Carbanions. 17. Rearrangements of 2,2-Diphenyl-4-pentenyl Alkali Metal Compounds[1]

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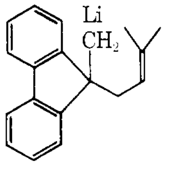
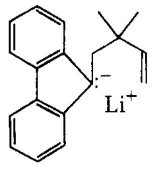
Abstract: 2,2-Diphenyl-4-pentenyllithium (**2**) rearranges in tetrahydrofuran at −50 to 0 °C to give, according to the products of protonation and carbonation, chiefly 1,1-diphenyl-4-pentenyllithium (**4**) (product of migration of allyl). With 2,2-diphenyl-4-pentenyl-*3*-^{14}C-lithium (**2***), carbon-14 was found in **4** either at the terminal C-5 position ("inversion" of the allyl group) or scrambled at positions C-3 and C-5; the amount of scrambling increased with increasing temperature. Potassium and cesium *tert*-butoxides (but not lithium *tert*-butoxide) with **2** in THF at −75 °C induced ready rearrangement to give chiefly 1-benzyl-1-phenyl-3-butenyl anion (product of migration of phenyl) and lesser amounts of the product of migration of allyl. Potassium *tert*-butoxide complexed with 18-crown-6 with **2*** gave chiefly 1,1-diphenyl-4-pentenyl anion with complete inversion of the allyl group. 5-Chloro-4,4-diphenyl-1-pentene reacts with potassium metal in THF at 65 °C to give, after carbonation, products similar to those from **2** with potassium *tert*-butoxide, along with 20% of an unknown carboxylic acid in the volatile acidic product. These results upon 2,2-diphenyl-4-pentenyl alkali metal compounds are interpreted on the basis that allyl migration occurs in a highly solvated transition state, likely in a loose ion pair, either by a [2,3]-sigmatropic process (with inversion) or by a dissociation–recombination mechanism (with scrambling of the label), while phenyl migration occurs in a more weakly solvated transition state, likely in a tight ion pair, by a [1,2]-sigmatropic process.

Rearrangements of carbanions containing only carbon and hydrogen are rare compared with the diversity of examples of rearrangements of anions containing heteroatoms.[2] While hydrocarbon anion rearrangements involving 1,2 migrations of aryl[3] and vinyl[4] groups by an intramolecular process and benzyl[5] by an intermolecular process are well known, the migration of allyl was unknown at the start of this investigation. Subsequently Baldwin and Urban[6] provided an example in the rearrangement of 9-(3-methylbut-2-enyl)-9-(lithiomethyl)fluorene (A) in tetrahydrofuran (THF) to give predominantly the lithium compound B at −20 °C along with C which was formed in increasing amounts as the temperature was raised. The interpretation[6] was that B was formed by an anionic [2,3]-sigmatropic rearrangement and C (and an unknown amount of B) resulted from a radical dissociation–recombination mechanism. Some 10 to 15% of 2-methylfluorene and comparable amounts of 2-methyl-2-butene, 2,7-dimethylocta-2,6-diene, and 3,3,6-trimethylhepta-1,5-diene were obtained and explained as arising from reduction and coupling of radicals. These results paralleled those observed for migration of allyl in sulfur[7] and nitrogen[8] ylides and in anions of ethers[9] and thio ethers.[10]



A



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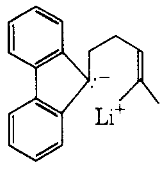


C

In the present work we report on the products and likely mechanisms of rearrangement of 2,2-diphenyl-4-pentenyl alkali metal compounds. This system has two advantages over that of Baldwin and Urban.[6] It permits competition between allyl migration and phenyl migration so that the factors favoring allyl vs. phenyl migration may be studied. In addition, the allyl group is much more symmetrical than γ,γ-dimethylallyl such that, with the aid of carbon-14 to label one end of the allylic system, it is possible to tell to what extent the allyl group becomes kinetically free during migration.

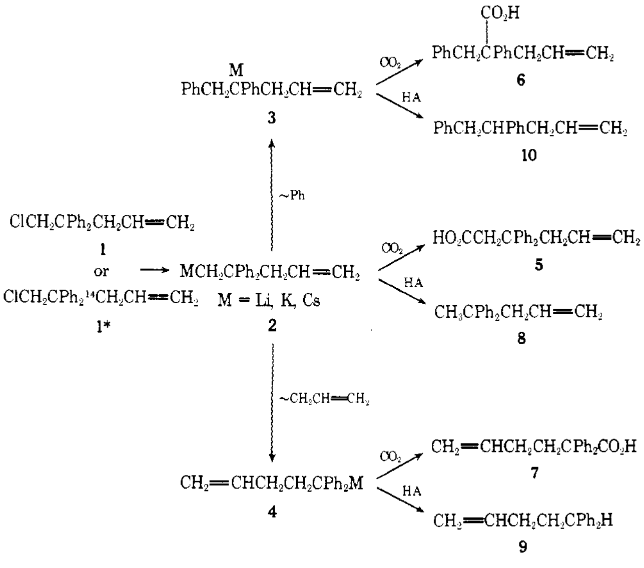
Results

5-Chloro-4,4-diphenyl-1-pentene (**1**) was prepared by alkylation of diphenylmethane with allyl chloride[11] and then with methylene chloride according to Scheme I. The same process, but with allyl chloride replaced by allyl-*1*-^{14}C chloride, served for the preparation of 5-chloro-4,4-diphenyl-1-pentene-*3*-^{14}C (**1***).

Scheme I

$$\begin{tikzcd}
Ph_2CH_2 \arrow[r, "KNH_2", "NH_3,\ Et_2O"'] & Ph_2CHK \arrow[r, "CH_2{=}CHCH_2Cl"] & Ph_2CHCH_2CH{=}CH_2 \arrow[d, "KNH_2", "NH_3,\ Et_2O"'] \\
 & ClCH_2CPh_2CH_2CH{=}CH_2 & KCPh_2CH_2CH{=}CH_2 \arrow[l, "CH_2Cl_2"']
\end{tikzcd}$$

Scheme II

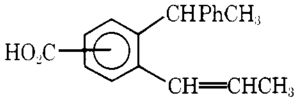


Reaction of chloride **1** with lithium metal in THF at −75 °C gave, as expected, 2,2-diphenyl-4-pentenyllithium (**2**) as shown by the products of carbonation and protonation (see Scheme II). When the solution of the organolithium reagent **2** was warmed to 0 °C, rearrangement occurred; according to the results of carbonation and protonation, the chief product was 1,1-diphenyl-4-pentenyllithium (**4**) (product of 1,2 migration of allyl) along with some 3% of 1-benzyl-1-phenyl-3-butenyllithium (**3**) (product of 1,2 migration of phenyl). In tetrahydrofuran the half-life of 2,2-diphenyl-4-pentenyllithium (**2**) was about 27 min at −32 °C or 19 h at −50 °C. When the chloride **1** was allowed to react with lithium metal in THF at −75 °C in the presence of about 0.5 molar equiv of *n*-butyllithium, no *n*-butyllithium incorporation product was obtained on carbonation at −75 °C; however, if the solution of organolithium reagents was warmed to 0 °C before carbonation, 2,2-diphenylheptanoic acid constituted some 6% of the acidic products of higher molecular weight than valeric acid.

The effect of alkali metal alkoxides upon the rearrangement of 2,2-diphenyl-4-pentenyllithium (**2**) was tested. Addition of some 20 molar equiv of lithium *tert*-butoxide to **2** in THF containing about 0.5 molar equiv of *n*-butyllithium brought about no detectable rearrangement of **2** after 40 min at −75 °C; after 1.5 h at 0 °C, carbonation afforded chiefly the product **7** of 1,2 allyl migration along with 4% of the product **6** of phenyl migration, 3% of 2,2-diphenylheptanoic acid, and 7% of unrearranged product **5.** Lithium *tert*-butoxide, therefore, did not catalyze the rearrangement of **2** at −75 °C and evidently retarded rearrangement at 0 °C. In contrast, addition of a similar large excess of potassium *tert*-butoxide to **2** (containing *n*-butyllithium) in THF at −75 °C gave complete rearrangement after 5 min according to the constancy of the products of protonation after 5- and 20-min intervals; carbonation gave a mixture of acids containing some 32 parts of **7** (product of allyl migration) to 68 parts of **6** (product of phenyl migration) and 2 to 4% of 2,2-diphenylheptanoic acid. In a similar experiment with cesium *tert*-butoxide after 10 min at −75 °C, carbonation gave 16 parts of **7** to 84 parts of **6** and 2% of 2,2-diphenylheptanoic acid. While 18-crown-6 had no detectable effect upon 2,2-diphenyl-4-pentenyllithium (**2**) according to the results of carbonation after 3 h at −75 °C, potassium *tert*-butoxide complexed with 18-crown-6 brought about complete rearrangement of **2** (prepared from **1***) in 15 min (or less) at −70 °C; carbonation gave 92 parts of **7** to 8 parts of **6.**

In some of the runs of the chloride **1** with lithium, the acidic product contained 3 to 6% of 2,2-diphenylpropanoic acid.[12] Also in most runs there were minor amounts of unidentified products in the volatility range of the major components; it is assumed that these are isomers resulting from rearrangement of the terminal double bond to a more stable position.

As an aid in interpretation of the reaction of potassium *tert*-butoxide upon 2,2-diphenyl-4-pentenyllithium (**2**), the reaction of the corresponding chloride **1** with finely divided molten potassium in THF at 65 °C was studied. Carbonation after some 4 min of reaction time gave about a 40% yield of volatile acids containing 16% of the product of allyl migration (**7**), 53% of phenyl migration (**6**), and 20% of unknown X. On the basis of the exact mass and the UV and NMR spectra of the methyl ester of X, which was separated by gas chromatography, the partial structure **11** is tentatively suggested for X.



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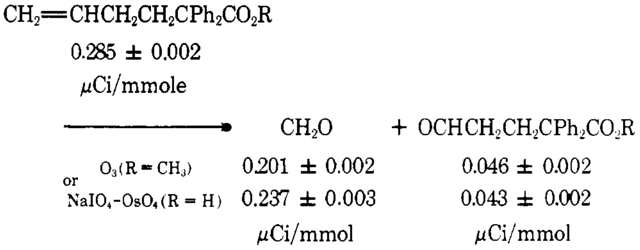
Isotopic tracer studies were run to ascertain the distribution of carbon-14 in the carboxylic acid **7** resulting from migration of allyl (see Scheme II) in 2,2-diphenyl-4-pentenyllithium (**2**) prepared from 5-chloro-4,4-diphenyl-1-pentene-*3*-^{14}C (**1***). In initial experiments the distribution of carbon-14 was determined by ozonization and assay of radioactivity in the dimethone derivative of the resulting formaldehyde, according to a general procedure which gave satisfactory results with simple aliphatic compounds.[13,14] A check with the milder oxidizing system sodium periodate-osmium tetroxide,[15] however, gave 18% high activity for the resulting formaldehyde as summarized in Scheme III. In another case in which the distribution of carbon-14 in the rearrangement product **7** (as free acid) was determined by the two techniques, the sodium periodate–osmium tetroxide procedure gave formaldehyde of 26% higher radioactivity than ozonization. Since the sum of the activities of the cleavage products from the sodium periodate–osmium tetroxide procedure is in good agreement with the activity of the starting acid while the sum of activities from ozonization is too low, only the former procedure appears to give reliable results with the present aromatic compounds.[16]

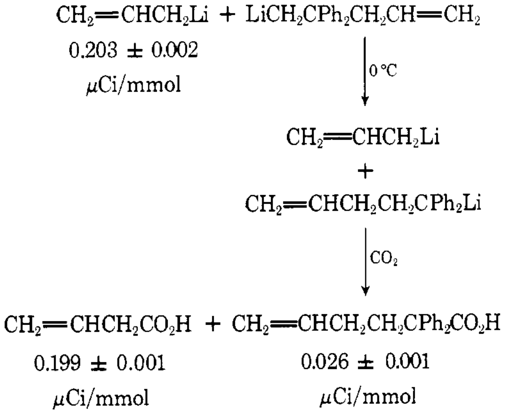
Scheme III



The starting chloride **1*** and the unrearranged carboxylic acid **5,** prepared from this chloride by reaction with lithium in THF at −75 °C followed by carbonation, were found to contain only 1 to 2% of their total radioactivity in the terminal methylene group according to the activity of the formaldehyde from ozonization; had the assay been by the sodium periodate–osmium tetroxide procedure, the activity of the formaldehyde should not have exceeded 2 to 3% of the total. Hence the chloride **1*** reacts with lithium metal in THF at −75 °C to give 2,2-diphenyl-4-pentenyllithium (**2**) without detectable isotope position migration such that at least 97% of the radioactive label was at C-3 in the lithium compound. The results upon the distribution of carbon-14 in the carboxylic acid **7** resulting from migration of allyl in 2,2-diphenyl-4-pentenyllithium-*3*-^{14}C are summarized in Table I. These results are presented according to whether the allylic migration occurred with distribution of the carbon-14 label equally at positions C-4 and C-6 of acid **7** ("scrambling") or with the label located solely at C-6 ("inversion").[17a] The rearrangements of 2,2-diphenyl-4-pentenyllithium-*3*-^{14}C reported in Table I are all ordinary thermally induced processes save that at −70 °C which was brought about by addition of potassium *tert*-butoxide complexed with 18-crown-6.

Finally 2,2-diphenyl-4-pentenyllithium was allowed to rearrange at 0 °C in the presence of 6 molar equiv of allyl-^{14}C-lithium. Assays for radioactivity indicated that carbon-14 became distributed in the products as shown in Scheme IV. On the assumption that the allyl group in the rearranged organolithium compound **4** (and in the acid **7** derived by carbo-

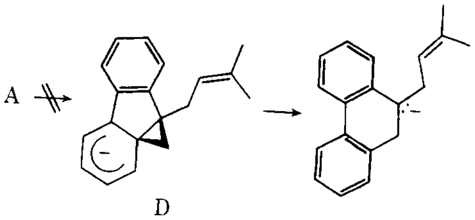
Scheme IV

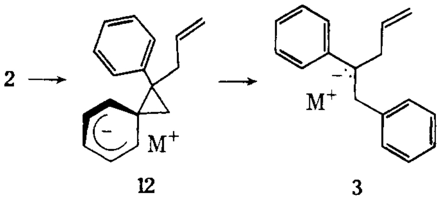


nation) should have the same activity as that of the allyllithium prevailing in the solution at the time of its formation, the activity of the rearranged acid **7** is calculated[17b] to be 0.188 μCi/mmol; the observed activity, however, is only 14% of this calculated value or 13% of that of the final allyllithium.

Discussion

A notable difference between the work upon 2,2-diphenyl-4-pentenyl alkali metal compounds (**2**) and that of Baldwin and Urban[6] upon 9-(3-methylbut-2-enyl)-9-(lithiomethyl)-fluorene (A) is that in the present work migration of phenyl occurred competitively with migration of allyl whereas in the work upon A only migration of the 3-methylbut-2-enyl group was reported. Migration of the aryl group in A would be expected to be difficult since the likely intermediate or transition state D, because of the restrictions on geometry imposed by the five-membeed ring, is expected to be strained[2g,18] relative to the intermediate **12** for migration of phenyl in **2**. Also Baldwin and Urban likely did not have the optimum countercation or solvent to promote migration of phenyl rather than allyl.





The importance of the proper cation is emphasized by the present observations that, whereas thermal rearrangement of the organolithium compound **2** at 0 °C gave about a 97:3 ratio of allyl to phenyl migration (i.e., ratio of **7**:**6**) catalysis of rearrangement of **2** by addition of potassium or cesium *tert*-butoxides gave ratios of 32:68 or 16:84, respectively, of allyl to phenyl migration at −75 °C. As was suggested for a related rearrangement,[19] catalysis of rearrangements of organolithium compounds by alkali metal alkoxides evidently involves an interchange of cations by a metathetical reaction:

$$\begin{aligned}&\mathrm{LiCH_2CPh_2CH_2CH{=}CH_2 + MO\text{-}\mathit{t}\text{-}Bu}\\&\quad\rightarrow \mathrm{MCH_2CPh_2CH_2CH{=}CH_2 + LiO\text{-}\mathit{t}\text{-}Bu}\qquad(1)\end{aligned}$$

This suggestion receives support in the present work by the observation that lithium *tert*-butoxide, unlike potassium and cesium *tert*-butoxides, fails to catalyze the rearrangement of 2,2-diphenyl-4-pentenyllithium (**2**). Also reaction by chloride **1** with potassium metal in THF at 65 °C gives a ratio of allyl migration to phenyl migration products (**7**:**6**) of 23:77 similar to that observed with potassium *tert*-butoxide at −75 °C.

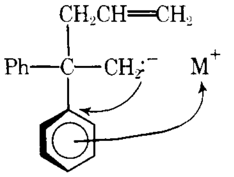
The importance of the state of solvation or of the presence of suitable ligands about the alkali metal cation is illustrated by catalysis of the rearrangement of the lithium compound **2** at −75 °C by potassium *tert*-butoxide containing 1 mol of 18-crown-6 for each mole of alkoxide. This reaction gave a 92:8 ratio of allyl to phenyl migration products (**7**:**6**); presumably phenyl migration could have been avoided all together had more 18-crown-6 been present to coordinate more completely with the potassium cation.

Table I. Rearrangement of 2,2-Diphenyl-4-pentenyllithium-*3*-^{14}*C*

	Distribution of carbon-14 in 2,2-diphenyl-5-hexenoic acid		
Temp, °C	% ^{14}C at C-6	% scrambling	% inversion
−20-0	66 ± 3	67	33 ± 6[c]
−32	77 ± 6[a]	46	54 ± 12
−50	81 ± 3	37	63 ± 6
−70[b]	100 ± 4	0	100 ± 8

[a] Corrected value: The large estimated uncertainty in this analysis arises from the uncertainty of the correction for the inherent error of the ozonization procedure used. All other oxidative cleavages reported in this table were by the sodium periodate-osmium tetroxide procedure. [b] Rearrangement at this low temperature was induced by addition of potassium *tert*-butoxide-18-crown-6. [c] Estimated uncertainty in the percentage scrambling or inversion.

The present observations on allyl vs. phenyl migration in 2,2-diphenyl-4-pentenyl alkali metal compounds (**2**) almost exactly parallel the more extensive observations reported earlier for benzyl vs. phenyl migration in 2,2,3-triphenylpropyl alkali metal compounds.[19] Conditions which favor loose or separated ion pairs favor migration of allyl or benzyl groups while those which favor tight or contact ion pairs[20] favor migration of phenyl. Evidently phenyl migration may occur in a tight ion pair since in the rearrangement leading to the spiro anion **12** the alkali metal cation may accompany the anionic center during bridging (see **13**) such that no great separation of charged centers is necessary at any time for cyclization. In contrast, the transition state for migration of allyl evidently has extensive charge separation; solvation of the alkali metal cation (as in a loose ion pair) is required to permit delocalization of the negative charge which rearrangement of the allyl group entails. What then is the mechanism for rearrangement of the allyl group?



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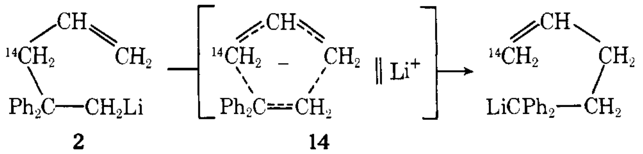
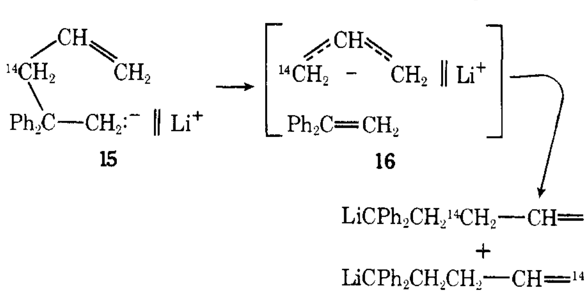
The results of the carbon-14 labeling experiments with 2,2-diphenyl-4-pentenyllithium-*3*-^{14}*C* (see Table I) suggest that there are two mechanisms for rearrangement of allyl: one giving rise to inversion in the allyl group and favored by low temperatures and the other giving scrambling of the label and favored by high temperatures. Our results are, therefore, very similar to those of Baldwin and Urban[6] for rearrangement of 9-(3-methylbut-2-enyl)-9-(lithiomethyl)fluorene (A) as they should be because of the general similarity of the two systems. A plot of the logarithm of the ratio of the percent scrambling to the percent inversion for the rearrangement of the organolithium compound **2** (data of Table I) gives an enthalpy of activation 3.6 ± 1.1 kcal/mol greater for the scrambling than the inversion process and an entropy of activation 15 ± 5 eu greater for scrambling than inversion. This unfavorable entropy for the inversion process is in good agreement with inversion occurring via a cyclic transition state such as **14** with loss of several degrees of rotational freedom as in related



Cope[21] and Claisen[22] rearrangements. Indeed this anionic [2,3]-sigmatropic rearrangement can be looked upon as the carbanion analogue of the Cope rearrangement. For this mechanism it is clear why solvation favors migration of allyl as opposed to phenyl; transition state **14** has the negative charge delocalized over the five carbons of the quasi-cyclopentadienide ring system as well as on the two phenyl groups whereas the transition state for phenyl migration (see **13**) has its negative charge more localized.

The detailed mechanism for migration of the allyl group with scrambling of the label is less clear. One possibility is elimination of allyllithium from a loose ion pair **15** derived from **2**. The experiment with unlabeled **2** and allyl-^{14}C-lithium showed that, under conditions (near 0 °C) where there is 67% allylic scrambling and 33% inversion, the rearranged product picked up only 14% of the maximum possible radioactivity from the allyllithium in the surrounding solution. Evidently the loose ion pair of allyllithium collapses to ordinary allyllithium at a rate of 14/67th or 21% that at which addition occurs to diphenylethylene. The rate of collapse of the loose ion pair is expected to be very fast and hence the rate of addition of the loose ion pair to diphenylethylene must be somewhat faster and much faster than the addition of ordinary allyllithium to diphenylethylene. The rate of the latter reaction has been measured[23] in THF at 22 °C and may be calculated to have a rate constant of about 1.1 $M^{-1}\ s^{-1}$. It is reasonable to assume that a loose ion pair is much more reactive than a tight ion pair in additions to olefins. Thus Szwarc and co-workers[24] have found rate constants of 6.5×10^4, 3.0×10^4, and ca. 80 $M^{-1}\ s^{-1}$ for the addition to styrene respectively of the free anion, the loose ion pair, and the tight ion pair of the sodium salt of "living" polystyrene in THF at 25 °C. Ordinary allyllithium evidently exists in THF at ordinary temperatures predominantly as a tight ion pair in which the carbon–metal bond is partially localized or covalent.[25]



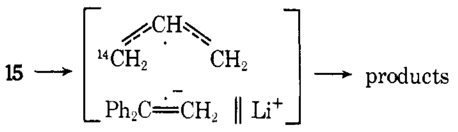
If the collapse of the loose allyllithium ion pair occurs, as seems likely, at nearly the diffusion controlled rate, then the intermediates **16** need to be described as existing within a solvent "cage".[26] On this basis, the loose ion pair of allyllithium must add to diphenylethylene at about the diffusion controlled rate; this high velocity may be facilitated by having diphenylethylene as a ligand of the lithium cation.[24,27] The occurrence of 1,1-diphenylhexyllithium in the reaction product from rearrangements carried out in presence of *n*-butyllithium may be explained on the basis that *n*-butyllithium[23] like external allyl-^{14}C-lithium adds to the diphenylethylene following collapse of the loose ion pair of allyllithium.

A somewhat similar mechanism has been proposed[5b,c] as the preferred mechanism for benzyl migration in 2,2,3-triphenylethyllithium (**17**):

$$\underset{\mathbf{17}}{PhCH_2CPh_2CH_2Li} \rightarrow PhCH_2Li + Ph_2C{=}CH_2 \rightarrow LiCPh_2CH_2CH_2Ph$$

In this case, however, when rearrangement is carried out in presence of benzyl-^{14}C-lithium, the benzyl group of the rearranged product has the *same* activity as that of the benzyllithium in the surrounding solution at the time of the rearrangement. In view of the similarity of mechanism and the report that benzyllithium adds to diphenylethylene in THF at a rate some 14 times faster than does allyllithium,[23] the differing extents of incorporation of radioactivity from benzyllithium and allylithium during rearrangement are surprising. Why does allyllithium arising as a loose ion pair from fragmentation of **15** add to diphenylethylene faster than benzyllithium evidently formed also as a loose ion pair from fragmentation of **17**? A possible explanation lies in the report[28] that toluene has a higher gas-phase acidity than propylene.[29] If these relative acidities prevail also in THF, then the benzyl anion in a loose ion pair would be expected to be less reactive than an allyl anion in a loose ion pair. On the other hand, since the charge on the α carbon in the benzyl anion and the terminal carbons of the allyl anion are the same, according to carbon-13 magnetic resonance[25c] on the contact ion pairs with potassium as counterion in THF solution, the loose ion pairs of benzyllithium and allyllithium would be expected to collapse at about the same rate. Therefore during rearrangement of **17** evidently the loose ion pair of benzyllithium collapses to comparatively unreactive tight ion pair faster than it adds to diphenylethylene; hence, it is external (^{14}C labeled) benzyllithium which adds to diphenylethylene.

While the above mechanism appears capable of explaining all that is known about the scrambling process for allyl migration, an alternative radical dissociation–recombination process remains a possibility. According to this mechanism the loose ion pair **15** dissociates into the radical pair **17** which collapses to give 1,1-diphenyl-4-pentenyllithium with carbon-14 scrambled at positions 3 and 5. We do not favor this mechanism since the intermediates **16** would appear to be more stable than **17** on the basis that, according to Hückel molecular orbital theory, an electron is more stable in a nonbonding orbital than in an antibonding orbital. Also, in order to account for the incorporation or radioactivity when **2** is rearranged in presence of allyl-^{14}C-lithium, one or more additional unsubstantiated reactions must be proposed. The radical dissociation–recombination mechanism may be favored by substitution of methyl groups for hydrogen in the allylic moiety since methyl groups generally increase the rate of formation of radicals and decrease the rate of formation of anions; perhaps such substitution accounts for the results of Baldwin and Urban[6] upon organolithium compound A. Certainly the radical dissociation–recombination process conveniently accounts for the 2,7-dimethylocta-2,6-diene and 3,3,6-trimethylhepta-1,5-diene obtained from A; however, since these were minor products, we cannot be sure that the rearrangement of A itself went by way of radical dissociation.



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In summary, under conditions which favor loose ion pairs of 2,2-diphenyl-4-pentenyl alkali metal compounds, allyl migration is observed. At low temperature (−70 °C), facile allyl migration occurs primarily by an anionic [2,3]-sigmatropic rearrangement with "inversion" of the allylic group; at higher temperatures allylic migration occurs increasingly by a dissociation–recombination process, apparently via a fragmentation into diphenylethylene and the loose ion pair of allyllithium. Under conditions which favor tight ion pairs of 2,2-diphenyl-4-pentenyl alkali metal compounds, 1,2-phenyl migration is observed. Facile phenyl migration occurs as the major process with potassium and cesium as counterions at −75 °C. At +65 °C with potassium ion still yet another rearrangement is observed, but the details of this process require further study.

Experimental Section[30]

Proton NMR spectra were ordinarily recorded at 60 mHz on a Varian A-60D or T-60 spectrometer using tetramethylsilane as an internal standard. Mass spectra were run upon a Varian A-66 or a Hitachi (Perkin-Elmer) RMU-7L mass spectrometer. Analyses by gas chromatography (GLC) were performed on instruments equipped with hydrogen-flame ionization detectors; qualitative GLC analyses are reported as "area percent" of total volatile constituents whereas quantitative GLC analyses are reported as "absolute" yields based upon use of known samples and internal standards.

Allyl-*1*-^{14}C alcohol was obtained from Tracerlab and from International Chemical and Nuclear Corp. Allyl-*1*-^{14}C chloride was prepared from allyl-*1*-^{14}C alcohol by the procedure of Sharman et al.[13,14] Cesium metal (99.9+ %) was obtained from MSA Research Corp. in sealed glass ampules. 2,2-Diphenylheptanoic acid was prepared in 77% yield by addition over a 15-min period of 1,1-diphenylethene to an equimolar amount of *n*-butyllithium (Foote Mineral Co.) in hexane–tetrahydrofuran solution at −78 °C, followed by carbonation; the acid after recrystallization from ethanol and then cyclohexane had mp 104.0–105.0 °C (lit.[31,32] 104–105 °C); NMR (CS_2) δ 11.82 (1 H, s, CO_2H), 7.22 (10 H, broad s, aromatic CH), 2.0–2.4 (2 H, m, CH_2), 0.6–1.2 (9 H, m, *n*-butyl CH). 2,2-Diphenyl-4-pentenoic acid was prepared by alkylation of the dipotassium salt of diphenylacetic acid with allyl chloride in diethyl ether at reflux temperature for 45 min according to the general procedure[33] for alkylation of the same salt with benzyl chloride; the acid had mp 140.0–142.0 °C (lit.[34] 141.5–141.9 °C); NMR (acetone-d_6) δ 7.3 (10 H, broad s, aromatic CH), 5.62 (1 H, m, vinylic CH), 4.89 (2 H, m, vinylic CH), 3.21 (2 H, d, $J = 6$ Hz, allylic CH). Lithium metal (0.05% Na max) was from Lithium Corporation of America. Liquid ammonia (99.9+ %) was from Matheson Co., Inc. and was distilled through a tube packed with barium oxide and potassium hydroxide pellets prior to condensation. Magnesium turnings for Grignard reactions was from Fisher Scientific Co. Osmium tetroxide was Baker and Adamson reagent grade supplied in a sealed ampule. Tetrahydrofuran (THF) was Baker reagent grade, dried over sodium wire and distilled from sodium aluminum hydride immediately before use.

Oxidative Degradation of Carbon-14-Labeled Compounds. A. With Ozone. Ozonizations (0.4 mmol of olefin) were conducted in 50 mL of chloroform at −50 ± 5 °C and the ozonides were decomposed by pouring into a mixture of 25 mL of water, 25 mL of acetone, 2 mL of acetic acid, and 1.0 g of zinc dust according to a general procedure previously described.[13,14] The solution after filtration was mixed with an alcoholic solution containing 2 molar equiv of 5,5-dimethyl-1,3-cyclohexanedione and, after the usual workup, yielded formaldimethone, mp 190.0–191.0 °C from 95% ethanol (lit.[35] mp 191.0–191.5 °C).

B. With Sodium Periodate–Osmium Tetroxide.[15] The olefin (0.4 mmol) was dissolved in 10 mL of ether, and to this solution was added 0.14 mmol of osmium tetroxide in 5 mL of ether. To the resulting amber-black solution after 5 min, 15 mL of water was added. The heterogeneous solution was stirred for 15 min and then 2 molar equiv of $NaIO_4$ was added with stirring continued for 12 h at room temperature. The layers were separated, and the ether layer was washed with 5 mL of water. The combined aqueous layers were mixed with 2 molar equiv of 5,5-dimethyl-1,3-cyclohexanedione in 25 mL of 95% ethanol and after the usual workup yielded formaldimethone. The ether phase was filtered through anhydrous $MgSO_4$, the ether was removed by distillation, and the residue was dissolved in 5 mL of 95% ethanol. The alcoholic solution was treated with 2,4-dinitrophenylhydrazine reagent according to the usual procedure to give the hydrazone derivative.[36]

Assay of Carbon-14. Radioactivity measurements were made by two independent methods. In the first method[14] samples (ca. 5 mg) were converted to carbon dioxide by a wet combustion method, and then the radioactivity of the carbon dioxide was measured in an ionization chamber with use of a vibrating-reed electrometer (Applied Physics Corp., Model 31). In the second method the sample (ca. 4 mg) was dissolved in 10.0 mL of the phosphor solvent *Insta-Gel*(Packard Instrument Co.) and its radioactivity measured directly in a liquid scintillation counter (Nuclear-Chicago, Model Mark I) at 9 °C. Specific activities by the two methods were converted to microcuries per millimole by references to a sample of benzoic acid of known activity which was assayed by each of the two methods. For either method samples were run in at least duplicate. In the present work half of the samples were assayed by both methods and agreed with the mean value from the two methods within an average deviation of ±1%. The remaining samples were counted only by the scintillation method.

4,4-Diphenyl-1-butene was prepared by reaction of diphenylmethylpotassium in liquid ammonia–ether with allyl chloride by a method similar to that of Kuznetsov and Libman.[11] The product after distillation in vacuo was obtained in 87% yield of product of bp 115 °C (2 Torr); $n^{20}{}_D$ 1.5704 [lit.[11] bp 114–116 °C (2 Torr); $n^{20}{}_D$ 1.5715)]; NMR (neat) δ 7.2 (10 H, m), 5.65 (1 H, m), 5.00 (2 H, m), 4.00 (1 H, t, $J = 8$ Hz), and 2.75 (2 H, t, $J = 8$ Hz).

4,4-Diphenyl-1-butene-*3*-^{14}C was prepared from diphenylmethylpotassium and allyl-*1*-^{14}C chloride by the procedure given above for the nonradioactive hydrocarbon.

5-Chloro-4,4-diphenyl-1-pentene (1). To potassium amide prepared from 39.4 g (1.01 g-atom) of potassium in 1 L of liquid ammonia under a nitrogen atmosphere was added with stirring 103.3 g (0.497 mol) of 4,4-diphenyl-1-butene in 100 mL of anhydrous ether. The reaction mixture was stirred at reflux for 1.5 h and then the red-black solution was forced (over a period of 15 min) by nitrogen pressure into 531 g (6.3 mol) of stirred methylene chloride kept at −75 °C. Some 4 min after completion of the addition, the red color of the solution disappeared and the excess KNH_2 was decomposed by addition of 30 g (0.56 mol) of NH_4Cl. The ammonia was allowed to evaporate, and the organic solvents were removed on a rotary evaporator. The residue was treated with water and extracted with ether. Analysis of the ethereal extract by GLC (6 ft Apiezon L column at 200 °C) showed that it contained 94 area % 5-chloro-4,4-diphenyl-1-pentene and 5% starting hydrocarbon. The product after distillation through a Vigreux column (15 cm in length) amounted to 105 g (83% yield) of bp 127 °C (50 μ) of 97 area % purity by GLC. The analytical sample after repeated distillation had NMR absorption (CCl_4) at δ 7.1 (10, H, broad s, aromatic CH), 4.8–5.4 (3 H, m, vinylic CH), 4.09 (2 H, s, CH_2Cl), and 3.00 (2 H, d, $J = 5.5$ Hz, allylic CH).

Anal. Calcd for $C_{17}H_{17}Cl$: C, 79.52; H, 6.67; Cl, 13.81. Found: C, 79.60; H, 6.83; Cl, 13.63.

The samples of 5-chloro-4,4-diphenyl-1-pentene used in the reactions with alkali metals were ordinarily of >95 area % purity according to analysis by GLC.[37]

5-Chloro-4,4-diphenyl-1-pentene-*3*-^{14}C (1*) was prepared from 4,4-diphenyl-1-butene-*3*-^{14}C by a procedure like that above for the nonradioactive compound. Ozonization of the chloride (activity of 0.42 ± 0.024 μCi/mmol) gave formaldimethane of activity of 0.010 ± 0.002 μCi/mmol. Thus since the mode of synthesis required the ^{14}C label to be at C-1 or C-3, the radioactivity assays indicated that 98% of the C-14 was at C-3. In most of the experiments this radioactive chloride was diluted further with nonradioactive chloride.

3,3-Diphenyl-5-hexenoic Acid (5). The acid was prepared by alkylation of 3,3-diphenylpropanoic acid (from Aldrich Chem. Co., Inc.) with excess of potassium amide and allyl chloride and liquid ammonia by a procedure similar to that reported for benzylation of diphenylacetic acid.[33] Analysis of the crude acidic product by qualitative GLC showed that it contained about 25% of starting acid with the remainder the desired acid. The product was purified by recrystallization from pentane and then chromatography on a 2.5 × 29 cm column of silica gel (70–325 mesh, E. Merck A.-G. Darmstadt) with elution by chloroform. A final recrystallization from pentane gave acid of mp 106.0–106.5 °C; NMR (CCl_4) δ 7.12 (10 H, broad s, aromatic CH), 4.8–5.3 (3 H, m, vinylic CH), 3.11 (4 H, unsymmetrical d, $J = 4$ Hz, allylic CH and CH_2CO_2H); mass spectrum *m/e* (rel intensity) 266 (0.07, M^+), 225 (100), 183 (68), 179 (13), 178 (21), 165 (29), 105 (24), 103 (50), 91 (12), 77 (21).

Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.26; H, 6.83.

2,2-Diphenyl-5-hexenoic Acid (7). Allyllithium (0.069 mol) was prepared from cleavage of allyl phenyl ether (0.111 mol) by excess lithium metal in 350 mL of tetrahydrofuran by the procedure of Eisch and Jacobs.[38] To the orange solution of allyllithium was added 13.8 g (0.077 mol) of 1,1-diphenylethene in 15 mL of diethyl ether at −5 ± 5 °C over a 10-min period with stirring. The black-red solution was then stirred for 15 min at 0 °C before carbonation. The usual work up gave a carboxylic acid containing some phenol. The crude product was dissolved in ether and the solution extracted well with water. After removal of ether and recrystallization from 95% ethanol, the product amounted to 3.5 g (19% yield) of acid of mp 138.0–139.0 °C; NMR (CCl_4) δ 7.23 (10 H broad s, aromatic CH), 4.6–6.1 (3 H, complex m, vinylic CH), 2.40 (2 H, t, J = 8 Hz, CH_2 at C-3), 1.81 (2 H, m, allylic C-H); mass spectrum m/e (rel intensity) 266 (3, M^+), 221 (34), 212 (86), 211 (22), 194 (21), 180 (19), 179 (22), 178 (25), 167 (71), 166 (40), 165 (100), 152 (18), 143 (17), 118 (16), 117 (55), 115 (19), 105 (30), 103 (37), 91 (87), 77 (45), 55 (15), 41 (15), 39 (19).

Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.31; H, 6.83.

2-Benzyl-2-phenyl-4-pentenoic Acid (6). Methyl 2,3-diphenylpropionate was prepared in 71% yield of distilled product of >99% purity (GLC) by benzylation of methyl phenylacetate with 10% excess each of potassium amide and benzyl chloride in liquid ammonia solution at reflux temperature according to a general procedure.[39] Methyl 2,3-diphenylpropionate (30.0 g, 0.125 mol) was then alkylated by a similar procedure with potassium amide (prepared from 0.158 g-atom of potassium) and allyl chloride (14.1 g, 0.184 mol) in 500 mL of liquid ammonia containing 65 mL of anhydrous ethyl ether. The crude product was dissolved in acetone; the solution deposited 4.2 g (12% yield) of crystalline methyl 2-benzyl-2-phenyl-4-pentenoate, mp 128.0–129.0 °C.

Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19. Found: C, 81.01; H, 6.88.

The acetone was removed from the mother liquor of the above recrystallization, and the residue was treated with 300 mL of 0.9 M aqueous alcoholic alkali for 93 h at reflux temperature. The usual work up gave 16.7 g (50% yield) of crude acid and 5.4 g of unsaponified ester. The acid after recrystallization from pentane had mp 85.5–87.0 °C; NMR (CS_2) δ 12.04 (1 H, s, -CO_2H), 6.7–7.4 (10 H, m, aromatic CH), 4.9–6.0 (3 H, m, vinylic CH), 3.27 (2 H, s, benzylic CH), 2.68 (2 H, d, J = 7 Hz, allylic CH); mass spectrum m/e (rel intensity) 266 (15, M^+), 225 (9), 181 (7), 179 (8), 178 (9), 175 (23), 131 (13), 129 (43), 128 (10), 115 (8), 107 (13), 103 (8), 91 (100), 77 (13).

Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.03; H, 6.90.

4,4-Diphenyl-1-pentene (8). To potassium amide (prepared from 0.112 g-atom of potassium) in 400 mL of liquid ammonia at reflux temperature was added 15.8 g (0.087 mol) of 1,1-diphenylethane (bp 63–65 °C at 0.14 Torr, prepared from catalytic hydrogenation of 1,1-diphenylethene) in 15 mL of anhydrous ethyl ether. To the deep-red solution after stirring for 10 min was added 9.03 g (0.118 mol) of allyl chloride in 20 ml of anhydrous ethyl ether over a period of 10 min. After 3 min of additional stirring the remaining KNH_2 in the cream-colored solution was decomposed with excess NH_4Cl. The crude product, after the usual work up, was distilled in vacuo to give 10 g (52% yield) of product of bp 88–90 °C at 0.08 Torr which was of 99.5% purity according to a qualitative GLC analysis: NMR (CCl_4) δ 7.10 (10 H, s, aromatic CH), 4.7–5.8 (3 H, m, vinylic CH), 2.82 (2 H, d, J = 6 Hz, allylic CH), 1.53 (3 H, s, CH_3); mass spectrum m/e (rel intensity) 222 (<0.1, M^+), 182 (35), 181 (100), 179 (12), 178 (11), 166 (24), 165 (34), 103 (43), 91 (10), 77 (19).

Anal. Calcd for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.60; H, 8.28.

5,5-Diphenyl-1-pentene (9). To allyllithium prepared[38] from cleavage of 14.7 g (0.110 mol) of allyl phenyl ether by 9.14 g (1.32 g-atom) of lithium in 400 mL of tetrahydrofuran was added 12.47 g (0.069 mol) of 1,1-diphenylethene over a period of 5 min, and the resulting deep-red solution was then stirred or 1.5 h at room temperature before decomposition with excess water. After standing overnight to decompose excess lithium, the tetrahydrofuran layer was separated and the aqueous layer extracted with ethyl ether. The combined ethereal phases were dried over anhydrous $CaCl_2$, concentrated, and then distilled through a 30-cm stainless steel spinning-band column until most of the phenol had been removed. The pot residue was finally distilled in a Hickman still at 4 Torr to give 11.5 g (75% yield) of product: NMR (CCl_4) δ 7.12 (10 H, s, aromatic CH), 4.7–6.1 (3 H, m, vinylic CH), 3.85 (1 H, t, J = 7.5 Hz, Ph_2CH-), 2.03 (4 H, m, -CH_2CH_2-); mass spectrum m/e (rel intensity) 222 (not detected, M^+), 181 (100), 166 (18), 165 (22), 103 (31), 77 (16).

Anal. Calcd for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.68; H, 8.34.

Allyl-^{14}C-lithium. Allyl phenyl ether was advantageously prepared from phenol (13.9 g, 0.148 mol) and 9.39 g (0.123 mol) of allyl chloride in 25 mL of 6.25 N NaOH, 50 mL of hexamethylphosphoramide,[40] and 30 mL of acetone at reflux overnight. Acetone was removed by distillation, 100 mL of water was added, and the mixture was extracted three times with ether. The combined ether layers were extracted with 10% sodium hydroxide, then with water, and finally dried over anhydrous $MgSO_4$. The product after distillation in vacuo amounted to 13.7 g (83% yield) of allyl phenyl ether of >99% purity according to GLC. Allyl phenyl ether, prepared from allyl-1-^{14}C chloride of activity of ca. 0.3 μCi/mmol was cleaved[38] to allyl-^{14}C-lithium by excess lithium in tetrahydrofuran.

General Procedure for Alkali Metal Reactions. All reactions with alkali metals were run under a nitrogen atmosphere in a Morton high-speed stirring apparatus according to the procedure given previously.[3j,k] In many of the experiments the Morton flask was advantageously modified[1] to six necks: the large central neck held the high-speed stainless-steel stirrer assembly; five standard-taper side necks contained a condenser, a pressure-equalizing dropping funnel, a thermometer well, a 4-mm bore Teflon stopcock protected on the end by a rubber septum for withdrawing samples with a syringe (which had been previously flushed with nitrogen), and an internal glass siphon tube fitted with a vacuum stopcock and a ball and socket joint on the end to permit transfer of large quantities of the alkali metal reagent without admitting air or water vapor to the system. All ethereal extracts of products were dried over anhydrous $MgSO_4$ before removal of ether.

Reactions of 5-Chloro-4,4-diphenyl-1-pentene (1) with Alkali Metals in Tetrahydrofuran. A. With Lithium. To 1.27 g (0.184 g-atom) of lithium wire cut into small pieces in 250 mL of tetrahydrofuran (THF) was added 0.5 mL (0.008 mol) of methyl iodide. The solution was cooled to −10 °C while some 10% of a solution of 10.7 g (0.042 mol) of 5-chloro-4,4-diphenyl-1-pentene (**1**) in 70 mL of THF was added. After 1 h of vigorous stirring at a temperature up to 0 °C, a pink color developed in the solution; the flask was then cooled at −65 ± 5 °C while the remainder of the chloride was added over a period of 10 min. After the solution had been stirred at this low temperature for 3 h, some 44% of the solution was forced onto crushed solid carbon dioxide (carbonation I) while the remainder of the red solution was stirred at 0 °C for 4 h before carbonation II. The THF was removed from the carbonated mixtures at reduced pressure, and the residues were treated with aqueous sodium hydroxide. The aqueous mixtures were extracted with ether to remove neutral material, acidified, and again extracted with ether to separate carboxylic acids. Carbonation I gave 2.6 g of neutral material and 2.0 g of acids. Analysis of the neutral product by GLC[41] at 175 °C gave the products, listed as area percent (relative retention time, identity): 41 (1.00, **8**), 1.5 (1.45), and 57 (2.5, **1**). The acids as methyl esters (prepared with diazomethane) by GLC[41] at 175 °C similarly contained: 4 (0.74, 2,2-diphenyl-4-pentenoic acid[12]), 14 (1.00, **7**), 81 (1.16, **5**), and 1 (1.33). The NMR spectrum of the crude acid was consistent with the major component being 3,3-diphenyl-5-hexenoic acid (**5**) according to comparisons with the authentic sample of this acid (prepared from alkylation of 3,3-diphenylpropanoic acid). Carbonation II gave 2.4 g of neutral material and 4.0 g of acids. The neutral product by similar GLC analysis contained: 72 (1.00, **8**), 13 (1.08, **9**), and 11 (2.3); while the acids contained: 7 (0.73, 2,2-diphenyl-4-pentenoic acid[12]), 86 (1.00, **7**), 4 (1.14, **6**). The acidic product after treatment with charcoal, recrystallization from aqueous ethanol, and washing the crystals with n-pentane gave crystals of mp 133–134°C; these crystals showed no mixture melting point depression and had NMR and infrared spectra identical with the sample of 2,2-diphenyl-5-hexenoic acid (**7**) prepared from 1,1-diphenylethene and allyllithium.

In another reaction 4.71 g (0.0184 mol) of **1** and 1.1 g (0.008 mol) of methyl iodide in 30 mL of THF were added over a 15-min period to 1.38 g (0.200 g-atom) of lithium in 250 mL of THF at −75 °C. Some twelve 1-mL aliquots were withdrawn at half-hour intervals and protonated by water. After 6 h of vigorous stirring the hydrolyzed aliquot contained, according to analysis by GLC,[42] no unreacted chloride and >98 area % of **8**. Mass spectral analysis at m/e 181 ($Ph_2C^+CH_3$) and 182 of an aliquot which had been decomposed with D_2O indicated that the 4,4-diphenyl-1-pentene contained 67% d_1 and 33% d_0 components or that 33% of the organolithium compound had been protonated by the solvent (or spurious protons) prior to addition of D_2O. The main reaction solution was warmed rapidly to −32 °C (±2 °C) and 1-mL aliquots of the deep rusty-red colored solution were withdrawn at various intervals over a period of 4 h and protonated by water. Analysis of these aliquots by GLC[42] indicated that the amount of rearranged hydrocarbon increased according to a first-order rate law ($k = 4.3 \times 10^{-4}\ s^{-1}$ or a half-life of 27 min) and that the final ratio of **9**:**8** was 68:32 (at retention times of 7.5 and 6.5 min, respectively, at 180 °C) in agreement with the mass spectral determination that about one-third of the organolithium reagent had been protonated prior to rearrangement. Carbonation of a portion of the final solution gave an acid fraction which upon analysis by GLC[42] consisted of >98 area % of **7** containing a trace of evidently **6** (as methyl ester at 1.09 times the retention time of **7** at 190 °C).

In another reaction, 3.58 g (0.517 g-atom) of lithium in 250 mL of THF was treated at room temperature with 1.1 g (0.008 mol) of methyl iodide. After 5 min of stirring, the reaction mixture was cooled to −75 °C and 0.44 g (0.0048 mol) of *n*-butyl chloride was added and allowed to react for 30 min. The chloride **1** (2.68 g, 0.0104 mol) in 12 mL of THF was then added over a period of 10 min. Reaction was indicated by the rapid development of a red color. A 1-mL aliquot of the solution was protonated after 4 h of stirring at −75 °C; analysis by GLC[43] at 167 °C gave 6 area % yield of unknown (relative retention time of 0.92), 91% of **8** (1.00), 3% of unknown (2.31), and no detectable chloride **1.** Carbonation of 6% of the −75 °C reaction solution gave 0.07 g of hydrocarbons and 0.25 g of acids. The latter upon GLC[44] analysis at 202 °C gave 3 area % yield of **7** (1.28), 89% of **5** (1.59), and 8% of unknown (1.96). A 100-mL aliquot of the reaction solution was held at −50 °C for 12 h before protonation of a small aliquot; analysis by GLC as previously gave 7% of unknown (0.92), 64% of **8** (1.00), 23% of **9** (1.17), and 7% of unknown (2.32). Carbonation of the solution remaining after 12.3 h at −50 °C gave 0.83 g of hydrocarbons and 0.30 g of acids; the latter upon GLC analysis as previously contained 39 area % yield of **7** (1.28), 2% of **6** (1.50), 53% of **5** (1.57), and 5% of unknown (1.94). The data for carbonation indicate that the first-order rate constant for rearrangement of 2,2-diphenyl-4-pentenyllithium (**2**) at −50 °C is $1.0 \times 10^{-5}\ \mathrm{s}^{-1}$ or the half-life is some 19 h at this temperature. Another 100-mL aliquot of the original reaction solution was warmed from −75 to 0 °C; 1-mL aliquots upon protonation after standing for 1, 2, and 3 h at 0 °C all gave upon analysis by GLC, as previously, 10 area % yield of unknown, possibly **10** (0.91), 15% of **8** (1.00), 73% of **9** (1.16), and 3% of unknown (2.29). Carbonation of the solution remaining after 4 h at 0 °C gave 0.54 g of hydrocarbons and 0.88 g of acids; the latter upon GLC analysis, as previously, gave products listed as area percent (relative retention time, identity): 1 (0.32), 1 (0.68, diphenylacetic acid?) 1 (1.17), 62 (1.29, **7**), 5 (1.36), 2 (1.49, **6**), 8 (1.58, **5**?), 6 (1.73, 2,2-diphenylheptanoic acid), 3 (1.96), and 7 (2.19).

B. With Potassium. Tetrahydrofuran (400 mL) was heated with 1.75 g (0.045 g-atom) of potassium at reflux temperature for 1 h. To the well-stirred mixture was added over a period of 1 min 5.16 g (0.0202 mol) of chloride **1** in 20 mL of THF. Stirring at reflux was continued for 3 min after addition of the chloride and then the flask was cooled to room temperature over a period of 3 min before forcing the deep-red solution onto crushed solid carbon dioxide. The usual work-up gave 2.2 g of neutral material and 3.7 g of crude acids. Of the acids only 2.2 g (41% yield) were volatile as methyl esters according to a quantitative analysis by GLC[44] at 201 °C which indicated that the volatile acidic product has the following composition listed as weight percent (relative retention time, identity): 1 (0.70, diphenylacetic acid), 2 (1.00, 2,2-diphenyl-4-pentenoic acid), 16 (1.27, **7**), 8 (1.36, unknown), 53 (1.47, **6**), and 20 (1.95, unknown X). The identification of 2,2-diphenyl-4-pentenoic acid, **7,** and **6** was confirmed by the mass spectra of samples collected from GLC.[43] Unknown X as methyl ester (separated by GLC[43]) gave an exact mass of 280.148 (calculated for $C_{19}H_{20}O_2$, 280.146); mass spectrum *m/e* (rel intensity) 280 (M^+, 23), 193 (23), 189 (18), 143 (29), 129 (69), 128 (26), 121 (18), 115 (33), 105 (15), 91 (100), 77 (16), 65 (16); NMR (CS_2) δ 7.13 and 7.05 (8 H, m, aromatic CH), 6.4–5.0 (2 H, m, vinylic CH), 3.9–3.1 (7 H, m; apparently an OCH_3 singlet at δ 3.55, a CH_3 doublet at δ 3.67 with $J = 18$ Hz, and a proton of high multiplicity), 1.25 (3 H, d, $J = 7$ Hz, $CHCH_3$); λ_{max} (95% EtOH) 245 nm (ϵ 7900).

C. With Lithium and then Alkali Metal *tert*-Butoxides. Lithium (6.45 g, 0.93 g-atom) was reacted with methyl iodide (2.3 g, 0.016 mol) and *n*-butyl chloride (0.88 g, 0.0095 mol) in 250 mL of THF at room temperature for 15 min and then the reaction mixture was cooled to −75 °C before adding 3.90 g (0.0152 mol) of chloride **1** in 25 mL of THF. After 4.3 h of vigorous stirring at −75 °C, a 125-mL aliquot of the solution was forced onto crushed carbon dioxide (carbonation I). To the remaining solution was added 125 mL of a THF solution containing 0.159 g formula weights of lithium *tert*-butoxide (prepared from *n*-butyl chloride and lithium in THF at −75 °C, and then addition of *tert*-butyl alcohol in an amount equal to the *n*-butyllithium produced). After 40 min of stirring at −75 °C, some 125 mL of the solution was forced onto solid carbon dioxide (carbonation II). The remaining solution was warmed rapidly to 0 °C and was kept at this temperature for 1.5 h before all of it was carbonated (carbonation III). After the usual work-up the acidic products were analyzed as methyl esters by a quantitative GLC procedure[44] at 215 °C. Carbonation I gave 1.80 g of volatile acids which had the following composition listed as weight percent (relative retention time, identify): 0.6 (1.21, **7**), 91 (1.49, **5**), 8 (1.77). Carbonation II gave 0.60 g of volatile acids of composition, listed as previously: 1.6 (1.22, **7**) 93 (1.53 **5**), 6 (1.81). Carbonation III gave 0.50 g of volatile acids: 1.6 (0.34), 0.7 (0.43), 0.9 (0.69, diphenylacetic acid), 0.9 (1.00, 2,2-diphenyl-4-pentenoic acid), 75 (1.25, **7**), 4 (1.36), 4 (1.45, **6**), 7 (1.50, **5**), 3 (1.65, 2,2-diphenylheptanoic acid), 2 (2.04).

In another run 7.4 g (1.06 g-atom) of lithium in 250 mL of THF was treated with 2.3 g (0.016 mol) of methyl iodide at room temperature. The flask was cooled to −75 °C, and then 0.88 g (0.0095 mol) of *n*-butyl chloride was added and allowed to react for 30 min with vigorous stirring before dropwise addition of 3.20 g (0.0125 mol) of chloride **1** in 10 mL of THF over a 15-min period. One hour after completion of the addition of **1,** 125 mL of the reaction mixture was forced onto solid carbon dioxide. The usual work up of the carbonation product gave 0.22 g of neutral product and 1.5 g of acids. Analysis of the neutral product by GLC[45] at 200 °C gave products listed as area percent (relative retention time, identify): 4 (0.78), 4 (0.82), 68 (1.00, **8**), 8 (1.11, **9**), 14 (1.68). The acidic product similarly contained by GLC of the methyl esters at 207 °C: 2 (1.26, **7**) and 98 (1.53, **5**); the mass spectrum of this product was essentially identical with that of an authentic sample of **5.** To the remaining reaction solution at −75 °C was added 125 mL of a THF solution (at −75 °C) containing 0.18 g formula weights of potassium *tert*-butoxide (prepared by addition of *tert*-butyl alcohol to excess finely divided, molten potassium metal in THF at reflux temperature with vigorous stirring continued for 2 h after completion of the addition). After 30 min of stirring the reaction solution at −75 °C was forced onto crushed solid carbon dioxide. The usual work up gave 1.1 g of neutral product and 0.95 g of acids. Analysis of the neutral product by GLC[45] at 200 °C gave products listed as area percent (relative retention time, identify): 6 (0.39), 18 (0.95, probably **10**), 53 (1.00, **8**), 12 (1.11, **9**), 5 (1.21), 5 (1.63). Analysis of the acids as methyl esters by GLC[45] at 207 °C gave products listed as previously: 2 (1.00, 2,2-diphenyl-4-pentenoic acid), 30 (1.26, **7**), 4 (1.32), 62 (1.46, **6**), 1.6 (1.69, 2,2-diphenylheptanoic aicd). The NMR and mass spectra confirmed the presence primarily of **6** and **7** in the crude acid according to comparisons with the spectra of authentic samples.

In a further run 8.02 g (1.16 g-atom) of lithium in 250 mL of THF was activated at room temperature with 0.5 mL (0.008 mol) of methyl iodide. The reaction mixture was cooled to −75 °C and then 0.44 g (0.0048 mol) of *n*-butyl chloride was added and allowed to react for 30 min, after which 3.90 g (0.0152 mol) of chloride **1** in 10 mL of THF was added over a 5-min period. After 4.5 h, a 75-mL aliquot of the organolithium solution was added ("inverse" addition) to 75 mL of potassium *tert*-butoxide (0.060 g formula weight) in THF at −75 °C; the mixture was shaken vigorously and after 10 min reaction time forced onto excess solid carbon dioxide (carbonation I). A second 75-mL aliquot of the organolithium solution was transferred to a storage vessel kept at −75 °C after which 75 mL (0.060 g formula weight) of potassium *tert*-butoxide in THF solution at −75 °C was added ("normal" addition); the mixture was shaken vigorously and after 10-min reaction time forced onto excess solid carbon dioxide (carbonation II). A third 75-mL aliquot of the organolithium solution at −75 °C was added to 75 mL (0.060 g formula weight) of cesium *tert*-butoxide (prepared from reaction of excess cesium with *tert*-butyl alcohol in THF like earlier preparation of potassium *tert*-butoxide) in THF solution at −75 °C; the mixture was shaken vigorously and after 10 min forced onto excess solid carbon dioxide (carbonation III). Finally, the remaining some 20 mL of organolithium solution after 6 h at −75 °C was carbonated (carbonation IV). The carbonated mixtures were worked up in the usual fashion. Carbonation I gave 0.57 g of crude neutral material and 0.9 g of acids; the latter upon quantitative GLC analysis[44] of the methyl esters at 210 °C contained 0.63 g of volatile acids of the composition, listed as weight percent (relative retention time, identify): 27 (1.27, **7**), 10 (1.35), 54 (1.48, **6**), 4.5 (1.70, 2,2-diphenylheptanoic acid), 4.5 (1.92). Carbonation II gave 0.5 g of neutral material and 0.9 g of acids; the latter upon similar quantitative analysis contained 0.67 g of volatile acids of composition listed as previously: 23 (1.28, **7**), 11 (1.35), 57 (1.49, **6**), 4.2 (1.71, 2,2-diphenylheptanoic acid), 4.5 (1.93). Carbonation III gave 0.25 g of neutral material and 1.2 g of acids; the latter upon quantitative analysis contained 0.69 g of volatile acids of composition: 0.7 (0.41), 3 (0.69, diphenylacetic acid), 13 (1.27, **7**), 8 (1.34), 70 (1.48, **6**), 1.6 (1.70, 2,2-diphenylheptanoic acid), 3 (1.92). Carbonation IV gave 0.08 g of neutral material and 0.24 g of acids; the latter upon quantitative analysis contained 0.18 g of volatile acids of composition: 2 (1.25, **7**), 1 (1.35), 89 (1.56, **5**), 8 (1.90).

D. With Lithium and then 18-Crown-6. 2,2-Diphenyl-4-pentenyllithium was prepared at −75 °C in the usual manner from 5.46 g (0.786 g-atom) of lithium, 0.6 g (0.004 mol) of methyl iodide, 0.2 g (0.002 mol) of *n*-butyl chloride, and 4.01 g (0.0156 mol) of chloride **1** in 250 mL of THF. After 5-h reaction time a 25-mL aliquot of the solution was added to 7.0 g (0.027 mol) of 18-crown-6 ether in 25 mL of THF and stored at −75 °C (test experiments showed that the solubility of the crown in THF was only 3 g/50 mL THF at −75 °C) for 3 h before carbonation. The usual work up and GLC analysis showed that the volatile carboxylic acid formed was >90% **5** just as in a similar aliquot without 18-crown-6. Another aliquot of the organolithium solution which had been warmed to 0 °C for 3 h before carbonation contained >90% of acid **7**.

E. With Lithium and then Allyl-^{14}C-lithium. 2,2-Diphenyl-4-pentenyllithium was prepared in the usual way from 5.7 g (0.83 g-atom) of lithium, 1.1 g (0.008 mol) of methyl iodide, and 3.98 g (0.0155 mol) of chloride **1** in 175 mL of THF at −75 °C. After 3.5 h of stirring at −75 °C, a double Gilman[46] titration indicated the presence of 0.0083 mol (53% yield) of organolithium compound. Carbonation of a 25-mL aliquot of the solution gave crude acid which by GLC analysis[43] contained 87 area % of **5**, 1% of **7**, 2% of 2,2-diphenyl-4-pentenoic acid, and small amounts of three unknowns. To the remaining organolithium reagent (6.9 mmol) was added 125 mL (44 mmol) of a THF solution of freshly prepared allyl-^{14}C-lithium at −75 °C. The solution of organolithium reagents was mixed well and then warmed rapidly (5 min to reach −5 °C) to 0 ± 5 °C and kept at this temperature for 3.2 h before carbonation. After the usual work up, the ethereal solution of acidic products was extracted four times with a total of 200 mL of 10% $NaHCO_3$. The $NaHCO_3$ extract was cautiously acidified with hydrochloric acid and then extracted with ether. The ether was removed through a short column packed with glass helices and the residue distilled in a microdistillation apparatus at 25 °C at 0.1 mm and collected in a trap cooled to −78 °C. The distillate (2.5 g) was dissolved in 95% ethanol and hydrogenated over 0.14 g of a 5% Pt on carbon catalyst (0.019 mol uptake of H_2). The resulting *n*-butyric acid was converted into its *p*-phenylphenacyl ester (mp 80.5–81.0 °C, lit.[47] 82 °C) which had an activity of 0.199 ± 0.001 μCi/mmol. The ethereal solution from the previous $NaHCO_3$ extraction yielded 2.7 g of crude crystals which according to GLC analysis[43] at 195 °C consisted of 85 area % of **7**, 5% of 2,2-diphenyl-4-pentenoic acid, and 10% of an unknown at 1.17 times the retention time of **7**. Two recrystallizations from aqueous methanol gave 0.9 g of crystals of **7** of mp 137–138 °C, which had an activity of 0.026 ± 0.001 μCi/mmol. While experimental difficulties prevented a direct assay of the starting allyllithium used in this experiment, this activity may be estimated from the activities of the products and the initial quantities of the reactants to be 0.203 ± 0.002 μCi/mmol, not appreciably different from the activity of the isolated *n*-butyric acid.

Reactions of 5-Chloro-4,4-diphenyl-1-pentene-*3*-^{14}C (1*) with Lithium in Tetrahydrofuran. A. At 0 °C. 2,2-Diphenyl-4-pentenyllithium was prepared from 1.30 g (0.187 g-atom) of lithium, 2.3 g (0.016 mol) of methyl iodide, 0.88 g (0.0096 mol) of *n*-butyl chloride, and 4.51 g (0.018 mol) of radioactive chloride **1*** (0.31 μCi/mmol) in the usual manner in 250 mL of THF at −75 °C. After 12 h at −75 °C a 75-mL aliquot was carbonated to give 0.91 g of acidic material containing 94 area % of **5** by GLC analysis. Crystallization of the acid from pentane gave 0.26 g of pure **5** (GLC) of activity 0.289 ± 0.002 μCi/mmol; ozonization of the acid gave formaldehyde whose methone derivative had an activity of 0.004 ± 0.001 μCi/mmol. The remainder of the organolithium reagent was warmed to 0 ± 2 °C over a period of 15 min and held at this temperature for 2.5 h before carbonation to give 1.4 g of acidic material containing by GLC analysis[45] 89 area % of **7**, 2% of **6**, 2% of **5**(?), and 7% of 2,2-diphenylheptanoic acid. Two recrystallizations from aqueous ethanol gave acid of >98% **7** by GLC with activity of 0.285 ± 0.003 μCi/mmol. Ozonization of the acid gave formaldehyde whose methone derivative had activity of 0.153 ± 0.004 μCi/mmol; however, oxidation with sodium periodate–osmium tetroxide gave formaldehyde whose methone derivative had an activity of 0.193 ± 0.004 μCi/mmol.

B. At −32 °C. 2,2-Diphenyl-4-pentenyllithium was prepared from 1.85 g (0.267 g-atom) of lithium, 3.4 g (0.024 mol) of methyl iodide, and 4.6 g (0.018 mol) of radioactive chloride **1*** (0.43 ± 0.02 μCi/mmol) in the usual manner in 250 mL of THF at −75 °C. After 9 h of stirring at −75 °C, 100 mL of the solution was carbonated to give an acid which by GLC analysis contained some 92 area % of **5** and 2% of **7**. The remainder of the organolithium reagent was kept at −32 ± 3 °C for 3 h before carbonation. The crude acidic product (3 g) by GLC analysis[48] at 208 °C contained products listed as area percent (relative retention time, identity): 1 (0.81, diphenylacetic acid), 3 (0.84, 2,2-diphenylpropanoic acid), 7 (1.00, 2,2-diphenyl-4-pentenoic acid[12]), 69 (1.14, **7**), and 18 (1.25, **5**). The crude acid was esterified with diazomethane and the methyl ester of acid **7** was separated (in 98 area % purity by GLC) by liquid chromatography on a 1 in. diameter column packed to a height of 10 in. with acid-washed alumina (Merck, reagent grade) with elution by hexane containing a little benzene. The ester of **7** had an activity of 0.447 ± 0.010 μCi/mmol. Ozonization of the ester gave formaldehyde which upon assay of its dimethone derivative had an activity of 0.281 ± 0.009 μCi/mmol.

C. At −50 °C. 2,2-Diphenyl-4-pentenyllithium was prepared at −75 °C in the usual manner from 7.3 g (0.047 g-atom) of lithium, 1.1 g (0.008 mol) of methyl iodide, and 5.18 g (0.0202 g-atom) of chloride **1*** (0.31 μCi/mmol) in 220 mL of THF. After 4.5 h of reaction a 20-mL aliquot of the solution at −75 °C was carbonated to give according to quantitative GLC analysis[44] at 211 °C 0.44 g of acids containing 6.6% of **7**, 91% of **5**, and 2% of an unknown at 1.47 times the retention time of **7**. The remainder of the organolithium solution was transferred to a tightly sealed storage vessel and kept at −50 ± 0.5 °C for 96.5 h before carbonation. The usual isolation gave 2.7 g of crude acids which according to quantitative GLC analysis[44] at 211 °C contained 2.22 g of volatile acids consisting of 94% of **7**, 2.3% of **6**, and 3.5% of **5**. The acid was recrystallized once for aqueous ethanol and twice from aqueous methanol to give 0.99 g of acid which was **7** of >99% purity (GLC). The total radioactivity of this acid was 0.285 ± 0.002 μCi/mmol. Ozonization of the methyl ester of this acid gave formaldehyde whose dimethone derivative had an activity of 0.201 ± 0.002 μCi/mmol. The aqueous ethanolic mother liquor from preparation of the dimethone was concentrated and extracted with ether. The ether was removed and the residue treated with 2,4-dinitrophenylhydrazine reagent[36] in aqueous ethanol with the solution being held briefly at its boiling point. The resulting red-orange 2,4-dinitrophenylhydrazone of methyl 2,2-diphenyl-5-oxopentanoate had mp 170–172 °C and radioactivity of 0.046 ± 0.002 μCi/mmol.

Anal. Calcd for $C_{24}H_{22}O_6N_4$: C, 62.33; H, 4.80; N, 12.12. Found C, 62.05; H, 4.87; N, 12.30.

Another portion of this purified acid **7** was oxidized by the sodium periodate–osmium tetroxide procedure to give formaldehyde whose dimethone derivative had activity of 0.237 ± 0.003 μCi/mmol. The ether phase from the osmium tetroxide oxidation yielded yellow crystals of the 2,4-dinitrophenylhydrazone of 2,2-diphenyl-5-oxopentanoic acid, mp 203–204 °C, activity 0.043 ± 0.002 μCi/mmol.

Anal. Calcd for $C_{23}H_{20}N_4O_6$: C, 61.60; H, 4.50; N, 12.50. Found: C, 61.36; H, 4.60; N, 12.37.

D. At −70 °C with Potassium *tert*-Butoxide–18-Crown-6 Complex. 2,2-Diphenyl-4-pentenyllithium was prepared in the usual way from 5.5 g (0.79 g-atom) of lithium, 1.1 g (0.008 mol) of methyl iodide, and 3.82 g (0.0149 mol) of chloride **1*** (activity of 0.306 ± 0.003 μCi/mmol) in 150 mL of THF at −75 °C. After 5 h of reaction at −75 °C a 10-mL aliquot was carbonated to give 0.20 g of crude acid whose GLC analysis[44] at 213 °C indicated the presence of 3 area % of **7**, 96% of **5**, and 1% of unknown (at 1.46 times the retention time of **7**). Recrystallization of the acid from pentane gave 0.11 g of **5** of total activity of 0.287 ± 0.003 μCi/mmol. To the remainder of the organolithium reagent at −75 °C was added dropwise a saturated solution of 0.078 g formula weight of potassium *tert*-butoxide and 20.8 g (0.079 mol) of freshly distilled 18-crown-6 in 125 mL of THF at room temperature; the addition of the alkoxide was made over a 15-min period such that the temperature of the solution was held at −70 ± 2 °C throughout the addition. Immediately after completion of the addition a 10-mL aliquot of the solution was carbonated; the remaining solution was stirred at −75 °C for 30 min longer before carbonation. The first carbonation yielded 0.026 g of crude acids while the second carbonation gave 0.77 g of crude acids and 1.9 g of neutral material. The acids from the two carbonations upon GLC analysis[44] at 213 °C had the same composition, listed as area percent (relative retention time, identity): 2 (0.58, diphenylacetic aicd), 6 (0.70, 2,2-diphenylpropanoic acid), 19 (1.00, 2,2-diphenyl-4-pentenoic acid[12]), 65 (1.27, **7**), 6 (1.46, **6**), and 2 (1.88). The crude acids were esterfied with diazomethane and the methyl ester of **7** was separated in 99% purity by preparative GLC[43] at 167 °C. The ester of **7** was saponified with 5% alcoholic KOH at reflux for 29 h and the acid **7** was then oxidized by the sodium periodate–osmium tetroxide procedure. The dimethone derivative of the resulting formaldehyde had an activity of 0.303 ± 0.004 μCi/mmol.

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(16) We are indebted to Professor Herbert O. House for bringing into question the reliability of the ozonization procedure.

(17) (a) The likely small isotope effect expected in reactions of an allyl group labeled at a terminal position will be ignored for simplicity in the present discussion. Note that protonation of allyl-*1*-^{14}C anion gives 6.4 ± 1.5% greater activity in the terminal methylene group than in the methyl group of the resulting propylene.[14] (b) The calculation is based on use of eq 5 of Grovenstein and Wentworth.[5b]

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(29) We wish to thank Professor Charles L. Liotta for a helpful discussion on this point.

(30) Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., and by Atlantic Microlab, Inc., Atlanta, Ga. Melting points and boiling points are uncorrected.

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(32) The previous report (ref 5b), that this acid has mp 131–133 °C is evidently in error; apparently the compound of mp 131–133 °C was 2,2-diphenylhexanoic acid [lit. mp 130–132 °C; A. L. Mndzhoyan, G. T. Tatevosyan, S. G. Agbalyan, and R. K. Bostandzhyan, *Chem. Abstr.*, **54**, 1412*e* (1960)] which was produced by inadvertent addition of *n*-propyllithium rather than *n*-butyllithium to 1,1-diphenylethylene.

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(37) We are indebted to Miss Kathleen Mary Taylor for synthesis of some of the 5-chloro-4,4-diphenyl-1-pentene.

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(39) W. G. Kenyon, E. M. Kaiser, and C. R. Hauser, *J. Org. Chem.*, **30**, 2937 (1965).

(40) Cf. J. E. Shaw, D. C. Kunerth, and J. T. Sherry, *Tetrahedron Lett.*, 689 (1973).

(41) The column used for GLC was a 6 ft, ⅛ in. column packed with 80–100 mesh Variport coated with 5% Apiezon L.

(42) The column used for GLC was a 6 ft, ⅛ in. column packed with 60–80 mesh Chromosorb W coated with 10% Apiezon L.

(43) The GLC column was 10 ft, ⅛ in. and was packed with 15% Carbowax 20M on 60–80 mesh Chromosorb W.

(44) The GLC column was 20 ft, ⅛ in. and was packed with 15% Apiezon H on 60–80 mesh Chromosorb W.

(45) The GLC column was 12 ft, ⅛ in. and was packed with 15% Apiezon H on 60–80 mesh Chromosorb W.

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(48) The GLC column was 6 ft, ⅛ in. and was packed with 5% Apiezon L on Diatoport S.