3, which is given in Table I along with other pertinent data. The observed value is consistent with those for related azirine derivatives and suggests that the s-character of the α-carbon atom is approximately 34%.

TABLE I

C^{13}–H COUPLING CONSTANTS

Compound	Group	$J_{C^{13}H}$, c.p.s.[a]
α-Lactam 3	Ring CH	168.5 ± 0.5
	t-Bu	126
N-Methylallenimine[b]	Ring CH_2	169
	Olefinic CH_2	162
	N-CH_3	135
2,2-Dimethylethylenimine	Ring CH_2	166
Ethylenimine	Ring CH_2	168.1 ± 0.5^c
Ethylene oxide	Ring CH_2	175.8 ± 0.5^c
Cyclopropane	Ring CH_2	161^d

[a] Determined with neat liquid using a Varian A-60 spectrometer. [b] We are indebted to Professor J. D. Roberts for a sample of this compound. [c] F. S. Mortimer, *J. Mol. Spectry.*, **5**, 199 (1960). [d] N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 768, 1471 (1959).

Although individual items among this experimental evidence and that cited earlier, taken one at a time, can be rationalized reasonably well on the basis of one or another of the alternative structures, consideration of the whole of the data appears to lend substantial support to the α-lactam structure. The results do *not* rule out the possibility that a delocalized intermediate may be involved in some of the further reactions of 3.[5] Experiments exploring this possibility (among others) are in progress.

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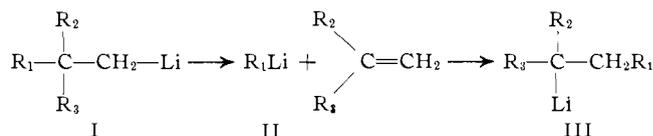LINCOLN, NEBRASKA   ROBERT D. THOMPSON
RECEIVED JULY 19, 1963

Carbanions. VI. The Mechanism of Rearrangement of 2,2,2-Triphenylethyllithium and 2,2,3-Triphenylpropyllithium
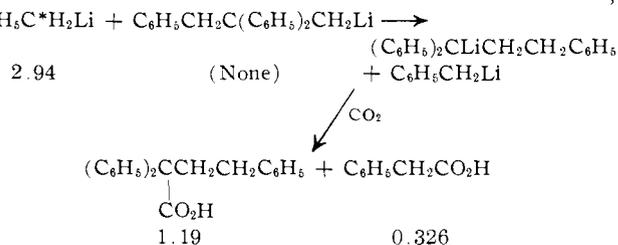
Sir:

A 1,2-shift of phenyl has been observed in 2,2,2-triphenylethyl derivatives of sodium,[1,2] potassium,[3] and lithium.[3] An analogous migration of phenyl has been observed in 2,2-diphenylpropyllithium and -potassium and of phenyl in preference to p-tolyl in 2-phenyl-2-(p-tolyl)-propyllithium.[4] Finally, a 1,2-migration of benzyl has been observed in 2,2,3-triphenylpropyllithium.[5] These rearrangements have been assumed, implicitly or explicitly, to be intramolecular in character.

By analogy with recent work[6] on the Wittig rearrangement of ethers, an elimination–readdition mechanism seems possible. Thus, the organolithium compound I could eliminate an organolithium compound II to form an olefin which could combine with II in the inverse manner to give the final product of rearrangement III. The general argument[4] in opposition to such a mechanism is that if addition of organolithium compound II to the olefin were possible, then the more basic organo-

(1) E. Grovenstein, Jr., *J. Am. Chem. Soc.*, **79**, 4985 (1957).
(2) H. E. Zimmerman and F. J. Smentowski, *ibid.*, **79**, 5455 (1957).
(3) E. Grovenstein, Jr., and L. P. Williams, Jr., *ibid.*, **83**, 412 (1961).
(4) H. E. Zimmerman and A. Zweig, *ibid.*, **83**, 1196 (1961).
(5) E. Grovenstein, Jr., and L. P. Williams, Jr., *ibid.*, **83**, 2537 (1961).
(6) U. Schoellkopf and W. Fabian, *Ann.*, **642**, 1 (1961); U. Schoellkopf 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).

lithium compound I, which is present initially in high concentration, should compete successfully in addition to the olefin; however, no products corresponding to addition of I have been found. As a further test for the elimination–readdition mechanism, Zimmerman and Zweig[4] 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.

We wish to report some experiments pertaining to the elimination–readdition mechanism for rearrangement of 2,2,2-triphenylethyllithium and 2,2,3-triphenylpropyllithium. A preliminary experiment, in which 1,1-diphenylethene was added to about a half-molar equivalent 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,[5] gave after carbonation only 3% recovery of 1,1-diphenylethene and much ill-defined polymeric material. This experiment must be regarded as indecisive, since the concentration of 1,1-diphenylethene was doubtlessly much higher than that likely to exist during rearrangement of 2,2,3-triphenylpropyllithium. Accordingly, benzyllithium was prepared by the procedure of Gilman[7] from benzyl methyl ether-α-C^{14}. A tetrahydrofuran solution (150 ml.) containing 11.2 mmoles of radioactive benzyllithium at $-65°$ was added to 450 ml. of a tetrahydrofuran solution containing 24.3 mmoles of 2,2,3-triphenylpropyllithium[5] at the same temperature and the well stirred mixture was allowed to warm to $0°$ and kept at this temperature for 30 min. before carbonation.[8] The initial specific activity of the starting benzyllithium was determined by carbonation of a portion of the same preparation of benzyllithium and assaying the resulting benzoic acid. In the following reaction sequence the activities of reactants and products are indicated below each compound assayed in units of microcuries per millimole. From this experiment it is obvious that the rearranged organolithium compound gained radioactivity at the expense of the benzyllithium; therefore, very likely,

$$C_6H_5C^*H_2Li + C_6H_5CH_2C(C_6H_5)_2CH_2Li \longrightarrow$$

2.94   (None)

$$(C_6H_5)_2CLiCH_2CH_2C_6H_5 + C_6H_5CH_2Li$$

$$\downarrow CO_2$$

$$(C_6H_5)_2CCH_2CH_2C_6H_5 + C_6H_5CH_2CO_2H$$
$$\overset{|}{CO_2H}$$

1.19   0.326

a benzyl group in a triphenylpropyllithium (or compound derived therefrom) exchanged with a benzyl group of benzyllithium. The 1,1,3-triphenylpropyllithium produced, however, is *not* at radiochemical equilibrium with the benzyllithium in the solution at the end of this experiment, since its
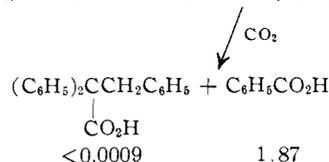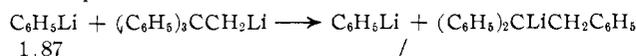
(7) H. Gilman and H. A. McNinch, *ibid.*, **26**, 3723 (1961); H. Gilman and G. L. Schwebke, *ibid.*, **27**, 4259 (1962).
(8) The concentrations of the organolithium compounds were determined by the double titration technique [H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.*, **66**, 1515 (1944)]. The radiochemical determinations were by the wet combustion method [O. K. Neville, *ibid.*, **70**, 3501 (1948)] with the oxidizers prepared according to Van Slyke and co-workers [D. D. Van Slyke, J. Plazin, and J. R. Weisiger, *J. Biol. Chem.*, **191**, 299 (1951)]. A vibrating-reed electrometer (Applied Physics Corp., Model 31) was used to assay the radioactive carbon dioxide. Benzoic acid-carboxyl-C^{14} (from Tracerlab, Inc.) was used to prepare benzyl methyl ether-α-C^{14}. The uniformly labeled chlorobenzene-C^{14} was from New England Nuclear Corp.

radioactivity is much greater than the final activity of the benzyllithium. Indeed, for the same reason we may conclude that no appreciable amount of exchange occurs between 1,1,3-triphenylpropyllithium and benzyllithium; that is, essentially no exchange occurs after rearrangement. Also, no major amount of exchange takes place (necessarily reversible) between 2,2,3-triphenylpropyllithium and benzyllithium prior to rearrangement. We must therefore conclude that an irreversible exchange of benzyl groups in the reactants occurs during rearrangement itself. The radioactivity data are in good quantitative agreement with this conclusion and the additional conclusion that the molar activity of the 1,1,3-triphenylpropyllithium being formed at any specific time is identical with that of the benzyllithium in the solution at the same time (i.e., a negligible isotope effect occurs). The molar activities of 2,2,4-triphenylbutanoic acid and phenylacetic acid calculated[9] on the basis of these conclusions and the initial quantities and activity of reactants are 1.20 and 0.335 μc./mmole, respectively. From these data it is obvious that the rearrangement of 2,2,3-triphenylpropyllithium is an *intermolecular* reaction. The elimination–readdition mechanism, involving elimination of benzyllithium followed by its readdition to 1,1-diphenylethene, fits all of the known data satisfactorily, provided that the benzyllithium which re-adds comes from the surrounding solution.

In a similar experiment phenyllithium (8.9 mmoles in 150 ml. of tetrahydrofuran), prepared from chlorobenzene[10] uniformly labeled with carbon-14, was added to 460 ml. of a tetrahydrofuran solution containing 15.0 mmoles of 2,2,2-triphenylethyllithium, all solutions[8] initially being at $-60 \pm 5°$. The resulting solution was allowed to warm with stirring to $5 \pm 5°$ and was maintained at this temperature for 4 hr. before carbonation. The results of this experiment are summarized in the following reaction sequence in which the activities of each compound assayed are given in units of microcuries per millimole.

$$C_6H_5Li + (C_6H_5)_3CCH_2Li \longrightarrow C_6H_5Li + (C_6H_5)_2CLiCH_2C_6H_5$$
1.87

$$\downarrow CO_2$$

$$(C_6H_5)_2CCH_2C_6H_5 + C_6H_5CO_2H$$
$$|$$
$$CO_2H$$
<0.0009   1.87

The 2,2,3-triphenylpropanoic acid obtained 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 could have become incorporated in the 2,2,3-triphenylpropanoic acid. On the basis of the present test, therefore, the migration of phenyl could be said to take place (as previously supposed[3–5]) by an *intramolecular* process, suitably by way of the transition state or reaction intermediate IV.[4] This is not a necessary,

Ph₂C——CH₂

IV
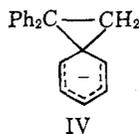
(9) These assumptions give rise to the expression $dx/dy = (A - x)/B$, where x and y are the number of microcuries and millimoles, respectively, of 1,1,3-triphenylpropyllithium formed at termination of reaction. A and B are the number of microcuries and millimoles, respectively, of benzyllithium at the start of reaction. Integration of this expression gives $y = 2.303B \cdot \log |A/(A - x)|$. Since rearrangement is complete under the conditions of the present experiment, y is taken to be equal to the number of millimoles of 2,2,3-triphenylpropyllithium initially present. The quantity of benzyllithium is assumed to remain constant throughout the reaction.

(10) H. Gilman and T. S. Soudy, J. Org. Chem., 22, 565 (1957).

explanation, however. An alternative mechanism is that while 2,2,2-triphenylethyllithium undergoes elimination of phenyl anion to give 1,1-diphenylethene, the phenyl anion and 1,1-diphenylethene exist in a solvent "cage" and recombine before radioactive phenyllithium can diffuse into the "cage." Future experiments are planned to try to distinguish between these and other mechanistic possibilities.

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Evidence for the Origin of the Ethyl Group of β-Sitosterol[1]

Sir:

Mechanistic considerations which are implicit in the accompanying formulas led us to believe that the C_2 unit at position-24 of β-sitosterol (VI) might be derived from two C_1-units, and we should like to present experimental evidence in favor of this hypothesis.
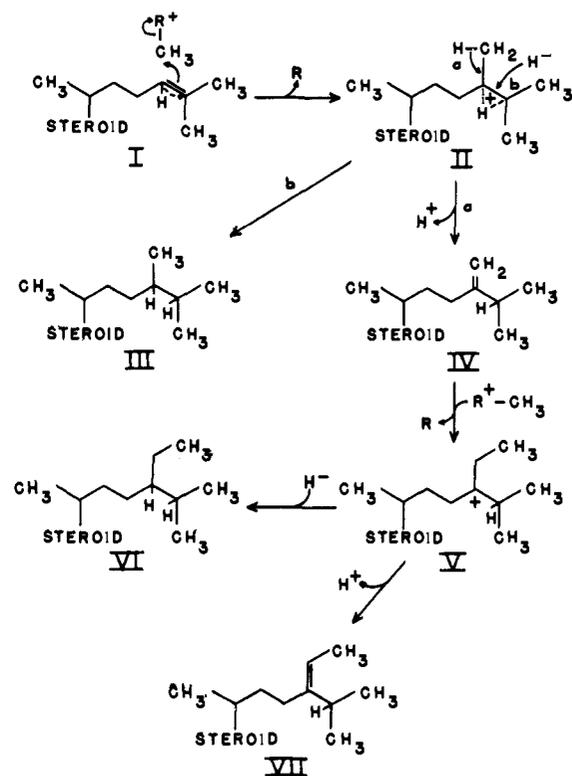
Twenty seeds of *Pisum sativum* (the pea) were germinated for 4 days in water and then for 1 day in a solution containing 86 mg. of nonradioactive sodium mevalonate and tracer amounts of L-methionine labeled with C^{14} at the methyl group. The neutral fraction after saponification of an acetone extract was chromatographed on alumina together with pure β-amyrin and