when chromatographed, vacuum-transfered aldehydes were used. The ampoules were not opened until immediately before analysis. 1-Pentene to 3-methyl-1-butene ratios increased with time in opened samples. Moreover, new low-boiling products which interfered with the analysis were formed when opened solutions were stored for prolonged periods of time. The chromatograph injection port and detector temperatures were maintained below 200°. Marked decomposition of the solutions occurred when the injection port was above 275°. Large changes (*e.g.*, $\times 10^4$) in chromatograph sensitivity altered the ratios somewhat. The ratios were less sensitive to moderate changes in analysis sample size. By varying the extent of decarbonylation and the analysis sample size, chromatograph sensitivity changes were limited to a range of about 100 over the entire aldehyde concentration range. Finally, in order to ensure uniformity and maximum accuracy, the largest olefin peak on the vapor-phase chromatograph was kept in the recorder range 70–90% of full deflection.

Product Studies. The decarbonylation reaction products of 3-methyl-4-pentenal and 2-methyl-4-pentenal were investigated employing the reaction conditions used in the study of the relationship between olefin ratios and initial aldehyde concentrations: 4.0 and 0.50 *M* solutions of both aldehydes were prepared and decarbonylated following the procedure outlined under Olefin Ratios. So little products were formed that it was necessary to characterize the various products by their retention times alone. Trace components were identified by peak augmentation with presumed products. The DIDP column proved most useful in both the qualitative and quantitative analysis of products, although the TCEP, CAWX, and PGSN columns were also employed. The latter column was particularly useful in separating *trans*- and *cis*-1,2-dimethylcyclopropane from 3-methyl-1-butene and 1-pentene. A precisely weighed quantity of *n*-heptane was added as an internal standard to each of the product solutions in order to determine the yield of olefins. A conversion factor was determined to relate chromatograph peak areas and mole fractions for *n*-heptane, 3-methyl-1-butene, and 1-pentene. Within experimental error, the conversion factors were the same for both olefins. The yields of trace components were estimated from their fractional relationship to the olefin products without correcting for detector response. The results of the analyses are reported in Tables III and V. Acetone, *t*-butyl alcohol, di-*t*-butyl peroxide, and unreacted aldehydes were present in substantial quantities, but were not included in the tables.

Acknowledgments. We thank Professers Cheves Walling and John D. Roberts and Mr. Tom Halgren for their comments concerning the preparation of this manuscript.

Homoallylic Free Radical Rearrangements. II. Evidence for a Substituted Cyclopropylcarbinyl Radical Intermediate in a Homoallylic Rearrangement[1]

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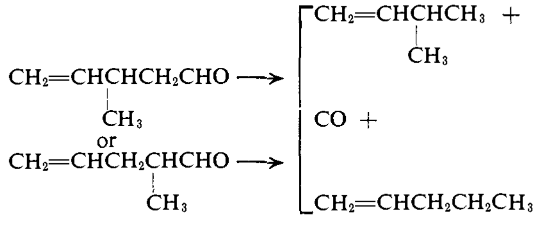
Abstract: The di-*t*-butyl peroxide-initiated radical-chain decarbonylations of 3-methyl-*trans*-4-hexenal and 2-methyl-*trans*-4-hexenal have been investigated in order to secure information regarding the possible intermediacy of cyclopropylcarbinyl-type radicals in homoallylic free radical rearrangements. The virtually exclusive hydrocarbon products from both aldehydes (chlorobenzene, 129.6°) were *trans*- and *cis*-2-hexene, 4-methyl-*trans*-2-pentene, and 4-methyl-*cis*-2-pentene. The distribution of olefinic products was examined as a function of aldehyde concentration. Measurements were made on aldehyde solutions varying in concentration from ~6 to 0.094 *M*. From these data it has been concluded that substituted cyclopropylcarbinyl radicals are important decarbonylation intermediates and, further, that these radicals lie along the reaction coordinate for rearrangement. The effect of structure variation on homoallylic free radical rearrangements is discussed briefly.

Recently, several well-defined homoallylic radical rearrangements have been reported.[3] In one such study[1b,4] we investigated the radical-chain decarbonylations (di-*t*-butyl peroxide, chlorobenzene, 129.6°) of 3-methyl- and 2-methyl-4-pentenal. 1-Pentene and 3-methyl-1-butene were the major hydrocarbon products from both aldehydes (eq 1). 1-Pentene to 3-methyl-1-butene ratios were measured for solutions of 3-methyl- and 2-methyl-4-pentenal varying in concentration from about 6 *M* (neat) to 0.094 *M*. In order to facilitate interpretation of the decarbonylation data, reaction was carried to only a few per cent conversion. The ratio of 1-pentene to 3-methyl-1-butene from 3-methyl-4-pentenal increased monotonically from approximately 5:1 to 9:1 as the aldehyde concentration was decreased from ~6 to 1.0 *M*. At concentrations below 1.0 *M* the ratio remained 9:1.



$$\left.\begin{array}{l} CH_2{=}CH\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CHO \longrightarrow \\ \text{or} \\ CH_2{=}CHCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCHO \longrightarrow \end{array}\right. \left[\begin{array}{l} CH_2{=}CH\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_3 \;+ \\ CO \;+ \\ CH_2{=}CHCH_2CH_2CH_3 \end{array}\right. \qquad (1)$$

From these observations it is clear that at least two radical intermediates are implicated in product formation. The rearrangements can be rationalized in terms of a 1,2-vinyl group migration involving homoallylic radicals I and II. Below 1.0 *M* the intercon-

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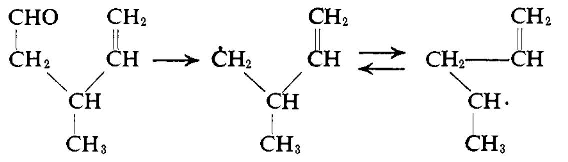
[1] (a) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work (Grants 1825-A4 and 2190-A4). (b) Presented in part at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964; Abstracts, p 29N.

[2] National Institutes of Health Predoctoral Fellow, 1965–1966.

[3] See ref 4 for a review of the literature in this area.

[4] L. K. Montgomery, J. W. Matt, and J. R. Webster, *J. Am. Chem. Soc.*, **89**, 923 (1967).

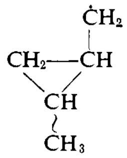


I II

version of I and II is presumed to be fast relative to chain-transfer processes. Under such circumstances the olefin ratio is determined solely by the equilibrium concentrations of I and II and the rate constants for the reactions of I and II with aldehyde. At concentrations above 1.0 *M* 3-methyl-4-pentenal, some of the unrearranged radicals (I) are trapped before they have a chance to rearrange; the 1-pentene to 3-methyl-1-butene ratio is lowered accordingly.

The partitioning of products from 2-methyl-4-pentenal also depended upon the initial aldehyde concentration. At 6 *M* the ratio of 1-pentene to 3-methyl-1-butene was 12.5:1. The ratio dropped to a value of about 10:1 by 1.5 *M*, where it remained down to 0.094 *M*. These data can also be accommodated utilizing homoallylic intermediates I and II. This time, however, the rearrangement scheme is entered *via* radical II. The limiting olefin ratio at low aldehyde concentrations need not be the same as that for 3-methyl-4-pentenal, for the pair of chain-transfer rate constants for 2-methyl-4-pentenal should be slightly different.

Although 1-pentene and 3-methyl-1-butene constitute the preponderance of hydrocarbon products from 3-methyl- and 2-methyl-4-pentenal, trace quantities of *trans*- and *cis*-1,2-dimethylcyclopropane were also *tentatively* identified by their vapor-phase chromatographic retention times. This suggests that some form of substituted cyclopropylcarbinyl radicals, *e.g.*, classical radicals III, play at least a minor role in the decarbonylation process. Since the rearrangements under discussion are intramolecular, structural entities like III must be implicated in the minimum as transition states for the interconversion of homoallylic radicals I and II. Detection of 1,2-dimethylcyclopropane implies that cyclopropylcarbinyl-type radicals are, in fact, rearrangement intermediates. Although III cannot be rigorously placed along the rearrangement reaction coordinate by this type of argument alone, such a positioning is definitely reasonable. In an attempt to gain further experimental evidence concerning the intermediacy of cyclopropylcarbinyl-type radicals in homoallylic free radical rearrangements, the decarbonylations of 3-methyl-*trans*-4-hexenal and 2-methyl-*trans*-4-hexenal have been investigated.



III

Results

3-Methyl-*trans*-4-hexenal was synthesized by the thermal rearrangement of α,γ-dimethylallyl vinyl ether. Burgstahler has shown that this transformation proceeds stereospecifically.[5] α,γ-Dimethylallyl vinyl ether was prepared from 3-penten-2-ol and ethyl vinyl ether utilizing the mercuric acetate catalyzed vinyl transetherification procedure of Watanabe and Conlon.[6] 2-Methyl-*trans*-4-hexenal was obtained from α-methallyl propenyl ether, which was synthesized by propenyl transetherification[4] starting from α-methallyl alcohol and ethyl propenyl ether. The double bond geometry in 2-methyl-*trans*-4-hexenal was assigned and the complete absence of the *cis* isomer demonstrated employing the usual physical methods.

A 0.9 *M* solution of 3-methyl-*trans*-4-hexenal in diphenyl ether was decarbonylated at 140°. Di-*t*-butyl peroxide was added periodically to maintain a steady evolution of carbon monoxide. A volume of gas was eventually liberated which exceeded the theoretical yield of carbon monoxide. Presumably gaseous products from the initiator contaminated the carbon monoxide. Vapor-phase chromatographic (vpc) analysis of the liquid products showed that the major products were *trans*- and *cis*-2-hexene, 4-methyl-*trans*-2-pentene, and 4-methyl-*cis*-2-pentene. The ratio of hexenes to methylpentenes was about 10:1. *trans*-2-Hexene, *cis*-2-hexene, and a mixture of 4-methyl-*trans*-2-pentene and 4-methyl-*cis*-2-pentene were isolated and carefully characterized by their nuclear magnetic resonance (nmr) and infrared spectra. So little 4-methyl-*cis*-2-pentene was present that it could not be collected separately or unambiguously identified in the 4-methyl-2-pentene mixture. The retention-time behavior of the compound presumed to be 4-methyl-*cis*-2-pentene on four different chromatographic columns was exactly the same as an authentic sample, however. Attempts to detect trace quantities of *trans*- and *cis*-1-ethyl-2-methylcyclopropane among the products of 3-methyl-*trans*-4-hexenal were unsuccessful. The search for these compounds was hampered somewhat by the fact that an authentic sample of 1-ethyl-2-methylcyclopropane was not available.

Two experiments furnish evidence that the aldehyde and the reaction products are not isomerized under the reaction conditions. First, unreacted 3-methyl-*trans*-4-hexenal was recovered by vpc. No products possessing vpc retention times similar to that of the reactant were noted. The recovered aldehyde possessed nmr and infrared spectra which were identical with those of the starting material. In a second experiment the stability of the olefinic products was explored by placing 4-methyl-*cis*-2-pentene in a reaction mixture where *n*-hexaldehyde was decarbonylated under reaction conditions similar to those used for 3-methyl-*trans*-4-hexenal. 2-Hexene or 4-methyl-*trans*-2-pentene were not formed.

Comparison of the decarbonylation products from 3-methyl-*trans*-4-hexenal solutions of different concentrations revealed that the ratio of 2-hexene to 4-methyl-2-pentene and the ratio of *trans* and *cis* isomers in the latter compound were not the same for all concentrations. A series of solutions of 3-methyl-*trans*-4-hexenal in chlorobenzene, extending from ~6 *M* (neat) to 0.094 *M*, were prepared and decarbonylated at 129.6°. Di-*t*-butyl peroxide (20 mole %) was used as the initiator. Following the procedure developed previously,[4] reaction times were selected so that less

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(5) A. W. Burgstahler, *J. Am. Chem. Soc.*, **82**, 4681 (1960).

(6) W. H. Watanabe and L. E. Conlon, *ibid.*, **79**, 2828 (1957).

than 10% decarbonylation occurred. The partially decomposed solutions were analyzed by vpc, employing a 1,2,3-(2-cyanoethoxy)propane column and a propylene glycol–silver nitrate column in series or, alternatively, the two columns separately. Both methods were time consuming. Decarbonylation data for 3-methyl-*trans*-4-hexenal are recorded in Table I. The reproducibility of the olefin ratios, both within a run and from run to run, was good at high aldehyde concentrations. The limited amounts of 4-methyl-2-pentene that were formed at concentrations below 1.0 *M* made reliable ratios difficult or impossible to obtain.

Table I. Product Ratios from the Decarbonylation of 3-Methyl-*trans*-4-hexenal in Chlorobenzene at 129.6°[a]

Initial aldehyde concn, *M*	2-Hexene/ 4-methyl- 2-pentene	*trans*-2-Hexene/ *cis*-2-hexene	4-Methyl-*trans*- 2-pentene/ 4-methyl- *cis*-2-pentene
Neat (6 *M*)	5.6 ± 0.1	2.1 ± 0.2	5.7 ± 0.3
4.0	6.5 ± 0.1	2.4 ± 0.1	6.0 ± 0.5
3.0	7.1 ± 0.1	2.6 ± 0.1	5.0 ± 0.2
2.0	7.7 ± 0.2	2.5 ± 0.1	4.9 ± 0.1
1.5	8.1 ± 0.1	2.6 ± 0.1	4.6 ± 0.5
1.0	8.7 ± 0.2	2.5 ± 0.2	4.4 ± 0.3
0.75	9.1 ± 0.1	2.4 ± 0.2	3.1 ± 0.3
0.50	9.6 ± 0.1	2.4 ± 0.2	3.2 ± 0.3
0.38	9.8 ± 0.4	2.4 ± 0.2	*b*
0.25	10.4 ± 0.2	2.2 ± 0.2	*b*
0.19	10.2 ± 0.2	2.2 ± 0.2	*b*
0.12	9.6 ± 0.2	2.6 ± 0.3	*b*
0.094	9.2 ± 0.3	2.3 ± 0.1	*b*

[a] Error quoted as maximum expected error and is based on two to four separate analyses. [b] Too little olefins for reliable quantitative analysis.

Product studies were conducted on partially reacted 4.0 and 0.50 *M* 3-methyl-*trans*-4-hexenal solutions like those employed to collect the data in Table I. All major products that were detected by vpc were identified. A summary of the nontrivial reaction products is provided in Table II. Qualitatively the products are very similar to those from the extensive decarbonylation mentioned above. Note that at both concentrations the extent of decarbonylation is less than 10%, as desired. The 2,4-hexadiene isomers are presumably chain termination products.

Table II. Reaction Products from the Di-*t*-butyl Peroxide-Initiated Decarbonylation of 3-Methyl-*trans*-4-hexenal in Chlorobenzene at 129.6°

Reaction product[a]	Analyzed yield, % 4.0 *M* aldehyde	0.50 *M* aldehyde
4-Methyl-*trans*-2-pentene	0.4	0.6
4-Methyl-*cis*-2-pentene	0.1	0.2
trans-2-Hexene	2.2	5.0
cis-2-Hexene	0.9	2.1
trans-2,*trans*-4-Hexadiene	0.02	0.06
trans-2,*cis*-4-Hexadiene	0[b]	Trace
cis-2,*cis*-4-Hexadiene	0[b]	0[b]

[a] Identification by retention times only. [b] None detected. Product would have been detected if present to the extent of 0.01%.

The decarbonylation products of 2-methyl-*trans*-4-hexenal were found to be similar to those from the 3-methyl isomer. A study of the effect of initial aldehyde concentration on the distribution of olefins is reported in Table III. Product studies were performed on incompletely reacted 4.0 and 0.50 *M* 2-methyl-*trans*-4-hexenal solutions (Table IV).

Table III. Product Ratios from the Decarbonylation of 2-Methyl-*trans*-4-hexenal in Chlorobenzene at 129.6°[a]

Initial aldehyde concn, *M*	2-Hexene/ 4-methyl- 2-pentene	*trans*-2-Hexene/ *cis*-2-hexene	4-Methyl-*trans*- 2-pentene/ 4-methyl- *cis*-2-pentene
Neat	14.0 ± 0.1	4.2 ± 0.2	4.7 ± 0.2
4.0	13.4 ± 0.1	3.5 ± 0.1	*b*
3.0	12.7 ± 0.2	3.1 ± 0.2	4.7 ± 0.1
2.0	12.9 ± 0.1	3.1 ± 0.1	4.4 ± 0.2
1.5	12.8 ± 0.1	3.0 ± 0.1	*b*
1.0	12.2 ± 0.1	2.7 ± 0.1	*b*
0.75	12.2 ± 0.2	2.7 ± 0.0	4.8
0.50	11.8 ± 0.3	2.5 ± 0.2	*b*
0.38	12.0 ± 0.1	2.6 ± 0.1	4.4 ± 0.3
0.25	12.5 ± 0.2	2.6 ± 0.0	*c*
0.19	12.5 ± 0.1	2.5 ± 0.2	*c*
0.12	12.3 ± 0.4	2.5 ± 0.2	*c*
0.094	12.6 ± 0.2	2.5 ± 0.3	*c*

[a] Error quoted as maximum expected error and is based on two to four separate analyses. [b] Ratios not determined at all concentrations owing to the difficulty of analysis. [c] Too little olefins for reliable quantitative analysis.

Table IV. Reaction Products from the Di-*t*-butyl Peroxide-Initiated Decarbonylation of 2-Methyl-*trans*-4-hexenal in Chlorobenzene at 129.6°

Reaction product[a]	Analyzed yield, % 4.0 *M* aldehyde	0.50 *M* aldehyde
4-Methyl-*trans*-2-pentene	0.25	0.6
4-Methyl-*cis*-2-pentene	0.05	0.1
trans-2-Hexene	3.3	6.0
cis-2-Hexene	1.0	2.4
trans-2,*trans*-4-Hexadiene	0.04	0.1
trans-2,*cis*-4-Hexadiene	Trace	Trace
cis-2,*cis*-4-Hexadiene	0[b]	0[b]

[a] Identification by retention times only. [b] None detected. Product would have been detected if present to the extent of 0.01%.

Discussion

4-Methyl-*trans*-2-pentene, 4-methyl-*cis*-2-pentene, and *trans*- and *cis*-2-hexene were detected in each decarbonylation listed in Tables I and III, disclosing that carbon skeletal rearrangement and double bond isomerization transpired in every reaction which was carried out. Since the reactants and the products are not isomerized under the reaction conditions, both of the observed types of transformations must take place during the radical-chain decarbonylation sequence.

Focusing first on carbon skeletal rearrangement, it can be seen from Table I that the 2-hexene to 4-methyl-2-pentene ratio almost doubles as the 3-methyl-*trans*-4-hexenal concentration is reduced from 6 to 0.50 *M*. Although the olefin ratios below 0.50 *M* vary somewhat, it is doubtful that these variations are mechanistically significant. In this work, as well as previous studies,[4] it was noted that the scatter from run to run is bad at low aldehyde concentrations, being considerably greater than the precision limits of a single run. In any case, all of the ratios lie within a range of 9.8 ± 0.4. Neat 2-methyl-*trans*-4-hexenal yields 2-hexene and 4-methyl-2-pentene in a ratio of 14:1 (Table III). The ratio drops sharply as the aldehyde concentration is decreased, then levels off at a value of about 12.5:1. Qualitatively, the patterns of carbon skeletal rearrangement which are observed for the isomeric 4-hexenals are much like those which were found for 3-methyl- and 2-methyl-4-pentenal. An obvious basis for this parallelism would be that the rearrangements in the two series take place by way of similar reaction mechanisms. Hence, an analogous rearrangement scheme for 3-methyl-*trans*-4-hexenal and 2-methyl-*trans*-4-hexenal is proposed in Figure 1. In this proposal homoallylic intermediates IV and V (neglecting, for the moment, double bond geometry) are interconverted by vicinal propenyl group migration.

1-Ethyl-2-methylcyclopropane was not detected among the products of either 3-methyl-*trans*-4-hexenal or 2-methyl-*trans*-4-hexenal. A direct demonstration of the intervention of cyclopropylcarbinyl radicals, like VI, is thus lacking. Two points are worth noting in this regard. First, as was mentioned above, it is possible that 1-ethyl-2-methylcyclopropane escaped detection. Secondly, the absence of any cyclopropane-containing products is compatible with the finding that no methylcyclopropane or isopropylcyclopropane were detected in a study of the decarbonylations of cyclopropylacetaldehyde and cyclopropyldimethylacetaldehyde.[7]

Although direct evidence for substituted cyclopropylcarbinyl radicals is lacking, the double bond geometries of the olefinic products and the distribution of products as a function of the initial concentrations of 3-methyl-*trans*-4-hexenal and 2-methyl-*trans*-4-hexenal furnish excellent evidence in support of such intermediates. Furthermore, these data lend experimental support to the proposed role of the cyclopropylcarbinyl radicals (VI) in the rearrangement sequence. Consider the interconversion of homoallylic radicals $\mathrm{IV^T}$ and $\mathrm{V^T}$. Structure VI must in the very least function as a transition state for propenyl group migration. If no energy minimum existed along the pathway which converts radicals of carbon skeleton IV into those of carbon skeleton V, $\mathrm{IV^T}$ would be transformed into $\mathrm{V^T}$ with no change in double bond geometry and *vice versa.* Crossing from intermediates with *trans* double bonds to those with *cis* double bonds is observed experimentally, however, for all four olefinic products are obtained starting from either $\mathrm{IV^T}$ or $\mathrm{V^T}$. A straightforward way to account for these facts is to postulate that radicals such as VI are rearrangement *intermediates* (Figure 1). If rotation occurs about the single bond in VI that replaces the double bonds in $\mathrm{IV^T}$ and $\mathrm{V^T}$, any one of the radicals $\mathrm{IV^T}$, $\mathrm{IV^C}$, $\mathrm{V^T}$, and $\mathrm{V^C}$ can, in principle, be formed from VI.[8]

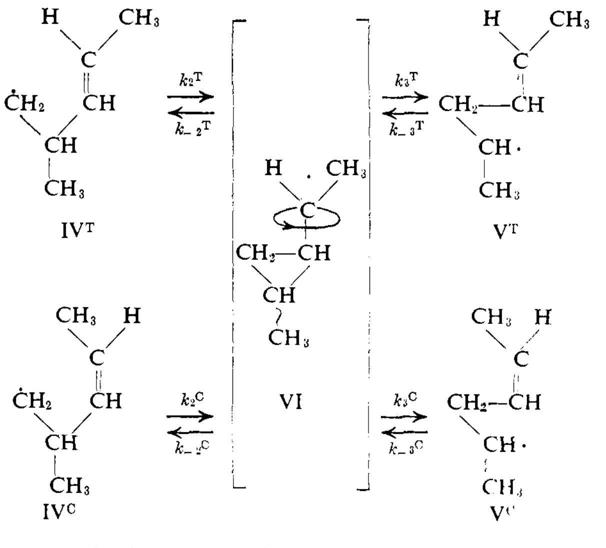

Figure 1. Key intermediates in the decarbonylations of 3-methyl-*trans*-4-hexenal and 2-methyl-*trans*-4-hexenal.

The *trans*-2-hexene to *cis*-2-hexene and 4-methyl-*trans*-2-pentene to 4-methyl-*cis*-2-pentene ratios in Tables I and III are highly compatible with this hypothesis. The ratio of *trans*- to *cis*-2-hexene from 3-methyl-*trans*-4-hexenal is constant within experimental error at all concentrations. This is consistent with the mechanism in Figure 1 in that all 2-hexene which is derived from $\mathrm{IV^T}$ must pass through VI. In contrast, the *trans* to *cis* ratio for 4-methyl-2-pentene decreases to almost to one-half its maximum value as the 3-methyl-*trans*-4-hexenal concentration is decreased from ~6 to 0.50 *M*. In terms of the proposed mechanism, this represents decreased trapping of $\mathrm{IV^T}$ as the aldehyde concentration is lowered. The ratio appears to be approaching a limiting value below 1.5 *M*, which it should if $\mathrm{IV^T}$, $\mathrm{IV^C}$, $\mathrm{V^T}$, and $\mathrm{V^C}$ are in equilibrium as suggested by the 2-hexene to 4-methyl-2-pentene ratios in this concentration range. It is unfortunate that the extreme difficulty in obtaining reliable *trans* to *cis* ratios for the more dilute solutions prohibits a clear-cut confirmation of this trend.

A number of other mechanisms are capable of yielding the data in Table I. For example, $\mathrm{IV^T}$ could rearrange directly to $\mathrm{IV^C}$ and $\mathrm{V^T}$ (both reversible). If $\mathrm{V^T}$ equilibrates rapidly with $\mathrm{V^C}$, the *trans*- to *cis*-2-hexene ratio would not be altered by changes in aldehyde concentration. Alternatively, $\mathrm{IV^T}$ could form $\mathrm{IV^C}$, $\mathrm{V^T}$, and $\mathrm{V^C}$ competitively (all reversible). Although these mechanisms are acceptable from the reaction kinetics point of view, they provide little insight as to why the double bond isomerizations occur.

Turning to the products from 2-methyl-*trans*-4-hexenal, Table III shows that here it is the ratio of 2-hexene isomers that changes, while the 4-methyl-2-pentene ratio remains constant. These data argue against the two alternative mechanisms outlined above. For the first mechanism to hold, $\mathrm{IV^C}$ and $\mathrm{IV^T}$ would have to interconvert rapidly at all 2-methyl-*trans*-4-hexenal concentrations but not at all 3-methyl-

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[7] D. I. Schuster, Ph.D. Thesis, California Institute of Technology, 1961.

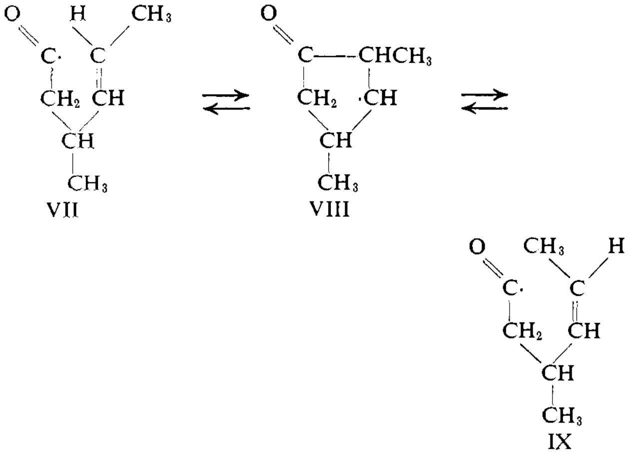
[8] Difficulties could arise in distinguishing between a transition state and a very short-lived intermediate. In general, any species which exists long enough[9] to undergo a limited amount of single bond rotation should be considerably longer lived than an activated complex.[10] In the specific case at hand the average lifetime of radical VI is orders of magnitude longer than presumed transition-state lifetimes,[10] if III's estimated 10^{-6}–10^{-8} sec lifetime[4] is at all realistic.

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

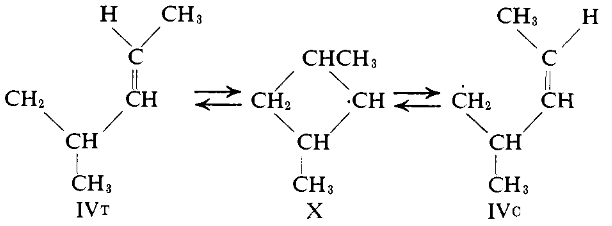
[10] S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p 189.

trans-4-hexenal concentrations. Also, the interconversion of V^T and V^C would have to be slow in the presence of the 2-methyl isomer and fast with the 3-methyl isomer. Restrictions of this kind are unreasonable. For the second mechanism to be operative, V^T and V^C would have to be formed from IV^T in very near their equilibrium concentrations. The same would be true for the production of IV^T and IV^C from V^T. Such compounded fortuity is unlikely. On the other hand, the products from 2-methyl-*trans*-4-hexenal harmonize nicely with the mechanism in Figure 1. The invariance of the 4-methyl-2-pentene ratios and the variance of the 2-hexene ratios complement the 3-methyl-*trans*-4-hexenal evidence supporting VI as a rearrangement intermediate. The limiting 2.5:1 value of the *trans*- to *cis*-2-hexene ratio below 1.0 *M* corresponds well to the equilibrium 2-hexene ratio for 3-methyl-*trans*-4-hexenal. The agreement of the constant 4.5:1 ratio for 4-methyl-2-pentene with the data in Table I is less satisfactory, though not alarming in view of the experimental difficulties encountered in obtaining reliable measurements below 1.0 *M*.

Two additional routes that might conceivably give rise to double bond isomerization during decarbonylation merit brief consideration. Acyl radical VII is in all likelihood an intermediate in the decomposition of 3-methyl-*trans*-4-hexenal. Cyclization of VII to VIII, followed by ring opening, leads to an acyl radical with a *cis* double bond (IX). This mechanism has some precedent in view of the facility[11] with which acyl radicals add to double bonds in intermolecular reactions.[12] It cannot by itself, however, satisfactorily account for the data in Table I. Among a variety of difficulties, the acyl radical cyclization mechanism would be expected to yield similar *trans* to *cis* ratios for 2-hexene and 4-methyl-2-pentene for each aldehyde concentration.


VII
VIII
IX

A second conceivable mode of isomerization involves the homoallylic radicals themselves. In addition to forming cyclopropylcarbinyl radical VI, IV^T could cyclize to cyclobutyl radical X, which in turn could give IV^C. Although it is known that the formation of cyclobutyl radicals from homoallylic radicals is not facile,[13] the most convincing argument against this mechanism is the fact that cyclobutyl radicals do not ring open under comparable reaction conditions.[7,13]


IV_T
X
IV_C

The results pertaining to olefin geometry in Tables I and III offer convincing evidence that substituted cyclopropylcarbinyl radicals are important intermediates in the decarbonylations of 3-methyl- and 2-methyl-*trans*-4-hexenal and, further, that these radicals lie along the rearrangement reaction coordinate. Since *trans*- and *cis*-1-ethyl-2-methylcyclopropane could not be detected, there is no hint as to whether *two* isomeric cyclopropylcarbinyl radicals are utilized in propenyl group migration. The experimental results require only one intermediate.

One consequence of adopting the mechanism in Figure 1 seems worth pointing out. An important feature of this mechanism is that rotation occurs about the single bond in VI that replaces the double bonds in IV^T and V^T. This implies that the chemical bonding in VI is essentially classical in nature. Although isomerization schemes involving nonclassical cyclopropylcarbinyl intermediates can be imagined, they are much more difficult to reconcile with the observed data.

The extent of carbon skeletal rearrangement at any given 3-methyl-*trans*-4-hexenal concentration is surprisingly similar to that which is found for 3-methyl-4-pentenal at the same concentration.[4] Such a likeness is also noted when the rearrangement products of 2-methyl-*trans*-4-hexenal and 2-methyl-4-pentenal are compared. The above parallelisms provide some indication as to how one important type of structure variation influences reactivity in a homoallylic free radical rearrangement. In the decarbonylations of both the methylhexenals and the methylpentenals, the observed double bond migrations interconvert primary and secondary radical centers. Moreover, the primary radicals (IV) and the secondary radicals (V) from the methylhexenals are very similar in structure to primary radical I and secondary radical II from the methylpentenals. Comparable pairs of chain-transfer rate constants for the two radical systems should bear a good quantitative resemblance to one another. In contrast, one way in which the systems do differ significantly is in the stability of their respective cyclopropylcarbinyl-type intermediates, III and VI. Secondary radical VI should be about 4 kcal/mole more stable (relative to the appropriate homoallylic radicals) than primary radical III.[14] This energy difference could in the limit make rate constants k_2 and k_{-3} of Figure 1 150 times larger than the corresponding rate constants for 1,2-vinyl

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[11] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp 273–278.

[12] A trace quantity of 3-methylcyclopentanone was detected among the decarbonylation products of 3-methyl-4-pentenal. A few brief attempts to convert γ,δ-unsaturated aldehydes to cyclopentanones at a lower temperature failed.

[13] (a) R. Breslow in "Molecular Rearrangements," Vol. I, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 293; (b) C. Walling and P. S. Fredricks, *J. Am. Chem. Soc.*, **84**, 3326 (1962).

[14] See ref 11, p 50.

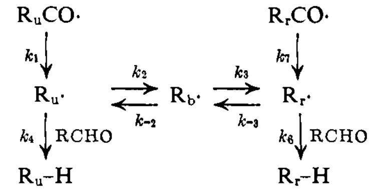

Figure 2. A general mechanistic scheme to account for the carbon skeletal rearrangements which accompany the decarbonylations of 3-methyl- and 2-methyl-*trans*-4-hexenal.

group migration. In view of the similarity of the rearrangement data for the methylhexenals and the methylpentenals, such a limiting case is most certainly not in operation.

A quantitative estimate can be made of the relative migratory aptitudes of propenyl groups and vinyl groups. If it is assumed that all $k_i^T = k_i^C$ in Figure 1, then the carbon skeletal rearrangements which take place during decarbonylation of the isomeric methylhexenals can be formalized as in Figure 2.[15] Acyl radical $R_uCO\cdot$ arises from 3-methyl-*trans*-4-hexenal, R_uCHO. Loss of carbon monoxide from $R_uCO\cdot$ yields a radical of unrearranged structure, $R_u\cdot$ (IV^T). IV^C is also designated $R_u\cdot$. Rearrangements from $R_u\cdot$ to radicals of rearranged structure, $R_r\cdot$ (V^T and V^C), proceed *via* substituted cyclopropylcarbinyl radicals, $R_b\cdot$. 4-Methyl-2-pentene, R_u–H, and 2-hexene, R_r–H, are obtained from $R_u\cdot$ and $R_r\cdot$, respectively. Decarbonylation of 2-methyl-*trans*-4-hexenal, R_rCHO, starts from R_rCO.

Provided that Figure 2 is an appropriate mechanistic model for rearrangement, the ratios of 4-methyl-2-pentene to 2-hexene from 3-methyl-*trans*-4-hexenal and 2-hexene to 4-methyl-2-pentene from 2-methyl-*trans*-4-hexenal are given[4] by eq 2 and 3. Additional u's and r's have been added to the subscripts of some

$$R_u\text{–}H/R_r\text{–}H = 2k_{4u}k_{-3}k_{-2} + k_{6u}k_{4u}(k_3 + k_{-2})[R_uCHO]/2k_{6u}k_3k_2 \quad (2)$$

$$R_r\text{–}H/R_u\text{–}H = 2k_{6r}k_3k_2 + k_{6r}k_{4r}(k_3 + k_{-2})[R_rCHO]/2k_{4r}k_{-3}k_{-2} \quad (3)$$

of the rate constants in order to indicate the aldehyde with which the rate constants are associated. Plots of R_u–H/R_r–H *vs.* the R_uCHO concentration and R_r–H/R_u–H *vs.* the R_rCHO concentration are shown in Figure 3 and 4. Both plots fit a linear relationship reasonably well at high aldehyde concentrations where the data are best. The rearrangement data are, therefore, at least compatible with the crude mechanism in Figure 2 and eq 2 and 3.

The slopes and the ordinate intercepts of the lines in Figure 3 and 4 can be used to estimate several different rate constant ratios, employing procedures outlined previously.[4] These ratios are recorded in Table V. Corresponding rate constant ratios for 3-methyl- and 2-methyl-4-pentenal are included for comparison. The most interesting comparisons are that k_2/k_{4u} and k_{-3}/k_{6r} are larger for the hexenals than for the pentenals. Since k_{4u} and k_{6r} should be about the same for the methylhexenals and the methylpentenals, k_2 and k_{-3} are probably larger for the hexenals. The striking thing, however, is that k_2 and k_{-3} are so similar in the two systems. Apparently the substantial difference in stability of the $R_b\cdot$ in the two rearrangement systems is not strongly felt in the transition states for ring closure. It is interesting in this connection that the magnitude of rate constants for the intermolecular addition of simple alkyl radicals to olefins does not depend markedly upon the stability of the radical which is formed upon addition.[16] A word of caution should be noted concerning the above rate constant comparisons. The k_2/k_{4u} and k_{-3}/k_{6r} ratios in Table V were obtained utilizing the assumption[4] that $k_3 = k_{-2}$. In actuality, k_3 is probably larger than k_{-2} in both systems,[4] if only by a small amount. Moreover, the difference between k_3 and k_{-2} is probably greatest for the hexenals, where the $R_b\cdot$ are more selective, secondary radicals. It is not necessary that k_3 be equal to k_{-2} in order to make k_2/k_{4u} or k_{-3}/k_{6r} comparisons. What is required is that k_3/k_{-2} be the same for both systems. If k_3/k_{-2} is larger for the hexenals than for the pentenals, the relative k_2/k_{4u} ratio of 77/59 in Table V is too large and the relative k_{-3}/k_{6r} ratio of 3.7/2.4 too small.

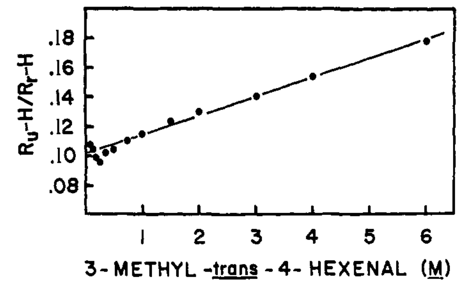

Figure 3. Plot of the ratio of 4-methyl-2-pentene, R_u–H, to 2-hexene, R_r–H, *vs.* the 3-methyl-*trans*-4-hexenal concentration.

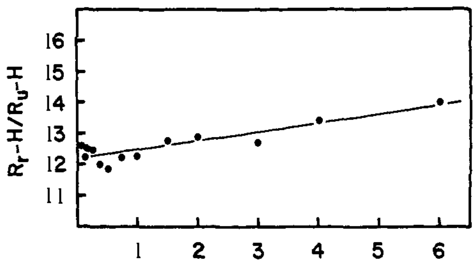

Figure 4. Plot of the ratio of 2-hexene, R_r–H, to 4-methyl-2-pentene, R_u–H, *vs.* the 2-methyl-*trans*-4-hexenal concentration.

Table V. A Comparison of Selected Rate Constant Ratios

	k_2/k_{4u}	k_{-3}/k_{6r}	k_{4r}/k_{4u}	k_{6r}/k_{6u}	k_4/k_6
3-Methyl-*trans*-4-hexenal	77		1.7	2.1	15
2-Methyl-*trans*-4-hexenal		3.7			12
3-Methyl-4-pentenal	59		2.5	2.7	16
2-Methyl-4-pentenal		2.4			15

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[15] The assumption that all $k_i^T = k_i^C$ would have to be justified in detail if subtle rate constant differences were being explored. The prime objective of this treatment is to obtain a semiquantitative estimate of relative migratory aptitudes of the two olefinic groups. For this purpose the assumption seems acceptable.

[16] (a) J. A. Kerr and A. F. Trotman-Dickenson, *Progr. Reaction Kinetics*, **1**, 117 (1961); (b) R. P. Buckley, R. Leavitt, and M. Szwarc, *J. Am. Chem. Soc.*, **78**, 5557 (1956); (c) R. P. Buckley and M. Szwarc, *ibid.*, **78**, 5696 (1956).

A number of chain-transfer rate constant comparisons are also listed in Table V. Ratios k_{4r}/k_{4u}, k_{6r}/k_{6u}, and k_4/k_6 are similar in the two systems, which is reasonable in view of the similarities in $R_u\cdot$, $R_r\cdot$, R_uCHO, and R_rCHO.

Experimental Section

General. Boiling points are uncorrected. Melting points were determined from samples in open capillary tubes employing a Büchi melting point apparatus. Nmr and infrared spectra were recorded routinely and are assumed to be in satisfactory agreement with authentic or predicted spectra when they are not explicitly discussed. The nmr spectra were obtained from dilute chloroform-d_1 or acetone-d_6 (2,4-dinitrophenylhydrazones) solutions using a Varian Associates A-60 spectrometer. The infrared spectra were obtained on a Perkin-Elmer Model 137 Infracord spectrometer. Preparative vpc was carried out using an Aerograph Autoprep, Model A-700, equipped with a 10-ft ($^3/_8$ in. o.d.) aluminum column packed with 30% Carbowax 20M on 60–80 mesh Chromosorb P. Quantitative vpc determinations were performed on an F & M Scientific Model 609 flame ionization gas chromatograph equipped with a Minneapolis-Honeywell recorder (Model V153-999) fitted with a Disc Instruments integrator. All of the columns used with the F & M instrument were stainless steel (8 ft, 0.25 in. o.d.) and employed a stationary support of 60–80 mesh Chromosorb P. The liquid phases that were used and their designations are: 20% 1,2,3-(2-cyanoethoxy)propane (TCEP); 20% Carbowax 20M (CAWX); 30% propylene glycol–silver nitrate (saturated) (PGSN). Microanalyses were obtained from Midwest Microlab, Inc., Indianapolis, Ind. 46226.

Specially Purified Materials. A. **Ethyl vinyl ether** (Eastman) was distilled, bp 35°, from sodium immediately prior to use.

B. **Reagent grade mercuric acetate** (Baker) was recrystallized from absolute ethanol and dried *in vacuo*.

C. **Di-t-butyl peroxide** was distilled, bp 55–56° (120 mm), immediately prior to use.

D. **Chlorobenzene** was purified by washing successively with concentrated sulfuric acid, 10% sodium carbonate solution, and distilled water. The chlorobenzene, so washed, was dried over anhydrous calcium chloride and distilled, bp 132°, from phosphorus pentoxide.

3-Methyl-*trans*-4-hexenal. α,γ-Dimethylallyl vinyl ether was prepared following vinyl transetherification method B of Watanabe and Conlon.[6] A solution consisting of 3-penten-2-ol (52.0 g, 0.60 mole), ethyl vinyl ether (259 g, 3.60 moles), and mercuric acetate (3.47 g, 10.9 mmoles) was refluxed for 6 hr at 36°. The reaction flask was protected from light. The reaction products were washed extensively with 5% sodium carbonate solution in order to remove 3-penten-2-ol, ethanol, and mercuric acetate. It was found that it was much easier to remove the 3-penten-2-ol by washing rather than by fractional distillation at some later stage. The washed product solution was dried over anhydrous calcium chloride (prolonged storage over calcium chloride resulted in a polymer formation). Diphenylamine was added to inhibit polymerization. Unreacted ethyl vinyl ether was removed by distillation. The residual material was distilled at atmospheric pressure.

Fractions within the boiling range 105–130° were sealed in a Pyrex ampoule without further purification and heated at 160° for 15 min. The resultant products were distilled, yielding 16.75 g (0.150 mole, 25% yield) of 3-methyl-*trans*-4-hexenal, bp 140° (lit.[5] bp 136–137°, 745 mm), $n^{25}D$ 1.4232 (lit.[5] $n^{25}D$ 1.4235), 2,4-dinitrophenylhydrazone mp 93.5–94° (lit.[5] 94–95°).

2-Methyl-*trans*-4-hexenal. Ethyl propenyl ether was prepared as described previously.[4] Ethyl propenyl ether (180.5 g, 2.10 moles), 3-buten-2-ol (75.6 g, 1.05 moles), mercuric acetate (15.0 g, 0.047 mole), and acetic acid (0.5 g, 0.008 mole) were combined and heated in a bath maintained at 74°. The reaction flask was protected from light. After 15 hr a 2-g sample was removed from the reaction flask, washed with 5% sodium carbonate solution, and dried over anhydrous calcium chloride. Nmr analysis of this sample indicated that the ratio of propenyl methyl protons to ethyl methylene protons had increased from 1.5:1 to 2.1:1. The reaction products were cooled, washed extensively with 5% sodium carbonate solution, and dried over anhydrous calcium chloride. Ethyl propenyl ether was removed by distillation. The residual products were fractionated. Material collected in the boiling range 130–150° was sealed in a Pyrex ampoule and heated at 170° for 1 hr. Final purification of 2-methyl-*trans*-4-hexenal was accomplished by preparative vpc (130°); 18.7 g (0.167 mole. 16% yield) of pure aldehyde was collected. bp 141°. $n^{25}D$ 1.4222. The 2,4-dinitrophenylhydrazone of 2-methyl-*trans*-4-hexenal was prepared,[17] mp 108–109°.

2-Methyl-*trans*-4-hexenal had characteristic aldehyde infrared absorption bands (neat film) at 2717 and 1724 cm^{-1}. The strong 1724-cm^{-1} absorption had a shoulder at 1675 cm^{-1}. A medium to strong band was present at 970 cm^{-1} (probably CH out of plane deformation for *trans* double bond), but there was no significant absorption near 690 cm^{-1} (absence of *cis*). The spectrum was acceptably clean above 3100 cm^{-1}. The nmr spectrum was in good agreement with the aldehyde's assigned structure and integrated well. The nmr spectrum consisted of a clean doublet (7 cps, 3 protons) at 1.07 ppm (tetramethylsilane, internal standard), a second multiplet (3 protons) centered at about 1.6 ppm which was essentially a doublet, complex absorption (3 protons) from 1.8 to 2.8 ppm, complex absorption (2 protons) from 5.0 to 6.0 ppm, and a doublet (∼1.5 cps, 1 proton) at 9.54 ppm. A reasonable attempt was made to obtain a good carbon–hydrogen analysis using chromatographed, vacuum-transfered aldehyde which appeared completely homogeneous on a variety of analytical vpc columns. An acceptable analysis was not obtained.

Decarbonylation of 3-Methyl-*trans*-4-hexenal. To a two-necked, round-bottomed flask fitted with a rubber septum and a reflux condenser which was connected in series to a Dry Ice–acetone trap and a gas buret was added 2.00 g (0.0178 mole) of 3-methyl-*trans*-4-hexenal and 20 ml of redistilled diphenyl ether. The reaction flask was placed in an oil bath maintained at 140° and allowed to come to thermal equilibrium. Di-*t*-butyl peroxide (1.30 g, 0.0178 mole) was added in small portions to initiate decarbonylation and to maintain a steady evolution of carbon monoxide. The reaction was halted after 418 cc of gas had been evolved. Reaction products from the reaction vessel and the Dry Ice trap were combined and subjected to vpc analysis (DIDP, 25–175°). The major products as identified by their vpc retention times were 4-methyl-*trans*-2-pentene, 4-methyl-*cis*-2-pentene, *trans*-2-hexene, *cis*-2-hexene, acetone, *t*-butyl alcohol, unreacted aldehyde, and unreacted peroxide. The olefins were formed in the relative yields of 4.45:1.00:33.4:6.55, respectively. *trans*-2-Hexene, *cis*-2-hexene, and a mixture of 4-methyl-*trans*-2-pentene and 4-methyl-*cis*-2-pentene were collected by vpc. The nmr and infrared spectra of the 2-hexenes were identical with those of authentic samples. The 4-methyl-2-pentenes were only available in a limited quantity and could not be characterized individually. Spectra of the mixture looked very much like 4-methyl-*trans*-2-pentene. Retention time behavior of the 4-methyl-2-pentenes on four different vpc columns (Table VI) left little doubt that both the *trans* and *cis* isomers were present. Unreacted 3-methyl-*trans*-4-hexenal was isolated by vpc and was found to have infrared and nmr spectra identical with those of the starting aldehyde. No other products were present in the 3-methyl-*trans*-4-hexenal portion of the chromatogram.

Table VI. Relative Retention Times of Olefinic Products

Column	Temp, °C	4-Methyl-2-pentene *cis*	*trans*	2-Hexene *cis*	*trans*
TCEP	25	1.00	1.00	1.57	1.42
DIDP	0	1.00	1.07	1.90	1.73
PGSN	47	2.02	1.00	2.84	1.24
TCEP + PGSN	47	1.71	1.00	2.49	1.29

Decarbonylation of *n*-Hexaldehyde with 4-Methyl-*cis*-2-pentene Added. *n*-Hexaldehyde (2.00 g, 0.020 mole), di-*t*-butyl peroxide 0.585 g, 0.004 mole), and 4-methyl-*cis*-2-pentene were combined and diluted to a total volume of 5.00 ml with chlorobenzene. The solution was heated in a sealed Pyrex ampoule at 130° for 30 min, cooled, opened, and analyzed by vpc (DIDP, 0°). The analysis did not detect any formation of 4-methyl-*trans*-2-pentene, *trans*-2-hexene, or *cis*-2-hexene.

Olefin Ratios. The general procedure for determining olefin ratios at selected aldehyde concentrations has been outlined pre-

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(17) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed, John Wiley and Sons, Inc., New York, N. Y., p 219.

viously.[4] All decarbonylations were carried out at 129.6 ± 0.1° using chlorobenzene as the solvent. The relative amounts of *trans*-2-hexene, *cis*-2-hexene, and the sum of 4-methyl-*trans*-2-pentene and 4-methyl-*cis*-2-pentene could be conveniently determined employing the TCEP column (30°). The *trans*- to *cis*-4-methyl-2-pentene ratio was determined separately on the PGSN column (26°). Alternatively, the two columns could be connected in series to resolve all four components (47°). The detector responses of the four olefins were the same within experimental error, so that the integrated peak areas could be compared directly. All the necessary precautions[4] were taken in order to obtain reproducible data. The aldehyde solutions were heated for varying lengths of time, depending upon their concentrations. The reaction periods used were: 6–4.0 *M*, 20 min; 3.0 *M*, 25 min; 2.0 *M*, 30 min; 1.5 *M*, 35 min; 1.0 *M*, 45 min; 0.75 *M*, 60 min; 0.50–0.38 *M*, 90 min; 0.25–0.094 *M*, 120 min. The products from 3-methyl- and 2-methyl-*trans*-4-hexenal (Tables II and IV) show that less than 10% decarbonylation occurred in the 4.0 and 0.50 *M* solutions. Additionally, it was shown that aldehyde solutions could be heated twice as long as the reaction periods listed above without significantly changing the olefin ratios obtained.

Product Studies. The decarbonylation reaction products of 3-methyl- and 2-methyl-*trans*-4-hexenal were investigated employing the reaction conditions used in the study of the relationship between olefin ratios and initial aldehyde concentrations. Solutions (4.0 and 5.0 *M*) of both aldehydes were prepared and decarbonylated following the procedure outlined under Olefin Ratios. So little products were formed that it was necessary to characterize the various products by their retention times alone. Trace components were identified by peak augmentation with presumed products. A precisely weighed quantity of methylcyclohexane was added as an internal standard to each of the product solutions in order to determine the yield of products. The results of the analyses are reported in Tables II and IV. Acetone, *t*-butyl alcohol, di-*t*-butyl peroxide, and unreacted aldehyde were present in substantial quantities, but were not included in the tables.

The Photocycloaddition of Fluorenone to Ketenimines

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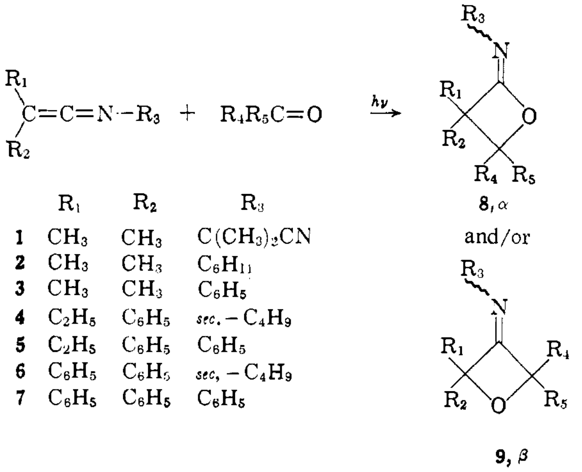
Abstract: The facile photocycloaddition of fluorenone across the carbon–carbon double bond of six ketenimines to give α-iminooxetanes (**8**) is described. Isomerization of the α adducts to β lactams has been observed. The use of mass spectroscopy in structural elucidation of the α adducts and β lactams and previously reported β adducts (**9**) is described in some detail. The relative rates of photocycloaddition of fluorenone to dimethyl-N-(cyclohexyl)- (**2**), dimethyl-N-(phenyl)- (**3**), ethylphenyl-N-(*sec*-butyl)- (**4**), ethylphenyl-N-(phenyl)- (**5**), diphenyl-N-(*sec*-butyl)- (**6**), and diphenyl-N-(phenyl)ketenimine (**7**) are within a factor of 4 of each other. The absence of a reactivity spread throughout this series suggests that energy transfer from triplet fluorenone to ground-state ketenimine is not competitive with photocycloaddition as was the case with the previously studied benzophenone–ketenimine system. The possible importance of dipole–dipole interactions between ground-state ketenimine and the electronically excited carbonyl compound in influencing the direction of cycloaddition is considered.

Recently, we described the photoinduced cycloaddition of aldehydes and ketones to ketenimines **1–7** to give iminooxetanes of α (**8**) or β (**9**) structure.[1,2] This reaction is an extension of the well-known Paterno–Büchi reaction in which aldehydes and ketones undergo photocycloaddition with simple olefins to give oxetanes.[3–7]



8, α

9, β

	R1	R2	R3
1	CH_3	CH_3	$C(CH_3)_2CN$
2	CH_3	CH_3	C_6H_{11}
3	CH_3	CH_3	C_6H_5
4	C_2H_5	C_6H_5	*sec.*–C_4H_9
5	C_2H_5	C_6H_5	C_6H_5
6	C_6H_5	C_6H_5	*sec*, –C_4H_9
7	C_6H_5	C_6H_5	C_6H_5

We[1] and others[6,7] have pointed out two important reactivity features of the Paterno–Büchi reaction involving olefins and ketenimines: (i) that there is correlation with the photoreduction reaction[8] to the extent that carbonyl compounds with n–π* triplet states are more reactive than those with π–π* triplet states[8,9] and (ii) that energy transfer from the triplet carbonyl compound to ground-state olefin or ketenimine is competitive with cycloaddition when the triplet level of the carbonyl compound is higher than that of the olefin or ketenimine. The first condition is demonstrated by the decreased reactivity of 2-acetonaphthone and 1-naphthaldehyde (π–π* triplet states[8]) toward olefins[6,7] and ketenimines[1a] and the second by the absence of oxetane formation when benzophenone is irradiated in the presence of dienes ($E_t \sim 60$ kcal/

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[1] (a) L. A. Singer and P. D. Bartlett, *Tetrahedron Letters*, 1887 (1964); (b) L. A. Singer and G. A. Davis, *J. Am. Chem. Soc.*, **89**, 598 (1967).

[2] The question of *syn–anti* isomers in these adducts is not yet resolved.

[3] E. Paterno and G. Chieffi, *Gazz. Chim. Ital.*, **39**, 341 (1909).

[4] G. Büchi, C. G. Inman, and E. S. Lipinsky, *J. Am. Chem. Soc.*, **78**, 876 (1956).

[5] J. F. Harris, Jr., and D. D. Coffman, *ibid.*, **84**, 1153 (1962).

[6] D. R. Arnold, R. L. Hinman, and A. H. Glick, *Tetrahedron Letters*, 1425 (1964).

[7] N. C. Yang, M. Nussim, M. J. Jorgenson, and S. Murov, *ibid.*, 3657 (1964).

[8] G. S. Hammond and P. A. Leermakers, *J. Am. Chem. Soc.*, **84**, 207 (1962).

[9] L. H. Piette, J. H. Sharp, T. Kuwana, and J. N. Pitts, Jr., *J. Chem. Phys.*, **36**, 3094 (1962).