 (9, $C_{13}H_{17}^+$), 171 (22, $C_{13}H_{15}^+$), 168 (51, $C_{13}H_{12}^+$), 167 (100, $C_{13}H_{11}^+$), 165 (28, $C_{13}H_9^+$), 117 (20, $C_9H_9^+$), and 91 (42, $C_7H_7^+$); the exact mass was 368.2506 (calcd for $C_{28}H_{32}$: 368.2504). Compound D is accordingly assigned the tentative structure of 4-*p*-cyclohexylphenyl-1,1-diphenylbutane.

Reactions of 4-Chloro-1-*p*-biphenylyl-1,1-diphenylbutane. A. With Lithium. In the usual apparatus was placed 250 ml of THF and 1.87 g (0.269 g-atom) of lithium wire cut into small pieces. Methyl iodide (0.1 ml) was added with vigorous stirring at room temperature and then the reaction mixture was cooled to −70° before dropwise addition of a solution of 6.76 g (0.0170 mol) of 4-chloro-1-*p*-biphenylyl-1,1-diphenylbutane in 20 ml of THF over a period of 30 min. After stirring for 2 more hr the deep red solution was forced onto solid carbon dioxide. The usual work-up gave 2.0 g of neutral material (glpc,[45] area per cent yields: 2% **10**, 77% **8**, 10% **9**, 8% starting RCl) and 4.8 g of crude acids (glpc analysis at 262°, area per cent yields (relative retention time, identity): 21 (1.00, **7**), 79 (1.08, **6**)).

In a second run which was conducted similarly at −70° with 1.86 g of lithium and 7.27 g (0.0184 mol) of chloride, the deep red solution after stirring for 2 hours following completion of the addition of chloride turned almost black over a period of 5 min. The reaction solution was then forced through a fine stainless steel screen on the end of a siphon tube (to remove excess lithium) into a nitrogen-filled flask for storage at 0° (ice bath). Hydrolysis of the residual reaction mixture in the flask gave a product which on glpc analysis at 262° gave area per cent yields (relative retention time, identity) of 1 (1.00, **10**), 3 (1.21, **8** + 6 H), 66 (1.49 **8**), 21 (2.08, **9**), 4 (2.44), and 5 (2.71, unreacted chloride = RCl). The organolithium reagent after storage at 0° for 4 hr was carbonated and the flask residue was hydrolyzed. The latter hydrolysate on glpc analysis gave products, listed as previously, 1 (1.00, **10**), 54 (1.49, **8**), 25 (2.08, **9**), 8 (2.44), 7 (2.71, RCl), 5 (3.05). The usual work-up of the carbonated mixture gave 1.2 g of crude acids and 4.3 g of neutral product. The acids on glpc as methyl esters at 262° contained products, listed as previously, 83 (1.00, **7**) and 17 (1.08, **6**), while the neutral product similarly contained 0.5 (1.00, **10**), 61 (1.49, **8**), 14 (2.08, **9**), 9.5 (2.44), 9.5 (2.71, RCl), and 6 (3.05).

A repetition of the last run yielded at −75° an initial organolithium reagent which upon carbonation of an aliquot gave a 22:78 ratio by weight of neutral material to acids, the acids consisting of a 78:22 ratio of **6** to **7**. Hydrolysis of another aliquot of the organolithium reagent gave a mixture of hydrocarbons which contained 22 area % of rearranged hydrocarbon **9**. After storage of the organolithium reagent for 8 hr at −11°, carbonation gave a 93:7 ratio by weight of neutral material to acids. The neutral material contained 65 and 19 area % **8** and **9**, respectively, while the acids consisted of a 26:74 ratio of **6** to **7**. Hydrolysis of an aliquot of the lithium reagent which had been stored at −11° gave a mixture of hydrocarbons containing 24 area % of **9** and 50% of **8**.

B. With Lithium Followed by Potassium *tert*-Butoxide. Two of the usual Morton high-speed stirring apparatuses were set up side by side such that the contents of one flask could be forced under pressure of nitrogen through a tube into the second flask. To one flask were added 300 ml of THF, 9.53 g (0.244 g-atom) of potassium, and then, after the solution came to reflux temperature, 8.9 g (0.12 mol) of *tert*-butyl alcohol dropwise over a period of 30 min with vigorous stirring under an atmosphere of nitrogen. The solution was kept at reflux with vigorous stirring for an additional 90 min before cooling, finally to −75°. To the other flask were added 250 ml of THF, 1.54 g (0.223 g-atom) of lithium, and 0.10 ml (1.6 mmol) of methyl iodide; the mixture was stirred vigorously for 10 min at room temperature before cooling to −75°. A solution of 0.943 g (0.0102 mol) of *n*-butyl chloride in 10 ml of THF was added with stirring to the cold solution over a period of 20 min. This was followed immediately by the addition of 4-chloro-1-*p*-biphenylyl-1,1-diphenylbutane (1.00 g, 2.53 mmol) in 15 ml of THF over a period of 20 min. When after 90 min of additional stirring at −75° the pink solution developed a black coloration, stirring was stopped and a 5-ml aliquot was decomposed with methanol (hydrocarbon A). To the remainder of the reaction mixture at −75° was added *ca.* 150 ml of the cold potassium *tert*-butoxide solution (freed from the coagulated potassium metal by passage through a fine-meshed stainless-steel screen on the end of the transfer tube). The solution instantly developed a dark pink color. The mixture was stirred for 0.5 min and then was kept at −75° for 10 min before methanolysis of a 5-ml aliquot (hydrocarbon B) and carbonation of the remainder. The carbonated mixture was worked up in the manner previously given[4] for carbonated organolithium compounds to give 0.34 g of crude neutral material (hydrocarbon C) and 0.67 g of acid. Analysis by glpc[45] at 266° indicated that hydrocarbon A had 52 area % of **8** and 46% of **9** while hydrocarbon B had 24% of **8** and 75% of **9** as well as 1–2% each of an unknown at 2.12 times the retention time of **8**. Quantitative glpc analysis of hydrocarbon C indicated the presence of 0.13 g (14%) of **8**, 0.07 g (8%) of **9**, and 7 area % of the same unknown hydrocarbon. Analysis of the acid fraction, by quantitative glpc as methyl esters at 258°, indicated the presence of 0.61 g (58% yield based on starting chloride) of **7** and no **6**, and the remainder (~0.06 g) consisted of approximately equal amounts of four unknowns at 0.65, 0.72, 1.19, and 1.62 times the retention time of **7**. A repetition of this run but with reaction times of 1, 2, and 3 hr at −75° after addition of potassium *tert*-butoxide gave on methanolysis three identical mixtures of hydrocarbons, essentially of the composition of hydrocarbon B, as expected if rearrangement is complete in less than 10 min at −75°.

In another run 0.976 g (0.141 g-atom) of lithium in 250 ml of THF was similarly treated with 0.03 ml of methyl iodide at room temperature and then 0.44 g (4.8 mmol) of *n*-butyl chloride and 3.00 g (7.58 mmole) of 4-chloro-1-*p*-biphenylyl-1,1-diphenylbutane at −75°. A 10-ml aliquot was decomposed with methanol (hydrocarbon A) and to the remainder was added *ca.* 150 ml of potassium *tert*-butoxide (0.044 mol) in THF at −75°. The mixture was stirred for 0.5 min and allowed to stand for 5 min at −75° before methanolysis of a 10-ml aliquot (hydrocarbon B) and carbonation of the remainder. From the carbonation there was isolated 1.4 g of neutral material (hydrocarbon C) and 1.58 g of acid. The usual glpc analysis gave for hydrocarbon A 61 area % of **8** and 36% of **9** and for hydrocarbon B 29 area % of **8** and 63% of **9**. Quantitative glpc analysis of hydrocarbon C gave 0.64 g (24% yield) of **8**, 0.19 g (7% yield) of **9**, and 0.02 g (0.7%) of 1-*p*-(1,4-dihydrophenyl)phenyl-1,1-diphenylbutane; similar analysis of the acid gave 1.51 g (49% yield) of **7**, no **6**, and traces of two unknown acids of 0.45 and 0.49 times the retention time of **7**. The nmr spectrum of the acid was essentially the same as that of an authentic sample of 5-*p*-biphenylyl-2,2-diphenylpentanoic acid.

C. With Lithium Biphenylide. To 300 ml of THF was added 0.701 g (0.101 g-atom) of lithium and 1.0 ml (16 mmol) of methyl iodide. The solution was stirred vigorously at room temperature for 10 min and then 7.7 g (0.050 mol) of biphenyl was added. Upon stirring the solution rapidly developed a deep blue color and was thereupon cooled to −75° with stirring continued for 4 hr. The cold solution was then siphoned through a fine stainless steel screen (to remove excess lithium metal) into an adjacent Morton flask equipped with a high speed stirrer. Double Gilman[47] titration indicated that the solution was 0.050 *M* in lithium biphenylide or that the remaining solution contained some 12 mmol of reagent. To the well-stirred solution at −75° was added dropwise first 0.219 g (2.37 mmol) of *n*-butyl chloride in 10 ml of THF (to scavage any impurities present) and then, over a period of 5 min, 0.956 g (2.41 mmol) of 4-chloro-1-*p*-biphenylyl-1,1-diphenylbutane in 20 ml of THF. Upon addition of the latter chloride, the solution gradually changed to a green-blue color and, 1 min after completion of the addition, to a pink color. The reaction mixture was carbonated and the small residue in the flask decomposed with methanol. The methanolysis product upon glpc analysis contained area per cent yields as follows: 90% of **8**, 8.1% of **9**, and 2% of unreacted chloride. The carbonated product afforded 0.84 g of crude acids and, according to quantitative glpc analysis, 0.05 g of volatile neutral products in the recovered biphenyl. The acids on quantitative glpc analysis (as methyl esters) contained 63% yield (based on starting chloride) of **6** and 5.1% of **7** while the neutral product similarly consisted of 3% yield of **8**, 0.13% of **9**, 0.08% of **10**, and 2% of unreacted chloride.

In a similar reaction of 1050 ml of 0.016 *M* lithium biphenylide with 2.6 mmol of *n*-butyl chloride and then 2.5 mmol of 4-chloro-1-*p*-biphenylyl-1,1-diphenylbutane, the product of methanolysis contained by glpc analysis area per cent yields: 4% **10**, 85% **8**, and 12% **9**. The product of carbonation, however, contained only some 8% yield of volatile acids, presumably because of experimental difficulties in working with such a dilute solution of organolithium compounds.

In a similar reaction of 240 ml of 0.26 *M* lithium biphenylide with 2.4 mmol of *n*-butyl chloride and then 2.5 mmol of 4-chloro-1-*p*-biphenylyl-1,1-diphenylbutane, the product of methanolysis contained, according to analysis by glpc, the area per cent yields: 6% **10**, 92% **8**, 2.0% **9**. The product of carbonation according to quantitative glpc analysis (yields based upon the starting chloride) contained, in the neutral product, 13% of **10**, 26% of **8**, and 1.1% of **9** and, in the acidic product, 39% of **6** and 1.0% of **7**.

Reaction of Neophyl Chloride with Lithium Biphenylide. To 300 ml of THF was added 1.23 g (0.177 g-atom) of finely cut lithium and 1.0 ml (16 mmol) of methyl iodide. The solution was stirred vigorously for 5 min at room temperature and then 26.3 g (0.171 mol) of biphenyl was added. After 5 min of additional stirring the deep blue solution was cooled to −75° with vigorous stirring continued for 4 hr. A solution of 1-chloro-2-methyl-2-phenylpropane (5.61 g, 33.3 mmol) in 20 ml of THF was added dropwise to the well-stirred mixture over a period of 80 min at −75°. After 15 more min of stirring the green mixture was forced onto crushed solid carbon dioxide. The usual work-up gave 4.5 g of crude acid. Analysis of the neutral and acidic product by glpc on a 6 ft × 0.25 in. column packed with 10% Apiezon L on 60–80 mesh Chromosorb G (acid washed and treated with dimethyldichlorosilane) at 148° gave absolute yields of 0.21 g (4.5%) of *tert*-butylbenzene, 0.93 g (17% recovery) of unreacted chloride, 0.055 g (0.9%) of 2,2-dimethyl-3-phenylpropanoic acid, and 4.5 g (76%) of 3-methyl-3-phenylbutanoic acid.

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References and Notes

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Photosensitized Decomposition of Methyl Diazoacetate. Triplet Carbomethoxycarbene *via* Energy Transfer

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Abstract: The mechanisms involved in the photosensitized decomposition of methyl diazoacetate (**1**) were studied by examining the effect of **1** on the CIDNP phenomena observed during the ultraviolet irradiation of benzaldehyde (**2**) and benzoin (**3**) in cyclohexane-benzene solutions. The CIDNP spectra generated by photolysis of **3** were not changed significantly by the addition of **1**. In contrast, the spectra observed during irradiation of **2** were suppressed by the addition of **1** and replaced by CIDNP signals of products formed by reaction of **1** with **2** or with cyclohexane. These results exclude a chemical sensitization mechanism and therefore support an alternative mechanism, energy transfer from triplet **2** to **1** leading to triplet carbomethoxycarbene.

The photolysis of diazo compounds and diazirines is generally assumed to produce divalent-carbon intermediates in the singlet state. If the reaction rates of these intermediates are faster than the rates of intersystem crossing (3), as for example in the case of methylene or carbomethoxycarbene, the characteristic reactions of singlet carbenes are observed: insertion into carbon–hydrogen bonds and stereospecific addition to olefins. For other carbenes such as diphenylmethylene, the rate of intersystem crossing is faster than the singlet reaction rates so that reactions typical for triplets are observed: abstraction of hydrogen atoms and nonstereospecific addition to olefins.[1]

$$\mathrm{RR'C{=}N_2\ (S_0)} \xrightarrow{h\nu} \mathrm{RR'C{=}N_2\ (S_1)} \qquad (1)$$

$$\mathrm{RR'C{=}N_2\ (S_1)} \longrightarrow \mathrm{RR'C\colon (S_1) + N_2} \qquad (2)$$

$$\mathrm{RR'C\colon (S_1)} \xrightarrow{\mathrm{isc}} \mathrm{RR'C\colon (T)} \qquad (3)$$

In cases where the singlet carbenes react sufficiently fast to prevent intersystem crossing, two techniques have been developed to observe the reactions of the corresponding triplet states. One method is based on the use of inert diluents such as hexafluorobenzene in order to statistically delay the encounter of the reactive intermediate with the substrate.[2] The second technique circumvents the formation of the singlet carbene by photosensitized decomposition[3] of the precursors, *i.e.*, by exciting the triplet state of the diazo compound *via* energy transfer (eq 6). Both methods have been employed with apparent success in studying addition reactions of various methylenes.

Mechanisms involving energy transfer and triplet carbenes have also been invoked to explain the abstraction-recombination products (eq 8 and 9) observed during the photosensitized decomposition of diazo compounds in the presence of hydrogen donors.[4] However, this assignment has not been generally accepted because an alternative

$$\mathrm{sens\ (S_0)} \xrightarrow{h\nu} \mathrm{sens\ (S_1)} \qquad (4)$$

$$\mathrm{sens\ (S_1)} \xrightarrow{\mathrm{isc}} \mathrm{sens\ (T_1)} \qquad (5)$$

$$\mathrm{sens\ (T_1) + RR'C{=}N_2\ (S_0)} \longrightarrow \mathrm{sens\ (S_0) + RR'C{=}N_2\ (T_1)} \qquad (6)$$

$$\mathrm{RR'C{=}N_2\ (T_1)} \longrightarrow \mathrm{RR'C\colon (T) + N_2} \qquad (7)$$

$$\mathrm{SH + RR'C\colon (T)} \longrightarrow \mathrm{RR'\dot{C}H + \dot{S}} \qquad (8)$$

$$\mathrm{RR'\dot{C}H + \dot{S}} \longrightarrow \mathrm{RR'CHS} \qquad (9)$$

reaction sequence amounting to chemical sensitization[5] was not excluded. In this sequence, the sensitizer initiates the formation of products by hydrogen abstraction from the substrate (eq 10); the resulting radicals induce the decomposition of the diazo compound by transfer of a hydrogen atom (eq 11) or by radical addition followed by loss of N_2 (eq 12). Products are formed by disproportionation (eq 13) or by chain transfer steps (eq 14).

$$\mathrm{sens\ (T_1) + SH} \longrightarrow \mathrm{\dot{s}ens\ H + \dot{S}} \qquad (10)$$

$$\mathrm{\dot{s}ens\ H + RR'C{=}N_2\ (S_0)} \longrightarrow \mathrm{sens + RR'\dot{C}H + N_2} \qquad (11)$$

$$\mathrm{\dot{S} + RR'C{=}N_2\ (S_0)} \longrightarrow \mathrm{RR'\dot{C}S + N_2} \qquad (12)$$

$$\mathrm{RR'\dot{C}S + \dot{s}ens\ H} \longrightarrow \mathrm{RR'CHS + sens} \qquad (13)$$

$$\mathrm{RR'\dot{C}S + SH} \longrightarrow \mathrm{RR'CHS + S\cdot} \qquad (14)$$

In an attempt to differentiate between the energy-transfer mechanism and the radical-induced decomposition route, we have studied the effect of methyl diazoacetate (**1**) on the photoreactions of benzaldehyde (**2**) and benzoin (**3**). These reactions were studied by applying the chemically in-