cell compartment. All measurements were made in the same set of 1-cm quartz cells. Samples were thermostated at least 15 min before recording the spectra. Near-infrared spectra were recorded on a Perkin-Elmer Model 125 spectrophotometer at ca. 40 °C. Cells with NaCl windows (optical path length of 10 mm) were used. All spectral measurements were performed at least in duplicate.

Acknowledgment. We thank Mr. J. Ebels for carrying out the VPO measurements.

Registry No. 1, 80243-88-5; picric acid, 88-89-1.

Carbanions. 21. Reactions of 2- and 3-*p*-Biphenylylalkyl Chlorides with Alkali Metals. Preparation of Labile Spiro Anions[1,2]

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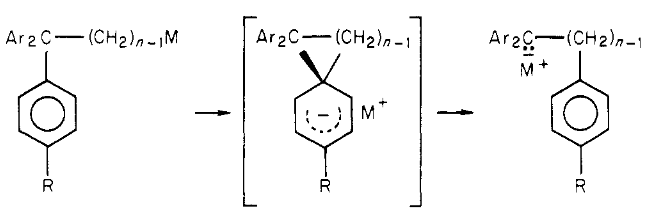
The present work was undertaken to see if (3-*p*-biphenylylpropyl)- and (2-*p*-biphenylethyl)cesium cyclize like (4-*p*-biphenylbutyl)cesium to stable spiro anions. Reaction of 1-*p*-biphenylyl-3-chloropropane (**5**) with Cs–K–Na alloy in THF at –75 °C gave, under the optimum conditions found, 36% of 7-phenylspiro[3.5]nona-6,5-dien-5-yl anion (**8**) besides 3-*p*-biphenylylpropyl (**7**), 1-*p*-biphenylylpropyl (**9**), and *p*-biphenylylmethyl (**10**) anions, according to the products of carbonation. The spiro anion **8** (Cs^+ as the counterion) has a half-life of about 13 min at –75 °C. In contrast, **5** reacts with lithium to give predominantly (3-*p*-biphenylylpropyl)lithium. Reaction of 1-*p*-biphenylyl-2-chloroethane with Cs–K–Na alloy gave no appreciable spiro anion under conditions which were successful with **5**. In the reaction of 1-*p*-biphenylyl-2-chloro-2-methylpropane (**28**) with Cs–K–Na alloy the α-*gem*-dimethyl group accelerates [1,2] migration of the *p*-biphenylyl group to give products similar to those from 2-*p*-biphenylyl-1-chloro-2-methylpropane (**24**); however, the expected intermediate spiro anion **26** was undetectable by the carbonation technique. With both α- and β-*gem*-dimethyl groups, 2-*p*-biphenylyl-3-chloro-2,3-dimethylbutane (**41**) reacts with Cs–K–Na alloy to give 1,1,2,2-tetramethyl-6-phenylspiro[2.5]octa-5,7-dien-4-yl anion (**43**) and 2-*p*-biphenylyl-1,1,2-trimethylpropyl anion (**42**) in about a 2:1 ratio according to the results of carbonation. The open anion **42** and the spiro anion **43** appear to be in mobile equilibrium (Cs^+ as the counterion) with half-lives of about 22 min in THF at –75 °C. With lithium as the counterion, only the open product (2-*p*-biphenylyl-1,1,2-trimethylpropyl)lithium (**50**) was detectable by carbonation.

Spiro anions **1** have been suggested as intermediates or transition states in [1,*n*] sigmatropic migrations of aryl groups in organoalkli metal compounds.[3] The preparation of the stable spiro anion **2a** by reaction of 4-chloro-1-*p*-biphenylylbutane with alkali metals[4] lends support to the interpretation of spiro anions as intermediates as does also the preparation[5] of the nitrogen analogue **2b**. Yet reaction of spiro[2.5]octa-4,7-diene with potassium amide in liquid ammonia at –65 °C or with *n*-butyllithium in tetrahydrofuran–hexane at room temperature gave no observable spiro anion **3a** but only products in which the cyclopropane ring was open. The related species[6a] **4** was, however, stable in liquid ammonia even at –30 °C. These results were explained on the basis that the product from cyclopropyl ring opening of **3a** contains an aromatic benzene ring and is therefore readily formed whereas that from similar ring opening of **4** contains a nonaromatic cyclooctatetraene ring. Attempts to prepare the nitrogen analogue **3b** were similarly unsuccessful and gave only the product of cyclopropyl ring opening, the [2-(4-pyridyl)ethyl]magnesium reagent,[5b] as did similar attempts to prepare the *gem*-dimethyl analogue[5c] **3c**. The present work was undertaken to probe the question as to what anions, containing only carbon and hydrogen, related in structure to **1** and **3a** may be stable species.



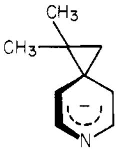
1

2a

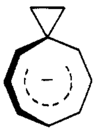
2b

3a

3b



3c



4

Results and Discussion

Reactions of 1-*p*-Biphenylyl-3-chloropropane (5) with Alkali Metals. In view of the successful preparation of the spiro anion **2a**, the preparation of the lower homologue **8** by reaction of 1-*p*-biphenylyl-3-chloropropane (**5**) with Cs–K–Na alloy was studied (see Scheme I) with the results reported in Table I. For reactions run for a few minutes in tetrahydrofuran (THF) at –75 °C and then carbonated, the acidic products which were volatile as

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[1] Based upon the Ph.D. Thesis of P.-C. L., Georgia Institute of Technology, Sept 1977, which should be consulted for more complete experimental details.

[2] A preliminary account of a portion of this work has appeared: Bertrand, J. A.; Grovenstein, E.; Lu, P.-C.; VanDerveer, D. *J. Am. Chem. Soc.* **1976**, *98*, 7835–7836. This publication should be consulted for some of the properties of 14, 41, and 44.

[3] For reviews see: (a) Grovenstein, E. *Adv. Organomet. Chem.* **1977**, *16*, 167–210. (b) *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 313–332.

[4] (a) Grovenstein, E.; Akabori, S.; Rhee, J.-U. *J. Am. Chem. Soc.* **1972**, *94*, 4734–4735. (b) Grovenstein, E.; Akabor, S. *Ibid.* **1975**, *97*, 4620–4626.

[5] (a) Fraenkel, G.; Cooper, J. W. *J. Am. Chem. Soc.* **1971**, *93*, 7228–7238. (b) Fraenkel, G.; Ho, C. C.; Liang, Y.; Yu, S. *Ibid.* **1972**, *94*, 4732–4734. (c) Rizvi, S. Q. A.; Foos, J.; Steel, F.; Fraenkel, G. *Ibid.* **1979**, *101*, 4488–4492.

[6] (a) Staley, S. W.; Cramer, G. M.; Kingsley, W. G. *J. Am. Chem. Soc.* **1973**, *95*, 5052–5054. (b) Maercker, A.; Troesch, J. *J. Organomet. Chem.* **1975**, *102*, C1–C3. Garst, J. F.; Pacifici, J. A.; Felix, C. C.; Nigam, A. *J. Am. Chem. Soc.* **1978**, *100*, 5974–5975. Maercker, A.; Eckers, M.; Passlack, M. *J. Organomet. Chem.* **1980**, *186*, 193–205.

0022-3263/82/1947-2928$01.25/0

Scheme I

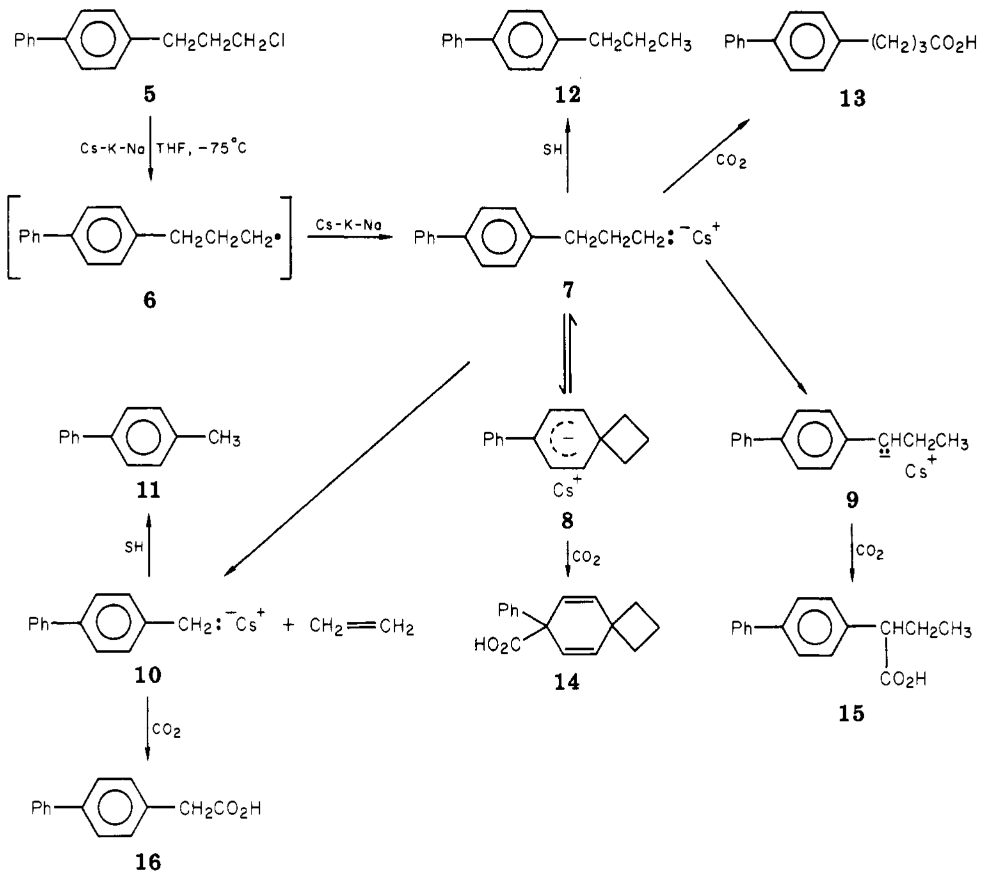


Table I. Reaction Products[a] from 1-*p*-Biphenylyl-3-chloropropane (5) with Cs–K–Na Alloy

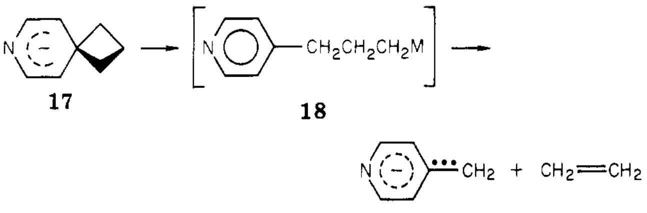
run	solvent	temp, °C	time, s	mol % yield based on 5[b]: 5	11[c]	12	13	14	15	16
1	THF	-75	540	0	1.5	19	2.0	0.4	6.5	5.8
2	THF	-75	360[d]	1.2	0.2	24	1.5	12.4	3.9	8.2
		-35	960	0.3	0.9	28	0.1	0	11	7.3
3	THF	-75	43	3.0	0.8	23	6.0	36	2.6	14
4	THF	-75	38	4.0		16	5.0	18	2.0	6.8
		-75	66	3.0		15	4.7	18	2.2	6.8
		-75	120	2.6		18	4.7	16	3.0	6.6
		-75	180	2.2		18	4.2	13	4.2	6.4
5	THF	-75	35	52		11	1.9	19.3	2.3	8.7
		-75	300[d]	3.6		24	0.5	12.1	3.1	5.2
		-75	600	2.5		22	0.6	9.4	4.1	4.1
		-75	900	2.0		27	0.1	7.1	4.5	3.5
6	THF + 18-C-6[e]	-75	30	0	0.1	19	0	9.1	9.3	4.6
7	THF + 18-C-6[e]	-75	60	0	0	20	0.3	12.3	10.4	3.0
8	Et_2O	35	1300	73	2.0	12	0.01	0	0.01	0.02
9	2-MeTHF[f,g]	-75	60	4	1.6	26	0	19.5	0	1.3

[a] See Scheme I for the structures of the products. [b] The theoretical yield for each horizontal column is 100%. [c] Where no yield is specified, the yield was less than 1%. [d] Mercury (60–110 g was added in a fine stream of tiny droplets shortly after addition of chloride 5 was complete. [e] 18-Crown-6 (2.3 mol/mol of 5 in run 6 and 5.8 mol/mol of 5 in run 7) was present prior to addition of 5. [f] The solvent was 2-methyltetrahydrofuran. [g] In addition, some 22% yield of 5-methylfuran-2-carboxylic acid was obtained.

methyl esters in gas chromatography consisted primarily of 4-*p*-biphenylylbutanoic acid (**13**), 7-phenylspiro[3.5]nona-5,8-diene-7-carboxylic acid (**14**), 2-*p*-biphenylylbutanoic acid (**15**), and *p*-biphenylylacetic acid (**16**). The appearance of the spiro acid **14** affirms the presence of the spiro anion **8**. The yields of the spiro acid decrease with time. The data for run 5 of Table I show that the spiro anion has a half-life of about 13 min in THF at -75 °C when the excess Cs–K–Na alloy was effectively removed by amalgamation or an even shorter half-life when the spiro anion was stirred with excess alloy (run 4) or warmed to -35 °C (run 2).

The loss of the spiro acid **14** and of the straight-chain acid **13** in these runs is paralleled by an increase in the amount of *p*-*n*-propylbiphenyl (**12**) and of the branched-chain acid **15**. These data suggest that the spiro anion **8** and the open anion **7** are interconvertible and with time or increase of temperature go to **12** and **9**, the precursor of **15**, as shown in Scheme I. This scheme would also suggest that the yield of *p*-biphenylylacetic acid **16** or its precursor anion **10** would also increase with time or increase in temperature, but Table I shows that the yield of this product generally decreased somewhat with time or temperature as though anion **10** were undergoing some subsequent reaction. Since all of the products from this reaction were not volatile and since some of the minor volatile products were not identified, Scheme I may be regarded as plausible but not fully established. The rearrangement of **7** to **9** is likely by an intramolecular [1,3] migration of a proton in the carbanion[6b] or could be by an intermolecular metalation of *p*-*n*-propylbiphenyl (**12**) at the benzylic position by the highly basic reagent **7**. The *p*-*n*-propylbiphenyl is a major product of the reaction and comes from protonation of the organoalkali compound **7** by a proton donor (SH), likely frequently the solvent itself.

Fragmentation of 3-arylalkyl anions such as **7** into an olefin plus a delocalized arylmethyl anion has many precedents.[5a,7] In particular, the spiro nitrogen analog **17** as a magnesium salt[5b] while stable in THF at room temperature undergoes fragmentation into **19** upon being heated at reflux in THF for 24 h. This fragmentation was interpreted as proceeding via an open-chain organometallic intermediate, **18**. In contrast, the lithium salt of **17** (in presence of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) decomposed into **19** during its attempted preparation[5b] at or below room temperature.



17 18 19

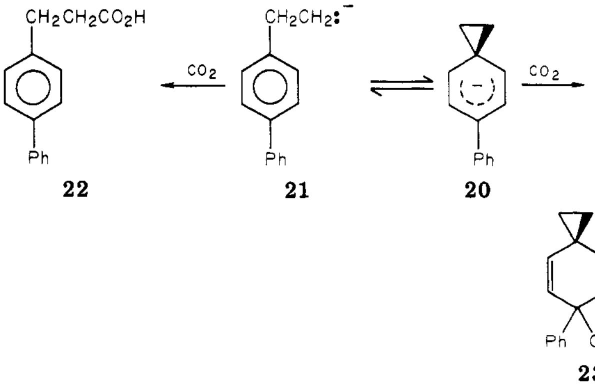
The effect of varying the solvent and solvent constituents for the reaction of 1-*p*-biphenylyl-3-chloropropane (**5**) with Cs–K–Na alloy was briefly studied. Addition of 2 or 6 mol of 18-crown-6/mol of **5** (runs 6 and 7, respectively of Table I) gave increased yields of the branched-chain acid **15** and decreased yields of the straight-chain acid **13** relative to the spiro acid **14**. These results may be understood on the basis that coordination of the cesium cation by the macrocyclic ligand 18-crown-6 should give a looser ion pair with a more reactive, "naked" carbanion and likely accelerates the irreversible conversion of **7** to the benzylic anion **9**. The opposite situation should prevail in a more poorly solvating medium. Attempts to test this postulate in diethyl ether at −75 °C were frustrated by the unreactivity of Cs–K–Na alloy with the chloride presumably because the surface of the alloy became covered with insoluble reaction product; even at 35 °C reaction was slow and the chief product was *p*-*n*-propylbiphenyl (**12**). With 2-methyltetrahydrofuran (run 9), reaction of the chloride proceeded much as with tetrahydrofuran; the yield of spiro acid **14** was one of the best obtained and might have been better save for the presence of 2-methylfuran as an impurity in the solvent. This impurity reacted likely with the open organoalkali compound **7** to give after carbonation 5-methylfuran-2-carboxylic acid; 2-methylfuran has been previously reported to undergo similar metalation with ethylsodium, phenylsodium, and benzylsodium.[8] In 2-methyltetrahydrofuran none of the branched-chain acid **15** was observed, and thus conversion of **7** to **9** was very slow in this solvent as expected. That **7** nevertheless cyclized in this solvent readily to the spiro anion **8** is in agreement with previous conclusions that aryl migration via spiro anions occurs readily from tight ion pairs with potassium or, better, cesium cations.[9]

Further experiments upon the 3-*p*-biphenylylpropyl anion involved a change of cation from primarily cesium with Cs–K–Na alloy[10] to lithium. Reaction of chloride **5** with lithium metal in THF at −75 °C gave chiefly (3-*p*-biphenylylpropyl)lithium since carbonation gave the straight-chain acid **13** accompanied by a few percent of the acids **14**–**16** of Scheme I. This result agrees with previous experience[3] that organolithium compounds do not ordinarily undergo rearrangement in THF at −75 °C. In order to catalyze rearrangement, we treated (3-*p*-biphenylylpropyl)lithium with potassium *tert*-butoxide and cesium *tert*-butoxide in THF at −75 °C. A catalytic effect was expected since by methathesis[9,11] the corresponding organopotassium or -cesium compound should be formed (see eq 1), and this should rearrange as shown for cesium

$$p\text{-}\mathrm{PhC_6H_4CH_2CH_2CH_2Li} + \mathrm{MO}\text{-}t\text{-}\mathrm{Bu} \rightarrow p\text{-}\mathrm{PhC_6H_4CH_2CH_2CH_2M} + \mathrm{LiO}\text{—}t\text{-}\mathrm{Bu} \quad (1)$$

in Scheme I. In fact, the α-metalation product **15** and the fragmentation product **16** were formed in yields as high as 9% and 3%, respectively, after 10 min, but the yield of spiro acid **14** did not exceed 0.4% in the most favorable case with CsO–*t*-Bu after 2 min and decreased upon longer reaction times. Evidently the environment in which the 3-*p*-biphenylylpropyl anion is generated in these experiments favors α-metalation and fragmentation over spirocyclization. One possibility is that (3-*p*-biphenylylpropyl)cesium (or potassium) is formed first as a loose alkoxide-separated ion pair; if true, this must be a looser ion pair than that formed upon reaction of Cs–K–Na alloy with the chloride **5** in THF in presence of 18-crown-6 since the yield of spiro anion **8** is so much less than that in presence of the crown ether.

Reaction of 1-*p*-Biphenylyl-2-chloroethane with Cs–K–Na Alloy. Reaction of 1-*p*-biphenylyl-2-chloroethane-*2,2-d*$_2$ with cesium, potassium, and Cs–K–Na alloy in THF has been reported[12] to give *p*-biphenylylethane in which the position of the label was appreciably rearranged or sometimes scrambled. These results were interpreted on the basis that rearrangement proceeded via the spiro anion **20**. In view of our success in characterizing the higher spiro analogue **8** by carbonation, we wondered if the spiro anion **20** could be characterized by the same technique to give **23** utilizing shorter reaction times and lower temperatures than those of the earlier study. Toward this



22 21 20 23

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[7] Wooster, C. B.; Morse, R. A. *J. Am. Chem. Soc.* **1934**, *56*, 1735–1737. Pines, H., Schaap, L. *Ibid.* **1958**, *80*, 4378–4381. Grovenstein, E.; Rogers, L. C. *Ibid.* **1964**, *86*, 854–861. Fischer, H. P.; Kaplan, E.; Neuenschwander, P. *Chimia* **1968**, *22*, 338–340.

[8] Gilman, H.; Breuer, F. *J. Am. Chem. Soc.* **1934**, *56*, 1123–1127.

[9] Grovenstein, E.; Williamson, R. E. *J. Am. Chem. Soc.* **1975**, *97*, 646–647.

[10] Grovenstein, E.; Longfield, T. H.; Quest, D. E., *J. Am. Chem. Soc.* **1977**, *99*, 2800–2802.

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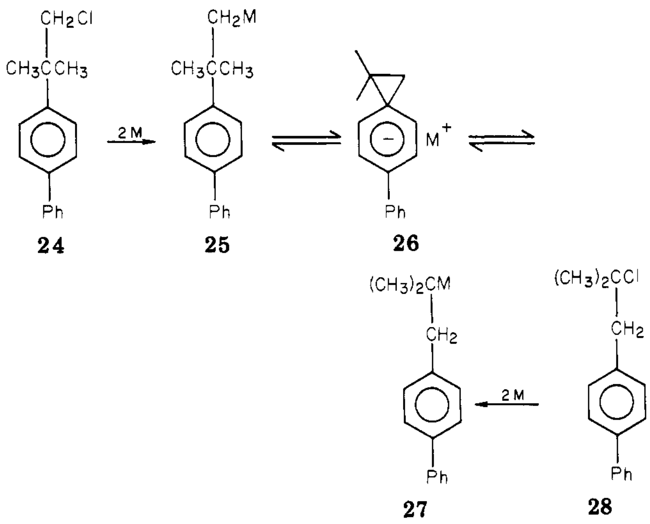
Scheme II

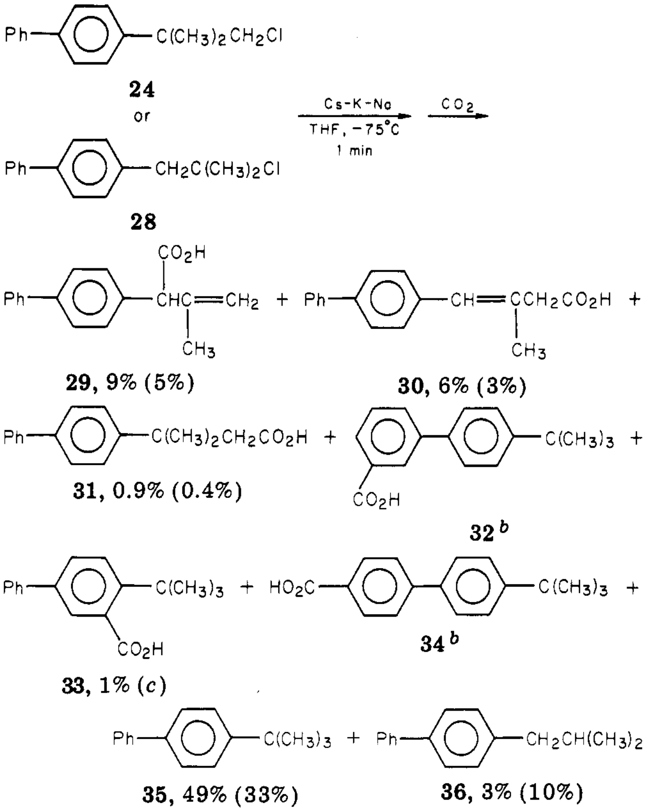


end, 1-*p*-biphenylyl-2-chloroethane was allowed to react with Cs–K–Na alloy in THF at −75 °C for about 48 s before quenching with carbon dioxide. The volatile acidic product contained only some 0.9% yield of 3-*p*-biphenylylpropanoic acid (**22**), 0.6% of 2-*p*-biphenylylpropanoic acid, and 0.5% of an unknown. The low yields discouraged attempts to ascertain if the unknown might be the desired spiro acid **23**.

Reactions of 2-*p*-Biphenylyl-1-chloro-2-methylpropane (24) with Alkali Metals. Since Maercker et al.[13] have reported that *gem*-dimethyl groups help to stabilize the cyclopropylmethyl form of the 3-butenyl Grignard reagent (Thorpe–Ingold effect[14]), we were encouraged to attempt to use *gem*-dimethyl groups to stabilize the spiro anion **20** relative to the open anion **21**. Reaction of 2-*p*-biphenylyl-1-chloro-2-methylpropane (**24**) with alkali metals (M) would be expected to give **25** (Scheme II) which could undergo cyclization to **26**. In fact, reaction of **24** with Cs–K–Na alloy in THF at −75 °C for some 65 s before carbonation gave a complex mixture of products with the more volatile products identified as shown in Scheme III. These products may be rationalized on the basis that 2-*p*-biphenylyl-2-methylpropylcesium (**25**, M = Cs) is initially produced as indicated by formation of acid **31**, whose yield decreased with time.

The initial organocesium compound (**25**) evidently reacts with the halide **24** by α elimination of HCl to give hydrocarbon **35** and the carbenoid rearrangement product 1-*p*-biphenylyl-2-methylpropene (**37**) which undergoes allylic metalation by **25** to give **35** and, after carbonation, acids **29** and **30**. In addition, minor amounts of **32–34** are formed by metalation of the biphenyl ring likely by an intramolecular process for **33** and an intermolecular process for **32** and **34**. The products identified from reaction of chloride **24** with Cs–K–Na alloy gave no evidence for formation of the spiro anion **26** nor appreciable evidence for its rearrangement product **27**. When the reaction of cesium alloy was repeated in presence of methanol (an agent which should serve as a "trap" for carbanions[11]), 12% of the hydrocarbons produced had the 4-isobutylbiphenyl carbon skeleton and the remainder the 4-*tert*-butylbiphenyl skeleton. The rearranged products are likely

Scheme III. Products from Reactions of 2-*p*-Biphenylyl-1-chloro-2-methylpropane (**24**) and 1-*p*-Biphenylyl-2-chloro-2-methylpropane (**28**) with Cs-K-Na Alloy[a]



[a] The yields from **24** are given first and those from **28** in parentheses. [b] The yield of **32** plus **34** was about 1% from both **24** and **28**. [c] Product **33** was not characterized from **28** but was likely present in a small amount.

formed by α elimination followed by reduction of intermediate 1-*p*-biphenylyl-2-methylpropene.

Reaction of lithium with 2-*p*-biphenylyl-1-chloro-2-methylpropane (**24**) in THF gave upon carbonation after reaction for 1 h at −75 °C about equal amounts of acidic and neutral products. The acidic product contained 11–12% of the rearrangement product 3-*p*-biphenylyl-2,2-dimethylpropanoic acid (**38**) in addition to the expected 3-*p*-biphenylyl-3-methylbutanoic acid (**31**) while the neutral material contained 4% of the rearranged hydrocarbon 4-isobutylbiphenyl (**36**) in addition of 4-*tert*-butylbiphenyl (**35**), for a total of 8% yield of rearranged products. When the reaction mixture was allowed to stand at −75 °C for another 2 h before carbonation, the acidic material now contained only 8% of the rearranged acid while the neutral material contained more of the rearranged hydrocarbon such that the total percentage of rearranged products remained essentially constant with time. Likewise, when the reaction mixture of organolithium compounds was warmed from −75 to −20 °C, the percentage of rearranged products did not increase. While the nonrearranged products likely arose from the organolithium compound **25** (M = Li) and the rearranged products from the rearranged organolithium compound **27**, the failure to obtain increasing amounts of rearranged products with increase in time or temperature argues against[15] appreciable **27** being formed

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(13) Maercker, A., Güthlein, P.; Wittmayr, H. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 774–775.

(14) Hammond, G. S. In "Steric Effects in Organic Chemistry"; Newman, M. S., Ed.; Wiley: New York, 1956; pp 460–469. Capon, B.; McManus, S. P. "Neighboring Group Participation"; Plenum Press: New York and London, 1976; Vol. 1 pp 58–75.

(15) Thus if the initial product after 1 h corresponded to equilibrium between **27** and **25**, then as **27** is irreversibly protonated by solvent (faster than protonation of **25**), to maintain equilibrium more **27** should be formed such that the percentage of total rearrangement products should increase with time.

from **25**. Instead, the rearranged organolithium compound **27** evidently is formed during the reaction of the chloride **24** with lithium, likely by rearrangement of an intermediate primary free radical to a more stable tertiary free radical followed by reduction of the radicals to the corresponding organolithium compounds as has been suggested for a related reaction.[16] In conformity with this view, when the reaction of the chloride **24** with lithium was conducted in presence of *tert*-butyl alcohol, which should trap intermediate carbanions prior to rearrangement, the amount of rearrangement was not reduced.

Since reaction of chloride **24** with lithium, unlike Cs–K–Na alloy, was not subject to the difficulty of α elimination with rearrangement, we reacted the organolithium reagent from **24** for 10 min at −75 °C with an excess of potasium *tert*-butoxide in order to form the organopotassium compound **25** by metathesis and see if it underwent cyclization to **26**. The chief product from this reaction after carbonation was *p*-*tert*-butylbiphenyl (**35**) in addition to small amounts of the unrearranged acid **31** and the acids **32**–**34** from metalation of the biphenyl ring. The spiro anion **26** was either not formed or was unstable with respect to decomposition into the observed products. The two methyl groups of **26** with M = Li, K, or Cs in THF evidently do not provide adequate stabilization for detection of **26** by ordinary chemical means. It is possible that **26**, nevertheless, is formed in these experiments but is unstable with respect to the open anionic reagent **25** which is more stable than the alternate open product **27**. To test this postulate, we next undertook the preparation of **27**.

Reactions of 1-*p*-Biphenylyl-2-chloro-2-methylpropane (28) with Alkali Metals. Reaction of chloride **28** with Cs–K–Na alloy for 1 min in THF at −75 °C gave on carbonation a complex mixture of products of which the major volatile products are identified as shown in Scheme III along with the products from the isomeric chloride **24**. The products from these two chlorides are remarkably similar. The unsaturated acids **29** and **30** likely came from chloride **28** via β elimination to 1-*p*-biphenylyl-2-methylpropene (**37**, which was identified in another run) followed by allylic metalation and carbonation. The considerable amount of 4-*tert*-butylbiphenyl (**35**) likely comes from cyclization of the initial tertiary organocesium compound **27** (see Scheme II) to the spiro anion **26** which undergoes ring opening to the primary organocesium compound **25**; the latter by protonation gives the observed 4-*tert*-butylbiphenyl. The formation of **25** is affirmed by identification of its carbonation product **31**. In this run some 65% of the volatile products had the rearranged carbon skeleton corresponding to **25** (or 79% if the olefinic products are ignored). When the run was repeated in presence of a little methanol, the product consisted of 1.3% of 4-*tert*-butylbiphenyl (**35**), 15% of 1-*tert*-butyl-4-cyclohexylbenzene (**39**), 2.7% of 4-isobutylbiphenyl (**36**), 44% of 1-isobutyl-4-cyclohexylbenzene (**40**), and the remainder unreacted chloride; only 26% of products of the rearranged structure corresponding to **25** were formed. Since for arylalkyl chlorides reductive cleavage of carbon–chlorine bonds is faster than reduction of benzene rings to cyclohexane rings,[11,18] the results in presence of methanol are consistent with chloride **28** being first converted to the organoalkali compound **27** which to a large extent is protonated by methanol to give 4-isobutylbiphenyl before it can rearrange to **25**. This "trapping" experiment with methanol, therefore, helps to confirm Scheme II.

The outstanding result from these reactions of 1-*p*-biphenylyl-2-chloro-2-methylpropane (**28**) and its isomer 2-*p*-biphenylyl-1-chloro-2-methylpropane (**24**) with Cs–K–Na alloy in THF at −75 °C is that, ignoring olefinic products from elimination reactions, the products from **28** are largely of rearranged skeleton and are identical with those from its isomer **24**, which gives negligible amounts of rearrangement products. In terms of Scheme II this result means that while the tertiary organocesium compound **27** rearranges to the primary organocesium compound **25**, the reverse rearrangement is inappreciable. These experiments, therefore, provide evidence that the primary organocesium compound **25** is thermodynamically more stable than the tertiary organocesium compound **27** in THF.[19] Also, **27** evidently more readily cyclizes in THF at −75 °C than does (2-*p*-biphenylylethyl-*1,1*-d_2)cesium[12] at −65 °C; in both cases, however, the spiro anions **26** and **20** are unstable with respect to corresponding open, primary, organocesium compounds.

Reaction of chloride **28** with lithium in THF at −75 °C for 35 min gave, upon carbonation, 28% of the unrearranged acid **38**, 8% of the rearranged acid **31**, 22% of 4-isobutylbiphenyl, and 20% of the 4-*tert*-butylbiphenyl; thus, of the volatile products, 64% were of unrearranged and 36% of rearranged carbon skeleton. Extension of the reaction time at −75 °C by 3 h did not alter the percentage of rearranged products but decreased the amount of carboxylic acids relative to hydrocarbons. Reaction of chloride **28** with lithium in THF at −75 °C in presence of *tert*-butyl alcohol gave 21% of hydrocarbons with the rearranged 4-*tert*-butylbiphenyl carbon skeleton, with the remainder having the unrearranged 4-isobutylbiphenyl skeleton. The reactions of the tertiary chloride **28** with lithium parallel those of the isomeric primary chloride **24** except that the tertiary chloride gives considerably more rearranged products. This result may mean that the tertiary chloride in its reaction with lithium proceeds to a larger extent than the primary chloride by way of radicals which are free enough and long-lived enough to rearrange. While experiments showed that the organolithium compound **27** itself does not rearrange appreciably in THF at −75 °C; it is possible that some precursor of the organolithium compound other than a free radical may be in part responsible for rearrangement during reaction of **28** with lithium. This could be a free carbanion or loose ion pair which may precede formation of organolithium compound **27**. The reduction in percentage of rearranged products by addition of *tert*-butyl alcohol during reaction of chloride **28** with lithium gives some support to this interpretation.

Reactions of 2-*p*-Biphenylyl-3-chloro-2,3-dimethylbutane (41) with Alkali Metals. Since the Thorpe–Ingold effect should be larger for four methyl groups than for two, the reactions of 2-*p*-biphenylyl-3-chloro-2,3-dimethylbutane (**41**) with alkali metals were studied. The results obtained from carbonation are reported in Table II for the GC volatile products.

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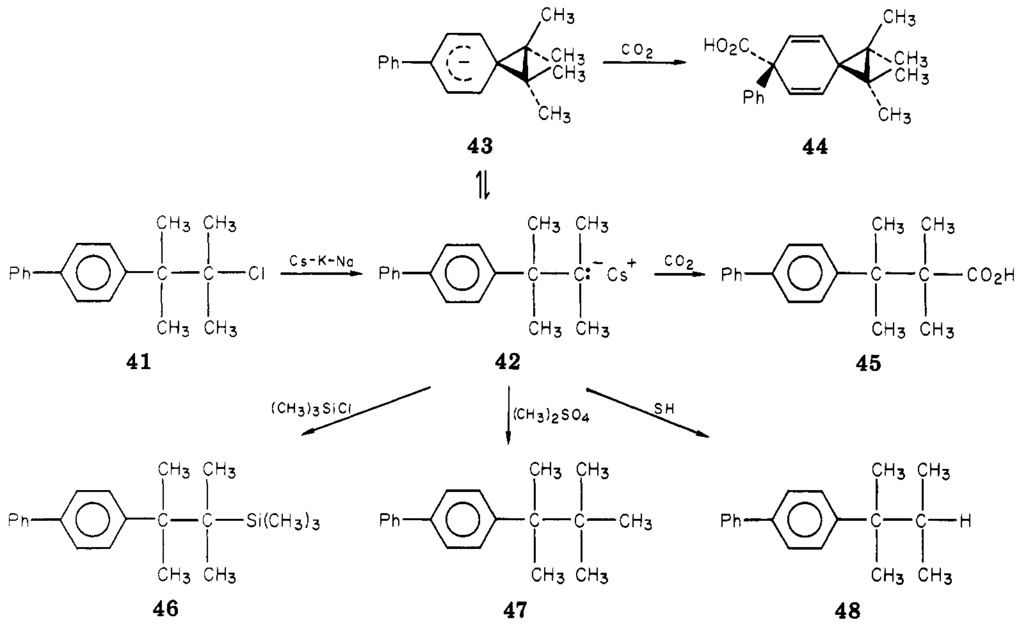
(16) Grovenstein, E.; Cheng, Y.-M. *J. Chem. Soc., Chem. Commun.* **1970**, 101–102.

(17) (a) Lochmann, L.; Pospisil, J.; Linn, D. *Tetrahedron Lett.* **1966**, 257–262. (b) Schlosser, M. *J. Organomet. Chem.* **1967**, *8*, 9–16. (c) Lochmann, L.; Lim, D. *Ibid.* **1971**, 153–158. (d) Schlosser, M.; Hartmann, J. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 508–509.

(18) Grovenstein, E. *J. Am. Chem. Soc.* **1957**, *79*, 4985–4990.

(19) We argue that the greater amount of 4-*tert*-butylbiphenyl from **25** as opposed to 4-isobutylbiphenyl from **27** reflects a larger concentration of **25** than of **27**. The counterargument that more 4-*tert*-butylbiphenyl is present than 4-isobutylbiphenyl becauses **25** protonates faster than **27** is refuted by the fact that observable **25** (as shown by its carbonation product **31**) is present after 1 min, but no **27** was detectable as its carbonation product **38** from either of the isomeric chlorides **24** and **28** in reactions with Cs–K–Na alloy.

Scheme IV



The most outstanding result of the Cs–K–Na alloy reactions is the formation of 1,1,2,2-tetramethyl-6-phenylspiro[2.5]octa-4,7-diene-6-carboxylic acid (**44**) in yields as high as 28%. The structure of **44** was in agreement with the spectroscopic properties of the acid and was confirmed by single-crystal X-ray diffraction.[2] In addition to the spiro acid **44**, the open acid 3-*p*-biphenylyl-2,2,3-trimethylbutanoic acid (**45**) was obtained. The ratio of **44** to **45** was nearly constant at 2.2 ± 0.3 to 1 throughout Table II wherever cesium was the countercation. The yields of **44** and **45** reached a maximum at short times (times long enough for all the chloride to react) and then decreased with longer times (see run 3). These results suggest that chloride **41** reacts with Cs–K–Na alloy according to Scheme IV. The spiro acid is assumed to come from the spiro anion **43** and the open acid from the open anion **42**. Since the half-lives of **42** and **43** are the same within experimental error (22 ± 2 min, as judged by the decreasing yields of **45** and **44** in run 3), these anions appear to be in mobile equilibrium. In contrast, the larger spiro anion **2a** with potassium as the counterion was previously shown *not* to ring open to (4-*p*-biphenylylbutyl)potassium in THF even at 65 °C.[4]

Carbonation of the reaction product of halide **41** with Cs–K–Na alloy also yielded 2-*p*-biphenylyl-2,3-dimethylbutane **48** along with hydrocarbons and acids which were nonvolatile under conditions of gas chromatographic analysis. Hydrocarbon **48** likely comes from protonation of the open anion by the solvent (SH) or acidic impurities (moisture) in the solvent. Also, hydrocarbon **48** was produced during reaction of Cs–K–Na alloy with chloride **41** in the presence of *tert*-butyl alcohol. No special importance is to be associated with our failure to observe the spiro cyclic hydrocarbon 1,1,2,2-tetramethyl-6-phenylspiro[2.5]octa-4,7-diene in the products from the Cs–K–Na alloy reactions since the more stable spiro anion **2a** gave only a low yield of 8-phenylspiro[4.5]deca-6,9-diene and mostly GC nonvolatile material upon protonation under all conditions tested.[4]

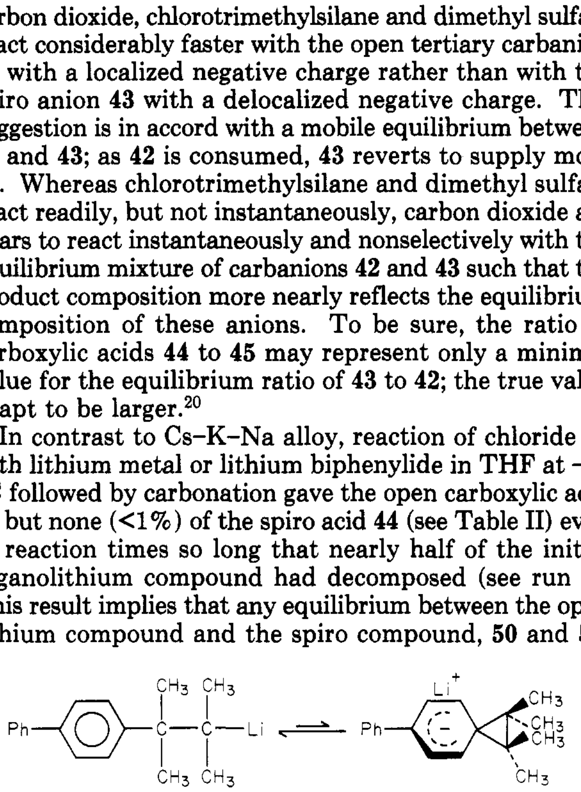
Table II. Reaction Products from Carbonation of 2-*p*-Biphenylyl-3-chloro-2,3-dimethylbutane (41) with Alkali Metals in THF at –75 °C

run	metal (other reagent)	time,[a] s	mol % yield based on 41: 41	44	45	48
1	Cs-K-Na	55	1.0[b]	28	10	32
2	Cs-K-Na	59	0.9[b]	26	10	30
3	Cs-K-Na	430	3.7	25	13	23
		910	1.2	20	10	20
		1300	1.2	16	8	21
		1720	0.8	13	6	21
4	Cs-K-Na (*t*-BuOH)[c]	35	74	0	0	15
5	Cs-K-Na	29	3	16	8	23
	(LiBr)[d]	30[e]	2	0.1	24	24
6	Li	3000	2[b]	0	37	41[f]
7	Li	3000	10	0	34	22[g]
		12000	4	0	19	41[h]
8	$\mathrm{Li^{+}Ph{-}Ph^{-}\cdot}$	600	4[b]	0	28	32
9	Li	2160	9	0	33	29
	(CsO-*t*-Bu)	300[i]	9	21	8	32
		1020[i]	9	17	7	35

[a] The time recorded is that measured from the point of half-addition of the alkyl chloride 41 to the midpoint of carbonation. [b] It is thought that all of the chloride in contact with the metal had reacted, the unreacted chloride being on the upper walls and side arms of the reaction flask. [c] The reaction with Cs-K-Na was run in the presence of *tert*-butyl alcohol. [d] The line starting with Cs-K-Na lists the product obtained upon carbonation of a small aliquot from reaction with Cs-K-Na while the line with LiBr lists the products similarly obtained after reaction of the remaining alkali metal reagent with LiBr containing LiOR. [e] The time is that measured from addition of LiBr until the midpoint of carbonation. [f] In addition, a 6% yield of 3-*p*-biphenylyl-2,3-dimethyl-1-butene (49) was obtained. [g] Also, a 9% yield of 49. [h] Also a 10% yield of 49. [i] The time recorded is from the midpoint of addition of CsO-*t*-Bu to the midpoint of carbonation.

It is, however, surprising and likely theoretically significant that spiro products were not identified (<5% yield, if any) from the reaction of chloride **41** with Cs–K–Na alloy in THF at –75 °C followed by addition of a large excess of chlorotrimethylsilane or of dimethyl sulfate. Instead, the open products 2-*p*-biphenylyl-2,3-dimethyl-3-trimethylsilylbutane (**46**) and 2-*p*-biphenylyl-2,3,3-trimethylbutane (**47**) were formed in yields of 35% and 30%, respectively. Failure to observe appreciable spiro product from either silylation or methylation cannot reflect the instability of these products because they are expected to be fully as stable as the spiro acid 44. Consequently, unlike carbon dioxide, chlorotrimethylsilane and dimethyl sulfate react considerably faster with the open tertiary carbanion **42** with a localized negative charge rather than with the spiro anion **43** with a delocalized negative charge. This suggestion is in accord with a mobile equilibrium between **42** and **43**; as **42** is consumed, **43** reverts to supply more **42**. Whereas chlorotrimethylsilane and dimethyl sulfate react readily, but not instantaneously, carbon dioxide appears to react instantaneously and nonselectively with the equilibrium mixture of carbanions **42** and **43** such that the product composition more nearly reflects the equilibrium composition of these anions. To be sure, the ratio of carboxylic acids **44** to **45** may represent only a minimal value for the equilibrium ratio of **43** to **42**; the true value is apt to be larger.[20]

In contrast to Cs–K–Na alloy, reaction of chloride **41** with lithium metal or lithium biphenylide in THF at −75 °C followed by carbonation gave the open carboxylic acid **45** but none (<1%) of the spiro acid **44** (see Table II) even at reaction times so long that nearly half of the initial organolithium compound had decomposed (see run 7). This result implies that any equilibrium between the open lithium compound and the spiro compound, **50** and **51**, respectively, greatly favors **50**. That equilibrium is in fact obtained under these conditions is implied by run 5 where the usual 2:1 mixture of organocesium compounds **43**/**42** (according to the results of carbonation) was first prepared; then, addition of lithium bromide followed by carbonation gave appreciably only the open acid **45** as expected if only the open organolithium compound **50** prevails following cation exchange with lithium bromide. The tertiary organolithium compound **50** has a half-life in THF at −75 °C of 180 min or about 8 times that of the organocesium compound **42**. It was also possible to convert the organolithium compound **50** into an equilibrium mixture of organocesium compounds **42** and **43** by metathesis[9] with

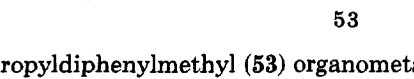


50 **51**

$$50 \xrightleftharpoons[\text{LiBr }(-\text{CsBr})]{\text{CsO-}t\text{-Bu }(-\text{LiO-}t\text{-Bu})} 42 \rightleftharpoons 43$$

cesium *tert*-butoxide in THF (run 9). The organometallic product 5–17 min following addition of cesium *tert*-butoxide had a half-life of some 38 min, as expected if cation exchange was nearly complete.

These studies on interconversions of **42**, **43**, **50**, and **51** parallel the equilibria between 4,4-diphenyl-3-butenyl (**52**)



52 **53**

and cyclopropyldiphenylmethyl (**53**) organometallic compounds reported by Maercker and Roberts.[21] In both studies the small lithium cation preferentially binds localized anions (**50**; **52** with M = Li in Et_2O) while large cations prefer to be bound to delocalized anions (**43**; **53** with M = K in Et_2O or THF). However, the tendency for the 4,4-diphenyl-3-butenyl anion to cyclize is greater than that of the 2-*p*-biphenylyl-2,2,3-trimethylpropyl anion such that in THF only **53** was detectable when M = Li, while with **43** appreciable open **42** exists even for the cesium compound in THF. The smaller tendency for cyclization to occur with addition to a phenyl group than to an ethylenic bond doubtlessly reflects in part loss of some π-delocalization energy in addition to the phenyl ring; other structural differences between the two systems complicate more detailed comparison.

In conclusion, the present work shows that in THF at −75 °C the rate of cyclization of (2-*p*-biphenylylethyl)cesium[12] (**21**) to the spiro anion (**20**) is accelerated by two α-methyl groups as in **27** → **26** (M = Cs); however, in order to give a stable spiro anion, two β-methyl groups are also needed as in **42** ⇌ **43**. With four methyl substituents **43**, unlike **26**, cannot ring open to a more stable anion. Two chief reasons may be cited for the increased equilibrium and rate constants leading from the open organometallic to the spiro anion upon methylation. First, methylation at the α-position increases the free energy of **21** relative to **20** or the transition state leading to **20** since primary organoalkali compounds are more stable in THF than tertiary organoalkali compounds. Second, for common and small rings, the introduction of *gem*-dimethyl groups tends to stabilize cyclic compounds relative to open analogues, independent of charge, because of changes in the number of gauche interactions and in rotational motion brought about by the methyl groups.[22]

Experimental Section[23]

Proton NMR spectra were recorded on a Varian A-60 or T-60A NMR spectrometer; ^{13}C NMR spectra were recorded at 25 MHz and ^1H spectra at 100 MHz with a JEOL Fourier transform spectrometer, Model PFT-100, with the multiplicity determined in off-resonance decoupled spectra. Both spectra are reported in parts per million (δ) downfield from tetramethylsilane as an internal standard. Mass spectra were run upon either a Varian M-66 or a Hitachi Perkin-Elmer RMU-7L mass spectrometer.

Gas chromatographic analyses, unless otherwise specified, were made on a Perkin-Elmer Model 881 chromatograph equipped with a hydrogen-flame ionization detector and utilized a 6 ft × $^1/_8$ in. column packed with 3% silicone gum rubber (SE-30) on 100–120-mesh Chromosorb G (acid washed and treated with dimethyldichlorosilane). Quantitative GC analyses were made with an internal standard and calibrations based upon authentic samples and are expressed in mole percent yield based upon the moles of starting organic reactant (alkyl chloride, unless otherwise specified). Acids were converted to methyl esters with diazomethane before GC analysis. Unless otherwise specified, products were identified by comparisons of GC retention times and mass spectra (of products collected frequently by preparative GC) with those of authentic samples.

p-Biphenylylacetonitrile was from Aldrich Chemical Co., Inc.; hydrolysis of the nitrile with concentrated hydrochloric acid yielded the acid **16**: ^1H NMR ($CDCl_3$) δ 7.3–7.7 (9 H, m), 3.66 (2 H, s); mass spectrum (methyl ester), *m*/*e* (relative intensity) 226 (57, M^+), 167 (100), 165 (23), 152 (10). 2-*p*-Biphenylylbutanoic acid (**15**) was synthesized by reaction of the potassium salt of *p*-biphenylylacetonitrile with ether bromide in ethereal solution and hydrolysis of the product according to a general procedure for other homologues.[24] The acid had the following: mp 119–121

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[20] Attempts to measure this equilibrium directly by ^1H NMR spectroscopy were unsuccessful in our hands both because of the low solubility of the organocesium compounds in THF (C_4D_4O) and their short lifetimes. By the carbonation technique we have sometimes measured ratios of **43**/**42** as high as 3.1:1.

[21] Maercker, A.; Roberts, J. D., *J. Am. Chem. Soc.*, **1966**, *88*, 1742–1759.

[22] Allinger, N. L.; Zalkow, V. *J. Org. Chem.* **1960**, *25*, 701–704. Hill, E. A.; Link, D. C.; Donndelinger, P. *Ibid.* **1981**, *46*, 1177–1182. Illuminati, G.; Mandolini, L. *Acc. Chem. Res.* **1981**, *14*, 95–102.

[23] Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, GA; melting points are uncorrected.

[24] Cavallini, G.; Massarani, E.; Nardi, D.; D'Ambrosio, R. *J. Am. Chem. Soc.* **1957**, *79*, 3514–3517.

°C (lit.[25] mp 123–125 °C); ^{1}H NMR ($CDCl_3$) δ 11.4 (1 H, s), 7.2–7.7 (9 H, m), 3.51 (1 H, t, J = 7 Hz), 2.00 (2 H, octet, J = 7 Hz), 0.92 (3 H, t, J = 7 Hz); mass spectrum (methyl ester), m/e (relative intensity) 254 (65, M^+), 195 (100), 167 (40). 4-*p*-Biphenylylbutanoic acid (**13**) was prepared by Dr. S. Akabori:[4] ^{1}H NMR ($CDCl_3$) δ 7.2–7.9 (9 H, m), 2.68 (2 H, t, J = 8 Hz), 1.9–2.6 4 H, m); mass spectrum (methyl ester) m/e (relative intensity), 254 (19, M^+), 223 (11), 180 (100), 167 (36), 165 (17), 152 (8).

1-*p*-Biphenylyl-3-chloropropane (5). Thionyl chloride (60.3 g, 0.564 mol) was added dropwise over a period of 2 h to 30.2 g (0.144 mol) of 3-*p*-biphenylyl-1-propanol and 11.4 g (0.145 mol) of pyridine at 0 °C with stirring. The solution was then heated on a steam bath for 20 min and finally poured onto crushed ice. From the ether extract of the mixture was isolated 30 g (90% yield) of product, mp 31–32 °C. Distillation in vacuo in a sublimation apparatus gave white crystals: mp 32–33 °C; ^{1}H NMR ($CDCl_3$) δ 7.4 (9 H, m), 3.49 (2 H, t, J = 7 Hz), 2.81 (2 H, t, J = 7 Hz), 2.11 (2 H, quint, J = 7.5 Hz); UV (EtOH) λ_{max} 253 nm (ϵ 25 500); mass spectrum, m/e (relative intensity), 232 (12, M^+, ^{37}Cl), 230 (39, M^+, ^{35}Cl), 167 (100), 165 (28).

Anal. Calcd for $C_{15}H_{15}Cl$: C, 78.09; H, 6.55; Cl, 15.36. Found: C, 78.12, H, 6.59; Cl, 15.25.

4-Isobutylbiphenyl (**36**) was prepared by Wolff–Kischner reduction[26] of 1-(4-biphenylyl)-2-methyl-1-propanone in triethanolamine: mp 32.5–33.0 °C (lit.[27] bp 282–286 °C); ^{1}H NMR ($CDCl_3$) δ 0.93 (6 H, d, J = 7 Hz), 1.9 (1 H, m), 2.52 (2 H, d, J = 7 Hz), 7.1–7.8 (9 H, m); mass spectrum, m/e (relative intensity) 210 (45, M^+), 167 (100), 165 (14), 152 (11).

1-Isobutyl-4-cyclohexylbenzene (**40**) was prepared according to a general method[11] of reduction of a 4-alkylbiphenyl to a 1-alkyl-4-cyclohexylbenzene by dropwise addition of a solution of 4-isobutylbiphenyl (0.61 g) in 40 mL of THF containing 4.8 g of *tert*-butyl alcohol to a suspension of 2.1 g of molten potassium stirred vigorously in 100 mL of THF at reflux. The solution was heated at reflux with continued stirring for 12 h before the usual workup; the product (0.55 g) had the following: bp 89–90 °C (0.11 mmHg); ^{1}H NMR ($CDCl_3$) δ 0.89 (6 H, d, J = 6 Hz), 1.1–2.1 (12 H, m), 2.44 (2 H, d, J = 7 Hz), 7.0–7.3 (4 H, m); mass spectrum, m/e (relative intensity) 216 (74, M^+), 173 (100), 160 (14), 159 (10), 117 (54); UV (95% EtOH) λ_{max} 252 nm (log ϵ 2.7), 257 (2.7), 263 (2.7), 265 (2.7), 273 (2.7).

1-*tert*-Butyl-4-cyclohexylbenzene (**39**) was prepared in a similar manner from 4-*tert*-butylbiphenyl: bp 88 °C (0.09 mm) [lit.[28] 103.5–104.5 °C (1.5 mm)]; ^{1}H NMR ($CDCl_3$) δ 1.32 (9 H, s), 1.1–2.1 (11 H, m), 7.2 (4 H, m); mass spectrum, m/e (relative intensity) 216 (40, M^+), 201 (100), 173 (11), 160 (7), 145 (14), 117 (20); UV (95% EtOH) λ_{max} 250 nm (log ϵ 2.3), 256 (2.4), 262 (2.5), 271 (2.5).

2-*p*-Biphenylyl-1-chloro-2-methylpropane (24). This compound was prepared by a modification of the procedure of Whitmore et al.[29] for neophyl chloride. To a 1-L Morton flask equipped with a high-speed stirrer and an addition funnel were added 10 mL of concentrated sulfuric acid (95–98%) and 188 g (1.22 mol) of biphenyl in 250 mL of carbon disulfide. The reaction flask was kept under a nitrogen atmosphere and cooled in a water bath at about 15 °C. To the solution was added dropwise over a period of 8 h 44.6 g (0.493 mol) of freshly distilled methallyl chloride diluted with 20 mL of CS_2 via a constant-drop-rate addition funnel (Kontes Glass Co.). The solution was stirred vigorously for another 10 h. The organic layer was separated, washed twice with 150-mL portions of 5% $NaHCO_3$ solution, dried over anhydrous $CaSO_4$, and concentrated. Distillation in vacuo gave a first fraction consisting of biphenyl and a second fraction at 0.025 mm and a bath temperature of 155–185 °C amounting to 43 g (35% yield) of 2-*p*-biphenylyl-1-chloro-2-methylpropane. The crude product after two recrystallizations from cyclohexane had the following: mp 63.5–64.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.3–7.8 (9 H, m), 3.67 (2 H, s), 1.45 (6 H, s); ^{13}C NMR ($CDCl_3$) δ 144.3 (s), 140.0 (s), 138.6 (s), 128.1 (d), 126.3 (d), 125.7 (d), 55.8 (t), 39.4 (s), 26.3 (q); UV (EtOH) λ_{max} 251 nm (ϵ 22 900), 204 (44 100); mass spectrum, m/e (relative intensity), 244 (0, M^+), 208 (100), 193 (40), 179 (18), 178 (41), 167 (26), 165 (36).

Anal. Calcd for $C_{16}H_{17}Cl$: C, 78.51; H, 7.00; Cl, 14.49. Found: C, 78.75; H, 7.18; Cl, 14.11, 14.19.

1-*p*-Biphenylyl-2-chloro-2-methylpropane (28). 1-*p*-Biphenylyl-2-methyl-2-propanol (6.35 g, 28.1 mmol) was allowed to react with 9.0 mL (125 mmol) of thionyl chloride in 200 mL of chloroform at 0 °C for 16 h. The solution was poured with stirring into a slurry of ice and water. The organic phase was separated, washed with 5% aqueous potassium hydroxide, and dried over anhydrous $MgSO_4$. Removal of the solvent in vacuo on a rotary evaporator gave 6.3 g of crude product whose ^{1}H NMR spectrum agreed with that expected for a mixture containing about 90% of the desired chloride (**28**) and 10% of an olefin, likely 1-*p*-biphenylyl-2-methylpropene (characteristic broad siglets at δ 1.92 and 6.27 in a ratio of 6:1). Recrystallization from hexane gave 5.4 g of product (mp 94.5–95.5 °C), which by NMR analysis contained 95% of **28** and 5% of olefin. This product was utilized in all the runs of **28** with alkali metals. Sublimation in vacuo and another recrystalliation from hexane failed to alter the composition of the chloride. A pure analytical sample was obtained by medium-pressure liquid chromatography of 0.75 g of the product through a 100-cm column (diameter, 2.5 cm) packed with silica gel (E. Merck, Darmstadt, 30–70 mesh) with elution by hexane–benzene (88:12 parts by volume). The pure chloride (28) after recrystallization from CCl_4 had the following: mp 97.0–97.5 °C; UV (95% EtOH) λ_{max} 252 nm (ϵ 22 400); ^{1}H NMR ($CDCl_3$) δ 7.3–7.7 (9 H, m), 3.12 (2 H, s), 6.61 (6 H, s); ^{13}C NMR ($CDCl_3$) δ 140.1 (s), 139.0 (s), 135.3 (s), 130.5 (d), 128.1 (d), 126.3 (d), 126.0 (d), 69.5 (s), 51.2 (t), 32.0 (q); mass spectrum, m/e (relative intensity) 244 (36, M^+), 209 (9), 208 (20), 193 (10), 178 (10), 167 (100). Anal. Calcd for $C_{16}H_{17}Cl$: C, 78.51; H, 7.00; Cl, 14.49. Found: C, 78.35; H, 7.10; Cl, 14.53.

2-*p*-Biphenylyl-3-chloro-2,3-dimethylbutane (41). 3-*p*-Biphenylyl-2,3-dimethyl-2-butanol (15.2 g, 0.0597 mol) was kept at room temperature for 19 h and then at reflux for 90 min in a solution containing 40.0 mL (0.556 mol) of purified thionyl chloride and 230 mL of chloroform. The mixture was then poured into 300 mL of ice–water and allowed to stand with stirring at room temperature overnight. The chloroform layer was separated, the aqueous solution was extracted with ether, and the combined organic phases were washed with 1% aqueous KOH and then water. The solution, after being dried over anhydrous $MgSO_4$, yielded 16.1 g of product. The crude product was crystallized from hexane, sublimed in vacuo at a bath temperature of 100–120 °C (50 μm), and finally recrystallized from hexane to give 11.9 g (73% yield) of white crystals:[2] mp 110.0–111.0 °C; UV (EtOH) λ_{max} 253 nm (ϵ 20 900); ^{13}C NMR ($CDCl_3$) δ 143.3 (s), 140.0 (s), 138.3 (s), 128.4 (d), 128.1 (d), 126.3 (d), 125.2 (d), 77.2 (s), 45.8 (s), 29.3 (q), 25.2 (q); mass spectrum, m/e (relative intensity) 272 (0, M^+), 236 (100), 221 (90), 195 (77), 179 (35), 178 (23), 167 (25), 165 (31). Anal. Calcd for $C_{18}H_{21}Cl$: C, 79.24; H, 7.76; Cl, 13.00. Found: C, 79.30; H, 7.77; Cl, 12.87.

General Procedure for Alkali-Metal Reactions. All reactions were run under a nitrogen atmosphere in a Morton high-speed stirring apparatus according to the procedure given previously.[11,12] For reactions with liquid alloys the solvent was generally stirred with the finely divided alloy for about 1 h at room temperature, cooled rapidly with stirring to the desired reaction temperature (normally about −75 °C as maintained with a dry ice–acetone bath), and stirred for 30 min more before the addition of alkyl halide. This procedure provided finely divided alkali metal and ensured that the solvent was free of impurities. After the reaction, the solution was normally forced onto solid carbon dioxide; solid carbon dioxide was also added to the residual contents of the reaction flask. Finally, excess 95% ethanol was added to both flasks to destroy any unreacted alkali metal. The contents of the two flasks were combined before proceeding with the usual workup procedure.

Reactions of 1-*p*-Biphenylyl-3-chloropropane (5) with Alkali Metals. (A) With Cs–K–Na Alloy. As an example of the general technique employed, run 3 of Table I is described. The chloride **5** (2.53 g, 11.0 mmol) in 25 mL of THF was added

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over a period of 12 s to finely divided and vigorously stirred Cs–K–Na alloy in 250 mL of THF in a 500-mL Morton flask at –75 °C. The alloy had been prepared from 5.56 g (0.0418 mol) of Cs, 1.81 g (0.0463 mol) of K, and 0.298 g (0.0129 mol) of Na. The solution was stirred for another 21 s. During this reaction the color of the solution changed from yellow, to red, to green, and finally to black. Then the solution was forced under nitrogen pressure over a period of 33 s onto solid carbon dioxide. Excess ethanol was added to destroy unreacted alkali metal. The solvent was removed on a rotary evaporator, 100 mL of water was added, and the mixture was extracted with ether. The ethereal layer was extracted with 5% aqueous KOH, washed with water, and finally dried over anhydrous $MgSO_4$. After filtration and removal of solvent, the ethereal solution yielded 0.68 g of neutral material. The combined alkaline extracts were acidified with hydrochloric acid and extracted with ether. This ethereal extract yielded 1.82 g of acids. Quantitative GC analysis of the neutral material on the 3% SE-30 column at 192 °C gave the following products (retention times in minutes, weight, % yield based on starting chloride): **11** (2.1, 0.015 g, 0.8%), **12** (4.0, 0.50 g, 23%), **5** (5.3, 0.08 g, 3%). Similar quantitative GC analysis of the methyl esters of the acids at 192 °C gave the following products, listed as before: **14** (7.6, 1.00 g, 36%), **16** (8.2, 0.32 g, 14%), unknown (10.0, 0.12 g, ca. 4%), **15** (11.8, 0.073 g, 2.6%), **13** (17.8, 0.17 g, 6.0%), six unknowns at retention times of 20.2, 26.2, 28.6, 30.6, 32.4, and 37.8 min in relative areas which suggest only a few percent yield of each of these components.

The acidic product (1.8 g from this run and 0.5 g from a similar run) was subjected to liquid chromatography through a column 25 mm in diameter packed with 240 g of silica gel (0.05–0.20 mm, E. Merck A.-G., Darmstadt). Acid **14**, 0.233 g of 95% purity by GC analysis, was eluted by a 20:40:40 mixture by volume of ether/cyclohexane/benzene. Recrystallization of the acid twice from hexane gave a 0.100-*g* sample of white crystals (mp 130.5–131.5 °C) which is assigned the structure of 7-phenylspiro[3.5]nona-5,5-diene-7-carboxylic acid (**14**) on the basis of its mode of synthesis and properties:[2] ^{13}C NMR ($CDCl_3$) δ 179.0 (s, CO_2H), 141.9 (s, C-1′ of phenyl), 133.7, 128.1, 126.4, 125.7, and 124.1 (all d, aromatic and vinylic CH), 52.8 (s, C-7), 39.3 (s, C-4), 34.7 (t, C-1 and C-3), 15.8 (t, C-2); UV (EtOH) λ_{max} 259 nm (ϵ 1039), 262 (1132), 265 (1184), 269 (1250), 279 (1211); mass spectrum, *m/e* (relative intensity) 240 (2, M^+), 212 (4), 211 (4), 196 (5), 195 (7), 194 (7), 178 (4), 167 (100), 165 (26), 153 (7), 152 (14); mass spectrum (methyl ester), *m/e* (relative intensity) 254 (4), 226 (16), 195 (33), 194 (13), 167 (100), 165 (19). Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.91, H, 6.75.

The other reactions in Table I were similarly performed by addition of 5.5–12.6 mmol of the halide **5** in 12–25 mL of the solvent to 6.0–8.4 g of finely *divided* Cs–K–Na alloy of eutectic composition[30] in 250 mL of solvent at the recorded temperature. The time reported in Table I is the interval from the midpoint of addition of chloride to the midpoint of carbonation; in runs 4 and 5, 50-mL aliquots were carbonated at the time intervals cited.

In run 1, from 1.28 g of chloride **5** there were obtained 0.263 g of neutral material and 0.91 g of acids. The neutral material after simple distillation at 0.09 mmHg at a bath temperature of 102 °C amounted to 0.222 g of clear oil which was identified as *n*-propylbiphenyl on the basis of its spectra: ^1H NMR ($CDCl_3$) δ 7.2–7.7 (9 H, m), 2.65 (2 H, t, J = 7 Hz), 1.64 (2 H, sextet, J = 7 Hz), 0.93 (3 H, t, J = 7 Hz; mass spectrum, *m/e* (relative intensity) 196 (28, M^+), 167 (100), 165 (17), 152 (9). The acids **13**, **15**, and **16** from this run were separated as methyl esters by gas chromatography and their identities confirmed by comparison of their mass spectra with those of authentic samples; the methyl ester of acid **14** was similarly separated from run 3 and identified by its mass spectrum.

In run 9 the solvent was 2-methyltetrahydrofuran (Aldrich Chemical Co.) which has been stored over sodium wire and distilled freshly from $NaAlH_4$. Fractional sublimation of the acidic product in vacuo gave a first fraction, which after two recrystallizations from cyclohexane had the following: mp 106.5–108.0 °C (lit.[31] mp 108.5–109.5 °C); ^1H NMR ($CDCl_3$) δ 11.4 (1 H, s, CO_2H), 7.28 (1 H, d, J = 3 Hz, H-3), 6.16 (1 H, d, J = 3 Hz, H-4), 2.38 (3 H, s, CH_3); mass spectrum, *m/e* 126 (molecular ion). All were as expected for 5-methylfuran-2-carboxylic acid.

(B) With Lithium and Then Potassium *tert*-Butoxide. To 1.94 g (0.280 mol) of finely cut lithium wire in 250 mL of THF at –15 °C was added 0.2 mL of methyl iodide and 2% of a solution of 1.62 g (0.007 01 mole) of chloride **5** in 15 mL of THF. The solution was stirred vigorously for 45 min until a pink color developed and then was cooled to –75 °C with a dry ice–acetone bath. The remainder of the chloride solution was added and the mixture stirred vigorously for 24 min until the brownish red solution just began to develop a greenish black color (likely due to formation of *n*-propylbiphenyl radical anion). Stirring was stopped, and a 20-mL aliquot of the solution was carbonated. According to quantitative analysis by GC and NMR the volatile product after the usual workup consisted of 47% of **12**, 31% of **13**, 0.8% of **14**, and 0.2% of **16** (yields listed as mole percent based on starting **5**). To the remainder of the solution was added 100 mL of THF containing 0.025 mol of potassium *tert*-butoxide. The solution was stirred at –75 °C for 50 s, and then an aliquot was carbonated. Analysis as before showed the presence of 73% of **12**, 7.9% of **13**, 0.3% of **14**, 0.9% of **15**, and 0.2% of **16**. Another fraction carbonated 8.5 min after addition of KO–*t*-Bu contained 76% of **12**, 7.2% of **13**, 0.1% of **14**, 2.3% of **15**, and 0.6% of **16**. A final fraction carbonated 29 min after addition of KO–*t*-Bu contained 79% of **12**, 4.5% of **13**, 3.6% of **15**, and 0.6% of **16**. In addition to the products listed above, all of the fractions from addition of KO–*t*-Bu contained small amounts (1% or less) of seven unknown acids whose methyl esters had relative retention times of 0.49, 0.72, 0.78, 1.08, 1.57, 1.70, and 2.22 times that of the methyl ester of **13**.

(C) With Lithium and Then Cesium *tert*-Butoxide. The organolithium compound was prepared as above from 1.12 g (0.048 86 mol) of chloride **5** with 1.17 g (0.169 mol) of lithium in 250 mL of THF at –75 °C. Carbonation of a 55-mL aliquot of the dark red solution gave on quantitative GC analysis 0.086 g (34% yield based on **5**) of **12** while the acid contained 0.085 g (27% yield based on **5**) of **13**; the remainder of the products were not GC volatile at 192 °C. To the remainder of the solution was added 80 mL of THF containing 0.0097 mol of CsO–*t*-Bu at –75 °C. The solution was stirred for 1 min; then aliquots were carbonated after an additional 1, 9, and 17 min. The usual workup and analysis gave in the first aliquot a 49% yield of **12**, 3.6% of **13**, 0.4% of **14**, 6.7% of **16**, and 2.9% of **16**, in the second aliquot 46% of **12**, 3.1% of **13**, 0.1% of **14**, 9.0% of **15**, and 2.7% of **16**, and in the third aliquot 48% of **12**, 2.6% of **13**, 9.7% of **15**, and 2.8% of **16** (all yields based on **5**). In addition, in the run with CsO–*t*-Bu there was about 2% of an unknown at 0.72 times the retention time of **13**.

Reaction of 1-*p*-Biphenylyl-2-chloroethane with Cs–K–Na Alloy. A solution of 1.98 g (0.009 16 mol) of 1-*p*-biphenylyl-2-chloroethane in 20 mL of THF was added to Cs–K–Na alloy containing 5.08 g of Cs, 1.97 g of K, and 0.269 g of Na in 220 mL of THF at –75 °C under the usual reaction conditions. The time of addition of the chloride was 28 s, and then the solution was carbonated after being stirred another 28 s. The usual workup gave 0.73 g of acid and 1.06 g of neutral product. Analysis of the methyl esters of the acid by quantitative GC at 179 °C showed the presence of 0.9% (based on chloride) of 3-*p*-biphenylylpropanoic acid, 0.6% of 2-*p*-biphenylylpropanoic acid, 0.5% of an unknown at 0.56 times the retention time of 3-*p*-biphenylylpropanoic acid, and no appreciable additional acids of retention times up to 1.5 times that of 3-*p*-biphenylylpropanoic acid. The neutral material contained *p*-biphenylylethane in 29% yield based on starting chloride and 27% of unreacted 2-chloro-1-*p*-biphenylylethane.

Reactions of 2-*p*-Biphenylyl-1-chloro-2-methylpropane (24) with Alkali Metals. (A) With Cs–K–Na Alloy. A solution of 2.50 g (0.0102 mol) of **24** in 16 mL of THF was added over a period of 11 s to 5.74 g of Cs–K–Na alloy (40.3 atom % Cs, 47.3 atom % K, 12.3 atom % Na) in 250 mL of THF stirred vigorously at –75 °C. After the mixture was stirred for another 60 s, a portion

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of the solution was carbonated to give, after the usual workup, 0.37 g of neutral material and 0.42 g of acids. Analysis of the neutral material by GC and NMR showed that is was 4-*tert*-butylbiphenyl[32] [49% yield based on **24**; ^{1}H NMR ($CDCl_3$) δ 7.2–7.7 (9 H, m), 1.34 (9 H, s); mass spectrum, *m/e* 210 (M^+)] containing a trace of 4-isobutylbiphenyl [3% yield based on **24**; ^{1}H NMR ($CDCl_3$) δ 0.92 (d, J = 7 Hz)]. Analysis of the acids by GC (of the methyl esters) at 189 °C gave the products in the following mole percent yields based on **24** (relative retention time, identity): 10 (0.93, a 10:1 mixture of **29** to probably **33** by NMR analysis), 0.9 (1.00, **31**), 7 (1.30, a 4:1 mixture of **30** to **32** + **34**(?) by NMR analysis). The remaining reaction mixture was stirred for 1 min more; then 5.2 mL of mercury was added as a very fine stream with stirring over a period of 2 min. Finally, the reaction mixture was carbonated 11 min after addition of **24**. The usual workup gave 0.43 g of neutral material and 1.00 g of acids. Analysis of the neutral material by GC and NMR showed the presence of 4-*tert*-butylbiphenyl (34% yield). Analysis of the acids as methyl esters by GC at 189 °C showed the same products and in the same amounts as those form the earlier carbonation save that the yield of **31** had fallen to 0.6%. In addition to the products which were identified, however, unknown methyl esters appeared at relative retention times of 1.17, 2.01, 2.40, 2.83, and 3.68 with GC peak areas which suggest the presence of 2–6% yields of each of these components. The acids from the two carbonations were combined and subjected to preliminary chromatography over 240 g of silica gel (0.05–0.20 mm, E. Merck A.-G., Darmstadt) with elution by ether–cyclohexane benzene mixtures to give a main fraction of 0.28 g of acids. The acids, now as methyl esters, were rechromatographed over 240 g of silica gel (column, 3.6 cm in diameter) with development by hexane–benzene with final elution by benzene. The first major fraction, after distillation at 0.05 mmHg at a bath temperature of 160–170 °C, amounted to 75 mg, showed a single peak on GC analysis, and had an NMR spectrum and GC retention time agreeing with the presence of about 9% of **33** (characteristic peaks in the methyl ester at δ 1.37 and 3.93 in about a 3:1 ratio) and 91% of a compound with the following: ^{1}H NMR ($CDCl_3$) δ 7.2–7.7 (after correction for **33**, 9 H, m), 5.07 (1 H, s), 4.97 (1 H, s), 4.41 (1 H, s), 3.72 (3 H, s), 1.75 (3 H, s); ^{13}C NMR ($CDCl_3$) δ 171.7 (s), 142.1 (s), 140.3 (s), 139.8 (s), 135.5 (s), 128.7 (d), 128.3 (d), 126.7 (d), 113.6 (t), 58.3 (d), 51.8 (q), 21.7 (q); mass spectrum, *m/e* (relative intensity) 266 (53, M^+), 207 (100), 192 (16), 191 (23), 179 (61), 165 (51); the spectral properties of the major component agree with those expected for 2-*p*-biphenylyl-3-methyl-3-butenoic acid (**29**). The next fraction contained 45 mg of a mixture which by GC analysis consisted of 25% of **29** and 75% of a compound with the following: ^{1}H NMR (in $CDCl_3$ after correction for **29**) δ 7.2–7.2 (9 H, m), 6.54 (1 H, br s), 3.68 (3 H, s), 3.24 (2 H, s), 1.95 (3 H, d, J = 1.5 Hz); mass spectrum (after purification by GC), *m/e* 266 (M^+). The spectral properties of the major component agree with those expected for 4-*p*-biphenylyl-3-methyl-3-butenoic acid (**30**). The third fraction contained 30 mg of a mixture containing by NMR analysis 60% of **30** and 40% of a compound having characteristic ^{1}H NMR peaks ($CDCl_3$) at δ 3.93 (3 H, s) and 1.35 (9 H, s). On the basis of NMR spectral and GC comparisons with authentic samples, the 40% component may be **32** or **34** but is likely a mixture of these isomers. A final 10-mg fraction was largely 3-*p*-biphenylyl-3-methylbutanoic acid (**31**). Two repetitive reactions of Cs–K–Na alloy with halide **24** gave similar results.

(B) With Cs–K–Na Alloy in the Presence of Methanol. To 5.96 g (0.0797 mol total) of eutectic Cs–K–Na alloy vigorously stirred in 250 mL of THF at −75 °C was added over a period of 16 s a solution of 1.08 g (4.4 mmol) of **24** and 1.10 mL (27.2 mmol) of methanol in 18 mL of THF. The mixture was stirred for 40 s more before being forced onto crushed solid carbon dioxide to give, by quantitative GC analysis at 155 °C, the following products [listed as mole percent yield based on **24** (retention time in minutes, identity)]: 55 (10.4, 1-*tert*-butyl-4-cyclohexylbenzene, **39**), 6 (11.0, 1-isobutyl-4-cyclohexylbenzene, **40**), 6 (13.7, 4-*tert*-butylbiphenyl, **35**), 2 (14.9, 4-isobutylbiphenyl, **36**).

(C) With Lithium. To 1.25 (0.179 mol) of finely cut lithium in 230 mL of THF at −7 °C were added 0.12 mL of methyl iodide and 15 drops of a solution of 1.43 g (5.8 mmol) of **24** in 18 mL of THF. After 40 min of vigorous stirring, a pink color developed. The solution was cooled to −75 °C, and the remainder of the chloride was added over a period of 13 min. After 11 min of continued stirring, the solution turned suddenly from deep red to green. Stirring was stopped and the solution forced onto solid carbon dioxide. The usual workup gave 0.45 g of neutral product, which by GC analysis consisted of a 96:4 ratio of **35** to **36**, and 0.98 g of carboxylic acids which by both NMR and GC/MS analyses at 200 °C consisted of an 89:11 ratio of **31** (retention time 14.6 min) to **38** (13.3 min). Acid **31** was separated by medium-pressure liquid chromatography on a 1-m glass column (2.6-cm diameter) packed with silica gel (30–70 mesh, E. Merck, Darmstadt) with elution by diethyl ether–cyclohexane in 30–70 parts by volume. After recrystallization from hexane, the 3-*p*-biphenylyl-3-methylbutanoic acid had the following: mp 122.0–123.2 °C; ^{1}H NMR ($CDCl_3$) δ 1.46 (6 H, s), 2.67 (2 H, s), 7.2–7.7 (9 H, m), 10.8 (1 H, br s); ^{13}C NMR ($CDCl_3$) δ 28.7 (q), 36.6 (s), 47.7 (t), 125.2 (d), 126.3 (d), 128.1 (d), 138.2 (s), 140.2 (s), 146.4 (s), 177.3 (s); UV (EtOH) λ_{max} 252 nm (ϵ 15 500); mass spectrum, *m/e* (relative intensity) 254 (28, M^+), 239 (3), 221 (5), 195 (100), 179 (9), 178 (16), 167 (10). Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.28; H, 7.16.

In a second run, 1.45 g (5.92 mmol) of the chloride (**24**) was allowed to react with 1.24 g (0.179 mol) of lithium in 250 mL of THF at −75 °C according to the general procedure of the first run. After 80 min of reaction the color of the solution turned from red to greenish black, stirring was stopped, and a 50-mL aliquot of the solution was carbonated to give, after the usual workup, 0.15 g of neutral material and 0.16 g of carboxylic acids. A quantitative GC and NMR analysis of these products gave the following yields (mole percent based on starting chloride in the aliquot): 38% of **35**, 1.6% of **36**, 40% of **31**, 5% of **38**. To the remainder of the solution was added 4 mL of mercury in a fine stream with stirring to amalgamate the excess lithium. The solution was then allowed to warm to −20 °C and held at this temperature for 60 min before carbonation of a 100-mL aliquot. Analysis of the products (0.34 g of neutral materials and 0.20 g of acids) as previously gave the following mole percent yields: 52% of **35**, 2.2% of **36**, 31% of **31**, 1.7% of **38**. The remaining solution was held at 0–5 °C for 2 h before carbonation to give negligible carboxylic acid and 0.51 g of neutral material which by analysis contained 81 mol % of **35** and 3.5 mol % of **36**. A third run of **24** with lithium at −75 °C for 65 min gave 30% of **35**, 1.2% of **36**, 28% of **31**, and 3.7% of **38**; after another 120 min at −75 °C 33% of **35**, 3.1% of **36**, 24% of **31**, and 2.1% of **38** were obtained.

(D) With Lithium in the Presence of *tert*-Butyl Alcohol. To 2.08 g (0.300 mol) of lithium in 250 mL of THF were added 15 drops of a solution of 1.92 g (7.8 mmol) of chloride **24** in 15 mL of THF and 0.1 mL of methyl iodide with stirring at −10 °C until a pink color developed. The reaction solution was then cooled to −75 °C, and the chloride solution now containing 1.76 g (23.7 mmol) of *tert*-butyl alcohol was added rapidly. The mixture was stirred vigorously for 1 h before carbonation. The usual workup gave 1.45 g of neutral material which by quantitative GC analysis (confirmed by ^{1}H NMR) contained the following mole percent yields based on starting chloride: 48% of **35**, 6% of **36**, 29% of **24**.

A repeat run with 3.26 g (0.470 mol) of lithium, 2.58 g (10.5 mmol) of chloride **24**, and 3.23 g (43.6 mmol) of *tert*-butyl alcohol gave 20% of **39**, 3% of **40**, 31% of **35**, and 7% of **36**.

(E) With Lithium Followed by Potassium *tert*-Butoxide. The organolithium reagent was prepared from 1.94 g (7.94 mmol) of the chloride **24** with 1.39 g (0.200 mol) of lithium (containing 1% sodium) and 0.15 mL (2.4 mmol) of methyl iodide in 250 mL of THF at −75 °C in the usual manner. Some of the organolithium reagent was carbonated to give, after the workup, 0.084 g of neutral material and 0.122 g of acid which by NMR and GC analysis contained the following mole percent yields (based on **24**): 37% of **35**, 4% of unreacted **24**, 47% of **31**, 6.5% of **38**. To the remainder of the reaction solution was added 75 mL (30 mmol) of potassium *tert*-butoxide in THF at −75 °C, and the solution was stirred for 30 s and then allowed to stand for 10 min at −75 °C before carbonation. The usual workup gave 1.28 g of neutral material which by NMR and GC analysis was essentially only **35** (78% yield) and 0.40 g of acids. The acids were analyzed by GC

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(32) Romadane, I. A.; Berga, I. E., *Zh. Obshch. Khim.* **1958**, *28*, 413–417; *Chem. Abstr.* **1958**, *52*, 13684*b*.

at 200 °C and gave major products at the following retention times in minutes (area percent yield, identify): 14.0 (19%, likely **33**), 15.1 (19%, **31**), 19.6 (38%, **32**), 20.5 (17%, **34**). In addition, minor amounts of other components were present. The major components as methyl esters were separated by liquid chromatography on silica gel and the structures confirmed by ^{1}H NMR, and, as necessary, mass spectral comparisons with authentic samples. The compound thought to be **33** had the following: ^{1}H NMR (CDCl$_3$) δ 1.39 [s, C(CH$_3$)$_3$], 3.90 (s, OCH$_3$); mass spectrum, *m/e* 268 (M$^+$).

Reactions of 1-*p*-Biphenylyl-2-chloro-2-methylpropane (28) with Alkali Metals. (A) With Cs–K–Na Alloy. A solution of 0.74 g (3.0 mmol) of chloride **28** [containing here and in all present runs with alkali metals 5 mol % of 1-*p*-biphenylyl-2-methyl-1-propene (**37**)] in 17 mL of THF was added over a period of 23 s to 6.6 g of finely divided eutectic Cs–K–Na alloy (0.036 mol of Cs) stirred vigorously in 230 mL of THF at −75 °C. After the mixture was stirred for another 277 s, the deep red solution was carbonated. The usual workup gave 0.54 g of neutral material and 0.11 g of carboxylic acids which contained, according to quantitative GC and NMR analyses (like those for the products from chloride **24**), products listed as follows in mole percent yields based on **28**: 24% of **35**, 6% of **36**, 12% of **37**, 38% of **28**, 2% of **29**, 0.6% of **31**, 3% of **30**, and three unknowns in yield of 3% or less, but only traces of **38** (<0.6%). A repeat run with 0.85 g (3.5 mmol) of chloride **28** added in 12 s to 5.4 g of Cs–K–Na alloy, with stirring continued for another 38 s before carbonation, gave 33% of **35**, 10% of **36**, 5% of **29**, 0.4% of **31**, 3% of **30**, 1% of a likely mixture of **32** and **34**, and three unknown dicarboxylic acids (whose methyl esters gave molecular ions at *m/e* 326).

(B) With Cs–K–Na Alloy in the Presence of Methanol. To 4.42 g of finely divided Cs–K–Na alloy (24.2 mol of Cs) vigorously stirred in 225 mL of THF at −75 °C was added in a period of 15 s 0.63 g (2.6 mmol) of chloride **28** dissolved in 15 mL of THF containing 1.00 mL (24.7 mmol) of methanol. The solution was stirred for 25 s longer and then carbonated. The usual workup gave by quantitative GC analysis (mole percent yields) **39** (15%), **40** (44%), **35** (1.3%), and **36** (2.7%) with the remainder of the GC volatile products being from GC pyrolysis of **28**.

(C) With Lithium. To 1.23 g (0.177 mol) of lithium in 250 mL of THF at −10 °C were added 0.2 mL of methyl iodide and 10 drops of a solution of 0.78 g (3.1 mmol) of a solution of chloride **28** in 16 mL of THF with stirring until a pink color developed. The solution was cooled to −75 °C, and the remainder of the chloride was added. After the mixture was stirred for 35 min, the color changed from red to deep purple, and the solution was forced onto solid carbon dioxide. The usual workup gave 0.35 g of neutral material and 0.44 g of carboxylic acids which by quantitative GC analysis (confirmed by ^{1}H NMR) contained (mole percent yields based on **28**) 28% of **38**, 8.0% of **31**, 20% of **35**, and 22% of **36**. The acidic product was separated by medium-pressure liquid chromatography (as described for the product from chloride **24** with Li). Acid **38** (0.13 g) was eluted first and, after recrystallization from CCl$_4$, yielded pure 3-*p*-biphenylyl-2,2-dimethylpropanoic acid (**38**): mp 148–149 °C; ^{1}H NMR (CDCl$_3$) δ 1.23 (6 H, s), 2.93 (2 H, s), 7.1–7.7 (9 H, m), 10.4 (1 H, br s); ^{13}C NMR (CDCl$_3$) δ 24.7 (q), 43.3 (s), 45.4 (t), 126.4 (d), 128.1 (d), 130.1 (d), 136.0 (s), 138.9 (s), 140.3 (s), 183.5 (s); UV (EtOH) $\lambda_{\max}$ 253 nm (ϵ 20 900); mass spectrum, *m/e* (relative intensity) 254 (10, M$^+$), 249 (1), 208 (1), 209 (1), 194 (4), 178 (3), 167 (100). Anal. Calcd for C$_{17}$H$_{18}$O$_2$: C, 80.28; H, 7.13. Found: C, 80.25; H, 7.14. Acid **31** was eluted in later fractions and found to be identical in ^{1}H NMR and mass spectra with **31** obtained from chloride **24** with lithium. Similar chromatography of the neutral product (0.33 g) on silica gel with elution by hexane give first 90 mg of **35**, then 70 mg of a mixture of **35** and **36**, and finally 110 mg of **36**. The identity of **35** and **36** were confirmed by comparisons of their NMR spectra and GC retention times with those of authentic samples and for **35** also by its mass spectrum.

Repetition of this reaction with 0.51 g (2.0 mmol) of chloride **28** and 0.81 g (0.12 mol) of lithium gave, upon carbonation of one-third of the solution after stirring it for 40 min at −75 °C, the following (in mole percent yields based on **28**): 18% of **35**, 20% of **36**, 19% of **38**, 3.8% of **31**. The remainder of the reaction solution was kept for 3 h more at −75 °C without stirring before carbonation to give 25% of **35**, 37% of **36**, 5.7% of **38**, 0.4% of **31**, 0.1% of **30** (?), and, both in the present and the prior carbonation, some 0.5% of an unknown methyl ester.

(D) With Lithium in the Presence of *tert*-Butyl Alcohol. To 1.31 g (0.189 mol) of finely cut lithium wire in 250 mL of THF at −75 °C were added 0.3 mL of methyl iodide and then after 30 min of stirring 2.0 mL of 2.5 M *n*-butyllithium in hexane. After the mixture was stirred for 15 min, 0.086 g (3.29 mmol) of chloride **28** in 18 mL of THF plus 3.38 g (45.6 mmol) of *tert*-butyl alcohol was added rapidly. Stirring was continued for 3 h at −75 °C. The reaction solution was forced onto solid carbon dioxide. Unreacted lithium was destroyed by additon of excess methanol. The workup gave 0.674 g of neutral organic product which by quantitative GC analysis contained (mole percent yields based on **28**) 12% of **39**, 29% of **40**, 2.8% of **35**, and 27% of **36**.

Reactions of 2-*p*-Biphenylyl-3-chloro-2,3-dimethylbutane (41) with Alkali Metals. (A) With Cs–K–Na Alloy. These reactions are summarized in Table II. In run 1 the chloride **41** (0.811 g, 2.97 mmol) in 20 mL of THF was added over a period of 13 s to 6.0 g of vigorously stirred eutectic Cs–K–Na alloy (containing 0.033 mol of Cs) in 250 mL of THF at −75 °C. The initially blue solution developed a deep red color and after being stirred another 31 s turned green. Stirring was stopped and, after an interval of 10 s, the solution was forced onto solid carbon dioxide over a period of 15 s. The usual workup gave 0.30 g of neutral material and 0.53 g of crude acids. Quantitative GC analysis confirmed by NMR gave the results reported in Table II. On the 3% SE-30 column at 202 °C the methyl esters of **45** and **44** had retention times of 17.4 and 9.6 min, respectively. Run 2 was similarly carried out with 1.40 g (5.12 mmole) of **41** and 5.66 g of eutectic Cs–K–Na (containing 0.0306 mol of Cs) and yielded 0.51 g of neutral material and 0.98 g of crude acids. The acidic products from the two runs were combined, and 1.28 g of the acids was subjected to liquid chromatography on a column (3.6-cm diameter) packed with 235 g of silica gel (0.05–0.20 mm, E. Merck A.-G., Darmstadt). The first component, collected with the use of hexane–ether (60/40 volume ratio) as the eluant, after one recrystallization from CCl$_4$ amounted to 0.116 g (6.0% yield) of crystals (mp 207.5–208.0 °C) which were identical with the sample of 3-*p*-biphenylyl-2,2,3-trimethylbutanoic acid (**45**) obtained from reaction of **41** with lithium. The second component collected with use of hexane–ether (20/80) as the eluant amounted to 0.27 g (14% yield[33]) of product or 0.14 g of white crystals after recrystallization from benzene–hexane; this acid[2] was identified as 1,1,2,2-tetramethyl-6-phenylspiro[2.5]octa-4,7-diene-6-carboxylic acid (**44**): mp 182–183 °C dec; ^{13}C NMR (CD$_3$COCD$_3$) δ 173.7 (s, CO$_2$H); 144.4 (s, C-1 of phenyl), 128.4, 128.3, 127.5, 126.5 and 126.4 (all d, aromatic and vinylic CH), 53.5 (s, C-6), 32.7, 32.5, and 32.1 (all s, cyclopropyl C), 19.2 and 19.0 (both q, CH$_3$); mass spectrum, *m/e* (relative intensity): 282 (5, M$^+$), 238 (20), 237 (41), 221 (7), 195 (21), 181 (100), 180 (6), 179 (14), 178 (13), 167 (22). Anal. Calcd for C$_{19}$H$_{22}$O$_2$: C, 80.82; H, 7.85. Found: C, 80.64, H, 7.85. The structure of this acid was confirmed by single-crystal X-ray diffraction analysis.[2]

The neutral products from runs 1 and 2 with Cs–K–Na and run 6 below with lithium were combined (1.26 g total), and, after short-path distillation at 0.04 mm, a 1.01-g sample was chromatographed on a column (2.3-cm diameter) which was packed with 100 g of silica gel (0.05–0.20 mm, E. Merck A.-G., Darmstadt) with cyclohexane as the eluant. The first substance collected was 0.28 g of 2-*p*-biphenylyl-2,3-dimethylbutane (**48**): UV (95% EtOH) $\lambda_{\max}$ 252 nm (ϵ 20 500); ^{1}H NMR (CDCl$_3$) δ 7.2–7.7 (9 H, m), 1.93 (1 H, septet, $J = 7$ Hz), 1.25 (6 H, s), 0.78 (6 H, d, $J = 7$ Hz); mass spectrum, *m/e* (relative intensity) 238 (9, M$^+$), 223 (1), 195 (100). Anal. Calcd for C$_{18}$H$_{22}$: C, 90.70; H, 9.30. Found: C, 90.75; H, 9.23. Subsequent fractions contained **48** along with increasing amounts of 3-*p*-biphenylyl-2,3-dimethyl-1-butene (**49**) which constituted about 10% of the hydrocarbon which was chromatographed. The purest sample of **49**, after correction for **48** had the following: ^{1}H NMR (CDCl$_3$) δ 7.2–7.7 (9 H, m), 5.01 (1 H, br s), 4.95 (1 H, br s), 1.58 (3 H, br s), 1.48 (6 H, s). A sample of this **49** which was purified by gas chromatography had the

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(33) It appears that only about half of the spiro acid **44** survived chromatography; on a closely related grade of silica gel, the acid was so readily converted into an insoluble material that the chromatographic column became plugged at the point of entrance of the sample onto the column.

following: mass spectrum, m/e (relative intensity) 236 (11, M$^+$), 221 (4), 195 (100).

In run 3 1.14 g (4.18 mmol) of 41 and 6.19 g of eutectic Cs–K–Na alloy (33.5 mol of Cs) were allowed to react according to the general procedure of run 1. After 7 min of vigorous stirring the color of the solution turned from red to green, and a portion of the solution was carbonated to give 0.180 g of acids and 0.089 g of neutral material. To the rest of the solution was added 15 mL of mercury in a very fine stream with vigorous stirring for 40 s. Fractions were then taken for carbonation with no additional stirring at the time intervals and with the results reported in Table II from quantitative GC analysis.

(B) With Cs–K–Na Alloy in the Presence of *tert*-Butyl Alcohol. To 6.17 g of finely divided Cs–K–Na alloy (33.4 mol of cesium) vigorously stirred in 250 mL of THF at −75 °C was added a solution of 0.806 g (2.95 mmol) of chloride 41 in 22 mL of THF containing 0.898 g (12.1 mmol) of *tert*-butyl alcohol during a period of 20 s. After being stirred for another 25 s, the solution was forced onto excess solid carbon dioxide to give 0.74 g of neutral material whose composition from NMR and GC analysis is given in Table II as run 4.

(C) With Cs–K–Na Alloy Followed by LiBr. The chloride 41 (0.0676 g, 2.48 mmol) was allowed to react with 6.58 g of eutectic Cs–K–Na alloy in the usual manner. After 29 s about 20% of the solution was carbonated. To the remainder after 37 s was added a THF slurry of LiBr (2.08 g, 0.0240 mol) containing 0.065 mol of LiOR (from *n*-BuLi added to remove any water). The products from carbonation were determined by GC analysis and are recorded in Table II run 5.

(D) Reaction with Cs–K–Na Alloy Followed by Chlorotrimethylsilane. The chloride 41 (0.909 g, 3.33 mmol) in 15 mL of THF was added over a period of 9 s to a well-stirred mixture of 6.35 g of Cs–K–Na eutectic alloy (0.0347 mol of Cs) in 200 mL of THF at −85 °C. After being stirred for another 34 s, the red solution turned green. The speed of stirring was reduced, and 12 mL (0.095 mol) of chlorotrimethylsilane (freshly distilled) diluted with 12 mL of THF was added over a period of 20 s. The reaction mixture was then forced onto solid carbon dioxide. The usual workup gave 1.00 g a neutral material (no carboxylic acids). Quantitative GC analysis showed the presence of (mole percent yields) 1% of **41**, 25% of **48**, and 35% of 2-*p*-biphenylyl-2,3-dimethyl-3-(trimethylsilyl)butane (**46**). Compound **46** had a retention time 3.7 times that of **48** on the SE-30 column at 201 °C. This analysis was confirmed by NMR spectroscopy which showed absence of vinylic protons in the crude product. Pure **48** and **46** were separated by preparative gas chromatography. The sample of **46** was distilled at 0.15 mm and a bath temperature of 90–110 °C to give white crystals: mp 50.5–52.0 °C; UV (95% EtOH) λ_{max} 255 nm (ϵ 17 700); ^{1}H NMR (CCl_4) δ 7.2–7.7 (9 H, m), 1.47 (6 H, s), 0.92 (6 H, s), 0.00 (9 H, s); mass spectrum, m/e (relative intensity) 310 (0, M$^+$), 268 (2), 267 (4),..., 211 (15), 195 (100),..., 73 (15). Anal. Calcd for $C_{21}H_{30}Si$: C, 81.22; H, 9.74. Found: C, 81.19; H, 9.76.

(E) Reaction with Cs–K–Na Alloy Followed by Dimethyl Sulfate. The chloride **41** (0.662 g, 2.43 mmol) in 16 mL of THF was added in 2 s to 4.52 g of Cs–K–Na eutectic alloy (0.0244 mol of Cs) rapidly stirred in 240 mL of THF at −75 °C. After 68 s, 40 mL (0.42 mol) of dimethyl sulfate was added in 2 s with stirring for 5 s before carbonation. The product by quantitative GC analysis contained 11% of **41**, 27% of **48**, and 30% of 2-*p*-biphenylyl-2,3,3-trimethylbutane (**47**). Compound **47** had a GC retention time 1.37 times that of **48** at 210 °C on the SE-30 column. Pure **47** was separated by preparative gas chromatography and was recrystallized from hexane as white crystals: mp 78–79 °C; UV (95% EtOH) λ_{max} 252 nm (ϵ 20 500); ^{1}H NMR δ 7.3–7.7 (9 H, m), 1.39 (6 H, s), 0.87 (9 H, s); mass spectrum, m/e (relative intensity) 252 (2, M$^+$), 236 (2), 221 (2), 209 (5), 195 (100). Anal. Calcd for $C_{19}H_{24}$: C, 90.42; H, 9.58. Found C, 90.28; H, 9.60.

(F) With Lithium. In run 6 of Table II, 0.83 g (0.120 mol) of lithium was stirred vigorously with 0.730 g (2.68 mmol) of **41** in THF at −78 °C for 50 min before carbonation and quantitive analysis by GC and NMR. Recrystallization of the acidic product from CCl_4 gave 0.22 g of pure 3-*p*-biphenylyl-2,2,3-trimethylbutanoic acid (**45**): mp 208–209 °C; UV (95% EtOH) λ_{max} 253 nm (ϵ 21 200); ^{1}H NMR ($CDCl_3$) δ 10.4 (1 H, s), 7.3–7.7 (9 H, m), 1.54 (6 H, s), 1.15 (6 H, s); ^{13}C NMR (CD_3COCD_3) δ 176.8 (s), 144.5 (s), 139.4 (s), 137.0 (s), 128.1 (d), 127.7 (d), 126.4 (d), 125.8 (d), 124.7 (d), 47.6 (s), 41.6 (s), 25.0 (q), 22.1 (q); mass spectrum, m/e (relative intensity) 282 (2, M$^+$), 264 (2), 249 (3), 237 (2), 222 (3), 221 (3), 195 (100), 194 (15),..., 167 (20). Anal. Calcd for $C_{19}H_{22}O_2$: C, 80.82; H, 7.85. Found: C, 80.63; H, 7.88.

(G) With Lithium Biphenylide. To 17.8 mmol of lithium biphenylide in 250 mL of THF at −75 °C was added a solution of 0.807 g (2.96 mmol) of halide **41** in 20 mL of THF over a period of 7 min, followed by dropwise addition of 2.5 mL (24 mmol) of *n*-butyl chloride. Carbonation of the mixture and the usual workup and analysis gave the products reported in Table II, run 8, in addition to valeric acid and recovered biphenyl.

(H) With Lithium Followed by Cesium *tert*-Butoxide. The chloride **41** (1.06 g, 3.89 mmol) was allowed to react in the usual manner with excess lithium (1.40 g, 0.204 mol, activated in the usual way with ca. 0.1 mL of CH_3I) at −75 °C in 240 mL of THF for 36 min. At this time 20%g of the solution was carbonated. To the remainder of the organolithium solution was added 9.1 mmol of CsO–*t*-Bu in 70 mL of THF at −75 °C. The compositions of the GC volatile products from carbonation are given in Table II under run 9 as determined by quantitative GC analyses and qualitatively confirmed by NMR spectra.

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Registry No. 5, 61221-46-3; **11**, 644-08-6; **12**, 10289-45-9; **13**, 6057-60-9; **13** methyl ester, 20637-07-4; **14**, 61221-49-6; **14** methyl ester, 81770-09-4; **15**, 959-10-4; **15** methyl ester, 81770-10-7; **16**, 5728-52-9; **16** methyl ester, 59793-29-2; **22**, 35888-99-4; **22** methyl ester, 37729-61-6; **24**, 81770-11-8; **28**, 81770-12-9; **29**, 81770-13-0; **29** methyl ester, 81770-14-1; **30**, 81770-15-2; **30** methyl ester, 81770-16-3; **31**, 81770-17-4; **31** methyl ester, 81770-18-5; **32**, 81770-19-6; **32** methyl ester, 81770-20-9; **33**, 81770-21-0; **33** methyl ester, 81770-22-1; **34**, 5748-42-5; **34** methyl ester, 81770-23-2; **35**, 1625-92-9; **36**, 10468-83-4; **37**, 10481-82-0; **38**, 81770-24-3; **39**, 4501-47-7; **40**, 81770-25-4; **41**, 61221-50-9; **44**, 61221-52-1; **44** methyl ester, 81770-26-5; **45**, 61221-51-0; **45** methyl ester, 81770-27-6; **46**, 81770-28-7; **47**, 81770-29-8; **48**, 81770-30-1; **49**, 81770-31-2; Cs–K–Na alloy, 37219-18-4; Li, 7439-93-2; KO–*t*-Bu, 865-47-4; CsO–*t*-Bu, 3934-09-6; LiBr, 7550-35-8; Li$^+$ Ph–Ph$^-$, 5143-35-1; *p*-biphenylylacetonitrile, 31603-77-7; 3-*p*-biphenyl-1-propanol, 78733-60-5; 1-(4-biphenyl)-2-methyl-1-propanone, 6976-20-1; biphenyl, 92-52-4; methallyl chloride, 563-47-3; 1-*p*-biphenylyl-2-methyl-2-propanol, 81770-32-3; 3-*p*-biphenyl-2,3-dimethyl-2-butanol, 81770-33-4; 5-methylfuran-2-carboxylic acid, 1917-15-3; 1-*p*-biphenylyl-2-chloroethane, 37729-56-9; 2-*p*-biphenylylpropanoic acid, 6341-72-6; methyl 2-*p*-biphenylylpropanoate, 74647-99-7; *p*-biphenylylethane, 5707-44-8; 4-biphenylcarboxylic acid, 92-92-2; methyl 4-biphenylcarboxylate, 720-75-2; 3-biphenylcarboxylic acid, 716-76-7; 2-*p*-biphenyl-2-propanol, 34352-74-4; 2-*p*-biphenylyl-2-methoxypropane, 72212-34-1; 2-*p*-biphenylyl-2-methylpropanoic acid, 48170-23-6; methyl 2-*p*-biphenylyl-2-methylpropanoate, 81770-34-5.

Supplementary Material Available: Experimental procedures for preparation of 3-*p*-biphenylyl-1-propanol, methyl 4′-*tert*-butyl-4-biphenylcarboxylate, methyl 4′-*tert*-butyl-3-biphenylcarboxylate, 1-*p*-biphenylyl-2-methyl-2-propanol, methyl 2-*p*-biphenylyl-2-methylpropanoate, and 3-*p*-biphenylyl-2,3-dimethyl-2-butanol and spectral properties of these compounds (4 pages). Ordering information is given on any current masthead page.