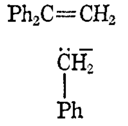
Carbanions. IX. Evidence for a Duality of Mechanism in Rearrangement of Carbanions[1,2]

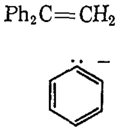
Erling Grovenstein, Jr., and Gary Wentworth

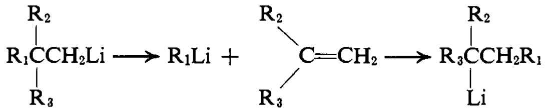
Contribution from the School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332. *Received November 5, 1966*

Abstract: Rearrangement of 2,2,3-triphenylpropyllithium to 1,1,3-triphenylpropyllithium in tetrahydrofuran solution in the presence of various organolithium reagents, RLi (phenyllithium, ethyllithium, *n*-butyllithium, isopropyllithium, and benzyllithium-α-C^{14}), gives detectable products (RCH_2CPh_2Li and $PhCH_2Li$) of reaction of the added organolithium reagent with 2,2,3-triphenylpropyllithium only in the cases of isopropyllithium and benzyllithium-α-C^{14}. These experiments indicate that 2,2,3-triphenylpropyllithium undergoes rearrangement by a preliminary cleavage into benzyllithium and 1,1-diphenylethene followed by readdition of benzyllithium to 1,1-diphenylethene to give 1,1,3-triphenylpropyllithium. Of the organolithium reagents tested, only isopropyllithium was able to compete with benzyllithium for the intermediate 1,1-diphenylethene. The direct addition of organolithium reagents to 1,1-diphenylethene under the general conditions of rearrangement was examined and from these results and those on rearrangement it is concluded that the reactivity of organolithium compounds toward 1,1-diphenylethene increases along the series $PhLi < EtLi, n\text{-}BuLi \ll i\text{-}PrLi < PhCH_2Li$. Rearrangement of 2,2,2-triphenylethyllithium to 1,1,2-triphenylethyllithium in tetrahydrofuran in the presence of phenyllithium-C^{14} or benzyllithium occurs without detectable incorporation of radioactive phenyl or benzyl in the products of rearrangement. These results indicate that rearrangement of 2,2,2-triphenylethyllithium occurs by an intramolecular mechanism. Similarly both Stevens and Sommelet rearrangements of dibenzyldimethylammonium halide brought about by benzyllithium-α-C^{14} in tetrahydrofuran occur without detectable incorporation of radioactivity in the dimethyl(1,2-diphenylethyl)amine and dimethyl(*o*-methylbenzylhydryl)amine produced and are therefore judged to be intramolecular rearrangements. Possible mechanisms for these intramolecular rearrangements are discussed.

Reaction of lithium with 1-chloro-2,2,3-triphenylpropane in tetrahydrofuran at −65° gives[3] 2,2,3-triphenylpropyllithium, which when warmed in the same solvent to 0° rearranges to 1,1,3-triphenylpropyllithium. This rearrangement, which involves over-all an exclusive 1,2 shift of benzyl, occurs more readily than a related 1,2 shift of phenyl in 2,2,2-triphenylethyllithium.[4] These and related rearrangements[5] have been assumed, implicitly or explicitly, to be intramolecular in character. The greater migratory aptitude of benzyl than phenyl could be explained on the basis of a contribution of a structure such as I to the transition state for benzyl migration; the corresponding structure II for phenyl migration would appear to be less important since here the negative charge is localized in an sp^2 orbital of the phenyl anion while in I the charge is delocalized over the π system of the benzyl anion. While I was regarded[3] as a contributing structure for an intramolecular route of migration of benzyl, this explanation for the greater migratory aptitude of benzyl over phenyl would apply even more forcefully if I is looked upon as a contributing structure to a transition state in which benzyl is being cleaved from 2,2,3-triphenylpropyllithium as a benzyl anion in an elimination–readdition mechanism.


I


II


III IV V

$$\underset{R_3}{\overset{R_2}{R_1CCH_2Li}} \longrightarrow R_1Li + \underset{R_3}{\overset{R_2}{}}C{=}CH_2 \longrightarrow \underset{Li}{\overset{R_2}{R_3CCH_2R_1}} \qquad (1)$$

The general argument[5] in opposition to such an elimination–readdition mechanism is that if addition of organolithium compound IV to the olefin were possible, then organolithium compound III, which is present initially in high concentration, should compete successfully in addition to the olefin; however, no products corresponding to addition of III have been detected in any of the rearrangements under discussion. In a direct test of the elimination–readdition mechanism, Zimmerman and Zweig[5] obtained little, if any, reaction of *p*-tolyllithium with α-methylstyrene using conditions under which 2-phenyl-2-(*p*-tolyl)propyllithium had undergone much rearrangement. Obviously the use of such arguments for or against the elimination–readdition mechanism required detailed knowledge of the reactivity of organolithium compounds (or carbanions) toward appropriate olefins under the condition of rearrangement; unfortunately such data do not appear to be available in most cases of interest.

On the basis of an intramolecular mechanism of carbanion rearrangement, Zimmerman and Zweig[5] have calculated, using simple LCAO molecular orbital theory, that phenyl should migrate more readily than benzyl (other factors being equal). Since an opposite result was found from experiment as stated above, these calculations suggest that a more complex mechanism may exist in practice for rearrangements of 2,2,3-

---

(1) Abstracted from the Ph.D. thesis of G. Wentworth, Georgia Institute of Technology, 1966.

(2) For a preliminary communication of some of this work, see E. Grovenstein, Jr., and G. Wentworth, *J. Am. Chem. Soc.*, 85, 3305 (1963).

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

(4) E. Grovenstein, Jr., and L. P. Williams, Jr., *ibid.*, 83, 412 (1961). See also E. Grovenstein, Jr., *ibid.*, 79, 4985 (1957); H. E. Zimmerman and F. J. Smentowski, *ibid.*, 79, 5455 (1957).

(5) H. E. Zimmerman and A. Zweig, *ibid.*, 83, 1196 (1961).

triphenylpropyllithium and 2,2,2-triphenylethyllithium or only for the former.

Finally recent work on the related Wittig rearrangement of ethers seems to establish an elimination–readdition mechanism in many cases. While in most cases the "migrating group" has been regarded as cleaving as a carbanion in an ion-pair complex with the carbonyl moiety,[6] more recently radical-pair cleavage of the metalated ether has been proposed at least for cases involving migration of *sec-* and *t*-alkyl groups.[7]

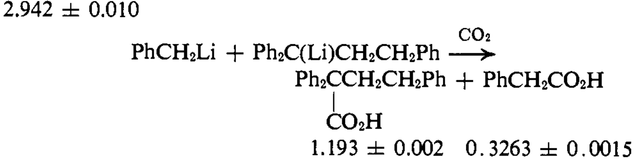
For these and other reasons[8] it seemed of interest to examine the mechanism of rearrangement of 2,2,3-triphenylpropyllithium and 2,2,2-triphenylethyllithium especially with respect to whether or not these rearrangements are intramolecular processes.

Results and Discussion

Rearrangement of 2,2,3-Triphenylpropyllithium in Presence of Benzyllithium-α-C^{14}. According to the elimination–readdition mechanism of carbanion rearrangement (see eq 1), it should *a priori* be possible to "trap" either the intermediate organolithium compound IV or the intermediate olefin V. A suitable trap for IV (benzyllithium in the present case), in absence of other complicating factors, would be isotopically labeled 1,1-diphenylethene; however, a preliminary experiment, in which 1,1-diphenylethylene was added to about 0.5 molar equiv of 2,2,3-triphenylpropyllithium in tetrahydrofuran at $-65 \pm 5°$ and the mixture warmed to 0° for 10 min under the general conditions required for rearrangement,[3] gave, after carbonation, only 3% recovery of 1,1-diphenylethylene and much ill-defined polymeric material. This experiment must be regarded as indecisive as far as mechanism is concerned, since the concentration of 1,1-diphenylethene was doubtlessly much higher than that likely to exist during rearrangement of 2,2,3-triphenylpropyllithium. Therefore, we next directed our attention toward the possibility of "trapping" the intermediate olefin V.

A suitable "trap" for the intermediate olefin, 1,1-diphenylethene, should be benzyllithium-α-C^{14}. This choice obviates the requirement of detailed knowledge concerning the relative reactivity of organolithium compounds toward 1,1-diphenylethene under the conditions of the rearrangement of 2,2,3-triphenylpropyllithium since obviously benzyllithium-α-C^{14} should differ in reactivity from the benzyllithium eliminated from 2,2,3-triphenylpropyllithium only by the amount expected for a carbon-14 isotope effect. Accordingly, benzyllithium-α-C^{14} was prepared in tetrahydrofuran by the general method of Gilman[9] and was added to a tetrahydrofuran solution of 2,2,3-triphenylpropyllithium[3] at −65°. The resulting solution was allowed to warm to 0° and was stirred at this temperature for 30 min before carbonation. The products 2,2,4-triphenylbutanoic acid (derived from 1,1,3-triphenylpropyllithium) and phenylacetic acid (derived from benzyllithium) after separation and purification had molar activities of 1.369 ± 0.08 and 1.229 ± 0.005 μcuries/mmole, respectively. This experiment clearly shows that radioactivity has been incorporated in the final 1,1,3-triphenylpropyllithium. While this result is in agreement with expectations for the elimination–readdition mechanism (eq 1), the molar activities of the two products are so similar as to suggest the possibility that radiochemical exchange between benzyllithium and 2,2,3-triphenylpropyllithium prior to rearrangement or between benzyllithium and 1,1,3-triphenylpropyllithium after rearrangement had occurred to almost any equilibrium extent; such exchange would, of course, invalidate any conclusions about the occurrence of the elimination–readdition mechanism. Detailed considerations show that while for (reversible) isotopic exchange prior to or following rearrangement the radioactivity of the final 1,1,3-triphenylpropyllithium cannot exceed that of the final benzyllithium by more than the amount (a few per cent) expected for an isotope effect, for isotopic exchange occurring irreversibly during rearrangement (as expected for the elimination–readdition mechanism) the radioactivity of the final 1,1,3-triphenylpropyllithium may greatly exceed that of the final benzyllithium if the initial concentration of radioactive benzyllithium is low compared to the starting concentration of 2,2,3-triphenylpropyllithium.

Since the initial quantity of radioactive benzyllithium likely exceeded that of 2,2,3-triphenylpropyllithium in the preliminary run, a second run was made in which the initial amount (11.2 mmoles) of benzyllithium was less than that of 2,2,3-triphenylpropyllithium (24.3 mmoles) as determined by Gilman's double titration technique.[10] Moreover the initial activity of the benzyllithium was measured by carbonating a portion of the solution and assaying the resulting phenylacetic acid. In the following sequence the activities of reactants and products are indicated below each compound assayed in units of microcuries per millimole. From this run it is obvious not only that the rearranged organolithium compound has gained radioactivity at the expense of the benzyllithium but also that the 1,1,3-triphenyl-



$$\underset{2.942 \pm 0.010}{\mathrm{PhC^{14}H_2Li}} + \mathrm{PhCH_2C(Ph)_2CH_2Li} \longrightarrow$$

$$\mathrm{PhCH_2Li + Ph_2C(Li)CH_2CH_2Ph} \xrightarrow{\mathrm{CO_2}} \underset{1.193 \pm 0.002}{\mathrm{Ph_2\underset{\displaystyle CO_2H}{\underset{|}{C}}CH_2CH_2Ph}} + \underset{0.3263 \pm 0.0015}{\mathrm{PhCH_2CO_2H}}$$

---

(6) D. J. Cram, C. A. Kingsbury, and A. Langemann, *J. Am. Chem. Soc.*, **81**, 5785 (1959); U. Schöllkopf and W. Fabian, *Ann.*, **642**, 1 (1961); U. Schöllkopf and D. Walter, *ibid.*, **654**, 27 (1962); P. T. Lansbury and V. A. Pattison, *J. Am. Chem. Soc.*, **84**, 4295 (1962); P. T. Lansbury and V. A. Pattison, *J. Org. Chem.*, **27**, 1933 (1962); U. Schöllkopf and H. Schäfer, *Ann.*, **663**, 22 (1963).

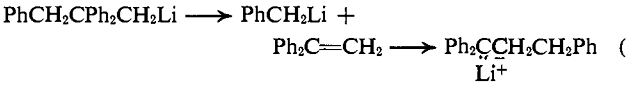
(7) P. T. Lansbury, V. A. Pattison, J. D. Sidler, and J. B. Bieber, *J. Am. Chem. Soc.*, **88**, 78 (1966).

(8) Dr. C. F. Koelsch (personal communication) pointed out to us prior to this investigation that 1,2 shift of aryl groups upon treatment of some 1,1,3-triarylindenes with sodium [W. Schlenk and E. Bergmann, *Ann.*, 463, 125 (1928); K. Ziegler and F. Crossman, *Chem. Ber.*, **62**, 1768 (1929); C. F. Koelsch, *J. Am. Chem. Soc.*, **56**, 480 (1934)] is probably mechanistically similar to rearrangement of 2,2,2-triphenylethyl anion (although rearrangement of the indenes likely occurs in a radical-anion intermediate followed by loss of sodium hydride and reduction of the indenyl radical to indenyl anion). Attempts to obtain migration of benzyl upon action of sodium with 1-benzyl-1,3-diphenylindene, however, gave toluene and 1,3-diphenylindenylsodium [C. F. Koelsch, *ibid.*, **56**, 1605 (1934)], likely by elimination of a benzyl anion. Dr. Koelsch suggested, by analogy, that 2,2,3-triphenylpropyllithium rearranges by elimination of benzyllithium followed by recombination with intermediate 1,1-diphenylethene to give 1,1,3-triphenylpropyllithium.

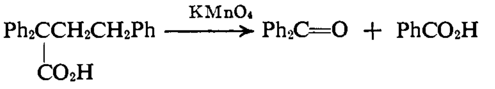
(9) (a) H. Gilman and N. A. McNinch, *J. Org. Chem.*, **26**, 3723 (1961); (b) H. Gilman and G. L. Schwebke, *ibid.*, **27**, 4259 (1962).

(10) H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.*, **66**, 1515 (1944); *cf.* H. Gilman and F. K. Cartledge, *J. Organometal. Chem.* (Amsterdam), **2**, 447 (1964).

propyllithium produced is *not* at radiochemical equilibrium with the benzyllithium in the solution at the end of the experiment since its radioactivity is much greater than the final activity of the benzyllithium. For this reason we may conclude that no appreciable exchange of radioactivity has taken place between benzyllithium and 2,2,3-triphenylpropyllithium prior to rearrangement or between benzyllithium and 1,1,3-triphenylpropyllithium following rearrangement. We must, therefore, conclude that an irreversible exchange of radioactivity occurs during rearrangement itself. That this exchange involves introduction of a radioactive benzyl group at the terminal position of 1,1,3-triphenylpropyllithium, as predicted by the intermolecular elimination–readdition mechanism (eq 2), is borne out by degradation of the 2,2,4-triphenylbutanoic acid resulting from carbonation of the 1,1,3-triphenylpropyllithium. As shown in the following scheme (eq 3), permanganate oxidation of the 2,2,4-triphenylbutanoic acid gave benzophenone and benzoic acid with all of the orginal activity of the 2,2,4-triphenylbutanoic acid in the benzoic acid. The slightly low value of the specific activity of benzoic acid may be due to oxidation of a small amount of the benzophenone to benzoic acid.[11]



$$PhCH_2CPh_2CH_2Li \longrightarrow PhCH_2Li + Ph_2C{=}CH_2 \longrightarrow \underset{Li^+}{Ph_2\bar{C}CH_2CH_2Ph} \quad (2)$$



$$\underset{CO_2H}{Ph_2CCH_2CH_2Ph} \xrightarrow{KMnO_4} Ph_2C{=}O + PhCO_2H \quad (3)$$

1.193 ± 0.002 μcuries/mmole; <0.0005 μcurie/mmole; 1.180 ± 0.010 μcuries/mmole

The radioactivity data of the second run are in good quantitative agreement with the intermolecular elimination–readdition mechanism (eq 2) provided that the benzyllithium which adds to the intermediate 1,1-diphenylethene has the same activity as that of the benzyllithium in the bulk of the solution, or, expressed differently, provided that, isotope effects being negligible, the instantaneous molar activity of the 1,1,3-triphenylpropyllithium being formed is the same as the instantaneous molar activity of the benzyllithium. These assumptions lead to the expression

$$dx/dy = (A - x)/B \quad (4)$$

where x and y are the numbers of microcuries and millimoles, respectively, of 1,1,3-triphenylpropyllithium formed; A and B are the number of microcuries and millimoles, respectively, of benzyllithium at the start of the reaction. Integration of this expression gives

$$y = B \ln [A/(A - x)] \quad (5)$$

Since rearrangement is complete under the conditions of the present experiment, y is taken to equal the number of millimoles of 2,2,3-triphenylpropyllithium initially present. The molar activities of 2,2,4-triphenylbutanoic acid and phenylacetic acid calculated using eq 5 are 1.20 ± 0.03 and 0.335 ± 0.010 μcuries/mmole, respectively; these values are in good agreement[12] with the experimental data. We conclude that the rearrangement of 2,2,3-triphenylpropyllithium occurs by the intermolecular elimination–readdition mechanism (eq 2).

Rearrangement of 2,2,3-Triphenylpropyllithium in Presence of Other Organolithium Reagents. In view of the establishment of the intermolecular elimination–readdition mechanism for rearrangement of 2,2,3-triphenylpropyllithium, it is peculiar that though 2,2,3-triphenylpropyllithium is present initially in high concentration, this organolithium compounds does not compete measurably with benzyllithium in addition to 1,1-diphenylethene. In order to provide further test of the elimination–readdition mechanism and to provide information about the relative reactivity of organolithium compounds toward addition to 1,1-diphenylethene under the conditions of rearrangement, a series of experiments was run, analogous to the above experiments with radioactive benzyllithium, in which 2,2,3-triphenylpropyllithium was allowed to rearrange in the presence of various organolithium reagents.

These experiments are summarized in Table I where product analyses are based on vapor phase chromatography (vpc) of the more volatile methyl esters of the final crude mixtures of carboxylic acids obtained on carbonation. Incorporation of the added organolithium reagent (RLi) onto 1,1-diphenylethene cleaved out of 2,2,3-triphenylpropyllithium during rearrangement is indicated by the appearance of methyl phenylacetate in the final product. Only in the case of isopropyllithium was any methyl phenylacetate detected; in the other cases the limiting quantity of methyl phenylacetate which the analytical procedure was capable of detecting is shown. Confirmation of these results is provided by the detection of methyl 2,2,4-triphenylbutanoate but not of methyl 2,2-diphenylpentanoate (product expected from addition of ethyllithium to 1,1-diphenylethene) on vpc analysis of the less volatile esters from rearrangement in presence of ethyllithium. Also 2,2-diphenyl-4-methylpentanoic acid (product expected from addition of isopropyllithium to 1,1-diphenylethene) was isolated in addition to methyl 2,2,4-triphenylbutanoate in the product from rearrangement in presence of isopropyllithium.

Table I. Rearrangements of 2,2,3-Triphenylpropyllithium in the Presence of Various Organolithium Reagents (RLi) in Tetrahydrofuran[a]

Reactants, mmoles		Maximum	More volatile products, mmoles	
RLi	$PhCH_2$-CPh_2CH_2Li	temp,[b] °C	RCO_2CH_3	$PhCH_2$-CO_2CH_3
PhLi, 31	22	0	22	<1.2
EtLi, 2.3	27	0	2.0	<0.014
n-BuLi, 50	20	0	46	<0.07
i-PrLi, 34	18	−15	15	4.9

[a] In 600 ± 50 ml of tetrahydrofuran. [b] The solutions of organolithium compounds were mixed at −62 ± 8° and then allowed to warm to the indicated maximum temperature for at least 10 min before carbonation.

In view of the failure to incorporate appreciable amounts of any reagents other than benzyllithium and isopropyllithium during rearrangement of 2,2,3-triphenylpropyllithium, a series of experiments (Table

---

[11] W. A. Bonner and C. J. Collins, *J. Am. Chem. Soc.*, 75, 5372 (1953).

[12] The rather large limits of error in the calculated values are primarily due to uncertainties in the concentrations of organolithium compounds.

Table II. Direct Addition of Organolithium Compounds to 1,1-Diphenylethene in Tetrahydrofuran Solution[a]

Reactants, mmoles		Temp,	Product[b] yield, %	
RLi	$Ph_2C{=}CH_2$	°C	RCH_2-CPh_2CO_2H	RCO_2H
PhLi, 34	40	5	18[c]	56[c]
n-BuLi, 38	40	0	26[e]	*d*
i-PrLi, 8.0	8.0	−15	95	*d*
$PhCH_2Li$, 20	25	0	80	None[f]

[a] The total volume of tetrahydrofuran was 275 ± 25 ml. [b] Yields are based on the amount of starting organolithium compound. [c] In addition 0.9 g of an unresolved mixture of these two volatile acids, 2.1 g of acids not volatile at 210° (0.1 mm), and 34% of the starting 1,1-diphenylethene were recovered. [d] The quantity of this acid was not determined. [e] In addition the acidic fraction contained an unidentified viscous oil. [f] The yield of phenylacetic acid was judged to be nil since the crude acid had the melting point of essentially pure 2,2,4-triphenylbutanoic acid.

II) was run to see if the organolithium compounds of Table I were capable of adding to 1,1-diphenylethene under conditions similar to those of rearrangement. The data of Table II are semiquantitative results from isolation experiments upon the carboxylic acids obtained on carbonation. Since the yields of carboxylic acids on carbonation are sometimes in our experience only 80% of that expected on the basis of the concentration of organolithium compounds as determined by Gilman titration[10] and since the times for these reactions were nearly the same except for that of phenyllithium which was some threefold that of the other reactions, we conclude that the additions of benzyllithium and isopropyllithium to 1,1-diphenylethene are fast and occur in essentially quantitative yield, while the addition of *n*-butyllithium is much slower and that of phenyllithium still slower with the latter two reactions occurring in competition with a side reaction (likely protonation and/or the addition of organolithium reagent to more than 1 molar equiv of 1,1-diphenylethene). These results are, therefore, in general accord with those of Table I and provide confirmation of the elimination–readdition mechanism (eq 1).

Previous workers report that phenyllithium adds rather slowly to 1,1-diphenylethene in ethyl ether[13] although it adds readily to some fulvenes.[14] Vinyllithium and phenyllithium are reported to be among the least reactive of the simple organolithium reagents as polymerization initiators for styrene in tetrahydrofuran solution at 20° as shown by the following reactivity series:[15] $n\text{-BuLi} \gg PhCH_2Li \sim CH_2{=}CHCH_2Li > CH_2{=}CHLi \sim PhLi$. The rate of addition of vinyllithium to 1,1-diphenylethene in tetrahydrofuran solution at 20° is slow enough to be followed by ordinary spectroscopic techniques;[16] under these conditions *n*-butyllithium is said to add to 1,1-diphenylethene "essentially instantaneously,"[16] although no details are given. Isopropyllithium adds to 1,1-diphenylethene in ethyl ether much more readily than phenyllithium but the yield of adduct was not specified.[13]

The literature, therefore, is in qualitative agreement with the relative rate of addition of organolithium compounds to olefins reported here save for the report[15] that *n*-butyllithium in tetrahydrofuran solution adds much more readily to styrene than does benzyllithium whereas we find that *n*-butyllithium adds much more slowly to 1,1-diphenylethene than does benzyllithium. Moreover, our data on competitive additions during rearrangement (Table I) indicate that isopropyllithium adds to 1,1-diphenylethene more slowly than does benzyllithium ($k_{i\text{-PrLi}}/k_{PhCH_2Li} = 8 \pm 4 \times 10^{-2}$ if each addition is assumed to be first order both in olefin and in organolithium compound, but see later discussion). In contrast isopropyllithium is reported to add readily to ethylene and propylene[17] whereas under corresponding conditions benzyllithium is "essentially unreactive" toward hexadecene-1 and tetradecene-1.[9b] The relative reactivity of the present organolithium compounds toward addition to olefins is, therefore, highly dependent upon the structure of the olefin; structural changes in the olefin which increase the degree of charge delocalization in the anionic adduct of the olefin increase the apparent relative reactivity[18] of benzyllithium to *n*-butyllithium or isopropyllithium along the series $CH_2{=}CH_2 < PhCH{=}CH_2 < Ph_2C{=}CH_2$. Only if the anionic charge is more highly delocalized in the addition product than in benzyllithium, does the apparent reactivity of benzyllithium exceed that of *n*-butyllithium or isopropyllithium. Similar structural factors should govern the relative reactivity or organolithium compounds in other types of reactions. Waack and West[19] have recently reported that the rates of metalation of triphenylmethane by organolithium reagents in tetrahydrofuran solution decrease in the order $PhCH_2Li > CH_2{=}CHCH_2Li > n\text{-BuLi} > PhLi > CH_2{=}CHLi > CH_3Li$. This order, in so far as comparisons are possible, is the same as that observed in the present work for additions to 1,1-diphenylethene and the high reactivity of benzyllithium and allyllithium might have been anticipated since the product of metalation provides greater delocalization of anionic charge than does the organometallic reactant. Evidently, it is only under these conditions that the high polarizability[19] of benzyllithium (or allyllithium) is able to become manifest in a high reactivity. Expressed in other words, the low basicity (large delocalization energy) of benzyllithium limits the reactivity of benzyllithium except where the organolithium product is even less basic (larger delocalization energy).

Another factor of importance in determining the reactivity of organolithium compounds is their extent of association in solution. Kinetic experiments indicate that in tetrahydrofuran solution benzyllithium and allyllithium are monomeric, phenyllithium is dimeric, and *n*-butyllithium is at least trimeric.[20] The assumptions generally made in analysis of the kinetic data are that monomeric species are much more reactive than dimers or higher aggregates and that a $(1/n)$th kinetic order dependence upon the concentration of organolithium compound indicates an *n*-fold degree of

---

(13) K. Ziegler and F. Dersch, *Chem. Ber.*, **64**, 448 (1931).

(14) K. Ziegler and W. Schaefer, *Ann.*, **511**, 101 (1934).

(15) R. Waack and M. A. Doran, *Polymer*, **2**, 365 (1961).

(16) R. Waack and P. E. Stevenson, *J. Am. Chem. Soc.*, **87**, 1183 (1965).

(17) P. D. Bartlett, S. Friedman, and M. Stiles, *ibid.*, **75**, 1771 (1953).

(18) Since it is not known whether or not these additions (especially those to ethylene and styrene) are reversible under the conditions used, a low apparent "reactivity" may, in fact, be due to an unfavorable equilibrium constant.

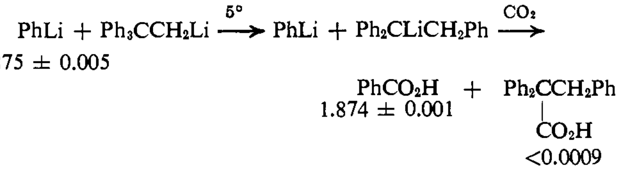
(19) R. Waack and P. West, *J. Am. Chem. Soc.*, **86**, 4494 (1964).

(20) R. Waack and P. West, *J. Organometal. Chem.* (Amsterdam), **5**, 188 (1966).

association; however, these assumptions have recently been questioned.[21] In view of the likely differing extents of association of organolithium compounds in tetrahydrofuran solution, the relative reactivity of a series of organolithium compounds may be concentration dependent. The concentrations of organolithium compounds in Tables I and II are of the same order of magnitude as those used by Waack and West.[19]

Finally returning to the question of why 2,2,3-triphenylpropyllithium, though present initially in high concentration, does not compete detectably with benzyllithium for 1,1-diphenylethene during rearrangement of 2,2,3-triphenylpropyllithium, we conclude that 2,2,3-triphenylpropyllithium is likely similar to ethyllithium or *n*-butyllithium and thereby is too unreactive to compete successfully with benzyllithium. The higher reactivity of benzyllithium as opposed to a *n*-alkyllithium can be attributed to a lower degree of association in solution and a higher polarizability. The carbon–metal bond in benzyllithium is likely predominantly ionic whereas that in a *n*-alkyllithium is predominantly covalent;[22] the interacting electrons in benzyllithium ion pair, therefore, are under less restraint by the lithium cation than in a covalent alkyllithium compound, especially one which is associated.

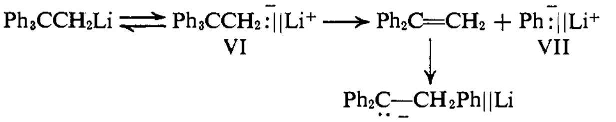
Rearrangement of 2,2,2-Triphenylethyllithium in Presence of Phenyllithium-C^{14} and Benzyllithium. In view of success in "trapping" 1,1-diphenylethene during rearrangement of 2,2,3-triphenylpropyllithium, similar experiments were undertaken for rearrangement of 2,2,2-triphenylethyllithium. Phenyllithium, prepared from chlorobenzene[23] uniformly labeled with carbon-14, was added to a tetrahydrofuran solution of 2,2,2-triphenylethyllithium[4] at −60°, and the solution was warmed to 5° for 4 hr before carbonation. The results of this experiment and of direct carbonation of a portion of the starting phenyllithium are summarized in the following reaction sequence in which the activities of each compound assayed are given in units of microcuries per millimoles.



$$\underset{1.875 \pm 0.005}{\mathrm{PhLi}} + \mathrm{Ph_3CCH_2Li} \xrightarrow{5^\circ} \mathrm{PhLi} + \mathrm{Ph_2CLiCH_2Ph} \xrightarrow{\mathrm{CO_2}} \underset{1.874 \pm 0.001}{\mathrm{PhCO_2H}} + \underset{<0.0009}{\mathrm{Ph_2C(CO_2H)CH_2Ph}}$$

The 2,2,3-triphenylpropanoic acid was indistinguishable in radioactivity from background radioactivity and it is accordingly estimated that less than 0.05% (if any) of the activity of the starting phenyllithium was incorporated in the 2,2,3-triphenylpropanoic acid.

This experiment implies that rearrangement of 2,2,2-triphenylethyllithium occurs by an intramolecular process; however, since, according to Tables I and II, phenyllithium is a comparatively poor reagent for addition to 1,1-diphenylethene, it is not clear that this experiment requires that rearrangements be intramolecular. For example, it could be imagined that covalent 2,2,2-triphenylethyllithium undergoes an initial ionization to give a solvent-separated ion pair[24] VI which in turn eliminates phenyl anion to form phenyllithium as a solvent-separated ion pair VII



$$\mathrm{Ph_3CCH_2Li} \rightleftharpoons \underset{\mathrm{VI}}{\mathrm{Ph_3CCH_2}\overset{-}{:}||\mathrm{Li^+}} \longrightarrow \mathrm{Ph_2C{=}CH_2} + \underset{\mathrm{VII}}{\mathrm{Ph}\overset{-}{:}||\mathrm{Li^+}} \qquad \mathrm{Ph_2C{=}CH_2} \downarrow \mathrm{Ph_2\underset{..}{C}{-}CH_2Ph||Li} \tag{6}$$

which then readds much more readily to 1,1-diphenylethene than does ordinary covalent phenyllithium (see eq 6). If the rate of the collapse of the phenyllithium ion pair VII is slow compared to its rate of addition to 1,1-diphenylethene and if only a very low concentration of this ion pair exists in equilibrium with covalent phenyllithium, then the present experimental results can be accommodated by a mechanism which is not in principle intramolecular. Since benzyllithium is very much more reactive[25] in addition to 1,1-diphenylethene than is phenyllithium, as was deduced from the results of Tables I and II, and since benzyllithium is expected to exist in tetrahydrofuran solution as an ion pair (likely a contact ion pair[26]) which should more nearly be able to complete with phenyllithium ion pair VII, 2,2,2-triphenylethyllithium was allowed to rearrange at 5° with a twofold excess of benzyllithium. Carbonation of the reaction mixture and vpc examination of the methyl esters of the more volatile acids produced gave methyl phenylacetate containing less than 0.06% (if any) of methyl benzoate; hence 2,2,2-triphenylthyllithium underwent rearrangement without detectable incorporation of benzyllithium. By this test also the rearrangement of 2,2,2-triphenylethyllithium appears to be an intramolecular process and the elimination–readdition mechanism of eq 6 appears unlikely.

As was pointed out earlier[2] another possibility is that 2,2,2-triphenylethyllithium undergoes elimination of phenyl anion to give 1,1-diphenylethene but that phenyl anion and 1,1-diphenylethene exist in a solvent "cage" and recombine before radioactive phenyllithium or benzyllithium can diffuse into the "cage." An attractive variation[27] of this idea is that rearrangement of 2,2,2-triphenyllithium occurs with elimination of phenyllithium as an ion pair to which 1,1-diphenylethene is bound as a ligand of the lithium ion; the ion pair–olefin complex then collapses to final product before an external organolithium compound can attack the 1,1-diphenylethene in the complex (see eq 7). While neither of these mechanisms which account for the intramolecular nature of the rearrangement of 2,2,2-

---

[21] T. L. Brown, *J. Organometal. Chem.* (Amsterdam), **5**, 191 (1966); H. L. Hsieh, *J. Polymer Sci.*, A3, 163, 173 (1965); R. Waack, *et al.*, *Chem. Ind.* (London), 1035 (1966).

[22] G. E. Coates, "Organo-Metallic Compounds," 2nd ed, Methuen and Co., Ltd., London, 1960, pp 1–3.

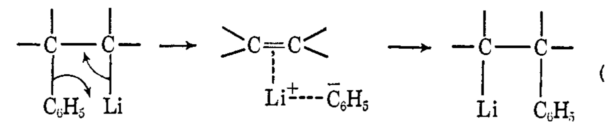
[23] H. Gilman and T. S. Soddy, *J. Org. Chem.*, **22**, 565 (1957).

[24] For a recent discussion of contact and solvent-separated ion pairs in organoalkali compounds, see T. E. Hogen-Esch and J. Smid, *J. Am. Chem. Soc.*, **88**, 307, 318 (1966).

[25] If it is assumed for purposes of comparison that the rates of addition of *n*-BuLi and $PhCH_2Li$ to 1,1-diphenylethene are first order in the stoichiometric concentrations of organolithium compound and first order in olefin, the data of Table I suggest that the relative reactivity of *n*-BuLi to $PhCH_2Li$ is less than $\sim 2 \times 10^{-6}$. The data of Table II and other data[13,15,16] suggest that phenyllithium is considerably less reactive than *n*-butyllithium. While quantitative comparison is complicated by the (unknown) extent of aggregation and/or nonideal behavior of solutions of organolithium compounds, such comparisons emphasize the real, very large differences in reactivity encountered in the present work.

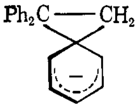
[26] A contact ion pair is suggested by the report [see R. Waack, M. A. Doran, and P. E. Stevenson, *J. Am. Chem. Soc.*, **88**, 2109 (1966), and references therein] of only small solvent effects on the absorption spectra of benzylic-type organoalkali compounds.

[27] D. J. Cram, "Fundamentals of Carbanion Chemistry " Academic Press Inc., New York, N. Y., 1965, p 237.



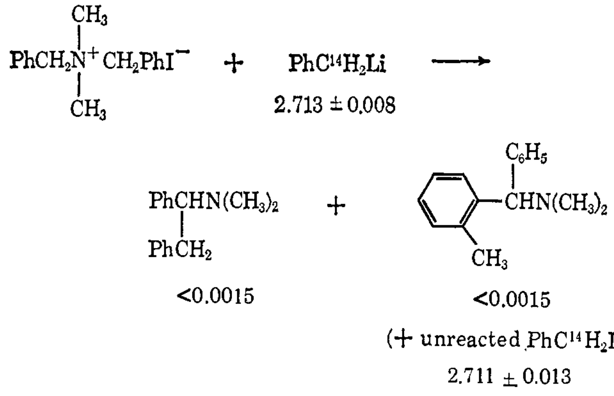
(7)

triphenylethyllithium is eliminated by the present work, a simpler explanation is that the rearrangement proceeds by way of the transition-state or reaction intermediate VIII.[3,5] Evidence in favor of an intermediate like VIII will be presented later.[28]

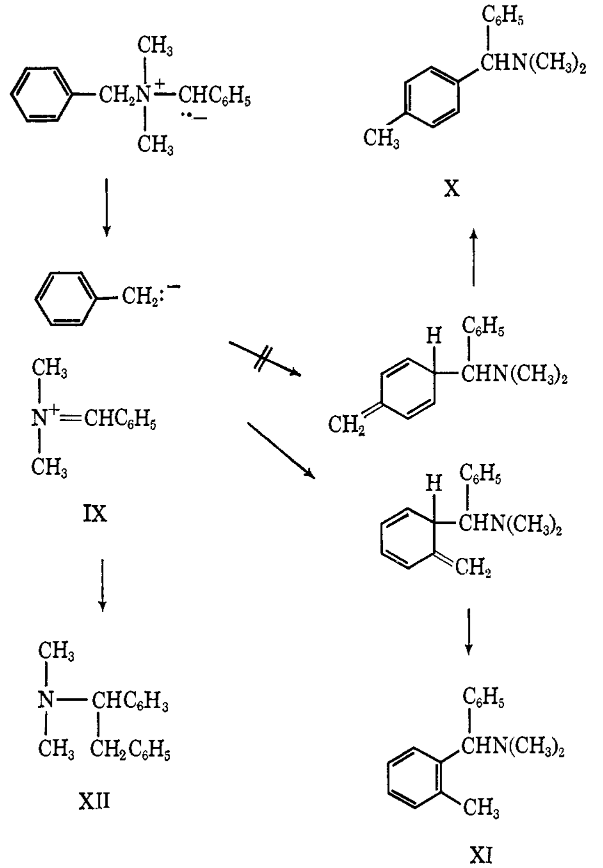


VIII

Rearrangement of Dibenzyldimethylammonium Halide by Benzyllithium-α-C^{14}. In view of the ease of incorporation of external benzyl anion during rearrangement of 2,2,3-triphenylpropyllithium, it seemed of interest to look for possible incorporation of external benzyl anion during Stevens and Sommelet rearrangements, which have generally been regarded as intramolecular rearrangements[29a] but which can also be interpreted[29b,c] as involving an elimination–readdition proceeding through an ion-pair intermediate. Wittig and coworkers[30] found that products of both Stevens and Sommelet rearrangements result from reaction of dibenzyldimethylammonium bromide with phenyllithium in ether. Accordingly, dibenzyldimethylammonium bromide was allowed to react with a 50% molar excess of benzyllithium-α-C^{14} in tetrahydrofuran at 20°. The dimethyl(1,2-diphenylethyl)amine (product of Stevens rearrangement) and dimethyl(*o*-methylbenzhydryl)amine (product of Sommelet rearrangement) produced in this reaction were found to have no detectable radioactivity (less than 0.09% of the activity of the starting benzyllithium). Since the dibenzyldimethylammonium bromide used was largely insoluble in the quantity of tetrahydrofuran employed as solvent, it was deemed advisable to repeat the reaction under homogeneous conditions. A dilute solution of dibenzylmethylammonium iodide in tetrahydrofuran was allowed to react at 25° with a 16-fold excess of benzyllithium-α-C^{14}; however, the amines produced were again devoid of any measurable amount of radioactivity as summarized in the following reaction sequence in which the activities of each compound assayed are given in units of microcuries per millimole (eq 8). These experiments show that the Stevens and Sommelet rearrangements, under both our homogenous or heterogenous conditions, are cleanly intramolecular rearrangements. The present work corroborates other data on the Stevens rearrangement, namely that rearrangements of mixtures of quaternary ammonium salts give only products[31] expected for purely intramolecular rearrangement (no "cross-bred" products), that 1,2-rearrangements of quaternary ammonium salts having an asymmetric migrating group (α-phenylethyl) proceed with nearly complete retention of configuration (97%,[32] >90%,[33] >93%[34]), and that the rearrangement of optically active allylbenzylmethylphenylammonium cation to 3-(N-methylanilino)-4-phenylbutene-1 occurs with transfer of asymmetry from nitrogen to carbon with apparently high conservation of optical purity.[35] Moreover, no case of incorporation of an external organolithium reagent during a Stevens rearrangement has been reported;[29] however, the organolithium reagent which has been used most commonly to initiate Stevens rearrangements is phenyllithium and this (if relative reactivity toward 1,1-diphenylethene is a proper guide) appears to be a poor choice if incorporation is desired.



(8)



---

[28] E. Grovenstein, Jr., and G. Wentworth, paper in preparation.

[29] (a) H. E. Zimmerman in "Molecular Rearrangements," Part 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp 378–391; (b) D. J. Cram, ref 27, pp 223–229; (c) U. Schöllkopf and W. Fabian, *Ann.*, **642**, 1 (1961).

[30] G. Wittig, H. Tenhaeff, W. Schoch, and G. Koenig, *ibid.*, **572**, 1 (1951).

[31] T. S. Stevens, *J. Chem. Soc.*, 2107 (1930); R. A. W. Johnstone and T. S. Stevens, *ibid.*, 4487 (1955).

[32] J. H. Brewster and M. W. Kline, *J. Am. Chem. Soc.*, 74, 5179 (1952); A. Campbell, A. H. J. Houston, and J. Kenyon, *J. Chem. Soc.*, 93, (1947).

[33] E. F. Jenny and J. Druey, *Angew. Chem. Intern. Ed. Engl.*, **1**, 155 (1952).

[34] B. J. Millard and T. S. Stevens, *J. Chem. Soc.*, 3397 (1963).

[35] R. K. Hill and T. H. Chan, *J. Am. Chem. Soc.*, **88**, 866 (1966).

The present work seems to offer perhaps the most direct evidence in favor of an intramolecular mechanism for the Sommelet rearrangement. Other general evidence is that if rearrangement proceeded by way of an elimination–readdition mechanism it is hard to understand why a product, dimethyl(*p*-methylbenzyhydryl)amine (X) in the present case, of attack at the *para* position of the benzyl anion has never been observed; the exclusive *ortho* nature of the Sommelet rearrangement argues strongly for a cyclic transition state. Moreover, if both the Sommelet and Stevens rearrangements proceeded by way of the same ion-pair intermediate (*e.g.*, IX), it is hard to understand why low temperature favors *ortho* attack (Sommelet product XI) while high temperature favors α attack (Stevens product XII) since the activation energy would be expected to be greater for *ortho* than for α attack because more resonance energy is lost in the *ortho* process (loss of aromaticity of benzenoid ring). Zimmerman[29a] has put forth an interesting explanation, based on a molecular orbital approach, for the temperature dependence of product composition from Sommelet–Stevens rearrangements; this explanation requires the assumption that these are concerted, cyclic processes.

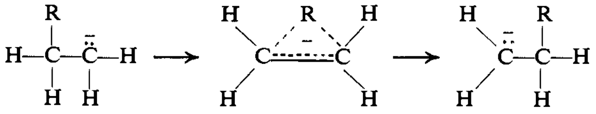
In summary, the present and related evidence demonstrates the intramolecular nature of Stevens and Sommelet rearrangements. While these rearrangements are most simply explained on the basis of a concerted cyclic process, occurrence of an elimination–readdition proceeding by way of a very tight ion pair is not rigorously excluded.

Conclusions. A duality of mechanism has been established for rearrangement of organolithium compounds. The 1,2-migration of benzyl in 2,2,3-triphenylpropyllithium takes place by way of an intermolecular process which consists of elimination of benzyl and readdition of benzyl from the surrounding solution to the 1,1-diphenylethene moiety. Most simply this elimination involves formation of benzyllithium and 1,1-diphenylethene *per se*, although fragmentation into benzyl radical and 1,1-diphenylethene radical anion in a process like that recently suggested[7] for the Wittig rearrangement of benzyl *t*-alkyl ethers is not completely excluded. The latter process would require sufficiently long-lived benzyl free radicals to bring about complete equilibration of carbon-14 prior to readdition.

$$\mathrm{PhCH_2\cdot + PhC^{14}H_2Li \rightleftharpoons PhCH_2Li + PhC^{14}H_2\cdot}$$

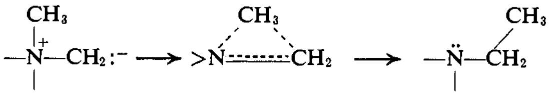
However, if the free radicals were long lived, some evidence of free-radical recombination to give dibenzyl and the dimer[36] of 1,1-diphenylethene radical anion might have been expected.[37]

The 1,2 migration of phenyl in 2,2,2-triphenylethyllithium takes place by way of an intramolecular processes, very likely by way of a nucleophilic addition to the migrating phenyl group to give the transition state or reaction intermediate VIII. The question arises as to whether or not a saturated alkyl group can undergo a 1,2 shift in a carbanion by way of a related transition state or intermediate such as XIII. The simple Hückel LCAO molecular orbital calculation of Zimmerman and Zweig[5] indicate that XI is endothermic relative to reactants by 1.22 β units when R is methyl and only 0.52 β when R is phenyl. These calculations make it evident that phenyl should migrate more readily than methyl, as found in 2,2-diphenylpropyllithium,[5] and suggest that methyl should migrate with difficulty, if at all, in simple anions such as *n*-propyl.

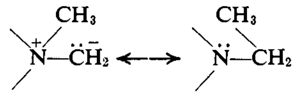


XIII

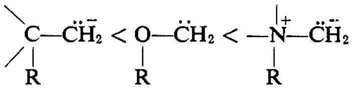
Extension by us of these calculations to the Stevens rearrangement indicates that XIV is endothermal relative to the starting ylide by only 0.11 β unit. While these calculations leave much to be desired in accuracy, they suggest that there is no theoretical reason why a simple alkyl group cannot undergo a 1,2 shift by way of a concerted cyclic process such as by way of XIV. We, therefore, prefer this mechanism to explain why Stevens rearrangements are cleanly intramolecular processes. Expressed in terms of resonance structures, the transition state XIV is stabilized by contributions from structures such as XVa and XVb; structure XVb is of special importance since here the more electronegative nitrogen atom has more electrons than in XVa. Indeed from molecular orbital calculations, even when the migrating methyl group of XIV is geometrically half-way in between nitrogen and carbon the charge on nitrogen (see XVa) has essentially disappeared and the methyl group is more strongly bound to carbon than to nitrogen. Such considerations suggest that concerted 1,2 shifts of alkyl groups (R) should occur with increasing ease along the series



XIV



XVa XVb



The same conclusion is reached if these rearrangements are regarded[38] as internal nucleophilic displacements of the negative carbon atom on the migrating group (R), for then it seems clear that an amine should be a better "leaving" group than an alkoxide, and the latter better than a carbanion.

Experimental Section

Reagents. Uniformly labeled chlorobenzene-C^{14} was from New England Nuclear Corp. Benzyl chloride-α-C^{14} was from Tracerlab,

---

[36] J. Jagur, M. Levy, M. Feld, and M. Szwarc, *Trans. Faraday Soc.*, 58, 2168 (1962).

[37] Carbonation of the dimer of 1,1-diphenylethene radical anion should have given 2,2,5,5-tetraphenyladipic acid (mp 290°) in the carbonation products of the rearrangement of 2,2,3-triphenylpropyllithium; however, the 2,2,4-triphenylbutanoic acid (mp 188°) isolated melted rather sharply (mp 182–186°) even before recrystallization, and all but some 3% of the product could be sublimed at a bath temperature of 210° (0.09 mm).

[38] C. R. Hauser and S. W. Cantor, *J. Am. Chem. Soc.*, 73, 1437 (1951); H. E. Zimmerman, ref 29a, p 399.

Inc., or was synthesized by reduction of benzoic acid-α-C^{14} (from Tracerlab, Inc.) with lithium aluminum hydride by the procedure of Nystrom[39] to give benzyl alcohol-α-C^{14} which was then converted to benzyl chloride-α-C^{14} by the method of Norris.[40] Benzyl methyl ether-α-C^{14} was prepared by reaction of benzyl chloride-β-C^{14} with methanolic sodium methoxide according to the procedure of Olson and co-workers.[41] Ethyl and benzyl bromides and *n*-butyl, *n*-propyl, isopropyl, and benzyl chlorides were of the best available commercial grades and were redistilled before use. 2-Chloro-1,1,1-triphenylethene was from an earlier preparation[42] and was recrystallized from ethanol.

Dibenzyldimethylammonium bromide, mp 176–177°, was prepared from benzyldimethylamine (Eastman Kodak Co., White Label grade) by reaction with benzyl bromide by the procedure of Nadar and Gyermek.[43] Dibenzyldimethylammonium iodide was prepared from the corresponding bromide by reaction with 10% excess of freshly prepared aqueous suspension of silver oxide (on a mechanical shaker for 8 hr), filtration to remove silver compounds, and neutralization with 48% HI. The resulting precipitate was washed with dilute sodium bicarbonate, dried *in vacuo*, and then recrystallized from ethanol–ether to give dibenzyldimethylammonium iodide, mp 192.5–194° (lit.[44] mp 191°).

1,1-Diphenylethene [bp 81–85° (0.1 mm), $n^{27.5}$D 1.6045] was prepared in 70–71% yield by reaction of benzophenone with methylmagnesium iodide according to a published procedure[45] for triphenylethene but with use of the Morton high-speed stirring apparatus.[46]

2,2-Diphenylpentanoic acid was prepared by reaction of the potassium salt of ethyl diphenylacetate with *n*-propyl chloride in liquid ammonia–ether solution according to the general method of Hauser and co-workers;[47] after saponification of the resultant ester by heating at reflux with a large excess of 15% aqueous potassium hydroxide for 5 hr, the acid was obtained in a yield of 74% of material, mp 150–154°. Two recrystallizations from benzene gave a product, mp 153–155° (lit.[48] mp 155–156°).

Lithium metal was from Lithium Corp. of America and contained 0.05% sodium maximum. Tetrahydrofuran was distilled from molten potassium and stored over sodium wire; immediately before use the tetrahydrofuran was heated at reflux over lithium aluminum hydride or, preferably for safety,[49] sodium aluminum hydride and distilled directly into the reaction flask.

1-Chloro-2,2,3-triphenylpropane. This compound has been previously synthesized[3] from 2-chloro-1,1,1-triphenylethane. A more convenient procedure is outlined below from 1,1,2-triphenylethylsodium prepared from triphenylethene by the procedure of Wooster.[50] In a 250-ml flask equipped with a mechanical stirrer and Dry Ice–acetone condenser, 125 ml of anhydrous ammonia was condensed upon 12.8 g (0.050 mole) of triphenylethene.[45] Under an atmosphere of dry nitrogen, 2.43 g (0.106 g-atom) of sodium was added rapidly in pieces of about 0.2 g. The solution turned red immediately upon addition of the sodium. The mixture was stirred for 10 min after completion of the addition of sodium and was then siphoned into a flask containing 75 ml of methylene chloride at −50°. The red color of the ammonia solution discharged rapidly. The ammonia was allowed to evaporate from the solution and 10 ml of 95% ethanol was added (to ensure decomposition of any unreacted sodium). The mixture was washed with 200 ml of water, the organic phase separated, and the aqueous phase extracted with methylene chloride. Evaporation of the combined methylene chloride solutions to dryness and recrystallization of the yellow-orange residue from acetone gave 5.9 g (40% yield) of white product, mp 127–128.5°. An attempt to carry out this preparation on an eightfold larger scale ran into the difficulty of an undissolved solid plugging the siphon tube during transfer of the 1,1,2-triphenylethylsodium; however, three similar large-scale preparations with potassium rather than sodium metal did not encounter this difficulty and gave an average yield of purified product of 46%.

General Procedures for Organolithium Reactions. All organolithium reactions were conducted in a Morton flask equipped with a Morton high-speed stirrer[46] and were run under an atmosphere of dry nitrogen. The lithium metal was in the form of a wire which was finely cut just before reaction. In reactions which involved the interaction of two organolithium compounds, the preparations of organolithium compounds were undertaken simultaneously in order to avoid unnecessary delay and decomposition of the organolithium compounds on storage. Unless otherwise indicated the concentrations and yields of organolithium reagents were determined by Gilman's double-titration technique.[10] The carbonation procedure consisted of forcing the solution through a glass outlet tube under nitrogen pressure into a flask containing a large excess of crushed solid carbon dioxide; the mixture was then allowed to stand overnight before work-up.

In the usual work-up procedure, 100 ml of water was added to the carbonated mixture, and the tetrahydrofuran was removed by distillation through a 20-cm column packed with glass helices (or a 30-cm Vigreux column). The remaining aqueous mixture was strongly acidified (*ca.* 100 ml of 10% hydrochloric acid) and extracted with at least five 50-ml portions of ether. The combined ether phases were extracted with 200 ml of 10% potassium hydroxide. The alkaline phase was separated and extracted with three 30-ml portions of ether. The combined ether extracts, which contained the neutral products, were dried over anhydrous magnesium sulfate. The alkaline phase was acidified with 150 ml of 15% hydrochloric acid and extracted with at least five 50-ml portions of ether. The combined ether extracts, which contained the acidic products, were dried over anhydrous magnesium sulfate. The magnesium sulfate was removed by filtration from the ether extracts of both the neutral and acidic products and these were further worked up as indicated for the individual experiments.

Rearrangement of 2,2,3-Triphenylpropyllithium. A. In Presence of 1,1-Diphenylethene. To 2,2,3-triphenylpropyllithium,[3] prepared from 8.0 g (0.026 mole) of 1-chloro-2,2,3-triphenylpropane, 1.0 ml (0.016 mole) of methyl iodide, and 0.31 g (0.044 g-atom) of lithium in 300 ml of tetrahydrofuran at −65 ± 5°, was added rapidly 4.6 g (0.026 mole) of 1,1-diphenylethene in 10 ml of tetrahydrofuran. The solution developed a brown color and after 10 min of stirring at −65° turned red-brown. The solution was allowed to warm to 0 ± 5° and maintained at this temperature for 10 min before carbonation. The reaction mixture was worked up in the usual manner. The ether extract of acidic products upon evaporation gave 1.4 g of acidic material. A portion of the acid after three recrystallizations from acetone had mp 265–285° (dec) and had a neutralization equivalent of about 1200 (phenolphthalein endpoint in 95% ethanol). The neutral product (9.4 g) was isolated by removing the ether from its extract by distillation through a 20-cm Vigreux column. Analysis by vpc revealed the presence of 0.13 g of 1,1-diphenylethene (2.8% recovery), 0.22 g (3.2% yield) of 1,1,3-triphenylpropane, and 0.49 g (6.9% yield) of 1,2,2-triphenylpropane; the remainder was ill-defined polymeric material.

B. In Presence of Benzyllithium-α-C^{14}. In the first run, 2,2,3-triphenylpropyllithium was prepared from 8.00 g (0.0261 mole) of 1-chloro-2,2,3-triphenylpropane, 0.5 ml of methyl iodide, and 0.70 g (0.100 g-atom) of lithium in 425 ml of tetrahydrofuran at −65 ± 5° in a 1-l. Morton flask. In a 500-ml Morton flask, benzyllithium[9] was prepared by dropwise addition of 4.83 g (0.0395 mole) of benzyl methyl ether-α-C^{14} in 10 ml of tetrahydrofuran to 4.11 g (0.593 g-atom) of lithium in 250 ml of tetrahydrofuran at −10 ± 5° (with prior initiation at 10°) with stirring for 3 hr. The temperature of the benzyllithium solution was then lowered to −65°, and the solution was siphoned into the flask containing the 2,2,3-triphenylpropyllithium. The resulting mixture was allowed to warm to 0 ± 5° over a period of 15 min with stirring, and stirring was continued at this temperature for 30 min before carbonation. The mixture was worked up in the usual manner. Evaporation of the ether extract of acidic products gave 5.66 g of brown solid. The

---

(39) R. F. Nystrom and W. G. Brown, *J. Am. Chem. Soc.*, **69**, 2548 (1947).

(40) J. F. Norris, *Am. Chem. J.*, **38**, 638 (1907).

(41) W. T. Olson, H. F. Hipsher, C. M. Buess, I. A. Goodman, I. Hurt, J. L. Lamneck, Jr., and L. C. Gibbons, *J. Am. Chem. Soc.*, **69**, 2451 (1947).

(42) E. Grovenstein, Jr., *ibid.*, **79**, 4985 (1957).

(43) K. Nadar and L. Gyermek, *Acta Chim. Acad. Sci. Hung.*, **2**, 95 (1952).

(44) H. Emde, *Arch. Pharm.*, 247, 355 (1909).

(45) H. Adkins and W. Zartman in "Organic Syntheses," Coll. Vol. II, A. H. Blatt, Ed., John Wiley and Sons, Inc., New York, N. Y., 1943, p 606.

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

(47) W. G. Kenyon, R. B. Meyer, and C. R. Hauser, *J. Org. Chem.*, 28, 3108 (1963); R. S. Yost and C. R. Hauser, *J. Am. Chem. Soc.*, **69**, 2325 (1947).

(48) A. L. Mndzhoyan, G. T. Tatevosyan, S. G. Agbalyan, and R. K. Bostandzhyan, *Dokl. Akad. Nauk Arm. SSR*, **28**, 11 (1959); *Chem. Abstr.*, **54**, 1412*e* (1960).

(49) Dr E. C. Ashby, personal communication.

(50) C. B. Wooster and J. F. Ryan, *J. Am. Chem. Soc.*, **54**, 2419 (1932).

solid was subjected to vacuum sublimation at 0.01 mm. The fraction collected at a bath temperature of 80–110° weighed 0.81 g and had mp 70–75°; the fraction collected at a bath temperature of 180–210° weighed 4.2 g and had mp 164–174°. The higher melting fraction was resublimed to give 3.1 g of product, mp 174–185°. After recrystallization from benzene, this material yielded 1.58 g of white crystals, mp 186.0–187.5°. This acid gave no mixture melting point depression with an authentic sample[3] of 2,2,4-triphenylbutanoic acid. The acid, mp 70–75°, was resublimed and then recrystallized from ethanol and cyclohexane to give 0.35 g of white crystals, mp 75.0–76.4°. This acid gave no mixture melting point depression with an authentic sample of phenylacetic acid. The two acids were then recrystallized to constant specific activity. After two more recrystallizations from cyclohexane and three more from 95% ethanol, the 2,2,4-triphenylbutanoic acid had mp 186.8–188.0° and activity of 1.369 ± 0.008 μcuries/mole. After one more recrystallization from cyclohexane and two recrystallizations from carbon tetrachloride, the phenylacetic acid had mp 75.4–76.7° and activity of 1.229 ± 0.006 μcuries/mmole. The technique of combustion and of counting of the radioactive compounds is the same as that described earlier.[51]

In the second run, 12.0 g (0.0392 mole) of 1-chloro-2,2,3-triphenylpropane was allowed to react with 1.04 g (0.150 g-atom) of lithium (activated by treatment with 0.5 ml of CH_3I) in 450 ml of tetrahydrofuran at −65°. Gilman titration[12] (on a total of 20 ml of the solution) indicated the formation of 24.3 mmoles of 2,2,3-triphenylpropyllithium (62% yield). Also 4.83 g (0.0395 mole) of benzyl methyl ether-α-C^{14} was allowed to react with 4.11 g (0.593 g-atom) of lithium in 250 ml of tetrahydrofuran at −10°. Gilman titration indicated the formation of 18.6 mmoles of benzyllithium-α-C^{14} (47% yield). A 150.0-ml aliquot of this solution, containing 11.2 mmoles of radioactive benzyllithium at −60 ± 10°, was transferred (by volumetric pipet which transferred little of the unreacted lithium) under nitrogen to the solution of 2,2,3-triphenylpropyllithium at the same temperature. The well-stirred mixture was allowed to warm to 0° over a period of 15 min and then was stirred at this temperature for 40 min before carbonation. The remainder of the benzyllithium was also carbonated in order that the initial specific activity of the benzyllithium could be determined. The crude acidic product (5.8 g) from the rearrangement was isolated as in the first run. Vacuum sublimation at 0.03 mm gave 0.89 g of product, mp 71–74°, and 4.02 g of mp 179–184°. The acids were then purified to constant melting point and constant radioactivity. After four recrystallizations from benzene and two recrystallizations from 95% ethanol, the higher melting acid (2,2,4-triphenylbutanoic acid) had mp 186.7–187.9° and activity of 1.193 ± 0.002 μcuries/mmole. After a second vacuum sublimation, four recrystallizations from cyclohexane, and two recrystallizations from carbon tetrachloride, the lower melting acid (phenylacetic acid) had mp 75.5–76.2° and activity of 0.3263 ± 0.0015 μcurie/mmole. From the carbonated mixture of starting benzyllithium, 0.152 g of phenylacid, mp 73.5–76°, was isolated after one recrystallization from cyclohexane. After two further recrystallizations from cyclohexane, one vacuum sublimation, and a final recrystallization from carbon tetrachloride, this acid had mp 75.2–76.3° and activity of 2.942 ± 0.010 μcuries/mmole.

In order to determine the position of the radioactive label in the 2,2,4-triphenylbutanoic acid obtained from the second run, oxidation of this acid was carried out according to the general procedure of Bonner and Collins.[11] A solution of 4.67 g (29.5 mmoles) of potassium permanganate in 20 ml of water and 0.05 ml of glacial acetic acid was added to a solution of 1.00 g (3.16 mmoles) of the 2,2,4-triphenylbutanoic acid in 40 ml of acetone, and the resultant mixture heated at reflux for 36 hr. The manganese dioxide formed in the reaction was removed by filtration and the filtrate condensed to a volume of about 20 ml. This aqueous residue was extracted with ether, and the ether extract treated with several portions of 10% potassium hydroxide to remove acidic products. The ether extract, after drying over anhydrous magnesium sulfate, was evaporated to dryness to give 0.280 g (1.54 mmoles, 49% yield) of sticky yellow solid, which, after two recrystallizations from ethanol, gave 0.197 g of white crystalline solid, mp 48.5–49.5°. This solid gave no depression in mixture melting point with an authentic sample of benzophenone. The combined aqueous alkaline solutions from the above extractions were acidified with 100 ml of 20% hydrochloric acid and extracted with ether. The ether extract, after drying over anhydrous magnesium sulfate, yielded on evaporation 0.191 g (1.57 mmoles, 50% yield) of almost white solid, mp 119–121°, which, after two recrystallizations from cyclohexane, gave 0.158 g of white needles, mp 121–122°. This acid gave no depression of mixture melting point with an authentic sample of benzoic acid. After recrystallization from ethanol and vacuum sublimation at 105° (0.02 mm), the benzoic acid had mp 121.7–122.8° and activity of 1.180 ± 0.010 μcuries/mmole. After two recrystallizations from methanol, the benzophenone had mp 49.2–50.1° and a radioactivity which was indistinguishable from background activity; if a 10% error in background activity is assumed (this is 40 times the average deviation in background activity), the activity of the benzophenone is calculated to be less than 0.005 μcurie/mmole.

C. **In Presence of Other Organolithium Reagents.** These reactions (Table I) were run like those for rearrangement in the presence of benzyllithium-α-C^{14} except as indicated below. The yield of 2,2,3-triphenylpropyllithium[3] from five reactions of 1-chloro-2,2,3-triphenylpropane with lithium in tetrahydrofuran at −65° averaged 61 ± 5% as measured by Gilman titration.

Phenyllithium was prepared in 46% yield by dropwise addition of 11.3 g (0.100 mole) of chlorobenzene in 10 ml of tetrahydrofuran to 2.08 g (0.300 g-atom) of lithium in 210 ml of tetrahydrofuran at 5 ± 5°. A 150-ml aliquot (31 mmoles of PhLi) of this solution at −60 ± 5° was added to 500 ml of a tetrahydrofuran solution of 2,2,3-triphenylpropyllithium (22 mmoles) at the same temperature, and the well-stirred mixture was warmed to 0 ± 5° and held at this temperature for 35 min before carbonation. After the usual isolation procedure, the acidic product amounted to 12.3 g of yellow solid which was sublimed at 0.01 mm. The first fraction, 3.6 g, mp 118–122°, was collected at a bath temperature of 70–125°; the second fraction, 5.5 g, was collected at 130–220°. Reaction of the first fraction with an excess of an ethereal solution of diazomethane and distillation gave 3.0 g (22 mmoles) of ester which according to vpc analysis was pure methyl benzoate containing less than 1% (if any) of methyl phenylacetate. Resublimation of the second fraction gave 0.29 g of forecut, which after recrystallization from methanol amounted to 0.23 g of mp 131–148°, and 4.6 g of main fraction of mp 181–187°. Recrystallization of the latter from benzene gave 4.3 g of acid, mp 185.5–187°, which showed no depression in mixture melting point with an authentic sample of 2,2,4-triphenylbutanoic acid.

Ethyllithium[10] was prepared by reaction of 16.2 g (0.085 mole) of ethyl bromide with 1.77 g (0.255 g-atom) of lithium in 260 ml of tetrahydrofuran at 15° for 1.8 hr. The temperature of the ethyllithium solution was lowered to −55 ± 5° and a Gilman titration indicated the presence of only 3.9 mmoles (4.6% yield) of ethyllithium. A 150-ml aliquot (2.25 mmoles) of this solution was added to 27 mmoles of 2,2,3-triphenylpropyllithium at −55 ± 5°, and the mixture was warmed to 0° over a 20-min period with stirring. After 30 min at 0 ± 5° the solution was carbonated. The reaction mixture was worked up in the usual manner except that the aqueous acidic solution after extraction of carboxylic acids and neutral products with ether was concentrated by removal of most of the water through a 30-cm Vigreux column. The remaining water was removed by azeotropic distillation with benzene through the same column, the residue extracted with 50 ml of ether, and this ether solution combined with the main ether extract of carboxylic acids. The ethereal solution of carboxylic acids was treated with excess diazomethane and analyzed by vpc. Methyl propionate (0.18 g, 2.0 mmoles) and methyl 2,2,4-triphenylbutyrate but no methyl phenylacetate or methyl 2,2-diphenylpentanoate were detected.

n-Butyllithium[52,53] was prepared in 84% yield by reaction of *n*-butyl chloride (0.100 mole) with excess lithium (0.500 g-atom) in 250 ml of tetrahydrofuran at −20°. To the solution of 2,2,3-triphenylpropyllithium at −60 ± 5° was added *n*-butyllithium at the same temperature, and the mixture was warmed to 0° and worked up like that for ethyllithium except that the carbonated reaction mixture (after decomposition with water, fractionation to remove tetrahydrofuran, and ether extraction of neutral components) was acidified and subjected to continuous ether extraction to remove all carboxylic acids. The results are summarized in Table I.

Isopropyllithium[52] was prepared in 37% yield by reaction of 11.8 g (0.150 mole) of isopropyl chloride with 5.2 g (0.75 g-atom) of

---

(51) E. Grovenstein, Jr., S. Chandra, C. E. Collum, and W. E. Davis, Jr., *J. Am. Chem. Soc.*, **88**, 1275 (1966).

(52) H. Gilman, F. W. Moore, and O. Baine, *J. Am. Chem. Soc.*, **63**, 2479 (1941).

(53) H. Gilman and B. J. Gaj, *J. Org. Chem.*, **22**. 1165 (1957).

lithium in 250 ml of tetrahydrofuran at −50 ± 5° in 1.5-hr reaction time. A preliminary experiment indicated that such a solution of isopropyllithium is 69% decomposed (according to Gilman titration) upon warming to 0 ± 5° over a period of 15 min and maintaining at this temperature for 10 min; accordingly, it was deemed desirable to carry out the rearrangement of 2,2,3-triphenylpropyllithium in the presence of isopropyllithium at a lower temperature than with the other organolithium reagents. An experiment showed that rearrangement of 2,2,3-triphenylpropyllithium was essentially complete when a tetrahydrofuran solution was warmed from −60 ± 5° to −15 ± 5° over a period of 15 min and then kept at the latter temperature 10 min, since the carboxylic acid (10.1 g) isolated upon carbonation had mp 181–186° and after recrystallization from benzene amounted to 9.7 g of acid, mp 185–186° (no mixture melting point depression with authentic 2,2,4-triphenylbutanoic acid). Also, isopropyllithium (0.22 *M* solution in tetrahydrofuran), when subjected to the same conditions, was decomposed to the extent of only 28% according to Gilman titration. Accordingly, isopropyllithium was added to 2,2,3-triphenylpropyllithium at −60 ± 5° and the well-stirred mixture was warmed to −15 ± 5° and held at this temperature for 10 min before carbonation. The reaction mixture was worked up as described for the reaction with *n*-butyllithium. The details are summarized in Table I which gives the quantities of the more volatile esters, methyl isobutyrate and methyl phenylacetate, found on vpc analysis. The methyl esters of the carboxylic acids obtained from this reaction were distilled through a 10-cm Vigreux column at 0.08 mm to give three fractions. Fraction I, bp 48–56°, was saponified with alcoholic potassium hydroxide and gave a product which upon recrystallization from cyclohexane amounted to 0.29 g (2.1 mmoles) of crystals of mp 74–76°, which gave no mixture melting point depression with an authentic sample of phenylacetic acid. Fraction II, bp 117–132°, was a viscous liquid which failed to give any crystalline product from common organic solvents or upon saponification. Fraction III, bp 135–160°, was a mixture of crystals and viscous liquid; upon washing with *n*-pentane, crystals were separated and these upon recrystallization from methanol amounted to 1.82 g (5.5 mmoles) of ester, mp 90–92°. These crystals were found to be identical (infrared spectrum and mixture melting point) with a known sample of methyl 2,2,4-triphenylbutanoate. The noncrystalline portion of fraction III upon saponification and acidification gave a mixture of acids which were separated mechanically according to whether (by chance?) they settled to the bottom or floated on the surface of the solution. The latter, after two recrystallizations from cyclohexane, gave 0.17 g of white crystals, mp 121–123°; these crystals gave no depression in mixture melting point with a sample of 2,2-diphenyl-4-methylpentanoic acid prepared (see below) from direct addition of isopropyllithium to 1,1-diphenylethene. The crystals which settled to the bottom of the solution after recrystallization from benzene amounted to 0.91 g of acid, mp 185–187°, as expected for 2,2,4-triphenylbutanoic acid.

The relative rate constants (*K*) for attack upon 1,1-diphenylethene of added organolithium reagent (RLi of initial molar amount *B*) *vs.* benzyllithium during rearrangement of 2,2,3-triphenylpropyllithium were calculated according to the equation

$$K = k_{\mathrm{RLi}}/k_{\mathrm{PhCH_2Li}} = [xB + B\ln(1 - x)]/-y$$

where x = fraction of RLi which adds to 1,1-diphenylethene and y = the molar amount of 1,1,3-triphenylpropyllithium formed. In the derivation and use of this equation it is assumed that the additions are first order in each reactant and that the effective molecular weights of the organolithium compounds are as implied by by their simple formulas.

Direct Addition of Organolithium Compounds to 1,1-Diphenylethene. The tetrahydrofuran solutions of organolithium compounds were prepared by the procedure given in the previous section and the concentrations determined by Gilman titration.[10] Known quantities (225 ml) of the solutions were measured in large volumetric pipets (which moreover separated the solution of organolithium compound from most of the unreacted lithium metal) and transferred to a Morton flask equipped with a high-speed stirrer, thermometer, and dropping funnel containing 1,1-diphenylethene in 50 ml of tetrahydrofuran. The solution of organolithium reagent was maintained under a nitrogen atmosphere at the temperature (±5°) indicated in Table II while the solution of 1,1-diphenylethene was added dropwise with vigorous stirring over a period of about 10 min (30 min for phenyllithium), followed by additional stirring for about 10 min (30 min for phenyllithium) before carbonation. The reaction mixtures were then worked up in the usual manner. The results are reported in Table II.

From the reaction of phenyllithium, the acidic products (7.1 g) were subjected to sublimation at 0.1 mm; benzoic acid (1.4 g, mp 120–122°) was collected in a first fraction (bath temperature up to 120°), and benzoic acid and a less volatile acid were obtained in a second fraction (3.6 g) (up to 210°). After two recrystallizations from methanol, the latter fraction gave 1.8 g of acid, mp 130–131.5°, which was identified as 2,2,3-triphenylpropanoic acid on the basis of infrared spectral comparisons with a known sample[4] of the acid. From the mother liquors after recrystallization from cyclohexane, 0.9 g of additional benzoic acid was obtained. Vapor phase chromatographic analysis of the neutral products (Perkin-Elmer column O, silicone grease on diatomaceous earth) indicated the presence of 2.4 g of unreacted 1,1-diphenylethene.

From the reaction with *n*-butyllithium, the acidic product consisted of a viscous oil which after two recrystallization from aqueous ethanol gave 2.7 g of white solid, mp 128–131°. Three further recrystallizations from ethanol gave 1.4 g of acid, mp 131–133° (lit.[48] mp 130–132° for 2,2-diphenylheptanoic acid).

From the reaction with isopropyllithium, the acidic fraction after two recrystallizations from cyclohexane amounted to 2.03 g, mp 120–122°. Two further recrystallizations from cyclohexane gave a white acid, mp 121–122° (lit.[54] mp 121.0–122.5° for 2,2-diphenyl-4-methylpentanoic acid).

From the reaction with benzyllithium, the acidic fraction gave 5.1 g of essentially white solid, mp 183–186°. One recrystallization from benzene gave 4.7 g of white crystals, mp 185–187°. This acid gave no mixture melting point depression with an authentic sample[3] of 2,2,4-triphenylbutanoic acid.

Rearrangement of 2,2,2-Triphenylethyllithium. A. In Presence of Phenyllithium-C^{14}. Reaction of 2-chloro-1,1,1-triphenylethane (10.0 g, 0.0343 mole) with lithium[4] (0.87 g, 0.124 g-atom) in 460 ml of tetrahydrofuran at −60° gave, after 3.5 hr, a 44% yield of 2,2,2-triphenylethyllithium (as indicated by titration[10]). Simultaneous reaction of chlorobenzene-C^{14} (4.43 g, 0.0393 mole) with lithium (0.82 g, 0.118 g-atom) in 260 ml of tetrahydrofuran at 10° for 4.5 hr gave 39% of phenyllithium-C^{14}. A 150-ml aliquot of this solution, containing 8.9 mmoles of phenyllithium-C^{14} at −60 ± 5°, was added to the solution of 2,2,2-triphenylethyllithium and the well-stirred mixture was allowed to warm to 5 ± 5° and kept at this temperature for 4 hr before carbonation. The remainder of the phenyllithium was also carbonated in order that its initial radioactivity could be determined. From the carbonated mixture of rearrangement products, 3.04 g of acidic product was isolated following the usual work-up procedure. This dark brown mixture, after several vacuum sublimations at 0.10 mm, gave a more volatile fraction of 0.157 g, mp 120–122°, and a less volatile fraction of 1.34 g. The more volatile fraction after recrystallization from cyclohexane yielded 0.137 g of white crystals, mp 121–122°. This acid gave no mixture melting point depression with an authentic sample of benzoic acid. Recrystallization of the less volatile fraction from methanol gave 0.79 g of white solid, mp 130–132°; this material gave no mixture melting point depression with an authentic sample of 2,2,3-triphenylpropanoic acid. The two acids were then recrystallized to constant activity. After three recrystallizations from cyclohexane and one recrystallization from water, the benzoic acid had mp 121.3–122.2° and an activity of 1.874 ± 0.011 μcuries/mmole. After two recrystallizations from methanol, the 2,2,3-triphenylpropanoic acid had mp 131.1–132.0° and an activity which was indistinguishable from the background count. If an error in the determination of 8% of background is assumed (this is 16 times the average deviation in background), the maximum possible specific activity of the 2,2,3-triphenylpropanoic acid is calculated to be 0.009 μcurie/mmole. From the carbonated solution of starting phenyllithium-C^{14}, 0.59 g of benzoic acid, mp 121–122[6], was isolated after one vacuum sublimation. After three recrystallizations from cyclohexane and two recrystallizations from water, the benzoic acid had mp 121.5–122.4° and specific activity of 1.875 ± 0.005 μcuries/mmole.

B. In Presence of Benzyllithium. Reaction of 8.78 g (0.030 mole) of 2-chloro-1,1,1-triphenylethane with 1.04 g (0.150 g-atom) of lithium in 500 ml of tetrahydrofuran at 60° gave (according to Gilman titration) 15.2 mmoles (51% yield) of 2,2,2-triphenylethyllithium. Reaction of 8.55 g (0.070 mole) of benzyl methyl ether with 7.29 g (1.05 g-atoms) of lithium in 260 ml of tetrahydrofuran at −10° gave 51 mmoles (73% yield) of benzyllithium. A 150-ml

---

(54) P. N. Craig and I. H. Witt, *J. Am. Chem. Soc.*, 72, 4925 (1950).

aliquot of this solution, containing 29.6 mmoles of benzyllithium at −60°, was added to the solution of 2,2,2-triphenylethyllithium at the same temperature, and the well-stirred mixture was allowed to warm to 5 ± 5° and maintained at this temperature for 4 hr before carbonation. After the usual work-up, the ethereal solution of carboxylic acids was allowed to react with excess diazomethane and then subjected to vpc analysis. Methyl phenylacetate (3.0 g, 20 mmoles) but less than 0.012 mmole (if any) of methyl benzoate were detected. Some white crystals, mp 128–130°, separated from the ethereal solution of esters and was identified as methyl 2,2,3-triphenylpropanoate by mixture melting point and infrared spectral comparisons with an authentic sample prepared from the corresponding acid.

Rearrangement of Dibenzyldimethylammonium Halide by Benzyllithium-α-C^{14}. Benzyllithium-α-C^{14} (70 mmoles, 64% yield) was prepared in the manner previously described by reaction of 13.8 g (0.110 mole) of benzyl methyl ether-α-C^{14} with 11.4 g (1.65 g-atoms) of lithium in a mixture of 400 ml of tetrahydrofuran and 200 ml of ethyl ether at −10°. A 225-ml aliquot of this solution was carbonated. To the remaining 44 mmoles of benzyllithium-α-C^{14} at 10° was rapidly added 9.57 g (29.3 mmoles) of crystalline dibenzyldimethylammonium bromide. The reaction was not noticeably exothermal at this temperature so the reaction temperature was raised to 20° and the mixture stirred vigorously for 2.5 hr. The reaction was quenched by adding 50 ml of water, and the organic solvents were removed by distillation through a 30-cm Vigreux column. The following work-up is based upon the procedure of Wittig and co-workers.[30] The aqueous residue was extracted with ether, and the ether extract was evaporated to leave a yellow, oily residue which was dissolved in 50 ml of 2 *N* sulfuric acid. Addition of 7 ml of concentrated hydrochloric acid caused the hydrochloride of dimethyl(*o*-methylbenzylhydryl)amine to precipitate. Treatment of the hydrochloride with 50 ml of 5% sodium hydroxide regenerated the amine (3.50 g, 53% yield), mp 48–50°. The product of Stevens rearrangement, dimethyl(1,2-diphenylethyl)-amine, was recovered from the acidic solution by adding excess sodium hydroxide, extracting with ether, and evaporating the ether extract. The resulting yellow oil (2.0 g, 30% yield) was dissolved in 10 ml of 95% ethanol and the solution added to 10 ml of a saturated solution of picric acid in 95% ethanol. The dark yellow solid (1.80 g) which precipitated immediately was isolated, recrystallized from ethanol-ether, and found to have mp 155–156° [lit.[30] 155–155.5° for the picrate of dimethyl(1,2-diphenylethyl)amine]. The bright yellow picrate of dimethyl(*o*-methylbenzhydryl)amine (1.30 g) was formed in the same manner and had mp 176–177° (lit.[30] mp 174.5–175°). Phenylacetic acid was isolated in the usual manner from the carbonated solution of benzyllithium-α-C^{14} and after three recrystallizations from cyclohexane amounted to 0.42 g, mp 75–76°. Three further recrystallizations from carbon tetrachloride gave acid, mp 75.6–76.4° and activity 2.224 ± 0.004 μcuries/mmole. The picrates of both amines were assayed, and the activity was found to be indistinguishable from the background. If 8% of the background activity is attributed to the picrates, the maximum activity of the picrates is calculated to be 0.002 μcurie/mmole.

For the reaction under homogeneous conditions, benzyllithium-α-C^{14} (87 mmoles, 88% yield) was prepared by reaction of 12.0 g (0.098 mole) of benzyl methyl ether-α-C^{14} with 10.2 g (1.47 g-atoms) of lithium in 275 ml of tetrahydrofuran at −10°. A 150-ml aliquot of this solution, containing 47 mmoles of benzyllithium at 25°, was added rapidly to a solution of 1.00 g (2.84 mmoles) of dibenzyldimethylammonium iodide in 550 ml of tetrahydrofuran, and the solution was stirred at 25 ± 5° for 3 hr before carbonation. The remainder of the initial solution of benzyllithium-α-C^{14} was also carbonated. Potassium hydroxide (5%, 200 ml) was added to the carbonated mixture of rearrangement products, and the tetrahydrofuran was removed by distillation through a 20-cm Vigreux column. The alkaline residue was extracted with ether and the ether extract of amines worked up as indicated above. There was obtained 0.18 g (29% yield) of dimethyl(*o*-methylbenzhydryl)amine, mp 49.5–51.0°, and 0.38 g (60% yield) of crude dimethyl(1,2-diphenylethyl)-amine. The former amine yielded a picrate which after two recrystallizations from ethanol amounted to 0.30 g, mp 177.0–178.0°. The crude dimethyl(1,2-diphenylethyl)amine gave 0.67 g of crude picrate, mp 152–155°, which after three recrystallizations from ethanol had mp 155.2–156.5°. The phenylacetic acid from the rearrangement was isolated in the usual manner from the alkaline solution after removal of the amines; the crude acid (2.0 g. 15 mmoles) after two recrystallizations from cyclohexane and two vacuum sublimations had mp 76.5–77.5° and an activity of 2.711 ± 0.013 μcuries/mmole. The phenylacetic acid-α-C^{14} obtained by direct carbonation was isolated in the usual manner and amounted to 3.1 g (23 mmoles), mp 70–75°. After two recrystallizations from cyclohexane and two vacuum sublimations the acid had mp 76.0–77.4° and activity of 2.713 ± 0.008 μcuries/mmole. The picrates of the two amines had a radioactivity which was indistinguishable from background activity. If 8% of the background activity is attributed to the picrates, the maximum activity of the picrates is calculated to be 0.0015 μcurie/mmole.

Analyses by Vapor Phase Chromatography. A Perkin-Elmer Model 154-D vapor fractometer equipped with a 2-m (0.25-in. diameter) column packed with diatomaceous earth coated with silicone grease (Perkin-Elmer column O) was utilized for all of the analyses. The following pairs of components were separated at the given retention times (temperature and flow rate of helium given in parentheses): methyl benzoate, 4.7 min, and methyl phenylacetate, 7.6 min (125°, 85 cc/min); methyl propionate, 0.7 min, and methyl phenylacetate, 10.1 min (125°, 62 cc/min); methyl valerate, 2.2 min, and methyl phenylacetate, 8.6 min (155°, 53 cc/min); methyl isobutyrate, 2.6 min, and methyl phenylacetate, 9.8 min (135°, 42 cc/min); methyl 2,2-diphenylpentanoate, 3.5 min, and methyl 2,2,4-triphenylbutanoate, 26.4 min (240°, 51 cc/min).

Molecular Orbital Calculations. These were done by the method and with all of the assumptions of the calculations of Zimmerman and Zweig.[5] In addition, the Coulomb integral for nitrogen was taken to be 1.5 $|\beta|$ units more negative than that of carbon while the bond integral of the C–N bond was taken to be the same as that (β) of the C–C bond.[55] For simplicity, these parameters for nitrogen were assumed to be the same for the initial state and the transition state (half-rearranged state).

Acknowledgments. Grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Rayonier Corp. for support of this work.

---

(55) *Cf.* A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 135.