# Communications to the Editor

Rearrangement of the Allylcarbinyl Radical[1]

Sir:

Extensive carbon skeletal rearrangement accompanies the solvolyses of allylcarbinyl derivatives. These fascinating rearrangements have been the subject of a number of studies.[2] Vicinal vinyl group migrations occur with facility in allylcarbinylmagnesium halides and diphenylallylcarbinyl radicals.[3] In this communication we wish to report two types of intramolecular structural transformations that allylcarbinyl radicals undergo, as well as several observations which are germane to the detailed mechanism of these changes.

In preliminary experiments it was determined that 4-pentenal decarbonylates by way of a radical chain process (di-*t*-butyl peroxide, chlorobenzene, 130°), yielding 1-butene as the virtually exclusive hydrocarbon product. In order to seek out conceivable carbon skeletal rearrangements that might take place during this reaction, the decarbonylation products of 4-pentenal-2,2-d_2 were examined. A 1.0 M solution of 4-pentenal-2,2-d_2 afforded 1-butene-4,4-d_2 and 1-butene-3,3-d_2 in roughly equal quantities (mass spectral analysis). Recovered, unreacted 4-pentenal-2,2-d_2 was not rearranged. Following a procedure developed previously in studies of the decarbonylations of 2- and 3-methyl-4-pentenals and 2- and 3-methyl-*trans*-4-hexenals[4] which facilitates quantitative interpretation of the rearrangement data, a series of 4-pentenal-2,2-d_2 solutions, varying in concentration from 0.50 to 6.0 M, was prepared and allowed to react to only a few per cent conversion. 1-Butene-4,4-d_2:1-butene-3,3-d_2 ratios were determined for each solution. Ratios for the 0.50–1.5 M solutions were all close to 1.0:1.0 There was, however, a small but clearly discernible monotonic increase in the ratios (10–20%) in going from the solutions in the concentration range 0.50–1.5 M to the 6.0 M solution.[5] The magnitude of this increase is in reasonable agreement with that which would be pre-

(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work (Grant 2190-A4).

(2) K. L. Servis and J. D. Roberts, *J. Am. Chem. Soc.*, 87, 1331 (1965), and pertinent references cited therein.

(3) (a) M. S. Silver, P. R. Shafer, J. E. Nordlander, C. Rüchardt, and J. D. Roberts, *ibid.*, 82, 2646 (1960); (b) D. J. Patel, C. L. Hamilton, and J. D. Roberts, *ibid.*, 87, 5144 (1965); (c) T. A. Halgren, M. E. H. Howden, M. E. Medof, and J. D. Roberts, *ibid.*, 89, 3051 (1967).

(4) (a) L. K. Montgomery, J. W. Matt, and J. R. Webster, *ibid.*, 89, 923 (1967); (b) L. K. Montgomery and J. W. Matt, *ibid.*, 89, 934 (1967).

(5) The presence of minor contaminants prohibited precise measurement of the 1-butene-4,4-d_2:1-butene-2,2-d_2 ratios. The ratios are presently being redetermined using chromatographed (glpc) 1-butene-x,x-d_2 samples. Preliminary experiments using this technique support the qualitative trend cited here.

dicted from the decarbonylation studies on 2-methyl- and 3-methyl-4-pentenals.[4a] The variation in ratios demonstrates that *a minimum* of two radical intermediates gives rise to the observed olefinic products. Classical[4a,6] radicals 1 and 2, which are interconvertible by vicinal vinyl group migration, suffice nicely as the required intermediates. Homoallylic radicals 1 and

$$CH_2=CHCH_2CD_2\cdot \underset{\overset{\sim CH=CH_2}{\rightleftharpoons}}{} \cdot CH_2CD_2CH=CH_2$$
$$\quad\quad 1 \qquad\qquad\qquad\qquad\qquad 2$$
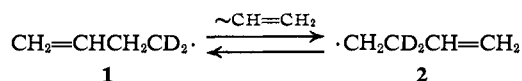
2 must interconvert moderately fast to be compatible with the data. In terms of the proposed mechanistic scheme, the decrease in the extent of rearrangement with increasing aldehyde concentration results from increased trapping of 1, which is formed initially from 4-pentenal-2,2-d_2.

If the interconversion of 1 and 2 is intramolecular, a reasonable assumption, a half-migrated entity of cyclopropylcarbinyl structure must be implicated in the very least as a transition state in the rearrangement sequence. The question arises as to whether a cyclopropylcarbinyl intermediate is also involved. In an effort to probe this point, *cis*-4-pentenal-5-d_1 (95% *cis* as inferred by proton nmr analysis) was synthesized and its decarbonylation products were examined. Radical chain decomposition of *cis*-4-pentenal-5-d_1 should generate homoallylic radical 3 initially. If half-migrated structure 4 is merely a transition state for carbon skeletal rearrangement, bond a should be formed
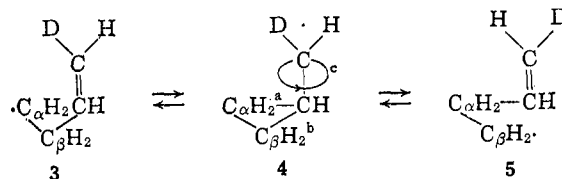
and bond b broken without a loss of geometrical identity about bond c, for transition-state lifetimes are generally considered to be short[7] relative to internal rotational lifetimes.[6] Decarbonylation of a 1.0 M solution of *cis*-4-pentenal-5-d_1 gave *cis*-1-butene-1-d_1 and *trans*-1-butene-1-d_1 in a 1.03:1.00 ratio (nmr). Recovered starting material had not rearranged. A straightforward explanation of these results is that a cyclopropylcarbinyl radical like 4 is a reaction intermediate and that the double bond geometry of the starting aldehyde is lost in intermediate 4 through rotation

(6) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 39, 2147 (1963).

(7) S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p 189.

about bond c. Finally, neat (6.4 M) cis-4-pentenal-5-d_1 was subjected to decarbonylation. The observed cis-1-butene-1-d_1 : trans-1-butene-1-d_1 ratio was 1.42 : 1.00, indicating that **3** can be trapped in a manner analogous to the trapping of **1**. This lends additional support to the proposed rearrangement scheme, particularly the contention that **4** lies along the rearrangement reaction coordinate.

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Evidence for Rapid and Reversible Equilibration of the γ,γ-Diphenylallylcarbinyl and Diphenylcyclopropylcarbinyl Free Radicals[1]

Sir:

We wish to report an example of an unusually facile and reversible free-radical rearrangement in which a substituted allylcarbinyl free radical is interconverted with the corresponding cyclopropylcarbinyl radical.[2] The investigation of the radical rearrangement complements previous studies on analogous carbanion[3] and similar carbonium ion[4] systems. Specifically, we have found that the γ,γ-diphenylallylcarbinyl radical (I) and the cyclopropyldiphenylcarbinyl radical (II) interconvert rapidly at 125° with respect to hy-

$$(C_6H_5)_2C=CH\diagdown_{CH_2}\diagup CH_2\cdot \qquad (C_6H_5)_2\dot{C}—\triangleleft$$
$$\text{I} \qquad\qquad\qquad \text{II}$$
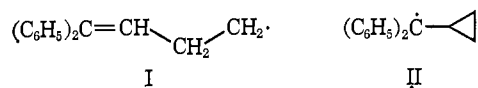
drogen abstraction by either from triethyltin hydride. Trialkyltin hydrides are known to be efficient hydrogen atom donors. For example, decarbonylation of the triphenylacetyl radical is competitive with hydrogen abstraction from tri-*n*-butyltin hydride only at low hydride concentrations.[5]

In the present work, the radicals were generated by thermolysis of either *t*-butyl (γ,γ-diphenylallyl)-peracetate (III) or *t*-butyl cyclopropyldiphenylperacetate (IV). The amounts of the principal C₁₆-hydrocarbon products formed in the presence of several different hydrogen donors are listed in Table I. Of these, 1,1-diphenyl-1-butene (V) and cyclopropyldiphenylmethane (VI)[6] are assumed for our purposes here to arise from the radicals I and II, respectively, while 1-phenyl-3,4-dihydronaphthalene (VII) is considered to arise from an *ortho* ring cyclization[7] of I to VIII, followed by loss of a hydrogen atom.

(1) Supported by the National Science Foundation. A preliminary account of the decomposition of *t*-butyl (γ,γ-diphenylallyl)peracetate and the theoretical problems posed thereby was presented at the Symposium on Small-Ring Compounds at the 142nd National Meeting of the American Chemical Society, Washington, D. C., March 22, 1962.
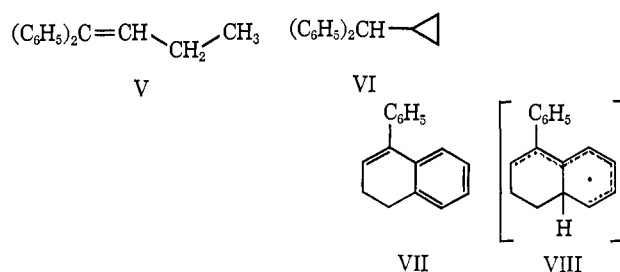
(2) For recent studies on related systems, see D. I. Schuster, Ph.D. Thesis, California Institute of Technology, 1961, and A. J. Rosen, Ph.D. Thesis, California Institute of Technology, 1964.

(3) A. Maercker and J. D. Roberts, *J. Am. Chem. Soc.*, **88**, 1742 (1966).

(4) K. L. Servis and J. D. Roberts, *ibid.*, **87**, 1331 (1965).

(5) H. G. Kuivila and E. J. Walsh, Jr., *ibid.*, **88**, 571 (1966).

(6) The formation of VI is reasonable on the basis of the stabilization of the radical I by the phenyl groups. In the absence of these groups, no cyclopropanes may be formed; *cf.* L. K. Montgomery and J. W. Matt, *ibid.*, **89**, 3050 (1967).

$$(C_6H_5)_2C=CH\diagdown_{CH_2}\diagup CH_3 \qquad (C_6H_5)_2CH—\triangleleft$$
$$\text{V} \qquad\qquad\qquad \text{VI}$$

$$\text{VII} \qquad\qquad\qquad \text{VIII}$$

The relative amounts of V and VII formed in 1,4-cyclohexadiene–cyclohexane mixtures as a function of the reaction temperature and of the cyclohexadiene concentration suggest that the *ortho* ring cyclization is

Table I. Yields of C₁₆-Hydrocarbon Products in the Thermal Decomposition of *t*-Butyl (γ,γ-Diphenylallyl)peracetate and *t*-Butyl Diphenylcyclopropylperacetate in Various Solvents

Solvent	Perester[a]	V	VI	VII
Triethyltin hydride, 0.14 M in *n*-octane	III[b]	23.5	1.63	10.0
1,4-Cyclohexadiene	III[d]	30.0	0.3[f]	11.9
Indene	III[c]	10.7	0.02[f]	16.0
Cyclohexane	III[d]	1.0	0.1[f]	26.5
Ether	III[d]	1.1	0.6[f]	31.5
Tetrahydrofuran	III[d]	1.0	0.05[f]	15.6
Cumene	III[d]	1.3	0.2[f]	e
1,4-Cyclohexadiene	IV[c]	45.0	14.6	11.0
Cyclohexane	IV[c]	1.1	7.5[f]	23.5
Ether	IV[c]	2.0	9.5[f]	28.5
Benzene	IV[c]	1.1	11.4	18.5

[a] The decomposition temperatures were 125–131° for III and 35° for IV. [b] 0.002 M. [c] 0.05 M. [d] 0.30 M. [e] Not determined. [f] As identification has been made by gas chromatographic retention time alone, this figure is an upper limit to the amount formed.

irreversible and that VIII disappears mainly through disproportionation or dimerization, or through loss of a hydrogen atom to, or coupling with, a cyclohexadienyl radical. The conversion of VIII to VII appears to be fairly efficient, and one may write approximately

$$d(V)/d(VII) = k_a(I)(ZH)/k_r(I)$$

so that

$$k_a/k_r = (V)/(VII)(ZH)_{av}$$

where k_a is the rate constant for hydrogen abstraction by I from the hydrogen donor, ZH, and k_r is the rate constant for the isomerization of I to VIII. Values of k_a/k_r estimated for triethyltin hydride, 1,4-cyclohexadiene, and indene at 125–131° are about 17, 0.4, and 0.1, respectively.[8] All of the other solvents are much less active as hydrogen donors; in fact, the similarity in the yields of V for decomposition of III or IV in cyclohexane, ether, tetrahydrofuran, and cumene suggests that the active hydrogen donor in these cases is

(7) For a previously reported example of a rearrangement of this type, see S. Winstein, R. Heck, S. Lapporte, and R. Baird, *Experientia*, **12**, 138 (1956).

(8) (a) The concentration of hydrogen donor was taken to be 8.7 M for 1,4-cyclohexadiene and 7.4 M for indene. (b) The values of k_a/k_r may not be strictly comparable because recent rate studies have shown that the perester III mainly undergoes induced decomposition in the presence of triethyltin hydride. Formation of large amounts of triethyltin γ,γ-diphenylallylacetate (*ca.* 50%) and of hydrocarbon products (V, VI, etc.) under a variety of conditions can be rationalized in terms of attack of triethyltin radicals at either of the peroxy oxygens of III. The nature of the induced decomposition will be discussed more fully in a later publication.