carried out as much as possible in the dark. This was particularly important in studying the cis → trans isomerization. This reaction, and its reverse, appear to be affected by prolonged exposure to light.

Buffer catalysis was observed for several of the processes (see text) and in these cases rate constants were extrapolated to zero buffer concentration. The total concentration of the buffers used in our studies ranged from 0.1 to 0.005 M. With the exception of the B2 $\rightleftarrows$ cC equilibration (eq 17), the contribution of the buffer to the overall rate was small, the buffer in the most concentrated solution accounting for no more than 25% of the rate.

Acknowledgments. The financial support of the Natural Sciences and Engineering Research Council of Canada and the Research Corporation is gratefully acknowledged.

Carbanions 20. Rearrangements in Reactions of 5-Chloro-4,4-diphenyl-2-pentyne, 1-Chloro-5,5-dimethyl-2,2-diphenyl-3-hexyne, and 5,5-Dimethyl-2,2-diphenyl-3-hexyne with Alkali Metals. Cation Effects on Migratory Aptitudes of Groups

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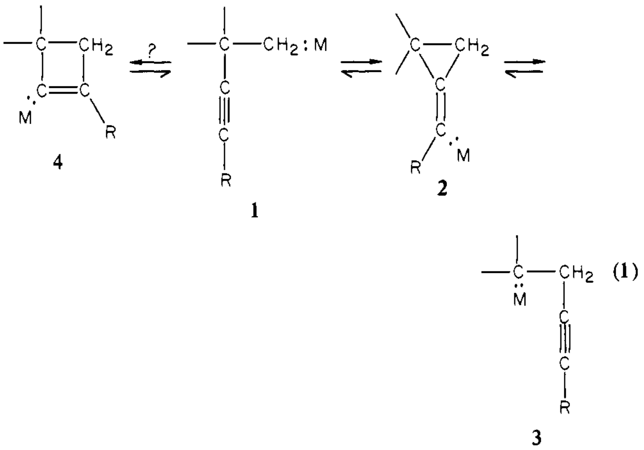
Contribution from the School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332. *Received March 17, 1980*

Abstract: Lithium reacts with 5-chloro-4,4-diphenyl-2-pentyne (**7a**) and with 1-chloro-5,5-dimethyl-2,2-diphenyl-3-hexyne (**7b**) in THF at -75 °C to give 2,2-diphenyl-3-pentynyllithium (**14a**) and 5,5-dimethyl-2,2-diphenyl-3-hexynyllithium (**14b**), respectively; when the THF solutions of these organolithium reagents are warmed to 0 °C, [1,2] migration of the acetylenic group of each occurs to produce 1,1-diphenyl-3-pentynyllithium (**16a**) and 5,5-dimethyl-1,1-diphenyl-3-hexynyllithium (**16b**), respectively, as deduced from the products of carbonation. Reaction of the organolithium compound **14a** with cesium *tert*-butoxide in THF at -75 °C gives a propargylic anion of unrearranged carbon skeleton from metalation of the methyl group; similar treatment of **14b** gives an organoalkali product derived from metalation of the ortho position of a neighboring phenyl group again without rearrangement of carbon skeleton. Reaction of the chloride **7b** with Cs-K-Na alloy in THF at -75 °C gives, evidently first, 5,5-dimethyl-2,2-diphenyl-3-hexynylcesium (**32**), which then undergoes [1,2] migration of phenyl to give 1-benzyl-4,4-dimethyl-1-phenyl-2-pentynylcesium (**27**). Much of **27** is metalated by **32** to give the dianion **28** and 5,5-dimethyl-2,2-diphenyl-3-hexyne (**18**). Hydrocarbon **18**, as confirmed by independent experiments, reacts with Cs-K-Na alloy to give a dianion **31** of rearranged carbon skeleton along with biphenyl. These products from the reaction with Cs-K-Na alloy were characterized as the hydrocarbons obtained by protonation and deuteration. The hydrocarbon from **31** is the novel compound 5,5-dimethyl-2-(1-phenyl-2,5-cyclohexadienyl)-2,3-hexadiene (**26**). An explanation is proposed for the change in relative migratory aptitude of acetylenic and phenyl groups with change of alkali metal cation from lithium to cesium. Also the protonation and alkylation of propargylic anions are discussed.

Vinyl groups have been observed to undergo [1,2] sigmatropic rearrangements in organoalkali compounds[1] and in Grignard reagents[2] while phenyl groups have been reported to migrate in organoalkali compounds but, so far, not in Grignard reagents[3] in ethereal solvents.[4] Some time ago one of us predicted[5] that a [1,2] shift of an acetylenic group in a carbanion was a likely possibility, e.g., **1** → **3** (M = alkali metal). By analogy with rearrangements of vinyl and phenyl groups in organometallic compounds, rearrangement of an acetylenic group would be expected to proceed by way of a cyclic intermediate or transition state such as **2** formed by addition of the organometallic moiety to the triple bond.



While a number of examples[2,6-8] of intramolecular cyclization of acetylenic Grignard and lithium reagents to give five- or six-membered rings are now known, only one example[9] of a [1,2] shift of an acetylenic group in a Grignard reagent (none in an orga-

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

(2) For reviews see: (a) Hill, E. A. *J. Organomet. Chem.* **1975**, *91*, 123-271. (b) *Adv. Organomet. Chem.* **1977**, *16*, 131-165.

(3) (a) Zimmerman, H. E.; Zweig, A. *J. Am. Chem. Soc.* **1961**, *83*, 1196-1213. (b) Grovenstein, E.; Cottingham, A. B.; Gelbaum, L. T. *J. Org. Chem.* **1978**, *43*, 3332-3334.

(4) Wittig ether rearrangement with phenyl migration has been observed in an organomagnesium compound in the good ionizing solvent hexamethylphosphoramide evidently by way of a solvent-separated ion pair (Ebel, H. F.; Dörr, V.; Wagner, B. O. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 163).

(5) Grovenstein, E.; Wentworth, G. *J. Am. Chem. Soc.* **1967**, *89*, 2348-2356.

(6) (a) Kandil, S. A.; Dessy, R. E. *J. Am. Chem. Soc.* **1966**, *88*, 3027-3034. (b) Richey, H. G.; Rothman, A. M. *Tetrahedron Lett.* **1968**, 1457-1460. (c) Hill, E. A.; Theissen, R. J.; Doughty, A.; Miller, R. *J. Org. Chem.* **1969**, *34*, 3681-3684.

(7) (a) Crandall, J. K.; Keyton, D. J. *Tetrahedron Lett.* **1969**, 1653-1656. (b) Moore, W. M.; Salajegheh, A.; Peters, D. G. *J. Am. Chem. Soc.* **1975**, *97*, 4954-4960.

(8) Courtois, G.; Masson, A.; Migniac, L. *C. R. Acad. Sci., Ser. C* **1978**, *286*, 265-268.

(9) Richey, H. G.; Rothman, A. M., personal communication to E. A. Hill quoted in ref 2a, p 150.

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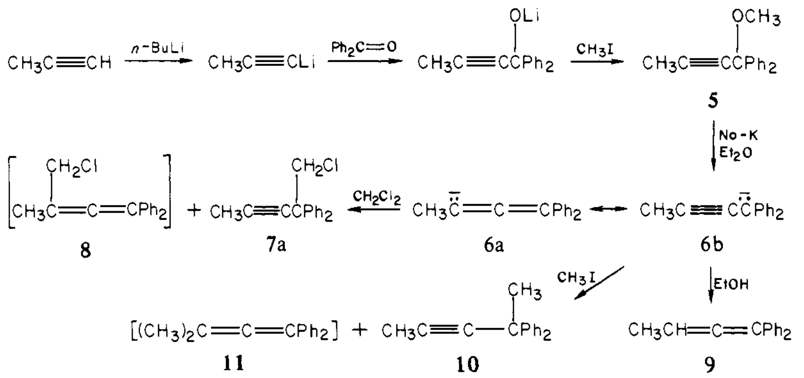
Scheme I



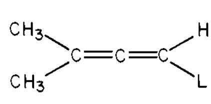
noalkali metal compound) has been reported, though detailed data is lacking. Also one example[10] of ring opening of a cyclopropylidenemethylmagnesium bromide ($2 \rightarrow 3$, M = MgBr) is known; in contrast 2-phenylcyclobutenylmagnesium bromide[10] was stable toward ring opening and 4-phenylbut-3-ynylmagnesium bromide did not cyclize to 2-phenylcyclobutenylmagnesium bromide ($\mathbf{4} \nrightarrow \mathbf{1}$). Organozinc compounds are said to undergo intramolecular addition to triple bonds with greater ease than organomagnesium compounds;[8] this qualitative observation suggests that organolithium compounds might be less reactive in such additions than organomagnesium compounds. However, since alkynyl Grignard reagents are reported to undergo intramolecular cyclization more readily than similar alkenyl Grignard reagents[2a,11] and since alkenyllithium compounds are known to cyclize, the intramolecular cyclization of alkynyllithium would appear to be a likely process. Formation of **2** from **1** nevertheless corresponds to a 3-exo-digonal ring closure which is disfavored by Baldwin's rules,[12] which predict that the 4-endo-digonal ring closure leading to **4** should be favored. Finally the topic of cyclization of organometallic compounds is complicated by cyclization occurring during formation of the organometallic compound by way of intermediate free radicals;[1a,2a] for example, cyclization during reaction of alkynyl halides with lithium biphenylide in THF occurs largely in intermediate free radicals.[7] In view of such complications and the uncertainty of a priori predictions and because of the general importance of knowing whether a given organoalkali compound is likely to rearrange or not, the present work was initiated to examine the question of [1,2] migration of an acetylenic group in an organoalkali compound vs. the alternative [1,2] migration of a phenyl group. The initial system chosen for study was 2,2-diphenyl-3-hexynyllithium.

Results and Discussion

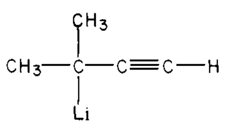
Preparation of 5-Chloro-4,4-diphenyl-2-pentyne (7a). The required 5-chloro-4,4-diphenyl-2-pentyne (**7a**) was conveniently made by the process outlined in Scheme I. The intermediate 1-methoxy-1,1-diphenyl-2-butyne (**5**) was prepared in 83% yield of purified crystalline product based upon benzophenone. Cleavage of **5** by sodium-potassium alloy gave the mesomeric carbanion (**6a** ↔ **6b**) which reacted with methylene chloride to give primarily the desired 5-chloro-4,4-diphenyl-2-pentyne (**7a**) along with 1,1-diphenyl-1,2-butadiene (**9**). The yield of purified crystalline **7a** was 67–70% from **5**. Interestingly protonation of the mesomeric anion with 95% ethanol gave preponderantly **9**.

That the crystalline chloromethylation product of the mesomeric anion **6a** ↔ **6b** had structure **7a** rather than **8** was affirmed by the IR spectrum,[13] which had a typical C≡C stretching band at 2235 cm^{-1} rather than a C=C=C band at 1940 cm^{-1} as found for the allenic hydrocarbon **9**. Furthermore, the ^{13}C NMR spectrum of the chloride had acetylenic carbon atoms at δ 80.6 and 81.8 but no absorption at δ 208–213 as expected for the strongly deshielded central sp carbon of an allenic group.[14] Finally, the mesomeric anion was observed to react with methyl iodide to give only the acetylenic product **10** with no detectable allenic product **11**. The distinction between structures **10** and **11** in principle is easy since in **11** the two methyl groups are equivalent while in **10** they are nonequivalent. In practice the ^{1}H NMR spectrum of the hydrocarbon in CCl_4 showed only a single signal at δ 1.88 integrating for six hydrogens in the region expected for the methyl groups on a 60-MHz instrument; however, on a 100-MHz instrument two peaks appeared at δ 1.90 and 1.92 in the solvent $CDCl_3$. Also the ^{13}C NMR spectrum of the hydrocarbon gave methyl carbon absorptions at δ 3.6 and 30.7 as expected for structure **10**. The reactions of the ambient anion in Scheme I may be summarized on the basis that soft electrophiles such as CH_3I and CH_2Cl_2 attack the anion preferentially on the carbon attached to the phenyl groups to give acetylenic derivatives, whereas hard electrophiles such as water and ethanol attack the opposite end of the propargylic anion to give allenic derivatives.[15]

Although reactions of polylithiated acetylenes and allenes with electrophiles have been subjected to considerable modern scrutiny,[16] the chemistry of monolithium and monopotassium derivatives is less well known. Recently Creary[17] reported a detailed study of the reactions of the monolithium derivative of 3,3-dimethylallene with electrophilic reagents; some but not all of these reactions could be rationalized in terms of Pearson's principle[18] of hard and soft acids and bases (HSAB). Other factors judged important were steric effects, product stability considerations, and "the unknown nature of the charge distribution" in the lithium compound which, on the basis of its NMR spectrum, was thought to have the allenic structure **12** rather than the acetylenic structure **13**.



12



13

In contrast to Creary's organolithium compound **12**, cation-anion interactions should be greatly reduced in our delocalized anion (**6a** ↔ **6b**) with potassium as countercation in tetrahydrofuran as solvent. One might hope, therefore, that with electrophiles of small steric bulk our correlation of reactivity by

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(10) (a) Derocque, J.-L.; Sundermann, F.-B. *J. Org. Chem.* **1974**, *39*, 1411–1416. (b) Derocque, J.-L.; Beisswenger, U.; Hanack, M. *Tetrahedron Lett.* **1969**, 2149–2152.

(11) Kossa, W. C.; Rees, T. C.; Richey, H. G. *Tetrahedron Lett.* **1971**, 3455–3458.

(12) Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734–736.

(13) Bellamy, L. J. "The Infra-Red Spectra of Complex Molecules", 3rd ed.; Chapman and Hall: London, 1975; pp 64–71.

(14) Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972; pp 76–77.

(15) (a) Ho, T.-L. *Chem. Rev.* **1975**, *75*, 1–20. (b) Gompper, R.; Wagner, H.-U. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 321–333.

(16) (a) Priester, W.; West, R.; Chwang, T. L. *J. Am. Chem. Soc.* **1976**, *98*, 8413–8421. (b) Priester, W.; West, R. *Ibid.*, **1976**, *98*, 8421–8432. (c) Klein, J. In "The Chemistry of the Carbon-Carbon Triple Bond", Patai, S., Ed.; Wiley: New York, 1978; Part 1, pp 343–379.

(17) Creary, X. *J. Am. Chem. Soc.* **1977**, *99*, 7632–7639.

(18) Pearson, R. G. *J. Chem. Educ.* **1968**, *45*, 581–587, 643–648.

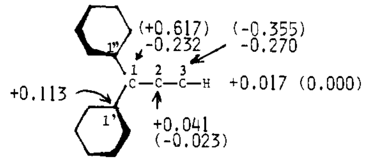


Figure 1. Net charge distribution and, in parentheses, coefficients of the HOMO (p_z orbital only, which is antisymmetric with respect to the plane of the drawing) for 1,1-diphenyl-2-propynyl anion in the CNDO/2 approximation. The two phenyl groups are equivalent according to the axis of rotational symmetry through C(1)–C(2).

the HSAB principle could be explained by generalized perturbation theory.[19] According to this theory reaction of an ambident nucleophile with a hard electrophile should occur at the atom carrying the highest electronic charge while reaction with a soft electrophile should occur at the atom with largest coefficient in its highest occupied molecular orbital (HOMO).

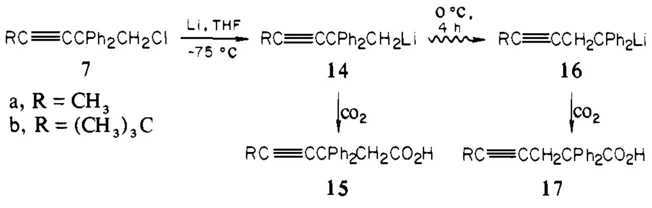
According to molecular orbital theory[20,21] at the level of approximation of CNDO/2, 1,1-diphenyl-2-propynyl anion in the gas phase has the geometry,[22] net charge distribution, and coefficients of its HOMO (shown in parentheses only at centers of interest) as given in Figure 1. Attack upon this anion by soft electrophiles would be predicted to occur preferentially at C(1) and by hard electrophiles at C(3) as we have found for 1,1-diphenyl-2-butynyl anion.[23] A methyl group at C(3) of the propynyl anion would be expected[24] to alter the coefficients at C(1) and C(3) only to a small and qualitatively unimportant extent. However, since the charge at C(3) is only a little larger than that at C(1) in this propynyl anion and since methyl groups in CNDO/2 calculations serve somewhat to delocalize negative charges on adjacent atoms, the charges at C(1) and C(3) in 1,1-diphenyl-2-butynyl anion are expected[24] to be approximately the same and, therefore, the charge densities at these carbon atoms per se are not expected to lead to preferential attack of hard electrophiles at C(3). In cases where an ambident nucleophile has about equal charges on its two nucleophilic atoms simple perturbation theory evidently needs to be modified to include secondary interactions with charges on adjacent atoms. It is notable that 1,1-diphenyl-2-butynyl anion has a charge of +0.11 on C(1′) and C(1″) of the two phenyl groups attached to C(1) and a charge of only about +0.04 on C(4) of the methyl group attached to C(3). Inclusion of these secondary interactions would lead to the prediction that hard electrophiles would attack C(3) of 1,1-diphenyl-2-butenyl anion as found by experiment.

Additional examples illustrating these general principles concerning the positions of preferential alkylation and protonation of ambident propargylic anions are given in later sections of this paper.

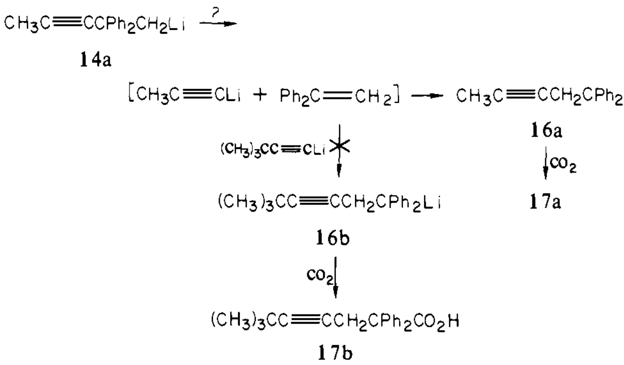
Reaction of 5-Chloro-4,4-diphenyl-2-pentyne (7a) with Lithium. The chloride **7a** was allowed to react with lithium in tetrahydrofuran (THF) at −75 °C. Carbonation of a portion of the reaction solution yielded 3,3-diphenyl-4-hexynoic acid (**15a**) and 4,4-diphenyl-2-pentyne (**10**) as the only volatile products in addition to some unreacted **7a**. The remainder of the reaction solution was warmed to 0 °C and held at this temperature for 4 h before carbonation. The only volatile products were now 2,2-diphenyl-4-hexynoic acid (**17a**) and 4,4-diphenyl-2-pentyne (**10**). The structure of the acid **15a** is in agreement with its spectral properties; its unrearranged structure is the normal result expected from reaction of halides with lithium metal in THF at low temperature.[1] The structure of the rearranged acid **17a** was suggested by its spectral properties and confirmed by independent synthesis through alkylation of the dilithium salt of diphenylacetic acid with 1-chloro-2-butyne:

$$Ph_2C{=}C(OLi)_2 + ClCH_2C{\equiv}CCH_3 \xrightarrow[HMPA]{THF} \xrightarrow{H^+} CH_3C{\equiv}CCH_2CPh_2CO_2H \quad (2)$$

Scheme II



Scheme III



The observations concerning the reaction of 5-chloro-4,4-diphenyl-2-pentyne with lithium are summarized in Scheme II. The initial lithium compound **14a** evidently undergoes rearrangement of carbon skeleton, ascribable to a [1,2] migration of the propynyl group to give **16a**. Both intermolecular and intramolecular mechanisms of [1,2] migration of groups in organolithium compounds are known.[25] The intermolecular mechanism consists of an elimination–readdition process as formulated in Scheme III for 2,2-diphenyl-3-pentynyllithium (**14a**). As a test of this mechanism the lithium compound **14a** was prepared at −75 °C as previously and then some 2.5 molar equiv of lithium *tert*-butylacetylide was added before the reaction mixture was warmed to 0 °C and carbonated. Only the previous product **17a** from [1,2] migration of the methylacetylene moiety was obtained; none (<0.5%) of the product **17b** from incorporation of lithium *tert*-butylacetylide[26] could be detected. An appreciable amount of 2,2-diphenylpropanoic acid was, however, produced; this acid likely arose from cleavage[27] of 4,4-diphenyl-2-pentyne to 1,1-diphenylethyl anion (and lithium methylacetylide?) by the excess lithium present during the 3-h period of stirring at 0 °C before carbonation. In conclusion, the elimination–readdition mechanism

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(19) Klopman, G. In "Chemical Reactivity and Reaction Paths", Klopman, G., Ed.; Wiley-Interscience: New York, 1974; pp 55–165.

(20) (a) Pople, J. A.; Beveridge, D. L. "Approximate Molecular Orbital Theory"; McGraw-Hill: New York, 1970; pp 57–79, 110–113. (b) Calculations by the approximate molecular orbital method CNDO/2 are believed to be adequate for the qualitative purposes of the present work; however, it is known that these calculations sometimes give results which are not in agreement with experiment for carbanions (cf. Jesaitis, R. G.; Streitwieser, A. *Theor. Chim. Acta* **1970**, *17*, 165–170).

(21) We are indebted to Professor Edward M. Burgess and Mr. Lewis R. Duckwall for aid in performing these calculations on a Control Data Corp. CYBER 70 Model 74 computer.

(22) In this calculation only the bond lengths of bonds C(1)–C(2) and C(2)–C(3) and the tilt angle which each benzene ring makes with respect to the plane containing C(1), C(2), C(3), C(1′), and C(1″) were optimized respectively at 1.42 Å, 1.22 Å, and 24°. Standard bond lengths and bond angles were assumed for the remaining geometry.[20a]

(23) Regrettably the CNDO/2 calculations could not be performed on 1,1-diphenyl-2-butynyl anion because this molecule was too large for our CNDO/2 program.

(24) This expectation was confirmed by performing CNDO/2 calculations on 1-phenyl-2-propynyl anion and its methylated derivative 1-phenyl-2-butynyl anion.

(25) Grovenstein, E.; Westworth, G. *J. Am. Chem. Soc.* **1967**, *89*, 1852–1862.

(26) While addition of organolithium reagents to 1,1-diphenylethene is well established, the addition of lithium acetylides is apparently unknown and may indeed *not* be a facile process as suggested by the some 3000-fold greater reactivity of *n*-butyllithium than of vinyllithium in this addition (Waack, R.; Doran, M. A. *J. Am. Chem. Soc.* **1969**, *91*, 2456–2461).

(27) Cf. the cleavage of 1,1,2-triphenylethane by sodium in liquid ammonia (Grovenstein, E.; Rogers, L. C. *J. Am. Chem. Soc.* **1964**, *86*, 854–861).

of Scheme III does not appear to be a viable mechanism of rearrangement of the acetylene moiety in 2,2-diphenyl-3-pentynyllithium (**14a**).

In order to learn more about this rearrangement, its dependence upon the nature of the alkali metal cation was next studied. Catalysis[28] of rearrangement of organolithium compounds by cesium *tert*-butoxide is believed to involve formation of the organocesium compound by the metathetical reaction

$$\mathrm{RLi} + \mathrm{CsO}\text{-}t\text{-}\mathrm{Bu} \rightarrow \mathrm{RCs} + \mathrm{LiO}\text{-}t\text{-}\mathrm{Bu} \qquad (3)$$

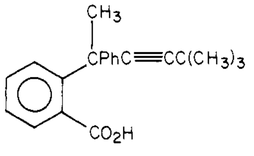
Hence reaction of 2,2-diphenyl-3-pentynyllithium (**14a**) with cesium *tert*-butoxide in THF at -75 °C was studied. Carbonation of the reaction mixture 30 min after addition of the alkoxide gave a complex mixture of carboxylic acids containing three major and two minor components. The major acids were identified as $CH_2{=}C{=}C(CO_2H)CPh_2CH_3$ and, likely, $HO_2CCH_2C{\equiv}CCPh_2CH_3$ and $HO_2CCH{=}C{=}CHCPh_2CH_3$. While these products may be formally regarded as derived from rearrangement products of 2,2-diphenyl-3-pentynyl anion, they likely result from metalation of 4,4-diphenyl-2-pentyne at the propargylic position by the powerful metalating agent[29,30] produced by reaction of alkyllithium reagents with alkoxides of alkali metals of higher atomic number than lithium. Small amounts of these same metalation products were also evidently produced when a preparation of the organolithium reagent **14a** was warmed to 0 °C in THF in the absence of added catalysts. Metalation at the propargylic position of 4,4-diphenyl-2-pentyne appears reasonable since hydrogens at the propargylic position of propyne are estimated, by an electrochemical technique,[31] to be 8 p*K* units more acidic than the tertiary hydrogen of isobutane but 10 p*K* units less acidic than the allylic hydrogens of propylene. Because propargylic metalation complicates the desired study of rearrangement of 2,2-diphenyl-3-pentynyl anion, the three acidic propargylic hydrogens of this anion were replaced by methyl groups and hence further studies were made upon 5,5-dimethyl-2,2-diphenyl-3-hexynyl anion.

Reaction of 1-Chloro-5,5-dimethyl-2,2-diphenyl-3-hexyne (7b) with Lithium. The required 1-chloro-5,5-dimethyl-2,2-diphenyl-3-hexyne (**7b**) was prepared by the same general procedure as for the preparation of 5-chloro-4,4-diphenyl-2-pentyne (**7a**) in Scheme I except that the starting material was *tert*-butylacetylene rather than methylacetylene. Reaction of **7b** with lithium in THF at -75 °C gave (see Scheme II) the expected organolithium compound **14b** as shown by carbonation to give 6,6-dimethyl-3,3-diphenyl-4-heptynoic acid (**15b**) in 74% yield of recrystallized product. When the organolithium compound **14b** was warmed to 0 °C and held at this temperature for 3 h, rearrangement to **16b** occurred as shown by carbonation to give 6,6-dimethyl-2,2-diphenyl-4-heptynoic acid (**17b**) in 67% yield of recrystallized acid. The structure of **17b** was in good agreement with its spectral properties and was confirmed by comparison with an authentic sample of this acid prepared by alkylation of the dilithium salt of diphenylacetic acid with 1-chloro-4,4-dimethyl-2-pentyne (cf. the synthesis of **17a**, eq 2). No evidence was obtained for formation of any isomeric products during rearrangement of **14b** to **16b**. Thus the chemistry of 5,5-dimethyl-2,2-diphenyl-3-hexynyllithium (**14b**) parallels that of 2,2-diphenyl-3-pentynyllithium (**14a**) but without some of the complications of the latter. The demonstration that the *tert*-butylacetylene moiety of **14b** undergoes ready [1,2] migration, just as does the methylacetylene moiety of **14a**, shows that the failure to obtain incorporation of lithium *tert*-butylacetylide during rearrangement of **14a** (see Scheme III) is not related to a low migratory aptitude of the *tert*-butylacetylene group. This observation strengthens the conclusion that [1,2] migration of the acetylenic group in **14a** (and similarly in **14b**) is not occurring by the elimination–readdition mechanism of Scheme III.

To investigate the effect of changing the countercation from lithium to cesium, a preparation of the lithium compound **14b**, which was demonstrated to contain 5,5-dimethyl-2,2-diphenyl-3-hexynyllithium in 89% yield by carbonation of a aliquot, was mixed at -78 °C with about 3 molar equiv of cesium *tert*-butoxide per mol of **14b**. After 30 min reaction time at -75 °C, the mixture was carbonated to afford a 28% yield of 5,5-dimethyl-2,2-diphenyl-3-hexyne (**18**) and 61% of a carboxylic acid which is assigned the structure of 2-(1,4,4-trimethyl-1-phenyl-2-pentynyl)benzoic acid (**19**). This structural assignment is in agreement

$CH_3CPh_2{\equiv}CC(CH_3)_3$

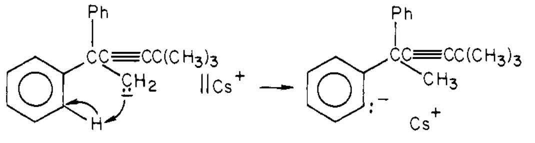
18



19

with the spectral properties of the acid. Thus the ^{1}H NMR spectrum has a nine-proton singlet at δ 1.21 attributable to a *tert*-butyl group, a three-proton singlet at δ 2.00 attributable to a deshielded methyl group, nine aromatic protons in a broad multiplet from δ 7.1 to 8.0, and a broad singlet at δ 9.2 attributable to a proton of a carboxylic acid. The ^{13}C NMR spectrum shows the presence of two acetylenic carbons at δ 83.7 and 92.8 and, in the region of δ 125.6–146.4, eight distinguishable aromatic carbons, three of which are not linked directly to hydrogen. That the carboxyl group in **19** is ortho to a bulky side chain is implied by the ultraviolet absorption spectrum, which has an absorption maximum at 220 nm (ϵ 3640) with a shoulder at 264 nm (ϵ 385) rather than more intense absorption at longer wavelengths as expected[32] for meta and para isomers.

The reaction of the organolithium compound **14b** with cesium *tert*-butoxide may be understood on the basis that the alkoxide induces formation of a powerful metalating agent,[29,30] which we regard as some type of solvent- or alkoxide-separated ion pair **20**, which reacts with a close-lying acidic proton on an ortho position of a neighboring phenyl group (eq 4). Indeed potassium *tert*-butoxide is known to catalyze the metalation of benzene by *n*-butyllithium.[30a] Also 2,2-diphenylpropyllithium when heated at reflux in diethyl ether gives some of the product of ortho metalation of a phenyl group in addition to chiefly the product of [1,2] migration of phenyl.[3a]



20 (4)

Reaction of 1-Chloro-5,5-dimethyl-2,2-diphenyl-3-hexyne (7b) with Cs–K–Na Alloy. In view of the fact that the product of cesium *tert*-butoxide catalyzed rearrangement of an organolithium compound may be different from the product of reaction of the corresponding alkyl chloride with cesium metal,[33] we also investigated the reaction of 1-chloro-5,5-dimethyl-2,2-diphenyl-3-hexyne (**7b**) with the eutectic alloy[34] of cesium, potassium, and sodium. Reaction of **7b** in THF with excess Cs–K–Na at -75

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(28) Grovenstein, E.; Williamson, R. E. *J. Am. Chem. Soc.* **1975**, *97*, 646–647.

(29) (a) Lockmann, L.; Pospisil, J.; Lim, D. *Tetrahedron Lett.* **1966**, 257–262. (b) Lochmann, L.; Lim, D. *J. Organomet. Chem.* **1971**, *28*, 153–158.

(30) (a) Schlosser, M. *J. Organomet. Chem.* **1967**, *8*, 9–16. (b) Schlosser, M.; Hartmann, J. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 508–509. (c) Hartmann, J.; Schlosser, M. *Helv. Chim. Acta* **1976**, *59*, 453–466.

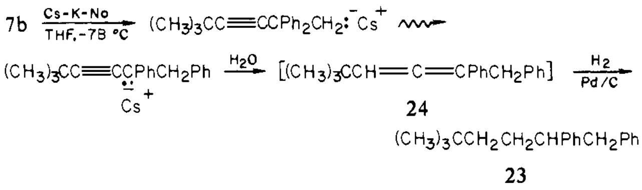
(31) Breslow, R.; Grant, J. L. *J. Am. Chem. Soc.* **1977**, *99*, 7745–7746.

(32) The UV spectrum of **19** is similar in intensity to that of 2,4,6-trimethylbenzoic acid [λ_{max} 235 nm (ϵ 3236) and 270 (417)] and different from that of 3-methylbenzoic acid [λ_{max} 231 nm (ϵ 10 200) and 278 (1190)] and 4-methylbenzoic acid [λ_{max} 236 nm (ϵ 13 500) and 280 (614)] (Grasselli, J. G., Ed. "CRC Atlas of Spectral Data and Physical Constants for Organic Compounds"; CRC Press: Cleveland, Ohio, 1973; pp B-307, B-316).

(33) Unpublished work with Dr. P.-C. Lu.

(34) Tepper, F.; King, J.; Greer, J. In "The Alkali Metals, an International Symposium Held at Nottingham on 19–22nd July, 1966"; The Chemical Society; London, 1967; pp 24–26.

Scheme IV



°C for 4 min followed by quenching with excess water gave a complex mixture of hydrocarbons. The mixture was hydrogenated over a palladium/carbon catalyst to simplify analysis. Since the prior reaction of **7b** with lithium suggested that one of the products would be 5,5-dimethyl-1,1-diphenylhexane (**21**) from hydrogenation of the product from [1,2] migration of the *tert*-butylacetylenic moiety, this hydrocarbon was synthesized by the process shown in eq 5. Surprisingly none of the hydrocarbon **21** was

$$Ph_2CHLi + ClCH_2C{\equiv}CC(CH_3)_3 \rightarrow Ph_2CHCH_2C{\equiv}CC(CH_3)_3 \xrightarrow[2H_2]{Pd/C} \underset{\mathbf{21}}{Ph_2CHCH_2CH_2CH_2C(CH_3)_3} \quad (5)$$

detected in the reaction product from **7b** upon analysis by gas chromatography and it is estimated that less than 2%, if any, of this hydrocarbon was produced. The major product (53 area % of the total volatile product) was instead identified as 5,5-dimethyl-1,2-diphenylhexane (**23**) by comparison with an authentic sample of this hydrocarbon prepared by the process outlined in eq 6.

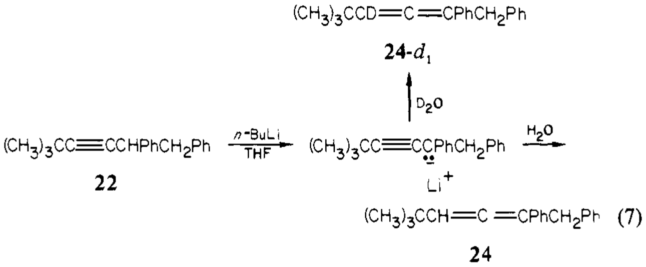
$$(CH_3)_3CC{\equiv}CLi + PhCH_2Br \rightarrow (CH_3)_3CC{\equiv}CCH_2Ph \xrightarrow[THF]{n\text{-BuLi}} (CH_3)_3CC{\equiv}C\underset{Li^+}{\ddot{C}}HPh \xrightarrow{PhCH_2Cl} \underset{\mathbf{22}}{(CH_3)_3CC{\equiv}CCHPhCH_2Ph} \xrightarrow[Pd/C]{2H_2} \underset{\mathbf{23}}{(CH_3)_3CCH_2CH_2CHPhCH_2Ph} \quad (6)$$

In this synthesis the structure of the intermediate hydrocarbon **22** is in agreement with our previous discussion of alkylation of the analogous ambident anion **6a,b**. The structure of **22** is confirmed by its spectral properties; the ^1H NMR of **22** has a two-proton doublet and a one-proton triplet (for each $J = 7$ Hz) at δ 2.88 and 3.72, respectively, as expected for the $-CHPhCH_2Ph$ moiety of **22**.

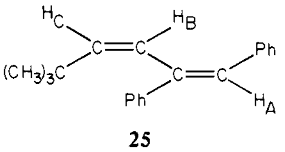
The production of hydrocarbon **23** from reaction of the chloride **7b** with Cs–K–Na alloy can be explained on the basis of a [1,2] sigmatropic migration of phenyl rather than of the *tert*-butylacetylene group in the expected intermediate organocesium compound (see Scheme IV). The resulting ambident anion would be expected to be protonated primarily to give 5,5-dimethyl-1,2-diphenyl-2,3-hexadiene (**24**) (cf. the discussion on protonation of the ambident anion **6a,b**). Hydrocarbon **24** or various isomers containing the same carbon skeleton would give the observed hydrocarbon **23** upon hydrogenation.

Since all of the products were not identified in this reaction of chloride **7b** with Cs–K–Na alloy, the reaction was repeated with some sixfold smaller ratio of Cs–K–Na alloy to chloride and finely divided mercury was added to amalgamate the excess of alloy prior to protonation. Analysis by gas chromatography revealed the presence of three major hydrocarbons. These products were separated by preparative gas chromatography and ultimately identified as some 37% yield of the above putative 5,5-dimethyl-1,2-diphenyl-2,3-hexadiene (**24**); 24% of a compound of similar carbon skeleton, 5,5-dimethyl-1,2-diphenyl-1,3-hexadiene (**25**); and 35% of a novel hydrocarbon, 5,5-dimethyl-2-(1-phenyl-2,5-cyclohexadienyl)-2,3-hexadiene (**26**).

Compound **24** is assigned the structure of 5,5-dimethyl-1,2-diphenyl-2,3-hexadiene both on the basis of its spectral properties and its identity with the authentic samples of this hydrocarbon prepared from 5,5-dimethyl-1,2-diphenyl-3-hexyne (**22**) by the procedure of eq 7.



Compound **25** is identified as 5,5-dimethyl-1,2-diphenyl-1,3-hexadiene, likely the (1*E*,3*Z*) isomer, on the basis of its spectral



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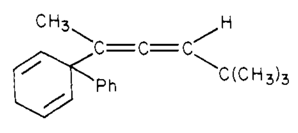

26

properties. Its ^1H NMR shows three characteristic vinyl hydrogens: a doublet for H_A at δ 6.77 ($J_{AB} = 2.5$ Hz), a doublet of doublets for H_B at δ 6.17 ($J_{BC} = 12.5$, $J_{AB} = 2.5$ Hz), and a doublet for H_C at δ 5.63 ($J_{BC} = 12.5$ Hz). The value of J_{BC} strongly implies that H_B and H_C are oriented cis to one another.[35] The ultraviolet absorption maximum of **25** at 290 nm (ϵ 31 000) is analogous to that of *trans*-stilbene (294 nm, ϵ 24 000) and unlike that of *cis*-stilbene (278 nm, ϵ 9350);[36] evidently the additional olefinic bond of **25** contributes little to alter the *trans*-stilbene chromophore of **25** because of steric inhibition of coplanarity of this bond with the stilbene moiety.

Compound **26** is assigned the structure of 5,5-dimethyl-2-(1-phenyl-2,5-cyclohexadienyl)-2,3-hexadiene based on its spectral properties. Its ^1H NMR spectrum contains a strong singlet at δ 0.98 for nine hydrogens as expected for a *tert*-butyl group but, unlike for the starting chloride or products **24** and **25**, this spectrum has only five aromatic protons. The expected second phenyl ring is present instead as a 2,4-cyclohexadienyl group exemplified by four vinyl hydrogens giving two broad resonances at δ 5.74 and 5.80 and two allylic hydrogens appearing as a multiplet at δ 2.61. Also compound **26** has a methyl group which appears as a doublet at δ 1.57 and is weakly coupled ($J = 3$ Hz) to a vinyl proton which appears as a quartet at δ 5.05; we assign these structural features to the grouping $-C(CH_3){=}CCH-$ in **26** and note that the long-range interproton coupling agrees with that in $(CH_3)_2C{=}C{=}CH_2$.[37] The absence of additional allylic hydrogens implies that the cyclohexadienyl group has two carbon substituents at allylic positions. The ^{13}C NMR spectrum agrees with these assignments and shows that the two allylic hydrogens of the cyclohexadienyl group exist on a methylene group (triplet at δ 26.0) and that the other allylic carbon of the cyclohexadienyl ring is a quaternary carbon (singlet at δ 47.7). Moreover, the peculiar carbon resonance at δ 199.4 (singlet) is near the value (δ 208–213) said to be characteristic of the central carbon of an allenic group.[14] The attachment of the phenyl group in **26** to the quaternary carbon of the 2,4-cyclohexadienyl is confirmed by the mass spectrum, which has as its most intense peak an ion at *m*/*e* 155 (expected for $C_{12}H_{11}^+$) and as its next most intense peak an ion at *m*/*e* 154 (expected for $C_{12}H_{10}^+$). These ions doubtlessly arise from cleavage of the phenylcyclohexadienyl group of **26**.

In order to identify the carbanions which gave rise to the hydrocarbons **24**, **25**, and **36** the last reaction of the chloride **7b** with Cs–K–Na alloy was repeated but with decomposition of the product by deuterium oxide. The deuterium derivative of hydrocarbon **24** by mass spectrometric analysis was a 28:72 ratio of monodeuterio and dideuterio compounds which are assigned the structures of **24**-d_1 and **24**-d_2, respectively. The deuterium

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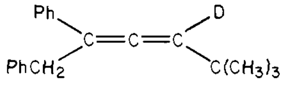
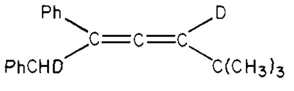
(35) Jackman, L. M.; Sternhell, S. "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed.; Pergamon Press: Oxford, 1969; pp 278, 302.

(36) Dyer, J. R. "Applications of Absorption Spectroscopy of Organic Compounds"; Prentice-Hall: Englewood Cliffs, N.J., 1965; p 20.

(37) Snyder, E. I.; Roberts, J. D. *J. Am. Chem. Soc.* **1962**, *84*, 1582–1586.

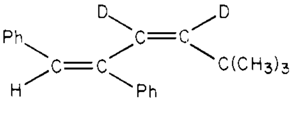


24-d_1

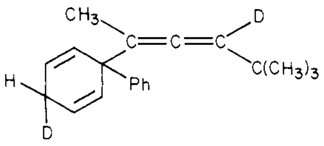


24-d_2

derivative of **25** by ^{1}H NMR and mass spectrometric analysis was the dideuterio compound **25**-d_2 while that of **26** was similarly the dideuterio compound **26**-d_2. The location of deuterium in **26** was confirmed by ^{13}C NMR, which showed triplets in the proton-decoupled spectrum for the carbons labeled with deuterium as well as small upfield shifts in the location of these resonances.[38]

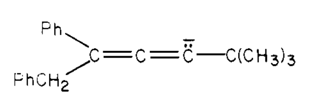


25-d_2

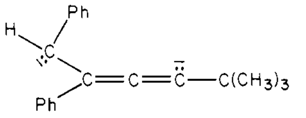


26-d_2

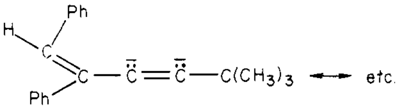
The structure of the deuterium derivative **24**-d_1 implies that the carbanionic precursor is the delocalized anion **27** (for which only a single canonical form is written for simplicity). This conclusion is confirmed by the alternate preparation of **24**-d_1 by metalation of 5,5-dimethyl-1,2-diphenyl-3-hexyne (**22**) with *n*-butyllithium followed by decomposition with deuterium oxide (see eq 7).



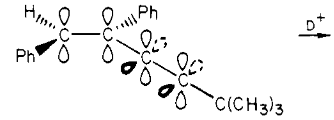
27



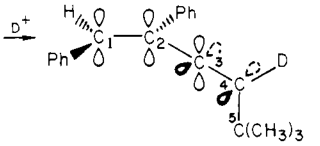
28a



28b



29



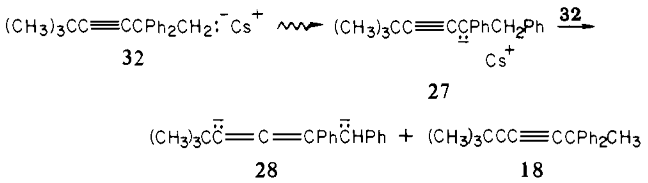
30

$\downarrow D^+$

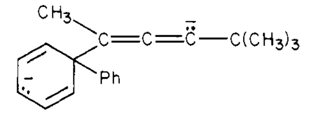
24-d_2 + **25**-d_2

The deuterium derivatives **24**-d_2 and **25**-d_2 likely come from the delocalized dianion **28a,b**; since these conventional structural formulas do not clearly show the π systems, these are redrawn in **29**. The basic carbon skeleton of **29** can be regarded as that of 5,5-dimethyl-1,2-diphenyl-1-hexen-3-yne; for the dianion two electrons are added to that lowest lying π^* orbital of this enyne conjugated system. These electrons are likely in the diene portion of the π^* system which is conjugated with the two phenyl groups, not in the orthogonal, isolated, π^* orbital near the *tert*-butyl group. The products **24**-d_2 and **25**-d_2 can be accounted for by preferential deuteration[39] at the *tert*-butyl terminus of the π system to give the monoanion **30**. This allylic anion has a π system like that in 1,2-diphenylallyl anion which, in the HMO approximation,[40] has equal charge density at C-1 and C-3; therefore, anion **30** should be deuterated approximately equally at C-1 and C-3 to give **24**-d_2 and **25**-d_2, respectively. Deuteration at C-3 may occur preferentially syn to deuterium because the bulky *tert*-butyl group hinders approach to the anion at C-3 on the side syn to the *tert*-butyl group. An alternative explanation for the cis orientation of the deuterium atoms in **24**-d_2 is provided by the theory of orbital distortion;[41] on the basis that the C(4)–C(5) bond in **30** perturbs the allyl moiety more than the C(4)–D bond, perturbation theory predicts that the electron density at C(3) will be greater in the region anti to the *tert*-butyl group than in the region syn for the highest occupied molecular orbital (HOMO). While the site of protonation is expected to correlate with the *total* electron density, the spacial distortion of the latter is difficult to assess; likely the effective distortion parallels the distortion of the HOMO.[42]

Scheme V



The structure of the deuterium derivative **26**-d_2 implies that the carbanionic precursor was the delocalized anion **31**. It is notable that **31** contains an allylic methyl group in place of the chloromethyl group of the starting chloride **7b**. This observation has important implications as to the reaction path leading to **31**.



31

The formation of **24**-d_1 via the anion **27** confirms the suggested mechanism (Scheme IV) for the product (**24**) of [1,2] phenyl migration; however, the deuterium study shows that much of **24** also comes from the dianion **28a,b** which in addition gives rise to **25**. This dianion likely comes from metalation of the initial rearranged monoanion (**27**) by a strong base, evidently 5,5-dimethyl-2,2-diphenyl-3-hexynylcesium (**32**), as shown in Scheme V. The byproduct of the metalation reaction, 5,5-dimethyl-2,2-diphenyl-3-hexyne (**18**), contains the methyl group of **31**; hence **18** seemed to us to be a possible precursor of **31**.

Reaction of 5,5-Dimethyl-2,2-diphenyl-3-hexyne (18) with Cs–K–Na Alloy. In independent experiments the hydrocarbon 5,5-dimethyl-2,2-diphenyl-3-hexyne (**18**) was allowed to react with Cs–K–Na alloy in THF at −75 °C under conditions like those used for the chloride **7b**. Protonation indeed gave the hydrocarbon **26** expected from the anion **31** along with some biphenyl. We suggest that these products are formed by the reactions of Scheme VI. The yield of biphenyl relative to 5,5-dimethyl-2-(1-phenyl-2,5-cyclohexadienyl)-2,3-hexadiene (**26**) increased with reaction time in agreement with biphenyl being formed from the precursor (**31**) of **26**.

The observed reaction of hydrocarbon **18** with Cs–K–Na alloy was rather surprising since the related hydrocarbons 1,1,1-triphenylethane and 2,2-diphenylpropane have previously been found[43] to react in a different manner; according to the previous results the expected product from **18** would be **34**. We suggest (see Scheme VI) that **34** is indeed formed reversibly from **18** along with **35**. At equilibrium the amount of **34** would be expected to

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(38) Doddrell, D.; Kitching, W.; Adcock, W.; Wiseman, P. A. *J. Org. Chem.* **1976**, *41*, 3036–3037.

(39) This preferential deuteration is to be expected if the enyne system is polarized as in 1-phenyl-1,3-butadiene which for its adduct of two electrons has a greater charge density at C-4 than at C-1 in the HMO approximation (Coulson, C. A.; Streitwieser, A. "Dictionary of π-Electron Calculations"; W. H. Freeman: San Francisco, 1965; pp 26–27).

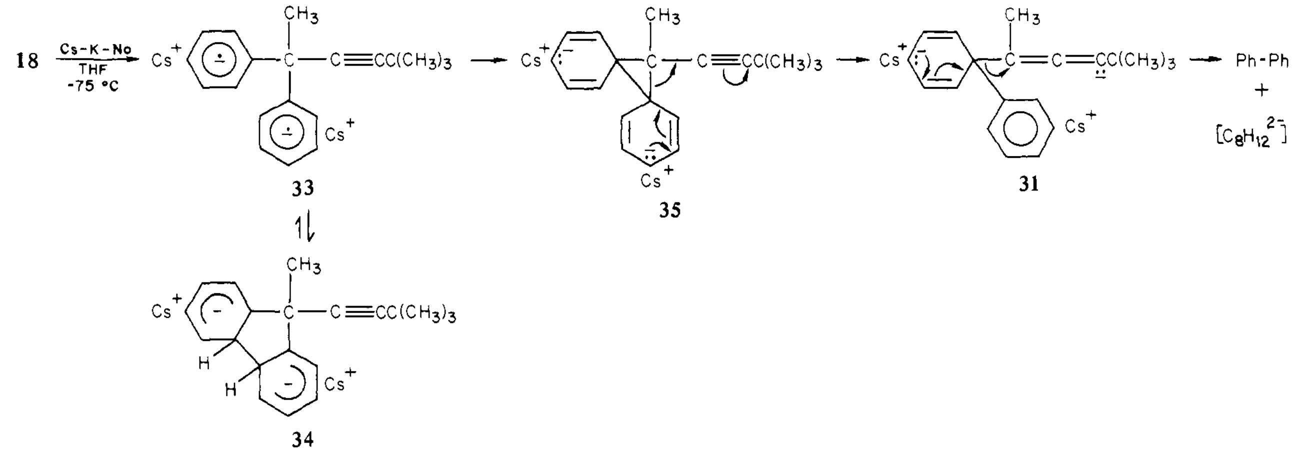
(40) Streitwieser, A.; Brauman, J. "Supplemental Tables of Molecular Orbital Calculations", Vol. I; Pergamon Press: Oxford, 1965; p 332.

(41) (a) Burgess, E. M.; Liotta, C. L. *Acc. Chem. Res.*, in press. (b) Klein, J. *Tetrahedron Lett.* **1973**, 4307–4310. (c) Inagaki, S.; Fukui, K. *Chem. Lett.* **1974**, 509–514. (d) Inagaki, S.; Fujimoto, H.; Fukui, K. *J. Am. Chem. Soc.* **1976**, *98*, 4054–4061. (e) Eisenstein, O.; Klein, J.; Lefour, J. M. *Tetrahedron* **1979**, *35*, 225–228.

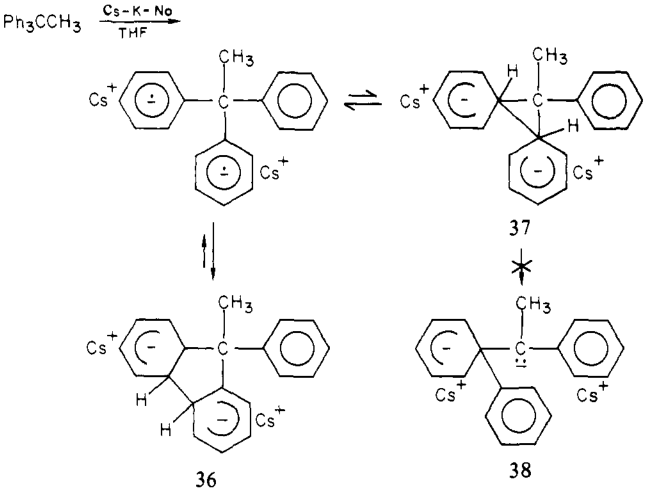
(42) We wish to thank Professor C. L. Liotta for helping us in this application of perturbation theory.

(43) Grovenstein, E.; Beres, J. A.; Cheng, Y.-M.; Pegolotti, J. A. *J. Org. Chem.* **1972**, *37*, 1281–1292.

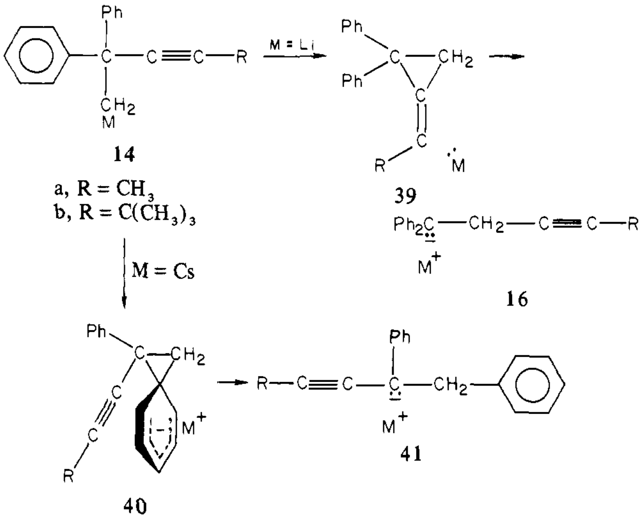
Scheme VI



Scheme VII



Scheme VIII



greatly exceed that of **35** because of the ring strain of **35**. The formation of **35**, however, is followed by its decomposition into **31**. Evidently **31** is thermodynamically more stable than **34**. The failure of 2,2-diphenylpropane to give products analogous to **31** is understandable in that a methyl group, unlike an acetylenic group, is unable to stabilize an adjacent negative charge as required for formation of **31**. The failure of 1,1,1-triphenylethane to give products (see Scheme VII) analogous to **32** is less obvious since a phenyl group is better than an acetylenic group[31] in stabilization of a negative charge on an adjacent carbon atom. An examination of molecular models reveals that, while the intermediate **37** from 1,1,1-triphenylethane is likely formed to some extent, its decomposition into the product of phenyl migration **38** is blocked by steric congestion in **37** which prevents the phenyl group from attaining an orientation which can stabilize the negative charge developing at the benzylic carbon in the transition state leading to **38** (steric inhibition of resonance). Hence, 1,1,1-triphenylethane gives only **36** under conditions whereby **18** gives **31**.

Conclusions

Sigmatropic [1,2] shifts of acetylenic groups have now been realized in two organolithium compounds, 2,2-diphenyl-3-pentynyllithium (**14a**) and 5,5-dimethyl-2,2-diphenyl-3-hexynyllithium (**14b**). These rearrangements were shown not to proceed by elimination of a lithium acetylide followed by readdition of the lithium acetylide to 1,1-diphenylethene formed in the elimination step (see Scheme III). We propose that the rearrangements proceed instead via a cyclic intermediate or transition state **39** (see Scheme VIII, M = Li) in analogy to related rearrangements of vinyl and phenyl groups.[1,2] The cyclic intermediate in Scheme VIII is depicted as being formed by a syn addition of the alkyllithium moiety of **14** to the triple bond in agreement with the known syn addition[44] of phenyllithium to cyclopropene. The simplest possibility is that **39** then undergoes an anti elimination to give **16** as shown. Known facts do not eliminate a more complex route such as isomerization of the syn adduct **39** to the anti adduct with syn elimination from the latter to give **16**.

The formation of **39** from **14** corresponds to 3-exo-digonal ring closure. Baldwin's rule[12] of 4-endo-digonal ring closure being favored in nucleophilic addition over 3-exo-digonal closure is *not* obeyed in the present examples. Recent theoretical studies[45] with ab initio molecular wave functions for the addition of H^- to acetylene to give vinyl anion suggest that the preferred geometry of addition corresponds to 3-exo-digonal ring closure for unperturbed acetylenic bonds as is also predicted by simple molecular orbital considerations for nucleophilic attack upon an acetylenic LUMO. Baldwin's rule of preferred 4-endo-digonal ring closure over 3-exo-digonal ring closure for intramolecular addition of a nucleophile to a triple bond appears to be without either experimental or theoretical justification. We conclude, therefore, that acetylenic bonds behave like ethylenic bonds for which Baldwin's rule states that 3-exo-trigonal nucleophilic ring closure is favored over 4-endo-trigonal closure. Hence acetylenic groups undergo [1,2] migrations in organolithium compounds much as do vinylic groups.

The above discussion omits the role of the countercation. We must emphasize that it is the *lithium* compounds **14a** and **14b** which undergo [1,2] migration of the acetylenic group. Also nucleophilic addition to a triple bond is expected to be anti (e.g., to give the geometrical isomer of **39**) in the absence of the lithium

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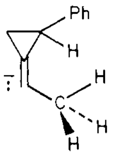
[44] Magid, R. M.; Welch, J. G. *J. Am. Chem. Soc.* **1968**, *90*, 5211-5217.

counterion if theoretical studies[45] upon addition of H^- to acetylene can be taken as a guide. An outstanding result of the present experiments is that, *when the countercation is changed from lithium to cesium,*[46] *the phenyl group migrates in exclusion of the acetylenic group*, i.e., **14b** gives **41b** and no detectable **16b** (see Scheme VIII).

As a basis for assessing the role of the countercation in the rearrangements of Scheme VIII, we have performed CNDO/2 calculations[20] upon the isomeric anions **42** and **43** as simplified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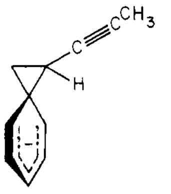

43

models for **39** and **40**, respectively. According to these calculations for the isolated anions (in the absence of solvent and countercation), **43** is some 9 kcal/mol more stable than **42**. Hence with cesium as countercation in THF as solvent the rearrangement of **14b** parallels the expected order of stabilities of the intermediates or transition states **39** and **40**; this is a reasonable result if **39** and **40** are stabilized approximately equally by interaction with solvent and cesium ions. It follows that with lithium as countercation the rearrangements of **14a** and **14b** can be explained only if lithium ion (together with solvent) stabilizes **39** considerably more than **40**. A restatement of these results is that the large cesium ion interacts approximately equally with the localized and delocalized anions,[48] **39** and **40**, respectively, whereas the small lithium ion interacts preferentially with the more localized anion. This result may be understood if the present rearrangements *all* occur within contact (or tight) ion pairs. This is not a surprising conclusion for cesium, since phenyl migration in 2,2,3-triphenylpropylcesium is believed to occur in a transition state resembling a contact ion pair[28] and organocesium compounds generally exist as contact ion pairs even with delocalized anions such as fluorenyl in THF at low temperatures.[49] In contrast organolithium compounds frequently exist as solvent-separated ion pairs, especially in THF at low temperature,[49] and benzyl migration in 2,2,3-triphenylpropyllithium is believed to occur in a transition state resembling a solvent-separated ion pair.[28] Also a detailed study of the kinetics of [1,2] vinyl rearrangement in 3-methyl-3-butenyl-*1,1-d*$_2$-lithium and solvent effects thereupon was interpreted on the basis that ionization of the organolithium compound preceded the rearrangement step.[51a] Nevertheless there is increasing evidence that organolithium compounds with localized negative charge tend to exist in solution as contact ion pairs.[50] Our proposal concerning participation of the lithium cation in [1,2] migration of the acetylenic group means that the mechanism of this migration is similar to the concerted, four-center mechanism[2] generally accepted for [1,2] vinyl migration in Grignard reagents.

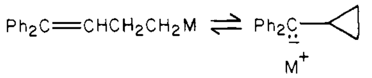
Are the present observations of cation effects upon migratory aptitudes of groups in rearrangements of organoalkali metal compounds likely to reflect general phenomena? We answer this question in the affirmative. By analogy with our present results, we predict that compound **44** with M = Li (or MgX) will undergo

$$CH_2{=}CHCPh_2CH_2M$$

44

preferential [1,2] migration of vinyl, and with M = Cs preferential migration of phenyl.

In related phenomena Maercker and Roberts[51b] found that 4,4-diphenyl-3-butenylalkali compounds undergo reversible cyclization (eq 8). For M = Li in diethyl ether only the open form



(8)

with localized negative charge was observable, while with M = Na or K only the cyclopropyl compound with delocalized charge was detectable; however, in the better solvent THF, only the cyclopropyl compound was detectable with any of these countercations. In yet another area, the rotational barrier about partial double bonds in allylic alkali metal compounds is dependent upon the alkali metal used, $\Delta G^{\ddagger}$ increasing some 7 kcal/mol from allyllithium to allylcesium in THF.[52] This result is likely due to the superior ability of lithium ion vs. cesium ion to stabilize localized negative charge in the transition state vs. the delocalized charge of the ground state.[53] The usual explanation of why lithium ion relative to heavier alkali metal cations preferentially stabilizes a localized anion vs. a delocalized anion is that carbon–lithium bonds possess more covalent character than carbon bound to heavier alkali metals.[51b,53] While recent ab initio SCF–MO calculations[54] suggest that the carbon–lithium bond in methyllithium, vinyllithium, and other simple organolithium compounds is predominantly ionic[55] with "essentially nil covalent character", we are unable to think of a better explanation for the present alkali metal effect than decreasing extent of covalent character of alkali metal carbon bonds in progressing from lithium to cesium. Solvation of organolithium compounds to give solvent-separated ion pairs can of course make organolithium compounds more ionic than corresponding cesium compounds and give rise to divergent behavior as Maercker and Roberts observed for their equilibrium (eq 8) in THF.

We would emphasize that bonding of cesium ions to carbanions in contact ion pairs is quite substantial[56] even though the bonding is largely ionic. Cesium cations stabilize carbanions in contact ion pairs and, therefore, greatly modify the chemistry of the carbanion. In the present work we have found that reaction of the organolithium compound **14b** with cesium *tert*-butoxide gives rise to the product of ortho metalation (eq 4), whereas reaction of the corresponding chloride with Cs–K–Na alloy gives [1,2] migration of phenyl (Scheme VIII) and sequential reactions. We attribute this differing behavior to the cesium *tert*-butoxide catalyzed process giving rise initially to a solvent- or alkoxide-separated ion pair (**20**), whereas reaction of the alkyl chloride with Cs–K–Na alloy evidently gives the contact ion pair (**14b**, M = Cs) without going through an intermediate solvent-separated ion pair. Carbanions separated from cesium cations by solvent (and/or alkoxide ions) are evidently more nucleophilic toward hydrogen than toward aromatic carbon while for carbanions in intimate contact with cesium ions the relative reactivities are reversed. In

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(45) (a) Dykstra, C. E.; Arduengo, A. J.; Fukunaga, T. *J. Am. Chem. Soc.* **1978**, *100*, 6007–6012. (b) Strozier, R. W.; Caramella, P.; Houk, K. N. *Ibid.* **1979**, *101*, 1340–1343.

(46) We assume in reactions of Cs–K–Na alloy with aromatic hydrocarbons and alkyl halides that cesium is the most reactive component in the alloy since this has been confirmed in all cases quantitatively investigated to date[47] in THF as solvent.

(47) (a) Grovenstein, E.; Longfield, T. H.; Quest, D. E. *J. Am. Chem. Soc.* **1977**, *99*, 2800–2802. (b) Quest, D. E., Ph.D. Dissertation, Georgia Institute of Technology, Atlanta, Ga., 1977.

(48) The terms "localized" and "delocalized" anions are only relative terms for differing extents of delocalization; thus according to CNDO/2 calculations only about half of the negative charge is localized as shown in structure **42**.

(49) (a) Hogen-Esch, T. E.; Smid, J. *J. Am. Chem. Soc.* **1966**, *88*, 307–318. (b) Smid, J. In "Ions and Ion Pairs in Organic Reactions", Szwarc, M., Ed.; Wiley-Interscience: New York, 1972; Vol 1, pp 85–151.

(50) Streitwieser, A.; Shen, C. C. C. *Tetrahedron Lett.* **1979**, 327–330.

(51) (a) Maercker, A.; Weber, K. *Justus Liebigs Ann. Chem.* **1972**, *756*, 43–78. (b) Maercker, A.; Roberts, J. D. *J. Am. Chem. Soc.* **1966**, *88*, 1742–1759.

(52) Thompson, T. B.; Ford, W. T. *J. Am. Chem. Soc.* **1979**, *101*, 5459–5464.

(53) Clark, T.; Jemmis, E. D.; Schleyer, P. v. R.; Brinkley, J. S.; Pople, J. A. *J. Organomet. Chem.* **1978**, *150*, 1–6.

(54) Streitwieser, A.; Williams, J. E.; Alexandratos, S.; McKelvey, J. M. *J. Am. Chem. Soc.* **1976**, *98*, 4778–4784.

(55) In contrast Pauling's electronegativity scale leads to the conclusion that the Li–C bond has only about 43% ionic character (Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, N.Y., 1960; p 102).

(56) For comparison, the bond strengths of CsCl and CsAu (as gaseous molecules) are 106 and 108 kcal/mol, respectively (Busse, B.; Weil, K. G. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 629–630.

a related case the separated ion pair deprotonated the solvent tetrahydrofuran faster than it added to a phenyl group.[33]

Finally, in the study of the reaction of 1-chloro-5,5-dimethyl-2,2-diphenyl-3-hexyne with Cs–K–Na alloy, we discovered that the hydrocarbon 5,5-dimethyl-2,2-diphenyl-3-hexyne reacts with the alloy to give a dianion of rearranged carbon skeleton (see Scheme VI). This reaction is dependent upon the great reducing power of cesium and some of its alloys, which is adequate to convert benzene and toluene to radical anions which dimerize.[47] The most novel aspect of the new work is the migration of a phenyl group onto another benzene ring. The closest analogy known to us is the reductive rearrangement of 1,1,3-triphenylindene to 1,2,3-triphenylindene brought about by sodium in ether, a reaction discovered by Schlenk and Bergmann[57] but first correctly interpreted by Ziegler and Crössman.[58-60] The great rapidity of the rearrangement of 5,5-dimethyl-2,2-diphenyl-3-hexyne by Cs–K–Na at −75 °C is noteworthy.

Experimental Section[61]

^1H NMR spectra were recorded at 60 MHz 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 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 a Varian M-66, a Hitachi (Perkin-Elmer) RMU-7L, or a Varian MAT 112S (with SS 200 data system) mass spectrometer.

Gas chromatographic (GC) analyses were ordinarily made on a Perkin-Elmer Model 881 chromatograph equipped with a hydrogen-flame ionization detector. Quantitative GC analyses were made with an internal standard and calibration based upon authentic samples. Qualitative GC analyses are reported as "area percent" of total volatile constituents.

All reactions with Na–K and Cs–K–Na alloys were run in the usual Morton[62] apparatus enclosed in a glovebox under an atmosphere of nitrogen to reduce fire hazards.

5-Chloro-4,4-diphenyl-2-pentyne (7a). Into a 1-L Morton flask equipped with a high-speed stirrer[62] 750 mL of diethyl ether was distilled from $LiAlH_4$. Eutectic Na–K alloy (17.1 g, 0.34 g-atom K) was added and the mixture stirred vigorously under a nitrogen atmosphere until the alloy was finely dispersed at reflux temperature (ca. 20 min). A solution of 23.6 g (0.107 mol) of 1-methoxy-1,1-diphenyl-2-butyne (mp 68–69 °C, lit.[63] mp 46–47 °C) in 50 mL of anhydrous ether was added dropwise over a 20-min period and the solution stirred at reflux for 2 h until analysis revealed that cleavage of the methyl ether was complete. The analytical sample was obtained by withdrawing a few milliliters of the solution with a syringe inserted through a rubber septum on a side arm of the flask. Decomposition of this aliquot with 95% ethanol and examination of the ^1H NMR spectrum of the product revealed the disappearance of the peaks at δ 3.34 (OCH_3) and 1.93 ($C{\equiv}CCH_3$) of the reactant and appearance of peaks at δ 1.77 (3 H, d, J = 7 Hz, $C{=}C{=}CHCH_3$) and 5.63 (1 H, q, J = 7 Hz, $C{=}C{=}CH$) attributed to the protonated product 1,1-diphenyl-1,2-butadiene. Mercury (10 mL, 135 g) was added dropwise to the reaction solution to amalgamate unreacted Na–K alloy. The brownish-red solution, containing a chocolate-colored, finely divided solid, was siphoned slowly under nitrogen into 400 mL of a solution composed of equal amounts by volume of CH_2Cl_2 and diethyl ether at −35 °C. The methylene chloride was kept mixed by swirling. The brownish-red color was gradually discharged upon warming the mixture to room temperature. Any unreacted alloy in the product was destroyed by addition of 95% ethanol. The volatile components were removed from the product on a rotatory evaporator, a nearly saturated brine solution was added, and the mixture was extracted with ether. Removal of the ether gave 22.2 g of crude product whose ^1H NMR analysis revealed the presence of 61% 5-chloro-4,4-diphenyl-2-pentyne, 19% 1,1-diphenyl-1,2-butadiene, and the remainder unidentified aromatic hydrocarbon. After two distillations through a Hickman still (at 0.05 mmHg and bath temperature of 115 °C) and recrystallization from *n*-pentane, the product amounted to 12.9 g (47% yield) of 5-chloro-4,4-diphenyl-2-pentyne of 99% purity: mp 60.5–61.0 °C; IR (neat melt) 3050 (m), 3020 (m), 2950 (m), 2920 (m), 2840 (m), 2235 (w), 1590 (m), 1490 (s), 1450 (s), 750 (s), 730 (s), 700 (s) cm^{-1}; ^1H NMR (CCl_4) δ 1.98 (3 H, s, $C{\equiv}CCH_3$), 4.07 (2 H, s, CH_2Cl), 7.2–7.6 (10 H, m); ^{13}C NMR ($CDCl_3$) δ 3.7 (q, $C{\equiv}CCH_3$), 51.4 (t, CH_2Cl), 51.6 (s, CCH_2Cl), 80.6 and 81.8 (each s, $C{\equiv}CCH_3$), 126.4 (d), 126.9 (d), 127.5 (d), 141.8 (s). Anal. ($C_{17}H_{15}Cl$) C, H, Cl. In two repetitions[64] of this synthesis, evidently with more complete exclusions of moisture, the yields of 5-chloro-4,4-diphenyl-2-pentyne after two distillations and recrystallization from pentane were 67 and 70% of product of mp 59.0–60.0 °C. The NMR spectrum of the crude product before distillation revealed the presence of 76% yield of the chloride and of about 10% yield of 1,1-diphenyl-1,2-butadiene which evidently is converted to nonvolatile material during distillation.

Reaction of 5-Chloro-4,4-diphenyl-2-pentyne (7a) with Lithium. Into a 500-mL Morton flask equipped with a high-speed stirrer 250 mL of tetrahydrofuran (THF) was distilled from $NaAlH_4$. Finely cut lithium wire (1.68 g, 0.242 g-atom) was added, the flask was cooled to −10 °C, and then 0.14 g of methyl iodide was added. The solution was stirred vigorously for 5 min and then 5% of 2.50 g (9.8 mmol) of 5-chloro-4,4-diphenyl-2-pentyne in 20 mL of THF was added. A pink color developed in the solution after continued stirring for 30 min. The flask was then cooled to −75 °C, the remainder of the chloride was added dropwise over a period of 30 min, and stirring was continued at −75 °C for 3 h before carbonation of a 140-mL aliquot (A). The remainder of the solution was warmed to 0 °C and held at 0 ± 5 °C for 4 h and then a final 110-mL aliquot (B) was carbonated by forcing the reaction mixture onto crushed solid carbon dioxide. In working up these aliquots the THF was removed under reduced pressure and the residue made distinctly alkaline by addition of 10% NaOH. The neutral material was extracted from the alkaline mixture with ether; the aqueous layer was acidified with hydrochloric acid and the organic acids were extracted with ether. Aliquot A yielded 0.69 g of neutral product and 0.52 g of acidic product. The neutral product according to quantitative GC analysis at 180 °C on a 6 ft × 0.125 in. column packed with 10% SE-30 (silicone gum rubber) on 100–120 mesh Chromosorb G with diphenylmethane (retention time 1.25 min) added as internal standard had components at 3.0 and 6.2 min corresponding respectively to 4,4-diphenyl-2-pentyne (33 wt %) and unreacted chloride (67 wt %). The acidic fraction as methyl ester (with methyl triphenylacetate, retention time 8.0 min, added as internal standard) by quantitative GC analysis on the same column at 200 °C contained 83 wt % of 3,3-diphenyl-4-hexynoic acid (**15a**) (retention time 4.0 min). 2,2-Diphenyl-4-hexynoic acid (**17a**) and 3,3-diphenyl-4-hexynoic acid (as methyl esters) have identical retention times under these GC conditions. The absence of appreciable 2,2-diphenyl-4-hexynoic acid (<1%) in the product was established with a 12 ft × 0.125 in. column packed with 15% Apiezon H on 60–80 mesh Chromosorb at 200 °C; on this column 2,2-diphenyl-4-hexynoic acid and 3,3-diphenyl-4-hexynoic acid as methyl esters had retention times respectively of 31.9 and 37.2 min. Recrystallization of the crude acid from hexane–cyclohexane mixture (4:1 by volume) gave pure 3,3-diphenyl-4-hexynoic acid; mp 174.0–174.5 °C; IR (Nujol) 1715 (s), 1695 (s), 1600 (m), 1490 (m), 1418 (m), 1350 (m), 1248 (s), 1188 (m), 1167 (m), 1086 (w), 982 (m), 966 (m), 771 (m), 761 (m), 710 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.94 (3 H, s, $-C{\equiv}CCH_3$), 3.33 (2 H, s, $-CH_2CO_2H$), 7.2–7.7 (10 H, m), 8.55 (1H, broad s, $-CO_2H$); MS *m/e* (rel intensity) 264 (23, M^+), 249 (4), 236 (43), 221 (45), 219 (9), 218 (7), 207 (27), 205 (100), 204 (20), 203 (24), 202 (17), 193 (56), 189 (11), 187 (18), 179 (23), 178 (40), 176 (6), 165 (17), 152 (60). Anal. ($C_{18}H_{16}O_2$) C, H.

Aliquot B yielded 0.55 g of neutral product and 0.42 g of acidic product. These were analyzed as for the previous aliquot. The neutral product contained 64 wt % of 4,4-diphenyl-2-pentyne and less than 1% of unreacted chloride. The acidic product contained 50 wt % of 2,2-diphenyl-4-hexynoic acid (**17a**) and less than 1% (if any) of 3,3-diphenyl-4-hexynoic acid. Two recrystallizations of the crude acid from a 4:1 (v:v) mixture of hexane and cyclohexane gave colorless crystals, mp 123.5–124.0 °C, which had identical IR and ^1H NMR spectra with those obtained for an authentic sample of 2,2-diphenyl-4-hexynoic acid (whose preparation is given below) and which gave no mixture melting point depression with the authentic acid. The 4,4-diphenyl-2-pentyne in the neutral products was identified by comparison of its ^1H NMR spectrum and GC retention time with those of a sample of this hydrocarbon prepared by an independent method described below.

Rearrangement of 2,2-Diphenyl-3-pentynyllithium (14a) in the Pres-

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(57) Schlenk, W.; Bergmann, E. *Justus Liebigs Ann. Chem.* **1928**, *463*, 125–127.

(58) Ziegler, K.; Crössman, F. *Chem. Ber.* **1929**, *62*, 1768–1770.

(59) (a) Koelsch, C. F. *J. Am. Chem. Soc.* 1933, *55*, 3394–3399. (b) *Ibid.*, **1934**, *56*, 480–484.

(60) Miller, L. M.; Boyer, R. F. *J. Am. Chem. Soc.* **1971**, *93*, 646–650.

(61) Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, Ga.; all melting points are uncorrected.

(62) Morton, A. A.; Redman, L. M. *Ind. Eng. Chem.* **1948**, *40*, 1190.

(63) Pavlova, L. A. *Zh. Obshch. Khim.* **1964**, *34*, 3270; *Chem. Abstr.* **1965**, *62*, 3970*e*.

(64) We wish to thank Mr. Douglas L. Streeter for these repetitions of the synthesis of **7a**.

ence of Lithium *tert*-Butylacetylide. 2,2-Diphenyl-3-pentynyllithium was prepared at −75 °C as described above from reaction of 2.55 g (10.0 mmol) of 5-chloro-4,4-diphenyl-2-pentyne with 1.68 g (0.242 g-atom) of lithium in 300 mL of THF under an atmosphere of nitrogen prepurified by passage over molecular sieves (8–12 mesh beads, 5 Å effective pore size, Davison Chemical), and then over a supported copper catalyst (Catalyst R 3-11 from Chemical Dynamics Corp.). A solution of lithium *tert*-butylacetylide was prepared from reaction of 0.65 g (7.9 mmol) of 3,3-dimethyl-1-butyne (freshly distilled material from Chemical Samples Co.) in 20 mL of THF at −40 °C for 5 min with 3.05 mL (7.5 mmol) of *n*-butyllithium (2.46 M in hexane); the solution was then held at −10 °C for 30 min. The solution of lithium *tert*-butylacetylide was added dropwise over a 20-min period to the well-stirred solution of 2,2-diphenyl-3-pentynyllithium at −78 °C. Then a 120-mL aliquot (36%) of the solution was carbonated (carbonation I). The reaction flask was warmed to 0 °C and held at this temperature for 3 h before carbonation of a 160-mL aliquot (49% of the original solution, carbonation II). The usual workup with quantitative GC analysis as previously (with confirmation by NMR analysis) gave from carbonation I, in the acid fraction, 0.31 g (1.18 mmol) of 3,3-diphenyl-4-hexynoic acid (**15a**), no detectable (<1 wt %) 2,2-diphenylpropanoic acid, 0.18 g (1.4 mmol) of 4,4-dimethyl-2-pentynoic acid, and, in the neutral fraction, 0.52 g (2.4 mmol) of 4,4-diphenyl-2-pentyne. Similarly carbonation II gave, in the acid fraction, 0.45 g (1.72 mmol) of 2,2-diphenyl-4-hexynoic acid (**17a**), 0.32 g (1.4 mmol) of 2,2-diphenylpropanoic acid, 0.47 g (3.7 mmol) of 4,4-dimethyl-2-pentynoic acid, and, in the neutral fraction, 0.28 g (1.28 mmol) of 4,4-diphenyl-2-pentyne. On the 12-ft Apiezon-H column at 210 °C, methyl 2,2-diphenyl-4-hexynoate had a GC retention time of 27.6 min while a known sample of methyl 6,6-dimethyl-2,2-diphenyl-4-heptynoate had a retention time of 31.7 min. In the acids from carbonation II there was a tiny peak of retention time 32.9 min and of 0.4 area % of the peak due to methyl 2,2-diphenyl-4-hexynoate. Hence the amount of methyl 6,6-dimethyl-2,2-diphenyl-4-heptynoate in carbonation II, if any, is estimated as less than 0.007 mmol. Also for carbonation II according to GC analysis on the SE-30 column at 210 °C methyl 2,2-diphenyl-4-hexynoate appeared at a retention time of 4.5 min followed by two unknown peaks at 5.5 and 6.2 min in amounts of 7 and 5 area %, respectively, of the hexynoate. These unknown methyl esters were separated by preparative GC and each gave MS *m*/*e* peaks at 278 as expected for molecular ions of isomers of methyl 2,2-diphenyl-4-hexynoate. The components of retention times 4.5, 5.5, and 6.2 min had identical retention times (this was checked by mixed GC injections) with those of the three major acids obtained below from 2,2-diphenyl-3-pentynyllithium and cesium *tert*-butoxide at −78 °C. The minor components of retention time 5.5 and 6.2 min are therefore likely methyl 5,5-diphenyl-3-hexynoate and methyl 5,5-diphenyl-2,3-hexadienoate, respectively; however, the major component is *not* 2-(1′,1′-diphenylethyl)buta-2,3-dienoic acid since the ^{1}H NMR spectrum of the crude acid had a characteristic quartet at δ 3.21 and triplet at δ 1.61 expected for 2,2-diphenyl-4-hexynoic acid. Minor amounts of 2-(1′,1′-diphenylethyl)buta-2,3-dienoic acid may have been present but were not detected in the NMR spectrum under the conditions run.

Reaction of 2,2-Diphenyl-3-pentynyllithium (14a) with Cesium *tert*-Butoxide. 2,2-Diphenyl-3-pentynyllithium was prepared from 2.55 g (10.0 mmol) of 5-chloro-4,4-diphenyl-2-pentyne with excess lithium in 250 mL of THF at −75 °C as described previously. Carbonation of a 100-mL aliquot of this solution gave 0.40 g of neutral material and 0.71 g of acid whose NMR spectrum agreed with that of 3,3-diphenyl-4-hexynoic acid. Cesium *tert*-butoxide was prepared by reaction in a Morton high-speed stirring apparatus at 3.3 g (45 mmol) of *tert*-butyl alcohol with excess cesium metal (71 mg-atoms) in 320 mL of THF at reflux temperature with stirring for 3 h. Titration of aliquots showed that the cesium *tert*-butoxide solution was 0.140 M. A measured portion (151 mL, 21 mmol) of the cesium *tert*-butoxide solution was withdrawn by syringe (care being taken to exclude excess cesium metal) and added dropwise with efficient stirring to the solution of 2,2-diphenyl-3-pentynyllithium at −75 °C. The solution was held at −75 °C with stirring for 30 min before carbonation. The usual workup gave 0.60 g of neutral material and 0.98 g of acids. The methyl esters of the acids upon GC analysis (on the SE-30 column at 210 °C) gave products at retention times in min (area % yield) 3.0 (6%), 4.1(3%), 4.5 (44%), 5.5 (22%), 6.2 (20%), and 10.4 (4%). The three major components were separated by preparative GC on the SE-30 column.

The component of retention time 4.5 min was identified as the methyl ester of 2-(1′,1′-diphenylethyl)buta-2,3-dienoic acid, $CH_2{=}C{=}C(CPh_2CH_3)CO_2CH_3$, mp 63–64 °C, on the basis of the following data: IR (neat melt) 3083 (m), 3060 (m), 3025 (m), 2983 (m), 2945 (m), 1957 (m), 1935 (m),[65] 1727 (s), 1605 (m), 1500 (m), 1453 (m), 1443 (m), 1380 (m), 1265 (s), 1135 (m), 1045 (s), 858 (m), 803 (s), 775 (s), 748 (m), 715 (s) cm^{-1}; ^{1}H NMR (CCl_4) δ 1.98 (s, 3 H, CH_3), 3.55 (s, 3 H, OCH_3), 4.85 (s, 2 H, $C{=}C{=}CH_2$), 7.13 (s, 10 H, aromatic H); MS *m*/*e* (rel intensity) 278 (5, M$^+$), 263 (3), 246 (3), 245 (4), 231 (5), 220 (18), 219 (100), 218 (8), 217 (3), 205 (5), 204 (15), 203 (7), 202 (7), 181 (30), 179 (4), 178 (4), 166 (6), 165 (7). Anal. ($C_{19}H_{18}O_2$) C, H.

The component of retention time 5.5 min was identified as likely the methyl ester of 5,5-diphenyl-3-hexynoic acid, $CH_3C(Ph)_2C\equiv CCH_2CO_2CH_3$, based on its method of preparation and the following data: ^{1}H NMR (CCl_4) δ 1.90 (s, 3 H, CH_3), 3.27 (s, 2 H, CH_2), 3.70 (s, 3 H, OCH_3), 7.0–7.5 (m, 10 H, aromatic H); MS *m*/*e* (rel intensity) 278 (21, M$^+$), 263 (33), 231 (8), 219 (70), 218 (100), 217 (12), 205 (36), 204 (51), 203 (43), 202 (26), 191 (9), 181 (21), 180 (13), 179 (9), 178 (12), 166 (6), 165 (10).

The component of retention time 6.2 min was tentatively assigned the structure of methyl 5,5-diphenyl-2,3-hexadienoate, $CH_3CPh_2CH{=}C{=}CHCO_2CH_3$, based on its mode of preparation and its mass spectrum: *m*/*e* (rel intensity) 278 (16, M$^+$), 263 (14), 247 (8), 246 (10), 245 (7), 231 (20), 219 (100), 218 (78), 217 (15), 205 (14), 204 (30), 203 (27), 202 (19), 200 (22), 181 (95, likely $M^+{-}CH{=}C{=}CHCO_2CH_3$), 180 (16), 179 (15), 178 (14), 173 (62), 166 (19), 165 (23). Also the ^{1}H NMR spectrum ($CDCl_3$) of the crude mixture of acids, after the peaks attributable to the other identified components were subtracted, had prominent peaks at δ 6.22 (1 H, d, J = 6 Hz, $CH{=}C{=}C\mathit{H}CO_2H$), 5.63 (1 H, d, J = 6 Hz, $C\mathit{H}{=}C{=}CHCO_2H$), 1.82 (3 H, s, CH_3).

1-Chloro-5,5-dimethyl-2,2-diphenyl-3-hexyne (7b). 1-Methoxy-4,4-dimethyl-1,1-diphenyl-2-pentyne (27.8 g, 0.100 mol, mp 52.5–53.0 °C, lit.[63] mp 47–48 °C) was cleaved by Na–K alloy (15.6 g, 0.400 g-atom of K) in 1.2 L of anhydrous ether according to the general procedure used in the preparation of 5-chloro-4,4-diphenyl-2-pentyne. The brown-red solution was then treated with 204 g (1.02 g-atoms) of mercury to amalgamate the excess Na–K alloy and then slowly siphoned with good mixing into 400 mL of 1:1 by volume dichloromethane–diethyl ether at −78 °C. The color was discharged gradually on warming to room temperature. The usual workup gave 26.1 g of crude product which by ^{1}H NMR analysis contained 63 mol % of 1-chloro-5,5-dimethyl-2,2-diphenyl-2-hexyne and 37 mol % of 4,4-dimethyl-1,1-diphenyl-1,2-pentadiene. The product was purified by chromatography on 800 g of 100–200 mesh silica gel (Fischer Scientific Co.) on a column 5.5 cm in diameter with elution first of the allene and then the chloride by petroleum ether–benzene (5:1 parts by volume). There was isolated 12.7 g (43% yield) of pure 1-chloro-5,5-dimethyl-2,2-diphenyl-3-hexyne: bp 160 °C (0.1 mmHg); IR (neat) 3086 (m), 3058 (m), 3028 (m), 2963 (s), 2928 (m), 2998 (m), 2868 (m), 2248 (w), 1602 (m), 1497 (s), 1479 (m), 1454 (s), 1368 (m), 1275 (m), 1210 (m), 1037 (m), 765 (m), 737 (m), 705 (s) cm^{-1}; ^{1}H NMR (CCl_4) δ 1.31 [9 H, s, $C(CH_3)_3$], 3.98 (2 H, s, CH_2Cl), 7.0–7.5 (10 H, m). Anal. ($C_{20}H_{21}Cl$) C, H, Cl.

A repetition of the above preparation but with bromochloromethane in place of dichloromethane gave essentially the same ratio of halide to pentadiene and in the same yield as with dichloromethane.

Reaction of 1-Chloro-5,5-dimethyl-2,2-diphenyl-3-hexyne (7b) with Lithium. Excess lithium (1.68 g, 0.242 g-atom) was allowed to react with 1-chloro-5,5-dimethyl-2,2-diphenyl-3-hexyne (2.17 g, 7.31 mmol) in 270 mL of THF at −75 °C according to the previous procedure given for 5-chloro-4,4-diphenyl-2-pentyne. After completion of the 3-h stirring period at −75 °C, a 155-mL aliquot (A) of the red solution was carbonated (i.e., forced onto crushed solid carbon dioxide). The remaining solution was warmed to 0 ± 5 °C and held at this temperature for 3 h before carbonation of the remaining 115-mL aliquot (B) of the now black-red solution. In working up each aliquot the THF was removed at reduced pressure on a rotary evaporator and the solid residue was dissolved in 150 mL of ether. The ethereal solution was extracted ten times with 100-mL portions of 5% aqueous sodium hydroxide (note the solubility of the lithium salt of the acid in ether and the low solubility of the salt of the acid in aqueous sodium hydroxide). The combined aqueous extracts were acidified with hydrochloric acid and the free acids extracted with ether. The ethereal extract was dried over anhydrous $MgSO_4$ before removal of ether.

Aliquot A yielded 1.09 g (3.56 mmol) of carboxylic acid which after recrystallization from *n*-pentane amounted to 0.95 g (3.10 mmol, 74% yield) of 6,6-dimethyl-3,3-diphenyl-4-heptynoic acid (**15b**): mp 145.0–145.5 °C; IR (Nujol) 1710 (s), 1607 (m), 1510 (m), 1426 (m), 1375 (m), 1336 (s), 1277 (s), 1249 (s), 1220 (m), 1172 (m), 1053 (m), 954 (m), 805 (m), 788 (m), 771 (s), 715 (s), 690 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.26 [9 H, s $(CH_3)_3C$], 3.27 (2 H, s, $C\mathit{H}_2CO_2H$), 7.1–7.6 (10

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(65) Doubling of the allenic $C{=}C{=}C$ stretching band as for the bands at 1957 and 1935 cm^{-1} is often found in systems like the present in which a polar group is directly attached to the allenic moiety (Bellamy, L. J. "The Infrared Spectra of Complex Molecules", Vol. 1, 3rd ed.; Chapman and Hall: London, 1975; p 70).

H, m, aromatic H), 9.7 (1 H, bd s, CO_2H); MS *m/e* (rel intensity) 306 (7, M^+), 250 (50), 249 (40), 247 (100), 232 (41), 231 (15), 229 (15), 217 (18), 216 (14), 215 (27), 207 (38), 205 (28), 204 (20), 203 (14), 202 (15), 191 (14), 179 (13), 178 (25), 165 (14). Anal. ($C_{21}H_{22}O_2$) C, H.

Aliquot B yielded 0.81 g (2.64 mmol) of crude acid which upon recrystallization from *n*-pentane gave 0.64 g (2.1 mmol, 67%) of pure 6,6-dimethyl-2,2-diphenyl-4-heptynoic acid (**17b**): mp 133–134 °C; IR (Nujol) 1702 (s), 1608 (w), 1505 (m), 1470 (s), 1407 (m), 1375 (m), 1290 (s), 1280 (s), 1270 (s), 1220 (m), 1200 (m), 1094 (w), 1048 (w), 1000 (w), 955 (m), 787 (m), 753 (s), 723 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.02 [9 H, s, $-C(CH_3)_3$], 3.19 (2 H, s, $-CH_2C\equiv C-$), 7.30 (10 H, s, aromatic H), 10.7 (1 H, bd s, $-CO_2H$); MS *m/e* (rel intensity) 306 (19, M^+), 291 (35), 261 (17), 249 (9), 215 (16), 212 (44), 211 (95), 205 (13), 204 (6), 203 (8), 202 (8), 194 (11), 193 (7), 192 (60), 191 (8), 189 (6), 183 (11), 180 (100), 179 (33), 178 (27), 167 (19), 165 (100). The melting point, mixture melting point, and spectral properties of this acid were identical with those of the sample of 6,6-dimethyl-2,2-diphenyl-4-heptynoic acid synthesized below from diphenylacetic acid.

Reaction of 5,5-Dimethyl-2,2-diphenyl-3-hexynyllithium (14b) with Cesium *tert*-butoxide. The organolithium compound was prepared as previously from 1.94 g (6.5 mmol) of 1-chloro-5,5-dimethyl-2,2-diphenyl-3-hexyne and 1.7 g (0.24 g-atom) of lithium in 265 mL of THF at −75 °C. After completion of the 3-h stirring period at −75 °C, 72 mL (27%) of the solution was forced onto crushed solid carbon dioxide (carbonation I). To the remaining solution was added dropwise with stirring at −75 °C 34 mL of 0.38 M cesium *tert*-butoxide (13 mmol) in THF. The solution was then stirred for 30 min at −75 °C before carbonation of a 173-mL aliquot (carbonation II) which was equivalent to about 58% of the starting chloride. After the usual workup, quantitative GC analysis of the methyl esters on the SE-30 column (confirmed by NMR) indicated that carbonation I gave 0.48 g (1.57 mmol, 89% yield) of 3,3-diphenyl-6,6-dimethyl-4-heptynoic acid. Similar analysis for carbonation II gave 0.28 g (1.07 mmol, 28% yield) of 5,5-dimethyl-2,2-diphenyl-3-hexyne (**18**), 0.019 g of 2,2-diphenylpropanoic acid, and 0.70 g (2.29 mmol, 61% yield) of an acid believed to be 2-(1,4,4-trimethyl-1-phenyl-2-pentynyl)benzoic acid (**19**). The acid assigned the structure of 2-(1,4,4-trimethyl-1-phenyl-2-pentynyl)benzoic acid after recrystallization from *n*-pentane had the properties mp 164.0–164.5 °C; IR (Nujol) 1707 (s), 1683 (s), 1583 (m), 1500 (s), 1424 (s), 1373 (m), 1315 (s), 1286 (s), 1217 (m), 1163 (m), 1078 (m), 1035 (m), 967 (m), 812 (m), 777 (s), 750 (m), 717 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.21 [9 H, s, $-C(CH_3)_3$], 2.00 (3 H, s, CH_3), 7.1–8.0 (9 H, m, ArH), 9.2 (1 H, bd s, $-CO_2H$); ^{13}C NMR ($CDCl_3$) 27.4 [s, $-\mathit{C}(CH_3)_3$], 30.8 [q, $-C(\mathit{CH}_3)_3$], 32.6 [q, CH_3], 44.2 [s, $Ar\mathit{C}Ph(CH_3)$], 83.7 [s, $-C\equiv \mathit{C}C(CH_3)_3$], 92.8 [s, $-\mathit{C}\equiv CC(CH_3)_3$], 125.6, 126.2, 127.2, 129.4, and 130.0 (all d, aromatic CH), 131.7 (s, aromatic $\mathit{C}CO_2H$), 144.3 and 146.4 (both s, quaternary aromatic C), 173.5 (s, $-CO_2H$); MS *m/e* (rel intensity) 306 (32, M^+), 291 (98), 273 (52), 261 (8), 258 (38), 250 (100), 249 (43), 232 (73), 231 (82), 216 (23), 215 (48), 209 (23), 208 (33), 207 (36), 206 (38), 205 (53), 204 (21), 203 (29), 202 (39), 193 (13), 191 (14), 189 (15), 178 (31), 165 (44), 157 (41). For further characterization, the acid of mp 164.0–164.5 °C was converted to its methyl ester (by reaction with ethereal diazomethane): ^1H NMR ($CDCl_3$) δ 1.23 [9 H, s, $-C(CH_3)_3$], 1.97 (3 H, s CH_3), 3.43 (3 H, s, OCH_3), 7.0–8.0 (9 H, m, ArH); UV (95% EtOH) λ_{max} 220 nm (ϵ 3640) and shoulder 264 (385); MS *m/e* (rel intensity) 320 (16, M^+), 319 (19), 305 (16), 273 (15), 264 (15), 263 (15), 258 (10), 249 (10), 246 (9), 245 (8), 234 (13), 232 (38), 231 (42), 222 (7), 219 (15), 216 (8), 215 (18), 205 (17), 204 (13), 203 (15), 202 (16), 178 (12), 165 (7), 157 (10), ..., 43 (100); exact mass 320.1768 (calcd for $C_{22}H_{24}O_2$, 320.1776).

Reaction of 1-Chloro-5,5-dimethyl-2,2-diphenyl-3-hexyne (7b) with Excess of Cs–K–Na Alloy Followed by Protonation. Into a 500-mL Morton flask equipped with a high-speed stirrer was distilled 250 mL of THF from $NaAlH_4$. To the flask under a nitrogen atmosphere was added 4.65 g of eutectic Cs–K–Na[34] (containing 0.0248 g-atom of Cs). The mixture was stirred vigorously at room temperature for 1.5 h and then at −75 °C for 20 min before addition of 0.425 g (1.43 mmol) of 1-chloro-5,5-dimethyl-2,2-diphenyl-3-hexyne in 10 mL of THF. After stirring for 4 min, stirring of the deep red solution was discontinued and the unreacted alloy was allowed to settle. The solution was forced through a cannula into 300 mL of water. After removal of THF on a rotatory evaporator, the aqueous phase was saturated with sodium chloride and the mixture extracted with ether. The ethereal extract yielded 0.38 g of a yellow oil which by GC analysis on the SE-30 column at 200 °C contained at least seven components in area percent yields (retention time, min) 35 (3.4), 8 (4.0), 19 (4.8), 6 (5.6), 8 (6.3), and after 9 min upon raising the temperature to 260 °C at 24 °C/min, 6 (11.5), 18 (13.0). The ^1H NMR spectrum of the crude product showed vinyl protons at δ 5.0–6.2 in an amount of 22% of the aromatic protons. To simplify analysis this mixture (0.24 g) was dissolved in 25 mL of 95% ethanol containing 15 drops each of glacial acetic acid and concentrated hydrochloric acid and reacted with hydrogen over 0.100 g of a 5% Pd on carbon catalyst (from Engelhard Industries) in a low-pressure (35 psi) Parr hydrogenation apparatus for 17 h at room temperature. After removal of the catalyst and the ethanolic solvent, the residual oil was dissolved in pentane and extracted with 5% aqueous sodium hydroxide. The pentane solution yielded 0.21 g of an oil whose ^1H NMR spectrum revealed the absence of vinylic protons in the region δ 4.5–6.5. Analysis by GC on the SE-30 column at 200 °C now revealed four components in area percent yields (retention time, min) 53 (3.4), 25 (3.8), 3.0 (5.0), and, after 9 min upon raising the temperature to 260 °C at 24 °C/min, 19 (13.0). Under these GC conditions the authentic sample of 5,5-dimethyl-1,1-diphenylhexane (**21**) (this hydrocarbon was expected from hydrogenation of the product from 1,2 migration of the acetylene group) had a retention time of 4.1 min and was clearly separable (as shown by a GC coinjection) from the reaction products. It is estimated that less than 2%, if any, of 5,5-dimethyl-1,1-diphenylhexane was present in the GC volatile reaction products. The major components of retention times 3.4 and 3.8 min were separated by preparative GC. The compound of retention time 3.4 min showed a MS molecular ion at *m/e* 266 and was identified as 5,5-dimethyl-1,2-diphenylhexane (**23**) on the basis of comparisons of its ^1H NMR, mass spectrum, and GC retention time (and mixture gas chromatograph) with those of an authentic sample of 5,5-dimethyl-1,2-diphenylhexane whose synthesis and properties are described below. The compound of retention time 3.8 min is likely 2,2-dimethyl-5-(1-phenylcyclohexyl)hexane based on identification of a compound with this carbon skeleton in a similar reaction, which is described later, and from the mass spectrum: *m/e* (rel intensity) 272 (3.5, M^+), 270 (92), 214 (65), 213 (52), 199 (27), 175 (16), 174 (15), 171 (13), 169 (10), 159 (47), 158 (13), 157 (26), 156 (7), 155 (15), 149 (24), 145 (17), 143 (18), 142 (10), 141 (27), 113 (100), ..., 91 (78). The peak at *m/e* 270 suggests, however, that there was an impurity containing two less hydrogens ($C_{20}H_{30}$) which gave an intense molecular ion.

Reaction of 1-Chloro-5,5-dimethyl-2,2-diphenyl-3-hexyne (7b) with Limited Amount of Cs–K–Na Alloy. A. Followed by Protonation. This reaction was conducted with 3.13 g (10.5 mmol) of 1-chloro-5,5-dimethyl-2,2-diphenyl-3-hexyne and 5.19 g of eutectic Cs–K–Na alloy (containing 0.028 g-atom of Cs) vigorously stirred over an 8-min period in 250 mL of THF at −75 °C under the general conditions for the previous reaction with Cs–K–Na alloy. Mercury (10 mL, 135 g) was then added in *very fine droplets* over a 15-min period followed by 20 min of additional stirring at −75 °C to amalgamate the unreacted alloy before forcing the deep red THF solution through a cannula into 300 mL of ice water. The usual isolation procedure gave 2.57 g of crude product. Analysis by GC on the SE-30 column at 200 °C gave peaks at retention time (min) (area % yield) 2.8 (35%), 3.3 (2%), 3.7 (37%), 4.1 (2%), and 4.6 (24%). A pure synthetic sample of the component of retention time 3.7 min was available for measurement of its GC calibration vs. 1,1,2-triphenylethane as internal standard (retention time 5.4 min). From use of this internal standard and calibration factor, it was calculated that the component of retention time 3.7 min constituted 40 wt % of the crude product; therefore, likely the other area percent yields are also essentially weight percent yields of product. The three major products were partially separated by chromatography on silica gel with elution by petroleum ether–benzene; final purification was accomplished by preparative GC on the SE-30 column. The major components were identified as follows.

The compound of retention time 2.8 min was identified as 5,5-dimethyl-2-(1-phenyl-2,5-cyclohexadienyl)-2,3-hexadiene (**26**): IR (neat) 3067 (m), 3038 (s), 2967 (s), 2937 (s), 2911 (s), 2873 (s), 2826 (w), 1961 (w), 1600 (m), 1487 (s), 1463 (m), 1450 (m), 1436 (m), 1364 (m), 1263 (w), 1222 (w), 1178 (w), 1078 (w), 1047 (w), 1013 (w), 947 (m), 764 (m), 741 (s), 704 (s) cm^{-1}; ^1H NMR (CCl_4) δ 0.98 [9 H, s, $-C(CH_3)_3$], 1.57 [3 H, d, $J = 3$ Hz, $-C(C\mathit{H}_3)=C=CH-$], 2.61 (2 H, m, CH_2 of 2,4-cyclohexadienyl group), 5.05 (1 H, q, $J = 3$ Hz, $-C(CH_3)=C=C\mathit{H}-$), 5.74 and 5.80 (2 H and 2 H, each bd s, vinylic CH of cyclohexadienyl group), 6.94–7.46 (5 H, m, $Ar\mathit{H}$); ^{13}C NMR ($CDCl_3$) δ 15.8 (q, $-C(\mathit{C}H_3)=C=C<$), 26.0 (t, CH_2 of 2,4-cyclohexadienyl group), 30.0 [q, $-C(\mathit{C}H_3)_3$], 32.3 [s, $-\mathit{C}(CH_3)_3$], 47.7 (s, quaternary C of 2,4-cyclohexadienyl group), 103.7 (d, $>C=C=\mathit{C}H-$), 106.6 (s, $>\mathit{C}=C=CH-$), 121.8, 122.4, 125.2, 126.7, 127.7, 130.3, and 131.1 (all d, aromatic CH and vinyl CH), 145.6 (s, quaternary aromatic C), 199.4 (s, $>C=\mathit{C}=C<$); MS *m/e* (rel intensity) 264 (6, M^+), 249 (2), 221 (3), 219 (2), 209 (3), 208 (6), 207 (18), 206 (3), 205 (4), 204 (2), 203 (3), 202 (2), 194 (2), 193 (3), 192 (6), 191 (6), 189 (3), 181 (3), 179 (11), 178 (7), 167 (3), 165 (11), 158 (5), 155 (100, $C_{12}H_{11}^+$), 154 (63), 153 (36), 152 (30), 151 (9), 150 (3); exact mass 264.192 (calcd for $C_{20}H_{24}$, 264.188).

The compound of retention time 3.7 min was identified as 5,5-dimethyl-1,2-diphenyl-2,3-hexadiene (**24**): IR (neat) 3090 (w), 3068 (m), 3036 (m), 2965 (s), 2908 (m), 2872 (m), 1948 (w), 1802 (w), 1759 (w), 1600 (m), 1495 (s), 1474 (m), 1454 (s), 1364 (m), 755 (s), 725 (s), 696 (s), 654 (m) cm^{-1}; ^{1}H NMR (CCl_4) δ 0.93 [9 H, s, $-C(CH_3)_3$], 3.72 (2 H, d, J = 3 Hz, $PhC\mathit{H}_2(Ph)C{=}C{=}CH-$), 5.35 (1 H, t, J = 3 Hz, $PhCH_2(Ph)C{=}C{=}C\mathit{H}-$), 7.0–7.5 (10 H, m, aromatic CH); MS *m/e* (rel intensity) 262 (22, M$^+$), 247 (34), 222 (12), 220 (16), 219 (23), 206 (17), 205 (53), 204 (15), 203 (15), 202 (14), 192 (8), 191 (12), 190 (5), 189 (7), 179 (13), 178 (13), 171 (12), 169 (6), 165 (10), 156 (20), 143 (13), 141 (12), 129 (16), 128 (18), 127 (11), 115 (23), 105 (92), 91 (100). This compound was found to be identical in spectral properties (IR, ^{1}H NMR, mass spectrum) with the authentic sample of 5,5-dimethyl-1,2-diphenyl-2,3-hexadiene whose synthesis is given later.

The compound of retention time 4.6 min was identified as (1*E*,3*Z*)-5,5-dimethyl-1,2-diphenyl-1,3-hexadiene (**25**): IR 3085 (m), 3060 (m), 3028 (m), 2960 (s), 2909 (m), 2870 (m), 1600 (m), 1492 (m), 1477 (m), 1465 (w), 1450 (m), 1387 (w), 1365 (m), 1360 (m), 1225 (w), 1202 (w), 1077 (w), 1032 (w), no appreciable absorption at 1000–965 cm^{-1} (therefore *cis*-CH=CH–), 917 (w), 897 (w), 878 (w), 759 (s), 747 (m), 696 (s) cm^{-1}; UV (95% EtOH) λ_{max} 228 (ϵ 1.7 × 10^4), 290 (3.1 × 10^4); ^{1}H NMR (CCl_4) δ 0.86 [9 H, s, $-C(CH_3)_3$], 5.63 (1 H, d, J = 12.5 Hz, *cis*-CH=C*H*-*t*-Bu), 6.17 (1 H, d of d, J = 12.5, 2.5 Hz, –CH=CPhC*H*=CH–), 6.77 (1 H, d, J = 2.5 Hz, –C*H*=CPhCH=CH–), 7.1–7.7 (10 H, m, ArH); MS *m/e* (rel intensity) 262 (24, M$^+$), 247 (21), 219 (25), 205 (47), 204 (17), 203 (12), 202 (13), 191 (11), 189 (8), 179 (7), 178 (13), 171 (19), 169 (19), 165 (12), 156 (7), 155 (9), 154 (7), 153 (7), 152 (9), 143 (9), 141 (17), 91 (100); exact mass 262.159 (calcd for $C_{20}H_{22}$, 262.172).

B. Followed by Deuteration. This reaction was run under identical conditions and with the same quantities of reactants as for the preceding protonation reaction (part A) except that, after stirring with mercury at –75 °C, the reaction solution was forced into 5 mL of D_2O (98.9 mol % D_2O) at 0 °C. The usual isolation procedure gave 2.76 g of crude product which by GC analysis on the SE-30 column at 200 °C gave peaks at retention time (min) (area % yield) 2.8 (32%), 3.3 (3%), 3.7 (24%), 4.1 (13%), and 4.5 (28%). The three major components were isolated by preparative GC on the same column and characterized by spectrometric methods.

The compound of retention time 2.8 min was identified as 5,5-dimethyl-2-(1-phenyl-2,5-cyclohexadienyl-*4-d*)-2,3-hexadiene-*4-d* (**26**-d_2): ^{1}H NMR (CCl_4) δ 0.98 [9.0 H, s, $C(CH_3)_3$], 1.58 [2.9 H, s, $-C(C\mathit{H}_3){=}C{=}CD-$], 2.63 (1.0 H, bd s, C*H*D of 2,4-cyclohexadienyl group), 5.05 [0.0 H, $-C(CH_3){=}C{=}C\mathit{D}-$], 5.74 and 5.81 (3.8 H, vinylic CH of cyclohexadienyl group), 6.9–7.4 (5.2 H, m, Ar*H*); ^{13}C NMR ($CDCl_3$, proton decoupled spectrum) δ 15.8 [s, $-C(\mathit{C}H_3){=}C<$], 256 (t, $J \simeq$ 18 Hz, CHD of 2,4-cyclohexadienyl group), 30.0 [s, $-C(\mathit{C}H_3)_3$], 32.2 [s, $-\mathit{C}(CH_3)_3$], 47.7 (s, quaternary C of 2,4-cyclohexadienyl group), 102.5 (t, $J \simeq$ 20 Hz, $>C{=}C{=}\mathit{C}D-$), 106.6 (s, $>\mathit{C}{=}C{=}CD-$), 121.6, 122.3, 125.2, 126.7, 127.6, 130.3, and 131.2 (all s, aromatic CH and vinyl CH), 145.6 (s, quaternary aromatic C), 199.4 (s, $>C{=}\mathit{C}{=}C<$); MS *m/e* (rel intensity) 266 (2.0, M$^+$), 265 (0.24), 251 (1), 210 (3), 209 (8), 208 (2), 207 (2), 206 (1), 205 (2), 195 (2), 194 (3), 193 (2), 192 (2), 181 (2), 180 (3), 179 (3), 178 (1), 177 (3), 177 (16), 168 (2), 167 (2), 166 (3), 165 (2), 158 (16), 157 (22), 156 (100, $C_{12}H_{10}D^+$), 155 (39), 154 (26), 153 (10), 152 (5).

The compound of retention time 3.7 min was identical in GC retention time and mixture GC retention time with the authentic sample of 5,5-dimethyl-1,2-diphenyl-2,3-hexadiene prepared by the method described below. This compound was identified as about a 28:72 ratio of 5,5-dimethyl-1,2-diphenyl-2,3-hexadiene-*4-d* (**24**-d_1) and 5,5-dimethyl-1,2-diphenyl-2,3-hexadiene-*1,4-d*$_2$ (**24**-d_2) on the basis of its mode of synthesis and mass spectrum: *m/e* (rel intensity) 264 (55), 263 (20), 249 (43), 248 (24), 221 (20), 220 (45), 219 (16), 207 (50), 206 (48), 205 (32), 204 (18), 203 (14), ..., 92 (100), 91 (59).

The compound of retention time 4.6 min was identified as 5,5-dimethyl-1,2-diphenyl-1,3-hexadiene-*3,4-d*$_2$ (**25**-d_2): ^{1}H NMR (CCl_4) δ 0.86 [9.0 H, s, $C(CH_3)_3$], 5.0–6.5 (no detectable peaks), 6.75 (1.0 H, s, PhC*H*=CPh–), 7.1–7.7 (10.0 H, m, ArH); MS *m/e* (rel intensity) 264 (47), 263 (3.7), 249 (42), 221 (21), 220 (38), 219 (11), 207 (85), 206 (32), 205 (21), 204 (17), 203 (11), 193 (9), 192 (13), 191 (9), 180 (8), 179 (11), 178 (11), 173 (9), 172 (32), 171 (25), 167 (8), 166 (19), 165 (8), 92 (100), 91 (47).

5,5-Dimethyl-2,2-diphenyl-3-hexyne (18). 1-Methoxy-4,4-dimethyl-1,1-diphenyl-2-pentyne (5.60 g, 20.0 mmol) was cleaved by Na–K alloy (3.50 g, 66.5 mg-atoms of K) in 250 mL of anhydrous ether according to the general procedure described in the preparation of **7a**. The excess alloy was amalgamated by addition of 10 mL of mercury; finally excess methyl iodide (25 mL) was added. The solution was stirred for 15 min after disappearance of the red color and then filtered through a fritted-glass Buchner funnel. The residue in the funnel was washed well with ether. The ethereal filtrate and washings were combined. The product, after removal of solvent, amounted to 5.2 g; after recrystallization from hexane, it had mp 45.0–46.0 °C. The analytical sample was sublimed in vacuo at a bath temperature of 65 °C to give crystals of mp 45.5–46.0 °C: ^{1}H NMR (CCl_4) δ 1.27 [9 H, s, $-C(CH_3)_3$], 1.87 (3 H, s, $-CPh_2C\mathit{H}_3$), 7.0–7.5 (10 H, m, ArH). Anal. ($C_{20}H_{22}$) C, H.

Reaction of 5,5-Dimethyl-2,2-diphenyl-3-hexyne (18) with Cs–K–Na Alloy. Into the usual Morton high-speed stirring apparatus was distilled from $NaAlH_4$ 200 mL of tetrahydrofuran; Cs–K–Na alloy (3.1 g, containing 0.015 g-atom of Cs) was added and the the mixture stirred for 1.5 h at 25 °C and then 0.5 h at –75 °C to give a fine suspension of the alloy. A solution of **18** (0.96 g, 3.7 mmol) in 15 mL of THF was added at once and the solution stirred vigorously for 10 min at –75 °C before addition of 10 mL of mercury in very fine droplets over a 10-min period with additional stirring for 20 min more at –75 °C before the dark red-brown solution was forced as a fine stream into 300 mL of ice water. The solvent was largely removed on a rotating evaporator and the residual liquid was extracted three times with ether. The ethereal extract after drying over anhydrous $MgSO_4$ and removal of solvent gave 0.68 g of an oil. Quantitative GC analysis at 170 °C on a 6 ft × 0.25 in. column packed with 5% SE-30 on 100–120 mesh Chromosorb G, with triphenylmethane (retention time 7.6 min) added as an internal standard and with the assumption that the calibration factor for **26** was the same as for the hydrocarbon **18**, gave the products specified as relative mol % yield (retention time (min), identity): 25 (1.2, biphenyl), 21 (3.2, **18**), and 54 (4.2, **26**). Inadequate Cs–K–Na alloy for complete reaction was likely present in this run because of loss of the alloy during the long stirring period at 25 °C prior to addition of **18**.

In a repetition of this run with 7.1 g of Cs–K–Na alloy (0.040 g-atom of Cs), which was stirred for only 30 min with THF at room temperature, and 3.70 g (14.1 mmol) of **18**, 2.5 g of crude product was isolated upon protonation. Quantitative GC analysis as previously gave products listed as relative mol % yield (retention time (min), identity): 37 (1.2, biphenyl), 52 (4.2, **26**), 11 (5.2, unknown assumed to have the same calibration factor as **26**). The crude product (1.6 g) was chromatographed on 60 g of silica gel (Woelm, 32–63 μm) on a 2-cm diameter column with elution by pentane to give 0.40 g of **26** which was indistinguishable by IR, ^{1}H NMR, and mass spectrum from the sample of **26** obtained from the chloride **7b** with Cs–K–Na alloy. The analytical sample of **26** was twice distilled at a bath temperature of 133 °C at 0.05 mmHg. Anal. ($C_{20}H_{24}$) C, H.

A third run was made with the same relative amounts of reactants and by the procedure as the second run except that the reaction mixture after reaction with mercury was kept at a bath temperature at –78 °C (no stirring) for a total reaction time of 4 h before protonation; the products analyzed and listed as previously were 60 (1.2, biphenyl), 33 (4.2, **26**), 7 (5.2). Since in some, but not all, of the above runs an unknown of retention time 5.2 min, likely an isomer of **26**, was observed, a fourth run was made like the second run except that immediately after the addition of mercury (20 min total reaction time) the cold mixture was siphoned into water. The product was isolated from the alkaline solution the same day by saturating with sodium chloride, separation of the THF layer, and extraction of the aqueous solution with ether. The organic solvents were removed through a 1-ft packed column, finally in vacuo at a temperature not exceeding 100 °C to give 1.28 g of product. Analysis by GC gave products listed as previously: 31 (1.2, biphenyl), 69 (4.2, **26**). None of the product of retention time 5.2 min was observed here and none appeared in the product kept stored at 0 °C in the dark for several days.

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Supplementary Material Available: Experimental procedures for the formation of compounds **5**, **9**, **10**, **17a**, **17b**, **21**, **22**, **23**, **24**, **24**-*d*, 1-methoxy-4,4-dimethyl-1,1-diphenyl-2-butyne, 1-methoxy-4,4-dimethyl-2-pentyne, 1-chloro-4,4-dimethyl-2-pentyne, and 5,5-dimethyl-1,1-diphenyl-3-hexyne and spectral properties of these compounds (8 pages). Ordering information is given on any current masthead page.