Homoallylic Free-Radical Rearrangements. IV. Rearrangements of the Allylcarbinyl Radical[1,2]

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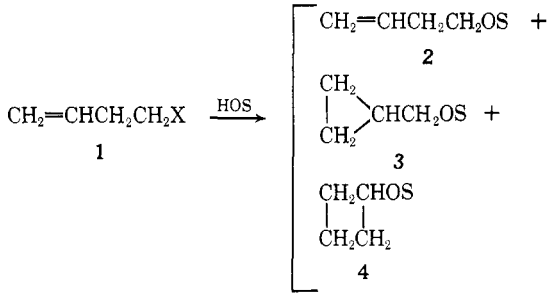
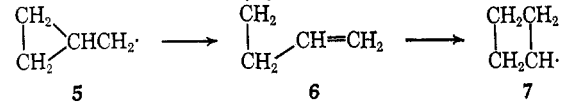
Abstract: The di-*t*-butyl peroxide initiated radical chain decarbonylations (chlorobenzene, 130°) of 4-pentenal, 4-pentenal-2,2-d_2, and *cis*-4-pentenal-5-d_1 have been examined in order to secure information regarding conceivable rearrangements of the allylcarbinyl radical. The virtually exclusive hydrocarbon product from 4-pentenal was 1-butene. Decarbonylation of 4-pentenal-2,2-d_2 afforded 1-butene in which the deuterium labels were distributed between the 3 and the 4 positions. The extent of deuterium scrambling was determined for a series of reactions in which the initial aldehyde concentration was varied from 0.50 to 6.0 *M*. The ratio of deuterons in the 4 position to those in the 3 position increased monotonically from 0.96 to 1.49 as the 4-pentenal-2,2-d_2 concentration was increased from 0.50 to 6.0 *M*. These observations suggest that vicinal vinyl group migration takes place in the allylcarbinyl radical. Decarbonylation of a 1.0 *M* solution of *cis*-4-pentenal-5-d_1 yielded a 1.03:1.00 mixture of *cis*-1-butene-1-d_1 and *trans*-1-butene-1-d_1. The ratio of olefins increased to 1.42:1.00 when the aldehyde concentration was increased to 7.3 *M*. From these results, it has been argued that cyclopropylcarbinyl radicals are important intermediates in the decarbonylation of 4-pentenal and, further, that they lie along the reaction coordinate for 1,2 vinyl group migration. The rearrangement data from 4-pentenal-2,2-d_2 and *cis*-4-pentenal-5-d_1 have been compared quantitatively.

Appropriately constituted allylcarbinyl derivatives (**1**) solvolyze yielding mixtures of allylcarbinyl (**2**), cyclopropylcarbinyl (**3**), and cyclobutyl (**4**) products.[4] These fascinating rearrangements have been the subject



of a number of investigations.[4,5] Rearrangements have also been noted in structurally analogous carbanionic systems.[6] For example, it has been shown that the α and β carbons in allylcarbinylmagnesium halides exchange positions by way of 1,2 vinyl group migration.[6a] The purpose of the present study was to ascertain whether or not allylcarbinyl radicals enter into rearrangements similar to those encountered with either cationic or anionic allylcarbinyl species.

Several observations in the literature bear directly or indirectly on the question under consideration. Allylcarbinyl–cyclopropylcarbinyl radical interconversion has been discussed in connection with the formation of minor quantities of methylcyclopropane in the preparation of allylmagnesium halides.[6b] A trace of methylcyclopropane has been detected in the tri-*n*-butyltin hydride reduction of allylcarbinyl bromide,[7] a reaction which is known to be a radical chain reaction.[8] Poutsma has found that the free-radical chlorination of 1-butene by molecular chlorine gives a mixture of addition and substitution products.[9] 4-Chloro-1-butene, which was presumably formed *via* an allylcarbinyl radical, was produced in 4.5% yield. Neither cyclobutyl chloride nor cyclopropylcarbinyl chloride was detected, however. In a contrasting observation, Walling and Fredricks[10] *tentatively* identified cyclobutyl chloride as a minor product in the *t*-butyl hypochlorite chlorination of methylcyclopropane. Inasmuch as simple ring expansion of cyclopropylcarbinyl radicals to cyclobutyl radicals is unlikely,[11] cyclobutyl chloride formation probably took place through allylcarbinyl radicals (**5** → **6** → **7**). Valuable information concerning the chemistry of allylcarbinyl radicals has been obtained



through a study of the vapor-phase photochlorination of methyl-^{13}C-cyclopropane.[12] Allylcarbinyl chloride and cyclopropylcarbinyl chloride were the principal monochlorination products in this reaction. The ^{13}C

(1) (a) Presented at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, Abstracts of Papers, O-48; (b) communicated in preliminary form: L. K. Montgomery and J. W. Matt, *J. Am. Chem. Soc.*, **89**, 3050 (1967).

(2) 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).

(3) National Institutes of Health Predoctoral Fellow.

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

(5) For a general review, see R. Breslow in "Molecular Rearrangements," Vol. I, P. deMayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp 259–272.

(6) (a) M. S. Silver, P. R. Shafer, J. E. Nordlander, C. Rüchardt, and J. D. Roberts, *J. Am. Chem. Soc.*, **82**, 2646 (1960); (b) D. J. Patel, C. L. Hamilton, and J. D. Roberts, *ibid.*, **87**, 5144 (1965).

(7) A. J. Rosen, Ph.D. Thesis, California Institute of Technology, 1964.[6b]

(8) H. G. Kuivila, L. W. Menapace, and C. R. Warner, *J. Am. Chem. Soc.*, **84**, 3584 (1962).

(9) M. L. Poutsma, *ibid.*, **87**, 2172 (1965).

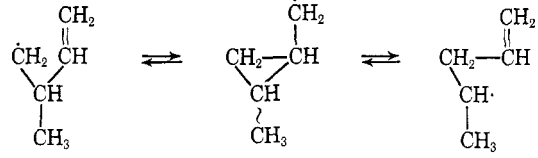
(10) C. Walling and P. S. Fredricks, *ibid.*, **84**, 3326 (1962).

(11) Vicinal alkyl group migrations have not been observed in this temperature range. For a discussion of this point, see C. Walling in "Molecular Rearrangements," Vol. I, P. deMayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp 417–421, 427–428. It is doubtful that the cyclopropylcarbinyl radical system is so different (the change in strain energy is slight) that a violation of this empirical rule would be expected.

(12) E. Renk, P. R. Shafer, W. H. Graham, R. H. Mazur, and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 1987 (1961).

label was found in a single position in each of the chlorides, the α-methylene position of the cyclopropylcarbinyl chloride and the terminal olefinic position of the allylcarbinyl chloride. These results demonstrate that extensive methylene group scrambling, like that observed in the corresponding carbonium ions,[4] does not occur in either cyclopropylcarbinyl or allylcarbinyl radicals under the experimental conditions employed. Finally, Fessenden and Schuler[13] have reported the electron paramagnetic resonance (epr) spectrum of the allylcarbinyl radical. There is little evidence of any homoconjugative interaction between the double bond and the primary radical center.[14,15] Moreover, the spectrum clearly indicates that if structural interconversions do occur in the allylcarbinyl radical they are slow relative to the hyperfine frequency ($\sim 1.5 \times 10^7$ sec^{-1}).

Although the literature pertaining to rearrangements involving simple allylcarbinyl radicals is limited, rearrangements have been reported for substituted allylcarbinyl radicals.[16] The skeletal isomerizations which accompany the radical chain decarbonylations of 3-methyl- and 2-methyl-4-pentenal[15] represent particularly relevant examples. 3-Methyl-1-butene and 1-pentene were the major hydrocarbon products from both aldehydes. Small amounts of *trans*- and *cis*-1,2-dimethylcyclopropanes were identified in both reactions. The observed rearrangements were formulated in terms of common free-radical intermediates (**8** ⇄ **9** ⇄ **10**). The role that substituted cyclopropylcarbinyl radicals (**9**) play in the rearrangement sequence has received support from other studies.[16c]



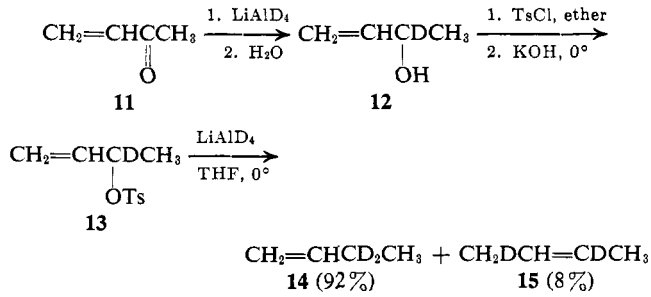
8 **9** **10**

Results

In the present investigation the radicals which were studied were generated by the di-*t*-butyl peroxide initiated radical chain decomposition of appropriate aldehydes. All of the reactions were carried out in chlorobenzene in sealed ampoules at 130°. The aldehydes which were employed were 4-pentenal, 4-pentenal-2,2-d_2, and *cis*-4-pentenal-5-d_1.

4-Pentenal-2,2-d_2 was prepared from 4-pentenal by triethylamine-catalyzed exchange with deuterium oxide in dioxane. Two exchange cycles provided extensively deuterated aldehyde in 56% yield. Proton nuclear magnetic resonance (nmr) analysis showed that the α positions were deuterium labeled to the extent of at least 98%. Two likely products from the decarbonylation of 4-pentenal-2,2-d_2, 1-butene-4,4-d_2 and 1-butene-3,3-d_2, were prepared. The synthesis of 1-butene-3,3-d_2 is shown in Scheme I. Deuterated olefins **14** and **15**

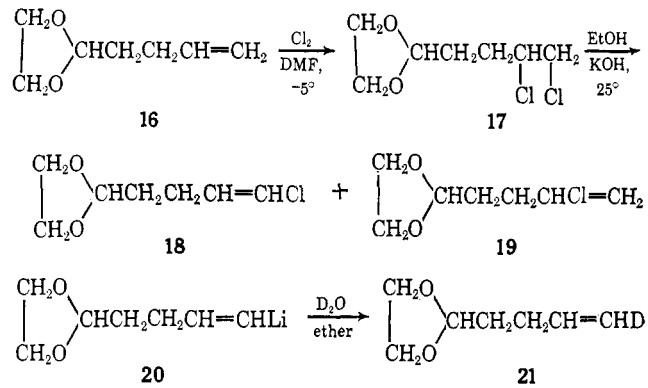
Scheme I



were separated using preparative gas–liquid partition chromatography (glpc). Secondary tosylate **13** was stable enough to characterize by nmr but decomposed upon standing at room temperature in chloroform-d_1 in 30 min. In the final reduction step, the ratio of terminal to internal olefins was somewhat greater than that obtained when either 3-bromo- or 3-chloro-1-butene is reduced with lithium aluminum hydride.[17] 1-Butene-4,4-d_2 was synthesized by a similar sequence, starting with a lithium aluminum deuteride reduction of the methyl ester of 3-butenoic acid.

Key steps in the synthesis of *cis*-4-pentenal-5-d_1 are shown in Scheme II. A dramatic solvent effect was

Scheme II



noted in the chlorination of acetal **16**. Chlorine could be bubbled through a carbon tetrachloride solution of **16** for 10 hr without achieving complete reaction. Low yields (less than 20%) of dichloride **17** were isolated. Most of the acetal ended up as high-boiling, chlorine-containing compounds. Under comparable reaction conditions, chlorine added readily to 1-hexene. In dimethylformamide the addition of chlorine to acetal **16** at −5° was complete in 2 hr; dichloride **17** could be isolated in 80% yield. Presumably, the acetal grouping inhibits the normal[18] radical chain reaction in carbon tetrachloride and polar addition takes place too slowly to compete effectively with undesirable side reactions. The *cis* and *trans* isomers of **18** and olefinic chloride **19** were separated by glpc. The isomeric chlorides were converted to the *cis*- and *trans*-deuterium-labeled acetals **21** *via* organolithium reagents (**20**). The deuterium content and stereochemistry of the acetals could be readily determined from the nmr absorption of the olefinic protons. The acetal of *cis*-4-pentenal-5-d_1 was 90.0% d_1 and 95.0% *cis* configuration. These analyses were utilized in all subsequent quantitative measurements.

(13) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).
(14) For a discussion of this point, see ref 15.
(15) L. K. Montgomery, J. W. Matt, and J. R. Webster, *J. Am. Chem. Soc.*, **89**, 923 (1967).
(16) (a) For a review of early studies in this area and related observations, see ref 15; (b) L. H. Slaugh, *J. Am. Chem. Soc.*, **87**, 1522 (1965); (c) L. K. Montgomery and J. W. Matt, *ibid.*, **89**, 934 (1967); (d) T. A. Halgren, M. E. H. Howden, M. E. Medof, and J. D. Roberts, *ibid.*, **89**, 3051 (1967).
(17) L. F. Hatch and R. E. Gilbert, *J. Org. Chem.*, **24**, 1811 (1959).
(18) M. L. Poutsma, *J. Am. Chem. Soc.*, **87**, 2161 (1965).

The *trans* and *cis* isomers of 1-butene-1-d_1 were synthesized starting from *trans*- and *cis*-1-chloro-1-butenes. The nmr spectra of the deuterium-labeled isomers indicated that *cis*- and *trans*-1-butene-1-d_1 mixtures could be analyzed accurately using nmr.

Previous studies[15] on the decarbonylation reactions of closely related unsaturated aldehydes showed that 40–70% of the stoichiometric quantity of carbon monoxide could be liberated by heating the aldehydes with 20 mole % di-*t*-butyl peroxide for 4–8 hr at 130°. The extent of decarbonylation in these aldehydes, as well as in saturated aldehydes, appears to be limited more by the buildup of inhibitory substances than by aldehyde-destroying side reactions. The decarbonylation reactions reported here were carried to low conversion in keeping with previously developed procedures.[15] Under such conditions side reactions are minimized and quantitative interpretation of the decarbonylation data is facilitated.[15] A decarbonylation product study was conducted on a 4.0 *M* solution of 4-pentenal in chlorobenzene. The results are presented in Table I. Two features of the data are worth noting at this point. First, only 5–6% decarbonylation occurred, which meets the low conversion guide lines established previously.[15] Secondly, 1-butene was the predominant hydrocarbon product.

Table I. Reaction Products from the Decarbonylation of a 4.0 *M* Solution of 4-Pentenal in Chlorobenzene at 130°

Product	Mole/mole of reactant[a,b]
1-Butene	0.054
Methylcyclopropane	0.00009
Cyclobutane	*e*
Carbon monoxide	0.061
t-Butyl alcohol	0.031[c]
Acetone	0.022[c]
Methane	0.013[c]
Residue[a,d]	0.67 g

[a] Reaction carried out on 6.730 g (0.0800 mole) of 4-pentenal (20 mole % di-*t*-butyl peroxide). [b] Reaction period of 30 min. [c] Relative to initial di-*t*-butyl peroxide. [d] Residual material which was left after distilling off unreacted aldehyde, volatile products, and chlorobenzene. [e] None detected (less than 10^{-5}).

In preliminary experiments, mass spectrometric analyses of the gaseous decarbonylation products of 4-pentenal-2,2-d_2 showed that 1-butene-4,4-d_2, the simple decarbonylation product, was not the only labeled 1-butene present. It appeared that 1-butene-3,3-d_2 was also formed in a roughly equal quantity. Owing to the fact that carbon monoxide and several minor contaminants were also present, it was difficult to tell if the 4,4-d_2 and 3,3-d_2 isomers were the only labeled 1-butenes formed.

A series of solutions of 4-pentenal-2,2-d_2 in chlorobenzene, varying in concentration from 0.50 to 6.0 *M*, were prepared and decarbonylated. Reaction times were selected so that less than 10% decarbonylation occurred.[15] The gaseous products from the partially decomposed solutions were analyzed by mass spectrometry. Known minor contaminants were substracted from the spectra of the various samples. The corrected spectra did not correspond to simple mixtures of 1-butene-4,4-d_2 and 1-butene-3,3-d_2. The spectra of glpc chromatographed samples did not correspond to mixtures either, making it clear that other labeled 1-butenes were present. Despite this fact, important qualitative trends could be discerned from the data. It was obvious, for example, that the relative distribution of products was similar for all 4-pentenal-2,2-d_2 solutions below 1.5 *M*. In the concentration range 1.5–6.0 *M*, the relative amount of 1-butene-4,4-d_2 increased in a regular manner.

The liquid products from several reactions were combined and the unreacted aldehyde was collected employing preparative glpc. Proton nmr analysis of the collected aldehyde revealed that 0.1–0.2 deuterium had been washed out during reaction. Thus, monolabeled 1-butenes account for at least a portion of the unidentified products. In view of this, an nmr analysis procedure was adopted. The nmr procedure permitted a position by position deuterium analysis but was more difficult experimentally and required a larger amount of 4-pentenal-2,2-d_2.

Chlorobenzene solutions of 4-pentenal-2,2-d_2 of four different concentrations were sealed in ampoules fitted with breakseals. Reaction times were lengthened somewhat in order to provide more products for analysis. The volatile reaction products were transferred on a vacuum line to a glpc gas-inlet system. The products were chromatographed and the 1-butene was collected in a total collection system which had an nmr tube attached. Chloroform-d_1 was added; the 1-butene solutions were analyzed using a Varian Associates HA-60 spectrometer. Table II contains the results of these experiments. Reasonable limits of error, as assessed by the Student's *t* distribution (99.5% confidence limits), are ±2% of indicated values. The relatively large error results from the fact that the analyses were performed on less than 1-mmole quantities of products.

Table II. 1-Butene Analyses for the Decarbonylation of 4-Pentenal-2,2-d_2[a,b]

Aldehyde concn, *M*	Protons per position 1	2[c]	3	4
0.50	1.99	1.00	1.48	2.50
2.0	2.05	1.00	1.15	2.17
4.0	2.05	1.00	1.49	2.40
6.0	2.00	1.00	1.41	2.12

[a] In chlorobenzene at 130° employing 20 mole % di-*t*-butyl peroxide as an initiator. [b] Error approximately ±2% of the values quoted. [c] Assigned.

Since only a limited amount of *cis*-4-pentenal-5-d_1 was available for decarbonylation studies, the products from this aldehyde were determined at only two concentrations. Using authentic samples of *cis*-1-butene-1-d_1 and *trans*-1-butene-1-d_1, it was shown these two olefins were the principal hydrocarbon decarbonylation products. Ratios of the *cis* to *trans* isomers were measured by nmr for 1.0 and 7.3 *M* (neat) solutions of *cis*-4-pentenal-5-d_1 which were carried to low conversion (Table III). The nmr spectrum of unreacted *cis*-4-pentenal-5-d_1 showed that the double bond had not undergone isomerization.

Discussion

1-Butene accounted for greater than 99% of the hydrocarbon products from 4-pentenal (Table I). No

Table III. Olefin Ratios for the Decarbonylation of *cis*-4-Pentenal-5-d_1[a]

Aldehyde concn, *M*	*cis*-1-Butene-1-d_1/*trans*-1-butene-1-d_1
1.0	1.03 ± 0.03[b]
7.3	1.42 ± 0.03[b]

[a] In chlorobenzene at 130° employing 20 mole % di-*t*-butyl peroxide as an initiator. [b] Error analysis by the Student's *t* distribution employing 99.5% confidence limits.

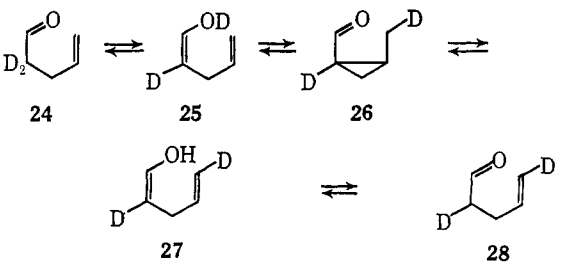
cyclobutane was detected. An important conclusion can be drawn from this observation, namely that allylcarbinyl radicals do not cyclize to cyclobutyl radicals in this system. This follows from the fact that cyclobutanecarboxaldehyde affords only cyclobutane under comparable experimental conditions.[19] The absence of cyclobutane among the products of 4-pentenal agrees well with the results of other studies (*vide supra*), the notable exception being the tentative identification of cyclobutyl chloride in the chlorination of methylcyclopropane with *t*-butyl hypochlorite.[10]

Methylcyclopropane was formed in about $^1/_{600}$ the yield of 1-butene. It does not follow by an analogous line of reasoning that cyclopropylcarbinyl radicals were not important intermediates, for it is well known that cyclopropylcarbinyl radicals open to allylcarbinyl radicals with unusual ease.[15] A good example of this behavior is that cyclopropylacetaldehyde decarbonylates to give 1-butene and no detectable methylcyclopropane.[19]

If 4-pentenal-2,2-d_2 underwent decarbonylation in a typical radical chain manner, 1-butene-4,4-d_2 would be the expected product. Experimentally it was found that 1-butene-3,3-d_2 is also a major product. Since it is unlikely that either the starting aldehyde or the products rearrange under the reaction conditions,[15,20] rearrangement must occur during the radical chain sequence. Formally, homoallylic radical **22** would be produced in this sequence. The formation of 1-butene-3,3-d_2 can be easily rationalized by assuming that 1,2-vinyl group migration occurs (**22** ⇄ **23**). Chain transfer from **23** provides 1-butene-3,3-d_2.

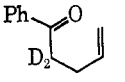
$$\underset{\mathbf{22}}{CH_2{=}CHCH_2CD_2\cdot} \rightleftarrows \underset{\mathbf{23}}{\cdot CH_2CD_2CH{=}CH_2}$$

When the mass spectral analyses of the products from 4-pentenal-2,2-d_2 indicated that 1-butenes other than 1-butene-4,4-d_2 and 1-butene-3,3-d_2 were present, two basic explanations seemed plausible. First, other d_2 isomers could have been produced. In the solvolyses of allylcarbinyl derivatives, extensive methylene-group scrambling takes place.[4] Comparable rearrangements in the allylcarbinyl radical would give rise to 1-butene-1,1-d_2 in addition to the 4,4-d_2 and 3,3-d_2 isomers. Another mechanism by which d_2 isomers could be formed would be by way of a preliminary rearrangement of 4-pentenal-2,2-d_2 (**24** ⇄ **28**). This type of isomerization has been observed with deuterated allylacetophenone **29**,[21] although it should be pointed out that



24 **25** **26** **27** **28**

only 0.2 deuterium is transferred to the terminal olefinic position of **29** after 17 hr of heating at 200°.



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From Table II it can be seen that the average number of protons in the 1-butene 1 position is close to 2.00 for each of the 1-butene mixtures. Thus, it is clear that neither of the above mechanisms produces the unidentified 1-butenes.[22] The second basic type of explanation which was considered was the possibility that deuteriums were lost at some stage during the reaction. This hypothesis is supported by the finding that recovered aldehyde contained only 1.8 deuteriums per molecule and is further substantiated by the data in Table II which show that the sum of the deuteriums in the 3 and the 4 positions is less than 2.00. It is likely that certain decarbonylation products, such as acetone or *t*-butyl alcohol, are involved in the exchange reaction. The details of the exchange process are being explored at present.

As far as the qualitative observation of rearrangement is concerned, a single deuterium label suffices almost as well as a double label. Having both singly and doubly labeled allylcarbinyl radicals does introduce problems concerning the quantitative interpretation of rearrangement data, however (*vide infra*). In Table IV ratios of unrearranged to rearranged 1-butenes, as inferred from the distribution of deuterium in the 3 and the 4 positions, are listed for the four initial 4-pentenal-2,2-d_2 concentrations. None of the ratios differ greatly from 1:1, indicating that deuterium scrambling between the α and β positions in the allylcarbinyl radical is rapid.

Table IV. Extent of Rearrangement As a Function of Initial 4-Pentenal-2,2-d_2 Concentration[a]

Aldehyde concn, *M*	Unrearranged 1-butenes[b]/ rearranged 1-butenes
0.50	0.96
2.0	0.98
4.0	1.18
6.0	1.49

[a] Chlorobenzene solvent, 130°. [b] Ratio of deuteriums in the 4 position of 1-butene to those in the 3 position.

While the observed rearrangements are adequately rationalized in terms of vicinal vinyl group migration, alternative mechanisms are conceivable. One alterna-

(19) D. I. Schuster, Ph.D. Thesis, California Institute of Technology, 1961.

(20) Spectra of the aldehyde recovered from partially reacted 4-pentenal-2,2-d_2 solutions were very similar to those of the starting aldehyde.

(21) R. M. Roberts and R. G. Landolt, *J. Am. Chem. Soc.*, 87, 2281 (1965).

(22) The analyses in Table II are relative proton analyses based on the protons in the 2 position. It is possible, though extremely unlikely, that the 2 position contains deuterium and that the observed 2:1 olefinic proton ratios result from deuteriums being introduced into the 2 position at precisely one-half the rate at which they are introduced into the 1 position.

tive would be a series of hydrogen atom migrations (**22** ⇄ **30** ⇄ **31**). *A priori*, this mechanism is not particularly appealing in view of the fact that 1,2 hydrogen atom transfers (monoradicals, thermally promoted, this temperature range) have not been reported.[11] A sounder argument against the mechanism utilized the observation that no 2-butene was formed. Intermediate **30** would be expected to give rise to products, the predominant one being 2-butene.[23]

$$\underset{\mathbf{22}}{CH_2{=}CHCH_2CD_2\cdot} \rightleftharpoons \underset{\mathbf{30}}{CH_2{=}\dot{C}H{-}CHCD_2H} \rightleftharpoons \underset{\mathbf{31}}{CH_2{=}CHCHDCHD\cdot}$$

The monotonic increase in the ratio of unrearranged to rearranged 1-butenes with increasing aldehyde concentration (Table IV) demonstrates experimentally that a minimum of two types of radical intermediates are involved in product formation. Homoallylic radicals **22** and **23** (plus their d_1 counterparts) serve nicely as the required intermediates.

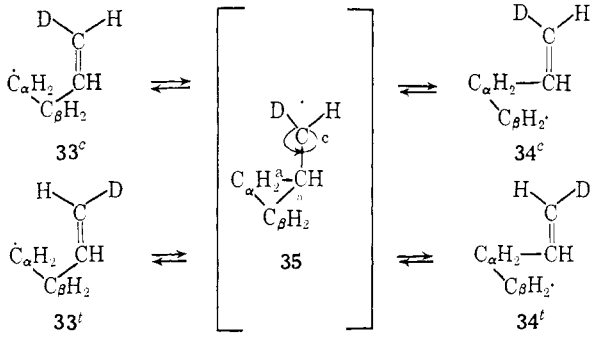
In the interconversion of **22** and **23**, a half-migrated entity similar to **32** must be implicated in the very least as a transition state. The mechanistically significant

$$\underset{\mathbf{22}}{CH_2{=}CHCH_2CD_2\cdot} \rightleftharpoons \underset{\mathbf{32}}{\overset{\dot{C}H_2}{\underset{CH_2{-}CD_2}{|\diagup\diagdown}}CH} \rightleftharpoons \underset{\mathbf{23}}{\cdot CH_2CD_2CH{=}CH_2}$$

question arises as to whether a cyclopropylcarbinyl intermediate is involved. In order to probe this point, *cis*-4-pentenal-5-d_1 was synthesized and its decarbonylation products were examined.

Radical chain decomposition of *cis*-4-pentenal-5-d_1 would generate radical **33**^{c} initially (Scheme III). If half-migrated structure **35** is merely a transition state

Scheme III. Rearrangement Scheme for *cis*-4-Pentenal-5-d_1



for carbon skeletal rearrangement, bond a should be formed and bond b broken without loss of geometrical identity about bond c (*i.e.*, **34**^{c} would be produced), for transition-state lifetimes are generally considered to be short relative to internal rotational lifetimes.[24,25] On the other hand, if cyclopropylcarbinyl radicals are formed and exist long enough to permit rotation about bond c, both *cis*- and *trans*-1-butene-1-d_1 would be observed.

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 (Table III). Since the double bond of *cis*-4-pentenal-5-d_1 is not isomerized under the reaction conditions, it is reasonable to assume that the two olefinic products are not interconverted. Accordingly, the formation of *trans*-1-butene-1-d_1 provides evidence that cyclopropylcarbinyl radicals are important decarbonylation intermediates. When neat (7.3 *M*) *cis*-4-pentenal-5-d_1 was reacted, the *cis* to *trans* ratio increased to 1.42:1.00 (Table III). This decrease in the extent of rearrangement suggests that an intermediate with *cis* double bond geometry precedes the cyclopropylcarbinyl radical in the decarbonylation sequence. Such a positioning is in harmony with Scheme III, thus lending support to the hypothesis that cyclopropylcarbinyl radical **35** lies along the reaction coordinate for carbon skeletal rearrangements.

At least two independent lines of evidence are in agreement with the idea that cyclopropylcarbinyl radicals are key intermediates in homoallylic rearrangements. Roberts and co-workers[16d] have found that if the cyclopropylcarbinyl radical is sufficiently stabilized (*e.g.*, **37**), substantial yields of cyclopropyl products are obtained.

$$\underset{\mathbf{36}}{\overset{\dot{C}H_2}{\underset{CH_2}{|\diagup}}CH{=}CPh_2} \rightleftharpoons \underset{\mathbf{37}}{\overset{CH_2}{\underset{CH_2}{|\diagdown}}C\dot{H}CPh_2}$$

The second line of support comes from an investigation of the decarbonylation reactions of 2-methyl- and 3-methyl-*trans*-4-hexenal,[16c] where it was shown that substituted cyclopropylcarbinyl radicals are intermediates in 1,2 propenyl group migrations.

The ratio of unrearranged to rearranged olefins from 4-pentenal-2,2-d_2 increased only 50% upon varying the aldehyde concentration from 0.50 to 6.0 *M*. It is known that a pair of deuteriums can exert secondary deuterium isotope effects of 25–30% on rate and equilibrium processes.[26] In view of the experimental difficulties which were faced in collecting the concentration-dependence data for 4-pentenal-2,2-d_2, it would be inappropriate to attach unqualified quantitative significance to the data in Table IV. There is, however, a very interesting comparison which can be made using the data from both 4-pentenal-2,2-d_2 and *cis*-4-pentenal-5-d_1. In order to make this comparison, it is necessary to have a general idea of how isotope effects might influence the 4-pentenal-2,2-d_2 data.

Provided that decarbonylation is carried to low conversion, the ratio of 1-butene-4,4-d_2 to 1-butene-3,3-d_2 which is obtained at a specific initial 4-pentenal-2,2-d_2 concentration [RCHO] is given by eq 1, where the rate constants are defined in Scheme IV.[15] Equation 1 predicts a linear relationship between the ratio of olefins and the aldehyde concentration. In Figure 1 the ratio

$$\frac{4,4\text{-}d_2}{3,3\text{-}d_2} = \frac{2k_{3D}k_{2H}k_{-2D} + k_{3H}k_{3D}(k_{-2H} + k_{-2D})[\mathrm{RCHO}]}{2k_{3H}k_{-2H}k_{2D}} \quad (1)$$

(23) C. Walling in "Molecular Rearrangements," Vol. I, P. deMayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp 433–438.

(24) (a) 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; (b) for information pertaining to the rate of rotation about bonds like bond c, see ref 13; (c) the results in ref 25 suggest that there might be a substantial barrier to rotation about bond c.

(25) G. A. Russell and H. Malkus, *J. Am. Chem. Soc.*, **89**, 160 (1967).

(26) E. A. Halevi, *Progr. Phys. Org. Chem.*, **1**, 109 (1963).

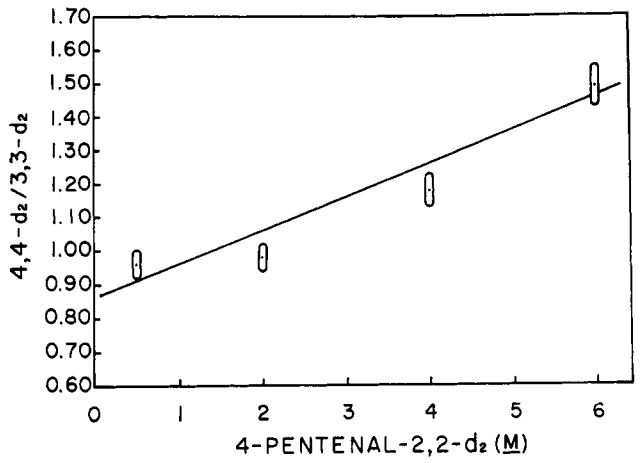
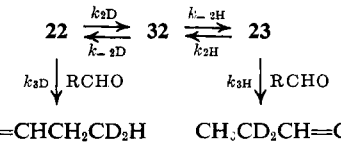


Figure 1. Plot of the ratio of unrearranged to rearranged 1-butenes *vs.* the initial 4-pentenal-2,2-d_2 concentration.

of deuterated 1-butenes is plotted *vs.* the initial 4-pentenal-2,2-d_2 concentration. Considering the uncertainties in the ratio measurements and the limited number of points, a reasonable fit to a straight line is obtained.

Scheme IV. Definintion of Rate Constants for the Rearrangement of the Allylcarbinyl-α,α-d_2 Radical, **22**



In the absence of secondary isotope effects, the intercept of the plot in Figure 1 would be 1.00 and the slope k_3/k_2. If isotope effects are included, the intercept is given by eq 2. This expression can be factored logically into two parts, the inverse of the equilibrium constant

$$\text{intercept} = \frac{k_{3D}k_{2H}k_{-2D}}{k_{3H}k_{-2H}k_{2D}} \qquad (2)$$

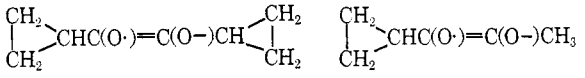
for the conversion of **22** into **23**, $k_{2H}k_{-2D}/k_{-2H}k_{2D}$, and the ratio of chain-transfer rate constants, k_{3D}/k_{3H}. Unfortunately, little is known concerning the magnitude of equilibrium isotope effects of the kind involved in the equilibrium between **22** and **23**.[26] A number of secondary kinetic isotope effects have been measured for systems where a tetrahedrally hybridized carbon is converted to a free-radical center. This is the type of transformation which takes place in converting **23** into **22** (*i.e.*, the CD_2 in **23** and **22**). Observed limiting rate constant ratios (k_H/k_D) for these systems fall in the range 1.13–1.17 per deuterium.[27] This range is similar to that which is found for many polar reactions[26] and is reasonable from the theoretical point of view.[28] If it is assumed for the purpose of the present discussion that the maximum expected α kinetic isotope effect is 15% per deuterium[29,30] and, further, that this limiting value can be used to estimate equilibrium isotope effects, then the value of $k_{2H}k_{-2D}/k_{-2H}k_{2D}$ becomes $1/(1.15)^2$ or 0.76. An inverse isotope effect would be expected for the chain-transfer step from **22**. This would place k_{3D}/k_{3H} between $(1.15)^2 = 1.32$ and 1.00, depending upon the extent of force constant changes in the abstraction transition state. Accordingly, the expected intercept range for products derived from intermediates **22** and **23** is 0.76–1.00. If singly labeled radicals are involved, this range reduces to 0.87–1.00. The least-squares intercept for the data in Figure 1 is 0.86.

According to eq 1, the slope in Figure 1 is given by eq 3. The $(k_{-2H} + k_{-2D})/2k_{-2H}$ component of eq 3

$$\text{slope} = \frac{k_{3D}(k_{-2H} + k_{-2D})}{2k_{2D}k_{-2H}} \qquad (3)$$

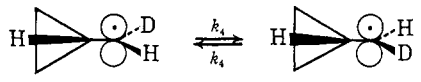
must lie between 0.88 and 1.16 ($k_{-2H} = 1.32k_{-2D}$ or $k_{-2D} = 1.32\ k_{-2H}$). Since the steps involving k_{3D} and k_{2D} should be subject to inverse isotope effects, k_{3D} and k_{2D} would differ from k_3 and k_2 in the allylcarbinyl radical by constants greater than 1.00 and less than 1.32. Combining the above estimates, it can be seen that the measured slope could, in the limit, differ from k_3/k_2 for the allylcarbinyl radical by a factor ranging from 1.53 to 0.67. In the case of monolabeled allylcarbinyl radicals, the range is 1.24–0.81. If the influence of isotope effects on the slope is considered in greater detail, it is found that the expected limits of influence fall in much narrower ranges than the estimates derived here. Without improved data, however, extended discussion of this point seems unwarranted. The least-squares value of the slope in Figure 1 is 0.100.

With some idea in mind of the extent to which secondary isotope effects might effect 1,2 vinyl group rearrangement in the allylcarbinyl radical, decarbonylation data from *cis*-4-pentenal-5-d_1 and 4-pentenal-2,2-d_2 can be compared. Recently, Russell and Malkus have explored the question of electron delocalization in cyclopropylcarbinyl radical systems by examining the epr spectra of cyclopropyl semidiones **38** and **39**.[25,31] These radical anions proved to be quite stable relative



38 **39**

to other cycloalkyl semidiones. The hyperfine splitting constants for the α-methine hydrogens of **38** and **39** are small and must result from highly preferred conformations in which the methine hydrogens are close to the nodal planes of the π systems. In the case of cyclopropylcarbinyl radical **35**, rotamers **35**^{c} and **35**^{t} would correspond to such conformations. If radical **35** exists



35^c **35**^{t}

either as **35**^{c} or **35**^{t}, then the rate of interconversion of **35**^{c} and **35**^{t} is of prime importance in determining how

(27) (a) S. Seltzer, *J. Am. Chem. Soc.*, **83**, 2625 (1961); (b) S. Seltzer, *ibid.*, **85**, 14 (1963); (c) S. Seltzer and F. T. Dunne, *ibid.*, **87**, 2628 (1965); (d) T. W. Koenig and W. D. Brewer, *Tetrahedron Letters*, 2773 (1965).

(28) (a) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey, and S. Suzuki, *J. Am. Chem. Soc.*, **80**, 2326 (1958); (b) S. Seltzer, *ibid.*, **83**, 1861 (1961); (c) M. Wolfsberg and M. Stern, *J. Pure Appl. Chem.*, **8**, 325 (1964).

(29) In typical acyclic systems, β kinetic isotope effects appear to be very small for free-radical reactions.[30]

(30) (a) S. Seltzer and E. J. Hamilton, Jr., *J. Am. Chem. Soc.*, **88**, 3775 (1966); (b) see also ref 27d; (c) T. Koenig and R. Wolf, *J. Am Chem. Soc.*, **89**, 2948 (1967).

(31) See also (a) N. K. Ray, R. K. Gupta, and P. T. Narasimhan, *Mol. Phys.*, **10**, 601 (1966) (see discussion in ref 25 regarding this investigation); (b) R. G. Kostyanovskii, S. P. Solodonikov, and O. A. Yuzhakova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 735 (1966).

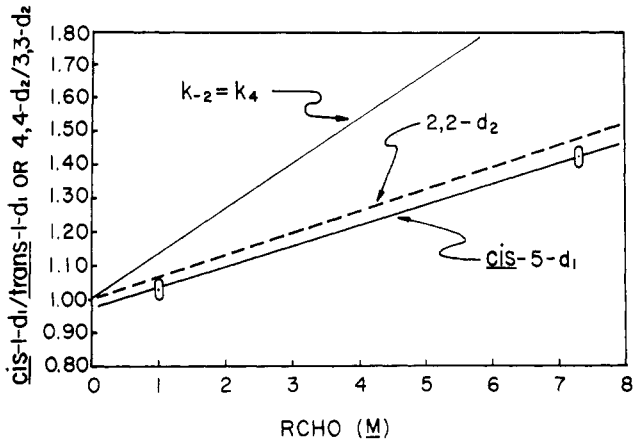


Figure 2. A comparison of the decarbonylation data for *cis*-4-pentenal-5-d_1 and 4-pentenal-2,2-d_2.

fast double bond isomerization occurs relative to carbon skeletal rearrangement.

Using the same general procedure which was employed to derive eq 1,[15] an expression can be obtained which relates the *cis*- to *trans*-1-butene-1-d_1 ratio to the rate constants k_2, k_{-2}, and k_3 (rate constants defined as in Scheme IV), the rate constant k_4 for the interconversion of **35**^{c} and **35**^{t}, and the initial *cis*-4-pentenal-5-d_1 concentration (eq 4). When k_4 is much greater than

$$\frac{cis}{trans} = \frac{k_4k_2 + k_3(k_{-2} + k_4)[\mathrm{RCHO}]}{k_4k_2} \qquad (4)$$

k_{-2}, the rate constant for ring opening of the cyclopropylcarbinyl radical, eq 4 reduces to eq 5. Moreover,

$$\frac{cis\text{-}1\text{-}d_1}{trans\text{-}1\text{-}d_1} = \frac{4,4\text{-}d_2}{3,3\text{-}d_2} = \frac{k_2 + k_3[\mathrm{RCHO}]}{k_2} \qquad (5)$$

if there are no isotope effects on the rearrangement of the allylcarbinyl-α,α-d_2 radical, eq 1 also reduces to eq 5. Thus, if **35**^{c} and **35**^{t} are interconverted rapidly relative to ring opening, a plot of the *cis*-1-d_1/*trans*-1-d_1 1-butene ratios *vs.* the *cis*-4-pentenal-5-d_1 concentration should be superimposable upon a plot of the 4,4-d_2/3,3-d_2 1-butene ratios *vs.* the 4-pentenal-2,2-d_2 concentration, once the latter plot has been corrected for isotope effects. The *cis*-4-pentenal-5-d_1 data are plotted in Figure 2. Within experimental error, the intercept is unity. The slope is 0.061. The minimum expected 4-pentenal-2,2-d_2 slope (isotope corrected, *vide supra*) is 0.067. These slopes are the same within the limits of precision of the measurements in the two systems. It is worth noting that if 0.067 is the true slope for the allylcarbinyl radical, then the *cis*-4-pentenal-5-d_1 slope would have to be 0.134 if $k_{-2} = k_4$. It is clear from Figure 2 that the 4-pentenal-2,2-d_2 and/or *cis*-4-pentenal-5-d_1 measurements would have to be seriously in error for such a condition to exist in fact. From the present data, it appears safe to conclude that k_4 is greater than k_{-2}. Just how much greater is difficult to say.

Experimental Section

All boiling points were recorded with standard-taper, partial-immersion thermometers but are otherwise uncorrected. Proton nuclear magnetic resonance (nmr) spectra (Varian Associates A-60 spectrometer) and infrared spectra (Perkin-Elmer Model 137 infrared spectrometer) were routinely recorded and are assumed to be in satisfactory agreement with authentic or predicted spectra when they are not explicitly discussed. Chemical shifts are reported as parts per million displacements downfield from tetramethylsilane as an internal standard. Chloroform-d_1 was used as the solvent for all nmr samples. Spin–spin decoupling experiments and quantitative nmr measurements were performed on a Varian Associates HA-60 spectrometer. Preparative gas–liquid partition chromatography (glpc) was carried out using an Aerograph Autoprep, Model A-700, equipped with 10-ft ($^3/_8$ in. o.d.) columns. The stationary phase for all columns was 60–80 mesh Chromosorb P. The liquid phases and their designations are 30% Carbowax 20M (CWP), aluminum column; 30% diisodecyl phthalate (DPP), stainless steel column; 30% silicone fluid XF-1150 (XFP), aluminum column; 30% silver nitrate–propylene glycol (SNP), copper column. Analytical glpc determinations were accomplished on an F & M Scientific Model 609 flame-ionization instrument equipped with a Minneapolis-Honeywell 1-mv recorder fitted with a Disc Instruments integrator. All of the columns which were used with the F & M instrument were stainless steel (8 ft, 0.25 in. o.d.) and employed 60–80 mesh Chromosorb P as a stationary support. The liquid phases that were used and their designations are 20% diisodecyl phthalate (DPA); 20% Carbowax 20M (CWA); 30% propylene glycol–silver nitrate (SNA). Mass spectrometric analyses were accomplished using a Consolidated Electrodynamics Corp. mass spectrometer, Model 21-620 A.

Allyl vinyl ether was prepared by the general transetherification method A of Watanabe and Conlon.[32] The ether was distilled as it was formed from a solution made up of allyl alcohol (122.0 g, 2.10 moles), 1,4-bis(vinyloxy)butane (129.5 g, 0.911 mole), and mercuric acetate (3.0 g, 0.00944 mole). Redistillation gave 124.5 g (81%) of allyl vinyl ether, bp 66° (lit.[32] bp 66–67°).

4-Pentenal was prepared in good yield by heating allyl vinyl ether (111.0 g, 1.32 moles) in a set of glass ampoules (nitrogen flushed) for 8 hr at 130°. Distillation of the combined products afforded 99 g (89%) of 4-pentenal, bp 105° (lit.[33] bp 101–105°).

2-Ethyl-2-methyl-1,3-dioxolane. Ethylene glycol (186.0 g, 3.00 moles), 2-butanone (216.0 g, 3.00 moles), 2.4 g of *p*-toluenesulfonic acid, and 250 ml of benzene were heated at the solution's reflux temperature. Water was formed and was removed with the aid of a Dean–Stark trap. Final distillation provided 246.1 g (71%) of 2-ethyl-2-methyl-1,3-dioxolane, bp 116–117° (lit.[34] bp 116°).

2-(3-Buten-1-yl)-1,3-dioxolane was prepared by removing 2-butanone as it was formed from a solution consisting of 4-pentenal (99.0 g, 1.175 moles), 2-ethyl-2-methyl-1,3-dioxolane (145.0 g, 1.25 moles), and 0.5 g of *p*-toluenesulfonic acid. Final distillation gave 137.0 g (91%) of 2-(3-buten-1-yl)-1,3-dioxolane, bp 64–65° (24 mm).

2-(3,4-Dichlorobutyl)-1,3-dioxolane. Several attempts to chlorinate 2-(3-buten-1-yl)-1,3-dioxolane in nonpolar media met with little success. For example, chlorine could be bubbled through a carbon tetrachloride solution of the unsaturated acetal for 16 hr without completely consuming the acetal double bond. 2-(3,4-Dichlorobutyl)-1,3-dioxolane could be isolated in no better than 20% yield. High-boiling, chlorine-containing compounds were the predominant products. Under comparable reaction conditions, chlorine added readily to 1-hexene. In dramatic contrast, chlorine added smoothly to the unsaturated acetal in dimethylformamide.

Chlorine was bubbled into a solution of 2-(3-buten-1-yl)-1,3-dioxolane (40.0 g, 0.341 mole) in 50 ml of dimethyl formamide at −3 to −5° for 2 hr. The reaction was monitored by nmr spectroscopy by following the disappearance of the acetal vinyl protons. Excess chlorine was removed with the aid of a water aspirator and the solvent was removed by distillation. Distillation at reduced pressure gave 48.2 g (76%) of 2-(3,4-dichlorobutyl)-1,3-dioxolane, bp 90–91° (2 mm).

Dehydrohalogenation of 2-(3,4-Dichlorobutyl)-1,3-dioxolane. 2-(3,4-Dichlorobutyl)-1,3-dioxolane (29.0 g, 0.145 mole) was added slowly to a mixture of 100 ml of absolute ethanol and 8.5 g (0.15 mole) of potassium hydroxide. The mixture was maintained at 25° for 1 hr and filtered. The ethanol was removed by distillation. Distillation at reduced pressure afforded 21.0 g (89%) of the vinyl chloride acetals, bp 90–95° (11 mm). 2-(3-Chloro-3-buten-1-yl)-

(32) W. H. Watanabe and L. E. Conlon, *J. Am. Chem. Soc.*, **79**, 2828 (1957).

(33) (a) R. F. Webb, A. J. Duke, and J. A. Parsons, *J. Chem. Soc.*, 4092 (1961); (b) C. D. Hurd and M. A. Pollack, *J. Am. Chem. Soc.*, **60**, 1905 (1938); (c) R. Paul, G. Roy, M. Fluchaire, and G. Collardeau, *Bull. Soc. Chim. France*, 121 (1950).

(34) C. D. Nenitzescu and V. Przemetzki, *Ber.*, **69**, 2706 (1936).

1,3-dioxolane, 2-(*cis*-4-chloro-3-buten-1-yl)-1,3-dioxolane, and 2-(*trans*-4-chloro-3-buten-1-yl)-1,3-dioxolane were present (DPA column) to the extents of 30, 28, and 42%, respectively. The isomers were separated using preparative glpc (DPP, 150°, 600 cc/min). The structures of the three isomers were assigned on the basis of nmr and infrared spectral data. The vinyl proton regions of the nmr spectra of the 4-chloro isomers are quite different from one another and are strikingly similar to the vinyl proton regions of *trans*- and *cis*-1-chloro-1-butene (*vide infra*). Double bond geometry assignments were made utilizing these similarities. Moreover, the chloro isomers were converted to *trans*- and *cis*-4-pentenal-5-d_1, where the double bond geometries can be assigned with certainty.

2-(*cis*-3-Buten-1-yl-4-d_1)-1,3-dioxolane. 2-(*cis*-4-Chloro-3-buten-1-yl)-1,3-dioxolane (4.90 g, 0.0304 mole) in 10 ml of anhydrous ether was slowly added to 50 ml of ether and 0.485 g (0.0700 equiv) of lithium dispersion which contained 2% sodium. The reaction was conducted at 0° under an argon atmosphere. After all of the acetal had been added, the solution was stirred for 1 hr at 0°. About 5 ml of deuterium oxide was added and the reaction mixture was stirred for 1 more hr at 0°. The ether solution was washed with two 20-ml portions of water and dried over anhydrous sodium sulfate. Distillation afforded 2.46 g (63%) of 2-(*cis*-3-buten-1-yl-4-d_1)-1,3-dioxolane, bp 64–65° (24 mm). The product was found by nmr analysis (see *cis*-1-butene-1-d_1 and *trans*-1-butene-1-d_1) to be 95.0% *cis* and 90.0% deuterated.

In the above procedure, reproducible results were obtained only when lithium containing 2% sodium was employed. A variety of other synthetic approaches to the organolithium intermediate gave varying rsults.

***cis*-4-Pentenal-5-d_1.** 2-(*cis*-3-Buten-1-yl-4-d_1)-1,3-dioxolane (2.46 g, 0.019 mole), *n*-decanal (8.92 g, 0.0571 mole), and a trace of *p*-toluenesulfonic acid were stirred at 60° at 50 mm. *cis*-4-Pentenal-5-d_1 (0.81 g, 50%) was collected in a Dry Ice–acetone-cooled trap. Final purification of the aldehyde was accomplished using preparative glpc (CWP, 75°, 100 cc/min).

***trans*-1-Butene-1-d_1.** The *cis* and *trans* isomers of commercial (Columbia) 1-chloro-1-butene were separated by preparative glpc (CWP, 80°, 200 cc/min). The structures of the two isomers were assigned by nmr. The olefinic protons in the *trans* isomer formed an AB system where the A–B chemical shift difference was much less than J_{AB} and, accordingly, did not give much of an indication of double bond structure. In the *cis* isomer, $\delta_A - \delta_B$ was greater than J_{AB}. From spin–spin decoupling experiments, it was found the J_{AB} = 7.2 cps, a reasonable value for a *cis*-substituted olefin. $\delta_A - \delta_B$ was 17 cps.

trans-1-Chloro-1-butene (3.50 g, 0.0387 mole) in 5 ml of ether was added over a 2-hr period to lithium pellets (0.536 g, 0.0774 equiv) in 15 ml of ether. The reaction was conducted under argon at 0°. After addition was completed, the solution was stirred at 0° for an additional 2 hr. The unreacted *trans*-1-chloro-1-butene and the ether were removed under reduced pressure. About 15 ml of tetrahydrofuran, which had been freshly distilled from lithium aluminum hydride, was slowly added (0°) to the nonvolatile residual material. The solution was maintained at 0° while 2.20 g of deuterium oxide was added. The solution was allowed to warm to room temperature. The reaction flask was warmed to 60° in order to transfer the *trans*-1-butene-1-d_1 to a collector which was cooled in a Dry Ice–acetone bath. The yield of *trans*-1-butene-1-d_1 was 1.55 g (70%).

It was found that if the reaction mixture was not evaporated to dryness, the final *trans*-1-butene-1-d_1 was contaminated with 1-butene and 1-butyne. Tetrahydrofuran was used as the final solvent because it dissolved the organolithium intermediate and was easier to separate from the *trans*-1-butene-1-d_1.

The nmr spectrum of *trans*-1-butene-1-d_1 (0.97 D per molecule by nmr analysis) consisted of a triplet (J = 7.5 cps, three protons) at 0.98 ppm, a multiplet approximating a quintet (pseudo $J \sim$ 7.5 cps, two protons) at 2.05 ppm, a doublet (J = 17 cps, one proton) split into triplets (J = 1.5 cps) centered at 4.93 ppm, and an 18-line multiplet (J = 1.5 cps, J' = 7.5 cps, J'' = 17 cps; one proton) extending from 5.5 to 6.2 ppm.

***cis*-1-Butene-1-d_1** was prepared in 50% yield (0.848 g) following the procedure used for the preparation of *trans*-1-butene-1-d_1. The nmr spectrum of *cis*-1-butene-1-d_1 (0.98 D per molecule, 93% *cis* by nmr analysis) consisted of a triplet (J = 7.5 cps, three protons) centered at 0.98 ppm, a multiplet approximating a quintet (pseudo $J \sim$ 7.5 cps, two protons) centered at 2.05 ppm, a doublet (J = 10 cps, one proton) split into triplets (J = 1 cps) centered at 4.87 ppm, and an 18-line multiplet (J = 2.5 cps, J' = 7.5 cps, J'' = 10 cps; one proton) extending from 5.6 to 6.1 ppm.

3-Buten-2-ol-2-d_1. Methyl vinyl ketone (6.00 g, 0.0856 mole) was added to a solution of 0.897 g (0.0214 mole) of lithium aluminum deuteride in 100 ml of anhydrous ether. The solution was stirred for 0.5 hr and cooled to room temperature. About 10 g of water was added dropwise. The organic layer was dried over anhydrous sodium sulfate and the ether was removed. The residual material was distilled; product in the boiling range 90–100° was chromatographed (CWP, 75°, 100 cc/min), yielding 4.80 g (77%) of 3-buten-2-ol-2-d_1 (at least 0.98 D per molecule by nmr analysis).

3-Buten-2-yl-2-d_1 tosylate was prepared following the general procedure of Wenkert and Mylari.[35] Powdered anhydrous potassium hydroxide (2.34 g, 0.0428 mole) was added over a 3-hr period to a solution of 1.566 g (0.0214 mole) of 3-buten-2-ol-2-d_1 and 4.09 g (0.0214 mole) of *p*-toluenesulfonyl chloride in 150 ml of ether which was maintained at 0°. The mixture was stirred for an additional 3 hr at 0°. The solid products were removed by filtration and washed twice with 50-ml portions of ether. The washings were combined with the filtrate and the ether was removed under reduced pressure. The flask was maintained at 0° during the solvent removal. 3-Buten-2-yl-2-d_1 tosylate was obtained in 73% yield (3.53 g). The tosylate was unstable at room temperature and decomposed (chloroform-d_1 solution) to a black tar over a 0.5-hr period.

The nmr spectrum of 3-buten-2-yl-2-d_1 tosylate consisted of a broad singlet (three protons) at 1.3 ppm, a singlet (three protons) at 2.4 ppm, absence of absorption from 4.4 to 4.8 ppm (at least 98% deuteration in the 2 position), a six-line multiplet from 4.9 to 5.3 ppm (two protons), a four-line pattern from 5.45 to 5.95 ppm (one proton), and an AB pattern (four protons) from 7.1 to 7.8 ppm.

1-Butene-3,3-d_2. A solution of 3.53 g (0.0156 mole) of 3-buten-2-yl-2-d_1 tosylate in 10 ml of tetrahydrofuran was added at 0° to a solution of 0.197 g (0.052 mole) of lithium aluminum deuteride in 50 ml of tetrahydrofuran. The solution was stirred for 1 hr and then heated to 65°. The butene gases which were collected (0.31 g, 28%) consisted of 92% 1-butene-3,3-d_2 and 8% 2-butene-x-d_2 (presumably 2-butene-1,3-d_2). The 1-butene-3,3-d_2 was purified by preparative glpc (SNP, 25°, 10 cc/min).

The nmr spectrum of 1-butene-3,3-d_2 consisted of a quintet (J = 1 cps, three protons) at 0.95 ppm, a six-line pattern (J = 2 cps, J' = 8 cps, J'' = 17.5 cps; two protons) extending from 4.75 to 5.15 ppm, and a basic four-line pattern (one proton) centered at 5.85 ppm in which each of the lines was split into quintets (J = 0.8 cps).

3-Buten-1-ol-1,1-d_2. A solution of 6.50 g (0.065 mole) of methyl 3-butenoate in 25 ml of ether was added to an ether solution (150 ml) containing 1.362 g (0.0325 mole) of lithium aluminum deuteride. After the addition was completed, the solution was refluxed for 0.5 hr. About 5 g of water was added, and the organic layer was dried over sodium sulfate. Distillation yielded 4.55 g (94%) of 3-buten-1-ol-1,1-d_2 bp 113–114°. The alcohol contained a minimum of 1.96 deuteriums per molecule in the 1 position (nmr).

3-Buten-1-yl-1,1-d_2 Tosylate.[35] Powdered anhydrous potassium hydroxide (4.50 g, 0.0804 mole) was added to a solution of 3.00 g (0.0405) of 3-buten-1-ol-1,1-d_2 and 7.72 g (0.0405 mole) of *p*-toluenesulfonyl chloride in 150 ml of anhydrous ether which was maintained at 0°. The addition took 3 hr; the solution was stirred for an additional 1 hr. The reaction solids were separated by filtration and washed with two 50-ml portions of ether. The ether washings and the filtrate were combined and the ether was removed under reduced pressure. 3-Buten-1-yl-1,1-d_2 tosylate was obtained in 91% yield (8.42 g).

1-Butene-4,4-d_2. 3-Buten-1-yl-1,1-d_2 tosylate (8.00 g, 0.035 mole) in 10 ml of tetrahydrofuran was slowly added at 0° to a solution of lithium aluminum deuteride (1.32 g, 0.0378 mole) in 50 ml of tetrahydrofuran. The resulting solution was stirred for 1 hr and heated to 65°. 1-Butene-4,4-d_2 (1.42 g, 69%) was collected in a cold trap.

The nmr of chromatographed (SNP, 25°, 10 cc/min) 1-butene-4,4-d_2 (1.98 D per molecule in the 4 position by nmr analysis) consisted of complex absorption (one proton) from 0.75 to 1.2 ppm, absorption approximating a broad-lined triplet (pseudo $J \sim$ 7 cps, two protons) at 2.05 ppm, complex absorption (two overlapping two-line patterns, two protons) from 4.7 to 5.2 ppm, and a 12-line pattern (one proton) extending to 5.5–6.2 ppm.

(35) E. Wenkert and B. L. Mylari, unpublished results.

4-Pentenal-2,2-d_2. A solution consisting of 18.0 g (0.214 mole) of 4-pentenal, 100 g (5.0 moles) of deuterium oxide, and 2.5 g of triethylamine in 300 ml of tetrahydrofuran was stirred at room temperature for 24 hr. The 4-pentenal was recovered by distillation and the process repeated. The 4-pentenal (10.0 g, 56% yield) which was isolated after the second exchange was chromatographed (CWP, 75°, 100 cc/min) and contained 1.97 D per molecule, as assessed by nmr.

Decarbonylation of 4-Pentenal. 4-Pentenal (6.73 g, 0.080 mole) and di-*t*-butyl peroxide (2.34 g, 0.016 mole) were placed in a 20-ml volumetric flask, which was made up to volume with chlorobenzene. The 4.0 *M* aldehyde solution was transferred to a 50-ml round-bottomed flask which was fitted with a side arm with a breakseal. The flask was sealed and heated at 130° for 30 min. The gaseous products were analyzed by mass spectrometry and the liquid products by glpc (DPA, CWA, and SNA columns under a variety of conditions). Simple distillation of the liquid products left a residue of 0.67 g. The results of the analyses are reported in Table I.

Decarbonylation of 4-Pentenal-2,2-d_2. A series (0.50–6.0 *M*) of solutions of 4-pentenal-2,2-d_2 in chlorobenzene were prepared and decarbonylated following the low-conversion procedure developed previously.[15] At the outset, it was anticipated that 1-butene-4,4-d_2 and 1-butene-3,3-d_2 would be the principal decarbonylation products and that these olefins could be conveniently and accurately analyzed by mass spectrometry. The latter presumption was fully realized while the former was not. The mass spectra of the decarbonylation products did not correspond to simple mixtures of 1-butene-4,4-d_2 and 1-butene-3,3-d_2 after known minor contaminants such as *t*-butyl alcohol, acetone, and methane were subtracted from the spectra. The products were chromatographed using the XFP and SNP columns (*vide infra*), but the situation was not improved. Other labeled 1-butenes were present. Several of the more concentrated aldehyde solutions were combined and the unreacted aldehyde was isolated employing preparative glpc (CWP). The aldehyde contained 1.8–1.9 deuteriums per molecule (nmr).

Since the protons in the 1, 2, 3, and 4 positions in 1-butene absorb in different regions in the nmr, an nmr analysis procedure was adopted to study the products from 4-pentenal-2,2-d_2. 4-Pentenal-2,2-d_2 (1–2-g samples) was used to make up 6.0, 4.0, 2.0, and 0.50 *M* aldehyde solutions (chlorobenzene, 20 mole % di-*t*-butyl peroxide). The solutions were heated in Pyrex ampoules at 130° for 60, 35, 50, and 100 min, respectively. Several of these reaction times are longer than those generally employed,[15] though still in the range of low conversion. The times were lengthened to increase the amount of product for nmr analysis. When it was noted that a substantial amount of deuterium was being washed out during the lengthened reaction periods (Table II), the periods were shortened, and the amount of 4-pentenal-2,2-d_2 was increased.

The ampoules containing the 4-pentenal-2,2-d_2 reaction products possessed breakseals. The volatile reaction products from each ampoule were transferred on a vacuum line to a glpc gas-inlet system. The products were chromatographed (SNP, 25°, 10 cc/min) and the 1-butene was collected utilizing a total collection system which had an nmr tube attached. Chloroform-d_1 was added; the 1-butene solutions were analyzed using the HA-60 spectrometer. The statistically analyzed results of a number of integrations are reported in Table II.

Decarbonylation of *cis*-4-Pentenal-5-d_1. *cis*-4-Pentenal (0.252 g, 2.97 mmoles) and di-*t*-butyl peroxide were added to a 1-ml Pyrex ampoule, which was subsequently flushed with argon and sealed. Density measurements showed that the aldehyde concentration was 7.3 *M*. The ampoule was heated at 130° for 101 min. About 3 ml of a 1.0 *M* solution of *cis*-4-pentenal-5-d_1 in chlorobenzene (20 mole % di-*t*-butyl peroxide) was sealed in a second ampoule which was about 6 ml in volume. The 1.0 *M* solution was heated at 130° for 120 min.

The 1-butene products were transferred on a vacuum line to nmr tubes. Chloroform-d_1 and tetramethylsilane were added and the tubes were sealed. The nmr spectra of the products corresponded to mixtures of *cis*-1-butene-1-d_1, *trans*-1-butene-1-d_1, and 1-butene. The ratio of *cis* to *trans* isomers was ascertained by careful integration of the vinyl proton region. All three of the butenes have one proton in the 2 position which absorbs at distinctly lower field than the rest of the olefinic protons. The *cis* and *trans* isomers have nonoverlapping triplets (H–D coupling) at 4.96 and 5.06 ppm, respectively. The ratio of *cis*-1-butene-1-d_1 to *trans*-1-butene-1-d_1 was calculated in a straightforward manner from the integrated intensities of these absorptions, after correcting for the 1-butene which was present. A number of integrations were performed and the results were evaluated statistically. The resulting data are reported in Table III.

Unreacted *cis*-4-pentenal-5-d_1 was recovered and analyzed by nmr spectroscopy. Integration of the absorptions in the vinyl proton region revealed that the double bond geometry of the starting aldehyde was not altered.

Acknowledgment. We wish to thank Dr. B. L. Mylari, W. O. Crain, and T. A. Halgren for valuable comments and/or experimental assistance.