

Homoallylic Free Radical Rearrangements. I.

The Di-*t*-butyl Peroxide-Initiated Decarbonylations of 3-Methyl-4-pentenal and 2-Methyl-4-pentenal¹

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Abstract: The principal hydrocarbon product from the di-*t*-butyl peroxide initiated decarbonylation of 3-methyl-4-pentenal in chlorobenzene at 129.6° was 1-pentene, an olefin of rearranged carbon skeleton. 3-Methyl-1-butene, the simple decarbonylation product, was formed in low yield. Under comparable reaction conditions 2-methyl-4-pentenal afforded a similar mixture of 1-pentene and 3-methyl-1-butene. Trace quantities of components possessing vapor-phase chromatography retention times identical with those of *trans*- and *cis*-1,2-dimethylcyclopropane were detected among the reaction products of both aldehydes. 1-Pentene/3-methyl-1-butene ratios, which were found to vary with initial aldehyde concentration, were determined for chlorobenzene solutions (about 6 *M* to 0.094 *M*) of 3-methyl-4-pentenal and 2-methyl-4-pentenal that were carried to only a few per cent reaction. The relationship of the olefin ratios so obtained to conceivable rearrangement mechanisms is discussed. A detailed reaction mechanism is proposed in which the decarbonylations and accompanying rearrangements of the two aldehydes proceed in part through common free radical intermediates. In this mechanism 1-pentene and 3-methyl-1-butene are formed from classical homoallylic radicals. These intermediates are interconverted by 1,2-vinyl group migration *via* short-lived (2-methylcyclopropyl)carbonyl radicals (both *trans* and *cis* isomers) of, as yet, unknown bonding type. General expressions for relating decarbonylation products and initial aldehyde concentrations are derived and discussed.

A substantial number of free radical rearrangements have been reported in recent years.^{4,5} Nevertheless, the scope of free radical rearrangements has not been clearly delineated, and there have been surprisingly few detailed studies of radical rearrangement mechanisms. Investigations pertaining to aryl group migrations represent a notable exception.⁶ Vicinal migrations of double bonds (homoallylic rearrangements) *via* both cationic⁷ and anionic⁸ pathways are well established. Studies dealing with homoallylic free radical rearrangements are few in number. Slaugh, Mullineaux, and Raley⁹ invoked 1,2-vinyl shifts to rationalize the carbon skeletal rearrangements which take place during the conversion of olefins to alkylbenzenes by iodine in the vapor phase at 450–500°. In support of their hypothesis they detected a small amount of a material possessing a vapor-phase chromatography retention time identical with that of a crucial intermediate. In 1964 we reported several well-defined vicinal migrations of double bonds in free radical reactions.^{1b} Slaugh¹⁰ has recently observed the rearrangement of the

Δ^2 -cyclopentenylmethyl radical to the 4-cyclohexenyl radical. Patel, Hamilton, and Roberts¹¹ have suggested that homoallylic radical rearrangements occur during the preparation of Grignard reagents from cyclopropylcarbonyl or allylcarbonyl halides. The purpose of this paper is to relate the experimental details and discuss selected mechanistic features of the homoallylic rearrangements which take place during the di-*t*-butyl peroxide-initiated decarbonylations of 3-methyl-4-pentenal and 2-methyl-4-pentenal.^{1b}

Early comparisons of the reactions of carbonium ions and structurally corresponding free radicals indicated that alkyl group migrations rarely, if ever, occurred in radical reactions. As future comparisons were made, the generality of this conclusion was questioned. Most of the controversy centered around reported radical rearrangements where the reaction mechanism was not known with certainty or where polar side reactions might have given rise to rearranged products.¹² Walling has critically reviewed the free radical rearrangement literature.⁴ No *bona fide*, thermally promoted, intramolecular 1,2 shifts of alkyl groups have been observed in radical reactions carried out in the range room temperature to 200°. A number of alkyl radical rearrangements do occur at higher temperatures but appear to be adequately formulated in terms of an elimination–addition mechanism.⁴ The remarkable difference in migration tendencies that alkyl groups display in carbonium ion and free radical reactions has been rationalized in terms of simple molecular orbital theory.¹³ It has been argued that the

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(2) National Institutes of Health Predoctoral Fellow, 1964–1966.

(3) National Science Foundation Undergraduate Research Participant, 1964–1965.

(4) C. Walling in "Molecular Rearrangements," Vol. I, P. DeMayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp 407–455.

(5) R. K. Freidlina, V. N. Kost, and M. Ya. Khorlina, *Russ. Chem. Rev.*, **31**, 1 (1962).

(6) For a summary of the research on vicinal aryl migrations see ref 4, pp 409–416.

(7) (a) J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 2509 (1951); (b) R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver, and J. D. Roberts, *ibid.*, **81**, 4390 (1959); (c) K. L. Servis and J. D. Roberts, *ibid.*, **86**, 3773 (1964).

(8) M. S. Silver, P. R. Shafer, J. E. Nordlander, C. Rüchardt, and J. D. Roberts, *ibid.*, **82**, 2646 (1960).

(9) L. H. Slaugh, R. D. Mullineaux, and J. H. Raley, *ibid.*, **85**, 3180 (1963).

(10) L. H. Slaugh, *ibid.*, **87**, 1522 (1965).

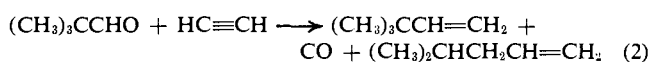
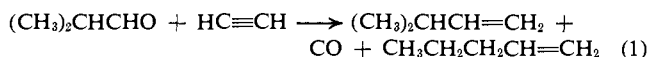
(11) D. J. Patel, C. L. Hamilton, and J. D. Roberts, *ibid.*, **87**, 5144 (1965).

(12) The historical development of this problem is summarized in ref 4.

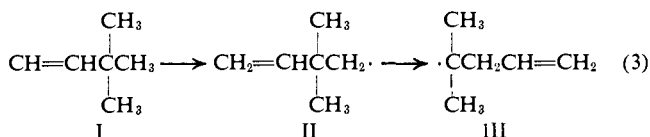
(13) (a) J. deHeer, as quoted by S. J. Cristol and G. D. Brindell, *J. Am. Chem. Soc.*, **76**, 5699 (1954); (b) H. E. Zimmermann and Z. Zweig, *ibid.*, **83**, 1196 (1961); (c) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, pp 380–384.

vicinal rearrangement of alkyl groups in radical reactions should be difficult relative to corresponding carbonium ion processes since the additional electron that a free radical possesses must be placed in an antibonding orbital in the rearrangement transition state.

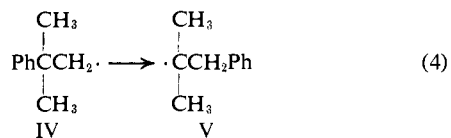
In light of the experimental and theoretical objections to alkyl group migrations in radical reactions, it was noteworthy when Dominguez and Trotman-Dickenson¹⁴ reported two novel gas phase rearrangements in 1962. They found that 1-pentene and 4-methyl-1-pentene accompany the formation of 3-methyl-1-butene and 3,3-dimethyl-1-butene, respectively, when isopropyl and *t*-butyl radicals (generated by the decarbonylation of isobutyraldehyde and pivalaldehyde) were added to acetylene at 100–200° (eq 1, 2). Isom-



erization of isopropyl radicals or *t*-butyl radicals under similar reaction conditions has not been reported.¹⁵ Dominguez and Trotman-Dickenson postulated that the rearranged products could only be formed if a methyl group migrated concomitantly with or subsequent to the addition step, although they offered no detailed mechanism for the isomerizations. A rearrangement pathway which seemed mechanistically reasonable to us¹⁶ and which does not involve methyl migration is presented in eq 3. Vinyl radical I is formed by the addition of a *t*-butyl radical to acetylene and un-



dergoes successively an intramolecular hydrogen atom transfer (I → II) and a homoallylic rearrangement (II → III). Cyclic hydrogen atom transfers are common, although they generally take place by way of six-membered transition states.^{4,5,17} The homoallylic rearrangement is analogous to the familiar rearrangement⁴ (IV → V) of the neophyl radical (IV) and should not be unfavorable in terms of chemical bonding since



the unpaired electron can be conveniently accommodated by a rearrangement transition state approximating the structure of a cyclopropylcarbinyl radical. The attractiveness of interpreting the Dominguez and Trotman-Dickenson rearrangements in terms of homoallylic rearrangements prompted us to assess in some detail

(14) J. A. G. Dominguez and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 940 (1962).

(15) J. A. Kerr and A. F. Trotman-Dickenson, *Progr. Reaction Kinetics*, **1**, 105 (1961).

(16) Slauch, Mullineaux, and Raley⁹ have also discussed the possibility of 1,2-vinyl shifts in these reactions.

(17) (a) J. W. ApSimon and O. E. Edwards, *Can. J. Chem.*, **40**, 896 (1962); (b) W. L. Meyer and A. S. Levinson, *Proc. Chem. Soc.*, 15 (1963); (c) R. F. C. Brown, *Australian J. Chem.*, **17**, 47 (1964); (d) D. H. R. Barton and J. R. Hanson, *Chem. Commun.*, 117 (1965).

the possibility of carrying out this type of reaction under less ambiguous circumstances.

Although the literature that explicitly pertains to homoallylic radical rearrangements is meager, a number of related studies provide considerable insight into the feasibility of achieving such rearrangements. For the purpose of discussion, it is convenient to regard 1,2-vinyl shifts as taking place by way of a two-step sequence, (1) ring closure of an allylcarbinyl radical to form a cyclopropylcarbinyl radical and (2) ring opening of the radical so formed to yield an allylcarbinyl radical of rearranged structure. The utility of such a formalization will depend upon whether cyclopropylcarbinyl radicals are actually rearrangement intermediates and/or whether the rearrangement transition state resembles a cyclopropylcarbinyl radical.

Information concerning the ring-closure reactions of simple, acyclic allylcarbinyl radicals is very limited. The thermal decomposition of *t*-butyl 5,5-diphenylperpent-4-enoate in chlorobenzene at 110° in the presence of tri-*n*-butyltin hydride affords a mixture of diphenylcyclopropylmethane (about 5%) and 1,1-diphenylbutene.¹⁸ The ratio of the two products is not significantly changed by a tenfold decrease in the tin hydride concentration. Traces (less than 0.25%) of methylcyclopropane and isopropylcyclopropane have been detected in the tri-*n*-butyltin hydride reductions of allylcarbinyl bromide and γ,γ -dimethylallylcarbinyl bromide.¹⁹ These reductions are presumably free radical in nature.²⁰

Examples of cyclizations of allylcarbinyl radicals in semirigid systems are more plentiful. For example, nortricyclene or substituted nortricyclenes are frequently observed as products from homoallylic bicyclo[2.2.1]heptenyl radical systems.²¹ It is not clear how much bearing such observations have on the question of the general feasibility of homoallylic rearrangements, however, for it is known that nortricyclene is slightly more stable than norbornene at the two compounds' reflux temperature.²² In contrast the heat of isomerization of propylene to cyclopropane is endothermic by about 8 kcal/mole.²³

The rearrangement of simple cyclopropylcarbinyl radicals is facile. Decarbonylation of cyclopropylacetaldehyde affords 1-butene as the sole hydrocarbon product.^{24,25} Similarly, cyclopropyldimethylacetaldehyde yields only 2-methyl-2-pentene.²⁵ When this decarbonylation is carried out in the presence of thio-

(18) (a) J. D. Roberts, Abstracts, 141st National Meeting of the American Chemical Society, Washington, D. C., March 1962, p 8-O; (b) M. E. H. Howden, Ph.D. Thesis, California Institute of Technology, 1962.

(19) A. J. Rosen, Ph.D. Thesis, California Institute of Technology, 1964.

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

(21) (a) D. J. Trecker and J. P. Henry, *ibid.*, **85**, 3204 (1963); (b) N. O. Brace, *J. Org. Chem.*, **27**, 3027 (1962); (c) S. J. Cristol, G. D. Brindell, and J. A. Reeder, *J. Am. Chem. Soc.*, **80**, 635 (1958); (d) S. J. Cristol and D. I. Davies, *J. Org. Chem.*, **29**, 1282 (1964); (e) M. M. Martin and D. C. De Jongh, *J. Am. Chem. Soc.*, **84**, 3526 (1962); (f) J. W. Wilt and A. A. Levin, *J. Org. Chem.*, **27**, 2319 (1962); (g) E. S. Huyser and G. Echeagaray, *ibid.*, **27**, 429 (1962); (h) S. J. Cristol, T. W. Russell, and D. I. Davies, *ibid.*, **30**, 207 (1965).

(22) P. von R. Schleyer, *J. Am. Chem. Soc.*, **80**, 1700 (1958).

(23) J. W. Knowlton and F. D. Rossini, *J. Res. Natl. Bur. Std.*, **43**, 113 (1949).

(24) W. H. Urry, D. J. Trecker, and H. D. Hartzler, *J. Org. Chem.*, **29**, 1663 (1964).

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

phenol, isopropylcyclopropane (18%) is obtained in addition to 2-methyl-2-pentene.²⁵ The free radical chlorination of methylcyclopropane yields both cyclopropylcarbinyl chloride and allylcarbinyl chloride, the ratio of the two monochlorination products being determined by a number of experimental variables.^{7a,26} Cyclopropylacetyl peroxide gives rise to cyclopropylcarbinyl cyclopropylacetate (56%) upon thermal decomposition in carbon tetrachloride.²⁷ It is likely, however, that all or a portion of the ester is formed by nonradical processes.²⁸ Radical chain additions of carbon tetrachloride or bromotrichloromethane to 2-cyclopropylpropene or vinylcyclopropane yield ring-opened addition products.²⁹ Thiophenol adds to 2-cyclopropylpropene giving 1-thiophenoxy-2-cyclopropylpropane, and methanethiol adds to the same olefin producing 1-methylthio-2-methyl-2-pentene and 1-methylthio-2-cyclopropylpropane.^{29a} The ratio of former compound to the latter decreased as the ratio of methanethiol to olefin was increased. 2,2'-Azobis-2-cyclopropylpropionitrile decomposes in hexane to yield *sym*-dimethyldicyclopropylsuccinonitrile (19%), 1-methylcyclopenten-5-one azine (7.3%), and polymer.³⁰

It would appear from the above summary that if 1,2 double bond migrations are to occur with any generality in acyclic systems, that the major question is whether allylcarbinyl radicals can cyclize to cyclopropylcarbinyl radicals and not whether the latter species can open to give rearranged radicals. In order to ascertain whether or not vicinal migrations of double bonds could be observed in a typical radical chain reaction in solution, the di-*t*-butyl peroxide-initiated decarbonylation reactions of 3-methyl-4-pentenal and 2-methyl-4-pentenal have been investigated. Winstein and Seibold³¹ first introduced this method of generating free radicals in their study of the neophyl radical rearrangement. The method has subsequently been employed to introduce radical centers at predetermined positions in molecules in a host of free radical investigations.

Results

3-Methyl-4-pentenal was synthesized by the thermal rearrangement of crotyl vinyl ether.³² The vinyl ether was conveniently prepared from ethyl vinyl ether and crotyl alcohol employing the mercuric acetate catalyzed vinyl transesterification procedure of Watanabe and Conlon.³³ This method was modified in order to prepare 2-methyl-4-pentenal. Ethyl propenyl ether enters into transesterification with allyl alcohol to yield allyl propenyl ether, although the reaction is somewhat sluggish. Allyl propenyl ether rearranges smoothly at 150° affording 2-methyl-4-pentenal.

(26) (a) H. C. Brown and M. Borkowski, *J. Am. Chem. Soc.*, **74**, 1894 (1952); (b) E. Renk, P. R. Shafer, W. H. Graham, R. H. Mazur, and J. D. Roberts, *ibid.*, **83**, 1987 (1961).

(27) (a) H. Hart and D. P. Wyman, *ibid.*, **81**, 4891 (1959); (b) H. Hart and R. A. Cipriani, *ibid.*, **84**, 3697 (1962).

(28) F. D. Greene, H. P. Stein, C. Chu, and F. M. Vane, *ibid.*, **86**, 2080 (1964).

(29) (a) E. S. Huyser and J. D. Taliaferro, *J. Org. Chem.*, **28**, 3442 (1963); (b) E. S. Huyser and L. R. Munson, *ibid.*, **30**, 1436 (1965).

(30) C. G. Overberger, M. Tobkes, and A. Zweig, *ibid.*, **28**, 620 (1963).

(31) S. Winstein and F. H. Seibold, Jr., *J. Am. Chem. Soc.*, **69**, 2916 (1947).

(32) R. F. Webb, A. J. Duke, and J. A. Parsons, *J. Chem. Soc.*, 4092 (1961).

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

Preliminary decarbonylation experiments with 3-methyl-4-pentenal showed that 40–70% of the stoichiometric quantity of carbon monoxide was liberated during 4–8-hr reaction. Diphenyl ether was used as the solvent in several early experiments. Chlorobenzene was employed in all subsequent studies. In a typical decarbonylation reaction, a 4.0 *M* solution of 3-methyl-4-pentenal (diphenyl ether, 20 mole % di-*t*-butyl peroxide) liberated 43% of the stoichiometric quantity of carbon monoxide in 359 min. Initial evolution of carbon monoxide was actually quite vigorous. The virtually exclusive hydrocarbon products from this reaction were 1-pentene and 3-methyl-1-butene, formed in the ratio of 10.8:1. The olefin of rearranged structure, 1-pentene, was isolated and unequivocally identified by physical methods. 3-Methyl-1-butene was added to a reaction mixture in which *n*-hexaldehyde was decarbonylated under comparable reaction conditions. No 1-pentene was produced, strongly implying that 3-methyl-1-butene is not isomerized to 1-pentene during the decarbonylation of 3-methyl-4-pentenal. A similar experiment showed that 1-pentene is not converted to 3-methyl-1-butene. Unreacted 3-methyl-4-pentenal was collected from the crude reaction products using vapor phase chromatography (vpc) and possessed nuclear magnetic resonance (nmr) and infrared spectra which were identical with those of the starting aldehyde. No other major reaction products were noted in the 3-methyl-4-pentenal portion of the vapor-phase chromatogram.

The ratio of 1-pentene to 3-methyl-1-butene was found to be a function of the initial 3-methyl-4-pentenal concentration. For a given initial aldehyde concentration, the ratio of olefins was invariant (within experimental error) through the first 10% of reaction. Characteristic, low-conversion ratios were determined for a series of aldehyde concentrations ranging from neat aldehyde (about 6 *M*) to 0.094 *M* aldehyde. 1-Pentene to 3-methyl-1-butene ratios could be conveniently measured by vpc even at the lowest aldehyde concentrations. The ratios are recorded in Table I. Re-

Table I. Olefin Ratios for the Decarbonylation of 3-Methyl-4-pentenal in Chlorobenzene at 129.6°

Aldehyde concn, <i>M</i>	1-Pentene/3-methyl-1-butene ^a	
	Run 1	Run 2
Neat ^b	4.7 ± 0.1	5.1 ± 0.1
4.0	5.4 ± 0.1	5.4 ± 0.1
3.0	6.4 ± 0.2	6.4 ± 0.2
2.0	6.9 ± 0.3	6.9 ± 0.2
1.5	7.4 ± 0.1	7.6 ± 0.1
1.0	7.7 ± 0.1	7.7 ± 0.1
0.75	8.5 ± 0.1	8.0 ± 0.1
0.50	8.3 ± 0.1	7.8 ± 0.1
0.38	9.1 ± 0.2	8.5 ± 0.1
0.25	8.6 ± 0.1	8.6 ± 0.1
0.19	12.0 ± 0.1	9.1 ± 0.1
0.12	9.8 ± 0.4	8.7 ± 0.1
0.094	10.1 ± 0.1	8.5 ± 0.7

^a Error quoted as maximum expected error based on two to four separate analyses. ^b At 6 *M* concentration.

producibility from run to run was satisfactory over the entire concentration range and was particularly good at high 3-methyl-4-pentenal concentrations. Poor re-

Table II. 1-Pentene to 3-Methyl-1-butene Ratios before and after Decarbonylation of *n*-Valeraldehyde

<i>n</i> -Valeraldehyde Concn, <i>M</i> ^b	1-Pentene/3-methyl-1-butene	
	Before	After
4.0	4.78	4.81
	9.56	9.44
	9.43	9.58
0.50	4.82	4.88
	9.50	9.60
	9.48	9.54

^a At 130°. ^b In Chlorobenzene solvent.

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

Reaction product ^a	Analyzed yield, %	
	4.0 <i>M</i> aldehyde	0.50 <i>M</i> aldehyde
3-Methyl-1-butene	0.3	0.9
1-Pentene	1.4	7.1
2-Pentene	0 ^c	0 ^c
<i>trans</i> - and <i>cis</i> -1,2-dimethyl- cyclopropane	0.02 ^b	0.08 ^b
<i>trans</i> -1,3-Pentadiene	0 ^c	0 ^c
<i>cis</i> -1,3-Pentadiene	0 ^c	0 ^c
2-Methyl-4-pentenal	0 ^d	0 ^d

^a Identification by retention times only. ^b Isomers approximately 1:1. ^c None detected. Product would have been detected if present to the extent of 0.01%. ^d None detected. Product would have been detected if present to the extent of 1%.

Table IV. Olefin Ratios for the Decarbonylation of 2-Methyl-4-pentenal in Chlorobenzene at 129.6°

Aldehyde concn, <i>M</i>	1-Pentene ^a / 3-methyl- 1-butene	Aldehyde concn, <i>M</i>	1-Pentene/ 3-methyl- 1-butene
Neat ^b	12.5	0.50	10.7
4.0	11.8	0.38	9.8
3.0	10.9	0.25	10.0
2.0	10.3	0.19	10.1
1.5	10.0	0.12	10.0
1.0	10.0	0.094	10.0
0.75	10.0		

^a Generally the average of two or more determinations. Maximum expected errors comparable to those in Table I. ^b At 6 *M* concentration.

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

Reaction product ^a	Analyzed yield, %	
	4.0 <i>M</i> aldehyde	0.5 <i>M</i> aldehyde
3-Methyl-1-butene	0.2	0.6
1-Pentene	2.4	6.0
<i>trans</i> - and <i>cis</i> -1,2-dimethyl- cyclopropane	0.04 ^b	0.12 ^c
<i>trans</i> -1,3-Pentadiene	0.003	0.012
<i>cis</i> -1,3-Pentadiene	0 ^d	0 ^d
2-Methyl-1,3-butadiene	0 ^d	0 ^d
3-Methyl-4-pentenal	0 ^e	0 ^e

^a Identification by retention times only. ^b Ratio of *trans* to *cis* isomers approximately 3.5:1. ^c Ratio of *trans* to *cis* isomers approximately 4.5:1. ^d None detected. Product would have been detected if present to the extent of 0.01%. ^e None detected. Product would have been detected if present to the extent of 1%.

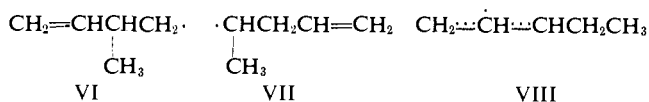
producibility was noted, however, when highly purified starting materials were not employed or when suitable (unreacted initiator did not decompose) vpc analysis conditions were not used. In order to show that the olefin ratios in Table I are not determined by preferential destruction of either 1-pentene or 3-methyl-1-butene, the two olefins were placed in reaction mixtures where *n*-valeraldehyde was decarbonylated. Ratios of 1-pentene to 3-methyl-1-butene were determined before and after decarbonylation. They did not differ within experimental error (Table II).

Decarbonylation product studies were performed at two aldehyde concentrations (Table III) on partially reacted solutions much like those used in the experiments above. Several possible reaction products which might provide information concerning the mechanism of decarbonylation were carefully sought.³⁴

2-Methyl-4-pentenal also yields 1-pentene and 3-methyl-1-butene, the former olefin predominating. The ratio of olefins again depends upon the initial aldehyde concentration (Table IV). Product studies on 4.0 *M* and 0.50 *M* 2-methyl-4-pentenal solutions are summarized in Table V.

Discussion

Straightforward decarbonylation of 3-methyl-4-pentenal should yield 3-methyl-1-butene, yet this olefin was present only as a minor olefinic product. 1-Pentene, the predominant olefin, possesses a carbon skeleton of rearranged structure. Since neither 3-methyl-4-pentenal nor the reaction products are isomerized under the reaction conditions, it must be concluded that rearrangement occurs during the radical chain sequence that leads to products. If 3-methyl-4-pentenal underwent decarbonylation in a typical radical-chain manner, homoallylic radical VI would be generated and react with 3-methyl-4-pentenal to give 3-methyl-1-butene. The formation of 1-pentene is conveniently rationalized by assuming that this olefin arises from the isomeric homoallylic



radical VII. Radicals VI and VII are interconvertible by 1,2-vinyl group migration. This mode of isomerization is not unique, however, since vicinal methyl migration (VI → VIII) yields the same carbon skeleton. *A priori*, the second mechanism is rendered less likely in view of the fact that simple, thermally promoted alkyl migrations have not been observed. However, Berson³⁵ has advocated caution in advancing this type of argument, pointing out that until such migrations have been reported (or, by implication, experimental limits placed on them) it is impossible to know the rigor of interdiction against them. In this regard, the molecular orbital calculations of Zimmerman and Zweig^{33b} indicate that methyl migration would be facilitated by the fact that rearrangement

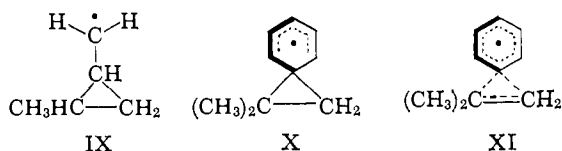
(34) Unreacted aldehyde was not determined in this experiment. In a related system, the decarbonylation of 4-pentenal, it has been found that the aldehyde can be recovered in good yield when decarbonylation is carried to low conversion.

(35) J. A. Berson, C. J. Olsen, and J. S. Walia, *J. Am. Chem. Soc.*, **84**, 3337 (1962).

yields a resonance-stabilized allylic radical. A more convincing argument against methyl migration utilizes the observation that no 2-pentene is formed in the reaction (Table III). 2-Pentene should be the *pre-dominant* olefin from an allylic intermediate such as VIII.⁴

The ratio of rearranged to unrearranged products from 3-methyl-4-pentalen is several times greater than the isobutylbenzene to *t*-butylbenzene ratio for β -phenylisovaleraldehyde under comparable decarbonylation conditions.³⁶ This difference in extent of rearrangement is probably most intimately tied (*vide infra*) to the rate constants for the isomerizations of homoallylic radical VI and the neophyl radical IV. If this is, indeed, the case, the rate constants for vicinal migration parallel those for the intermolecular addition of alkyl radicals to olefins and aromatics.³⁷

The relative migratory tendencies of vinyl and phenyl groups are reasonable in terms of first-order energetic considerations. The intramolecular nature of these rearrangements requires that a half-migrated or bridged species be implicated in the *minimum* as a rearrangement transition state. Cyclization of homoallylic radical VI to half-migrated structure IX starts



from and ends up with a primary radical. This transformation should be endothermic by some 8 kcal/mole.²³ Structure X would be formed from the neophyl radical by an analogous ring closure. The strain energy in X should be similar to that in IX, since the HCH bond angle in cyclopropane is about 118°. In the formation of X, however, the $1.46|\beta|$ delocalization energy of the pentadienyl radical system does not compensate for the $2|\beta|$ loss of delocalization energy in the aromatic ring of the neophyl radical.^{13c} More extensive electron delocalization in the half-migrated structure (*e.g.*, XI) might reduce this unfavorable change in delocalization energy. It is possible that future, more quantitative comparisons of homoallylic and vicinal aryl migrations will permit a reliable assessment of aryl-migration energetics and, perhaps, an evaluation of the relative importance of structures like X and XI in the rearrangement transition state.

From Table V it can be seen that the principal decarbonylation products from 2-methyl-4-pentalen are also 1-pentene and 3-methyl-1-butene. The pair of interconvertible radicals, VI and VII, can again be used to formulate the production of 1-pentene and 3-methyl-1-butene. This time VII is formed initially from 2-methyl-4-pentalen.

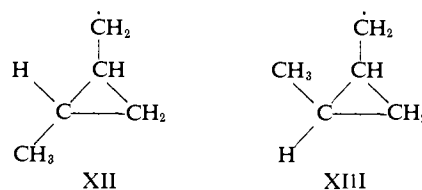
Certainly the most interesting products from 3-methyl-4-pentalen (Table III) and 2-methyl-4-pentalen (Table V), outside of rearranged olefinic products,

(36) C. Rüchardt, *Ber.*, **94**, 2599 (1961).

(37) (a) R. P. Buckley, F. Leavitt, and M. Szwarc, *J. Am. Chem. Soc.*, **78**, 5557 (1956); (b) M. Levy and M. Szwarc, *ibid.*, **77**, 1949 (1955); (c) J. Smid and M. Szwarc, *ibid.*, **78**, 3322 (1956).

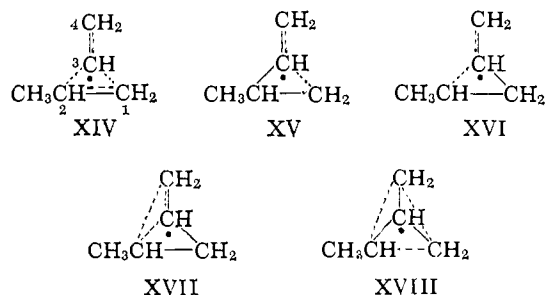
(38) (a) O. Hassel and H. Viervoll, *Acta Chem. Scand.*, **1**, 149 (1947); (b) O. Bastiansen and O. Hassel, *Tidskr. Kjemi, Bergvesen Met.*, **6**, 71 (1946); *Chem. Abstr.*, **40**, 6059 (1946).

are the trace quantities of the *trans*- and *cis*-1,2-dimethylcyclopropanes. Although the chromatographic identification of these compounds was conducted with considerable care, retention time evidence alone cannot unequivocally establish product identity, and the assignments must be considered tentative. The detection of substituted cyclopropanes implies that substituted cyclopropylcarbinyl radicals are involved as *intermediates* in the rearrangements. Homoallylic radicals VI and VII can yield two isomeric radicals upon ring closure, one *trans* ring fused (XII) and the other *cis* ring fused (XIII). Chain transfer to 3-methyl-4-pentalen or 2-methyl-4-pentalen from XII and XIII would give the isomeric 1,2-dimethylcyclo-



propanes. That the cyclopropanes are only very minor products is consistent with the known facility with which cyclopropylcarbinyl radicals ring open and particularly with the observations that no cyclic products were detected in the decarbonylations of cyclopropylacetaldehyde^{24,25} and cyclopropyldimethylacetaldehyde.²⁵ The case for intermediates like XII and XIII is strengthened considerably by the detection of similar radical species by an independent method in the homoallylic rearrangements which take place during the decarbonylations of *trans*-2-methyl-4-hexenal and *trans*-3-methyl-4-hexenal.³⁹

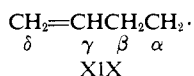
The formation of reaction products from 3-methyl-4-pentalen and 2-methyl-4-pentalen has been rationalized employing only classical radical intermediates. It is conceivable that nonclassical intermediates give rise to one or more of the decarbonylation products, although it is noteworthy that a compelling case in support of the existence of a single nonclassical radical has not been advanced at the present time. This is somewhat surprising, for the theoretical arguments for some form (*e.g.*, intermediates XIV–XVII below) of homoconjugative delocalization in homoallylic radicals are reasonably convincing.⁴⁰ Several experimental observations in the literature bear directly on the question of the existence of nonclassical homoallylic radicals and, as such, warrant at least brief comment.



(39) L. K. Montgomery and J. W. Matt, *J. Am. Chem. Soc.*, **89**, 934 (1967).

(40) (a) M. Simonetta and S. Winstein, *ibid.*, **76**, 18 (1954); (b) R. J. Piccolini and S. Winstein, *Tetrahedron, Suppl.*, **2**, 423 (1963); (c) M. E. H. Howden and J. D. Roberts, *ibid.*, **2**, 403 (1963).

A number of types⁴⁰ of nonclassical radicals can be derived from classical allylcarbonyl radicals VI and VII. These are illustrated in structures XIV–XVIII. A single radical such as XIV could yield all of the products mentioned thus far, affording 3-methyl-1-butene, 1-pentene, and dimethylcyclopropane by way of chain transfer at carbons 1, 2, and 4, respectively. An interconverting pair of radicals like XV and XVI would also represent an acceptable system. In related carbonium ion rearrangements, three interconverting bicyclobutonium ions⁷ possessing structures like XVII have been employed to rationalize the results of extensive rate and product studies. Pyramidal radical XVIII, like XIV, can give all three types of products. Radical XVIII is the only species out of XIV–XVIII with two bonding molecular orbitals.^{40c} This is an important consideration, for all of the radicals are three-electron systems. The favorable bonding situation in XVIII is opposed, however, by considerable strain energy.^{40c} ¹³C tracer experiments have shown that a rapidly equilibrating set of radicals like XVII or pyramidal radical XVIII are not intermediates in the radical-chain chlorination of methylcyclopropane, thus reducing the likelihood of their involvement in the present study. Fessenden and Schuler⁴¹ have reported the electron paramagnetic resonance spectrum of the 3-butenyl radical (XIX).



The hyperfine splitting in this spectrum shows little evidence of homoconjugation like that in hypothetical intermediates XV and XVI. The α and β hyperfine coupling constants of XIX, a_α and a_β , are 22.23 and 29.71 gauss, respectively. These constants are typical of the α and β constants for acyclic alkyl radicals.⁴¹ The value of a_β was slightly temperature dependent. The a_β of a number of simple radicals such as the *n*-propyl radical behave similarly; this behavior has been associated with changes in rotamer populations about the C_β – C_α bond as the temperature changes. Small couplings with the γ ($a_\gamma = 0.65$ gauss) and one of the δ ($a_\delta = 0.35$ gauss) protons were also noted. These slight splittings are reminiscent of the long-range, spin-spin splitting in the nmr spectra of 1-alkenes.⁴² The magnitude of a_β demonstrates that there is little spin density on the δ -carbon atom. In light of the above findings, additional consideration of nonclassical intermediates does not seem appropriate; classical intermediates VI and VII have been employed as the sole olefin-determining radical species in the remaining text.

In 1953 Seubold introduced a valuable technique for probing the number and type of intermediates in a free radical rearrangement.⁴³ He showed that the ratio of isobutylbenzene to *t*-butylbenzene which is obtained upon decarbonylating β -phenylisovaleraldehyde depends upon the initial aldehyde concentration, demonstrating that *at least* two intermediates are involved in the rearrangement sequence. R uchardt

has made a thorough, quantitative study of this system.³⁶ In designing experiments similar to those of Seubold and R uchardt to study the rearrangements encountered in the decarbonylations of 3-methyl- and 2-methyl-4-pentenal, it was noted that carbon monoxide was liberated more slowly from these aldehydes than from saturated aliphatic aldehydes or from β -phenylisovaleraldehyde.³⁶ Degradative chain transfer,⁴⁴ a process which frequently complicates the radical chain reactions of olefins, or some other undesirable reaction involving the double bond apparently moderate the chain reactions. It was realized from the outset that complications of this sort might arise.^{21j} Nevertheless, it was felt that the somewhat greater reactivity of aldehydic hydrogens compared to allylic hydrogens toward simple alkyl radicals¹⁵ might permit radical chain reactions of workable kinetic chain lengths to take place. The fact that up to 70% of the stoichiometric quantity of carbon monoxide was liberated from 3-methyl-4-pentenal and, further, that the initial evolution of carbon monoxide was vigorous indicated that decarbonylation studies of these unsaturated aldehydes were practical.

Several general problems must be considered in using decarbonylation olefin ratios to explore rearrangement reaction mechanisms. For example, if the decarbonylations were carried to completion, it would be necessary to derive and integrate an appropriate rate expression for the olefin ratio for each hypothetical mechanism under consideration. For all but the most elementary mechanisms, this would be difficult, if not impossible. Integration is simplified considerably if reaction is halted after only a few per cent conversion. Independent of what the detailed rearrangement mechanism or mechanisms are, it is reasonable to assume that all of the radical processes that lead to products are unimolecular radical interconversions or bimolecular radical-aldehyde reactions. Since the aldehyde concentration does not change significantly at low conversion, the steps leading to 1-pentene or 3-methyl-1-butene are thus either unimolecular or pseudo-unimolecular. Provided that the preponderance of decarbonylation products are produced under steady-state conditions and that the radical chains are long, there should be a characteristic 1-pentene to 3-methyl-1-butene ratio for each aldehyde concentration which is determined by the detailed mechanism for rearrangement. These characteristic, low-conversion olefin ratios can be related with relative ease (*vide infra*) and greater reliability to postulated mechanisms. Accordingly, the 1-pentene to 3-methyl-1-butene ratios in Tables I and III were determined at low percentage reaction. An added advantage of such a procedure is that side reactions are minimized by employing short reaction periods.

An important consideration in discussing the relationship of olefin ratios and possible rearrangement mechanisms is knowing just how rearrangement enters into the radical chain decarbonylation sequence. Some knowledge of the kinetic chain length is also important. The radical chain decomposition of aldehydes, initiated by either thermal or photochemical means, has been studied most extensively in the gas phase,⁴⁵ although the reaction was first explored in

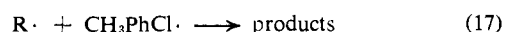
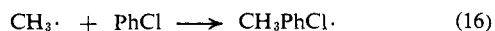
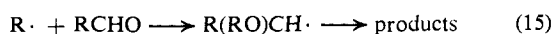
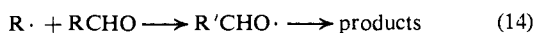
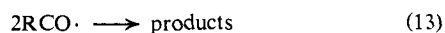
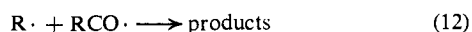
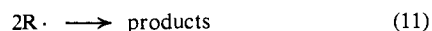
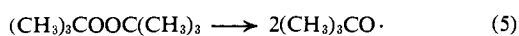
(41) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

(42) A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **83**, 231 (1961).

(43) F. H. Seubold, Jr., *ibid.*, **75**, 2532 (1953).

(44) P. D. Bartlett and R. Altschul, *ibid.*, **67**, 812 (1945).

solution where it was shown that light and peroxides catalyzed and hydroquinone inhibited carbon monoxide evolution.⁴⁶ The di-*t*-butyl peroxide-initiated decarbonylation of aldehydes³¹ can be discussed employing eq 5-18. As is the case in many free radical



chain reactions, the chain propagation steps, decarbonylation of the acyl radical (eq 9) and chain transfer (eq 10), are the best understood portions of the decarbonylation sequence. Structural changes in R occur in R· prior to chain transfer. Equations 5 and 6 probably represent the most important mechanism of chain initiation. Equation 8 should be less important under the experimental conditions employed (solvent chlorobenzene, 129.6°). Attack on the solvent by methyl radicals (eq 16) should be facile at this temperature^{37b} and compete effectively with initiation (eq 8), particularly at low aldehyde concentrations. It is possible, in fact, that methyl radicals, acting *via* their solvent-attacked derivatives, CH₃PhCl·, actually function as inhibitors (eq 17 and 18). Chain termination step 11 is the predominant mode of chain termination in many gas-phase reactions.⁴⁵ Only a small quantity of *trans*-1,3-pentadiene was detected among the decarbonylation products of 2-methyl-4-pentenal (Table V) and no disproportionation products were observed in the case of 3-methyl-4-pentenal (Table III). Radical combination products were not present in greater than trace quantities. Either reaction 11 is not an important termination reaction or the kinetic chain lengths are very long. It is doubtful that the latter is the case. The temperatures at which most gas-phase studies have been carried out are well above the 129.6° employed in this study. As the temperature decreases, the likelihood of chain termination involving acyl radicals increases⁴⁷ (eq 12, 13, and 18). Termination could also occur by degradative chain transfer (eq 14)^{44,48} or by radical attack on the carbonyl oxygen (eq 15).⁴⁹ Temperature-

programmed, vapor-phase chromatograms of the reaction products of both aldehydes revealed no unidentified products in significant yield that might be attributed to chain termination products. This is not, of course, a foolproof method of tracking down chain-termination products. Fortunately, in the current investigation it is not as important to know the precise nature of chain termination as it is to know that a significant portion of decarbonylation products does not arise from chain-termination reactions (*e.g.*, eq 11). Rough estimates of the kinetic chain lengths for 3-methyl-4-pentenal and 2-methyl-4-pentenal can be obtained from carbon monoxide yields and rate data for the thermal decomposition of di-*t*-butyl peroxide. These estimates indicate that the kinetic chain lengths are ten or greater.⁵⁰

The data in Table I reveal a dependence of the extent of rearrangement on the initial 3-methyl-4-pentenal concentration. The 1-pentene to 3-methyl-1-butene ratio increases steadily as the aldehyde concentration is decreased from 6 to 1.0 *M*. Below 1.0 *M* the ratio changes slowly, eventually assuming a constant value of about 8.7:1 at 0.38 *M* (run 2). Two intermediates, homoallylic radicals VI and VII, were used above to *rationalize* the formation of the observed olefinic products. The data in Table I *demonstrate* that a minimum of two radicals are involved. The invariance of the 1-pentene to 3-methyl-1-butene ratio below 0.38 *M* can be explained by assuming that in this concentration range the interconversion of intermediates VI and VII is fast relative to the chain-transfer, product-forming steps. Under these conditions the limiting olefin ratio is determined by the equilibrium concentrations of radicals VI and VII and the individual chain-transfer rate constants for the two radicals. Radical VII should be present in highest concentration at equilibrium, since it is a secondary radical. On the other hand, VII should be least reactive toward 3-methyl-4-pentenal. Since the limiting olefin ratio is 8.7:1, the relative concentrations of VI and VII must be the dominant factor. The progressive lowering of the 1-pentene to 3-methyl-1-butene ratio at aldehyde concentrations above 0.38 *M* is a consequence of the fact that all of the radicals that are generated from 3-methyl-4-pentenal must enter the rearrangement system through radical VI. At high aldehyde concentrations a substantial number of newly formed VI radicals are trapped before they have a chance to rearrange.

When the olefin ratios from 2-methyl-4-pentenal are compared for various initial aldehyde concentrations (Table IV), it is noted that the 1-pentene to 3-methyl-1-butene ratio drops rapidly from 12.5:1 for neat aldehyde to a constant value of about 10:1 at 1.5 *M* 2-methyl-4-pentenal. The data in Table IV can be interpreted in a manner which is analogous to that for the results in Table I. All rearrangement now

(45) E. W. R. Stacie, "Atomic and Free Radical Reactions," 2nd ed, Reinhold Publishing Corp., New York, N. Y., 1954, pp 206-217, 284-317.

(46) (a) A. Franke and E. Pollitzer, *Monatsh.*, **34**, 797 (1913); (b) J. B. Conant, C. N. Webb, and W. C. Mendum, *J. Am. Chem. Soc.*, **51**, 1246 (1929).

(47) (a) R. Cramer, *ibid.*, **79**, 6215 (1957); (b) C. H. Bamford and R. G. W. Norrish, *J. Chem. Soc.*, 1531, 1544 (1938); (c) F. E. Blacet and J. G. Calvert, *J. Am. Chem. Soc.*, **73**, 667 (1951).

(48) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., p 261.

(49) (a) J. A. Berson and C. J. Olsen, *J. Am. Chem. Soc.*, **84**, 3178 (1962); (b) F. F. Rust, F. H. Seubold, Jr., and W. E. Vaughan, *ibid.*, **70**, 3258 (1948).

(50) For example, a *minimum* (eq 16-18 neglected) average kinetic chain length of six was calculated for the first 130 min of carbon monoxide evolution from a 4 *M* solution of 3-methyl-4-pentenal in diphenyl ether at 129.6° where 20 mole % of di-*t*-butyl peroxide was employed as an initiator, assuming a first-order rate constant of $1.6 \times 10^{-5} \text{ sec}^{-1}$ for the initiator.⁵¹

(51) F. P. Lossing and A. W. Tickner, *J. Chem. Phys.*, **20**, 907 (1952).

starts from homoallylic radical VII. The limiting olefin ratio is not the same as for 3-methyl-4-pentenal. This is reasonable, for the ratio of chain-transfer rate constants need not be the same for 3-methyl-4-pentenal and 2-methyl-4-pentenal.

Greater insight regarding the relationship of the olefin ratios in Tables I and IV and the rearrangement reaction mechanism can be gained through a detailed, consideration of the scheme in Figure 1. Rearrange-

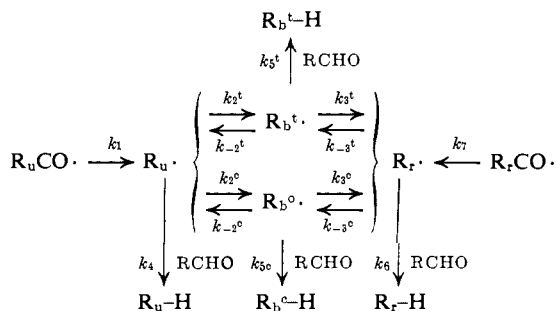


Figure 1. A general scheme for the decarbonylations of 3-methyl-4-pentenal and 2-methyl-4-pentenal.

ments originating from 3-methyl-4-pentenal, $R_u\text{CHO}$, enter the scheme by way of acyl radical $R_u\text{CO}\cdot$. Loss of carbon monoxide from $R_u\text{CO}\cdot$ gives a radical of unrearranged structure, $R_u\cdot$ (VI). $R_u\cdot$ either reacts with $R_u\text{CHO}$ yielding 3-methyl-1-butene, $R_u\text{-H}$, or rearranges to a radical of cyclopropylcarbinyl structure but of unspecified bond type which possesses either *trans*-fused ($R_b^t\cdot$) or *cis*-fused ($R_b^c\cdot$) ring geometry. Although intermediates of this type cannot be rigorously placed along the rearrangement reaction coordinate, such a positioning is definitely reasonable. The *trans*- and *cis*-1,2-dimethylcyclopropanes are formed from $R_b^t\cdot$ and $R_b^c\cdot$. Rearrangement is completed from $R_b^t\cdot$ or $R_b^c\cdot$ by ring opening to a radical of rearranged structure, $R_r\cdot$ (VII). 1-Pentene, $R_r\text{-H}$, is formed from $R_r\cdot$ in a chain transfer reaction with 3-methyl-4-pentenal. The decarbonylation of 2-methyl-4-pentenal, $R_r\text{CHO}$, can also be formulated in terms of the intermediates in Figure 1, but this time the scheme is entered through acyl radical $R_r\text{CO}\cdot$. It could be argued that since the experimental evidence at this time does not make $R_b^t\cdot$ and $R_b^c\cdot$ necessary rearrangement intermediates and, further, since so little 1,2-dimethylcyclopropane is observed, $R_b^t\cdot$ and $R_b^c\cdot$ should be omitted from the scheme in Figure 1. This would not seem to be the most acceptable approach, for it is shown below that the rate constants leading to and from $R_b^t\cdot$ and $R_b^c\cdot$ markedly affect the ratio of olefinic products.

The rates of change of the free radical intermediates which are involved in the decarbonylation of 3-methyl-4-pentenal are given in eq 19–23. Additional u 's have been added to the subscripts of some of the rate constants to denote that the decarbonylation of $R_u\text{CHO}$

$$d[R_u\text{CO}\cdot]/dt = I_{n_u} + k_{6u}[R_u\text{CHO}][R_r\cdot] + k_{4u}[R_u\text{CHO}][R_u\cdot] + k_{5u}^t[R_u\text{CHO}][R_b^t\cdot] + k_{5u}^c[R_u\text{CHO}][R_b^c\cdot] - k_1[R_u\text{CO}\cdot] - T_u \quad (19)$$

$$d[R_u\cdot]/dt = k_1[R_u\text{CO}\cdot] + k_{-2}^t[R_b^t\cdot] + k_{-2}^c[R_b^c\cdot] - (k_2^t + k_2^c + k_{4u}[R_u\text{CHO}])[R_u\cdot] - T_u \quad (20)$$

$$d[R_b^t\cdot]/dt = k_2^t[R_u\cdot] + k_{-3}^t[R_r\cdot] - (k_3^t + k_{-2}^t + k_{6u}^t[R_u\text{CHO}])[R_b^t\cdot] - T_u \quad (21)$$

$$d[R_b^c\cdot]/dt = k_2^c[R_u\cdot] + k_{-3}^c[R_r\cdot] - (k_3^c + k_{-2}^c + k_{6u}^c[R_u\text{CHO}])[R_b^c\cdot] - T_u \quad (22)$$

$$d[R_r\cdot]/dt = k_3^t[R_b^t\cdot] + k_3^c[R_b^c\cdot] - (k_{-3}^t + k_{-3}^c + k_{6u}[R_u\text{CHO}])[R_r\cdot] - T_u \quad (23)$$

is being considered. I_{n_u} represents the rate of formation of $R_u\text{CO}\cdot$ from initiation steps. The T_u are rates of termination reactions for the various radicals. In developing a relationship between the two olefins, $R_u\text{-H}$ and $R_r\text{-H}$, and the initial $R_u\text{CHO}$ concentration, several simplifying assumptions are necessary or desirably employed. First, it must be assumed that the chains are long (*vide supra*). All terms involving the reactions of $R_u\text{CHO}$ with $R_b^t\cdot$ and $R_b^c\cdot$ can be neglected. The aldehyde concentration is treated as a constant.

In the decarbonylation of 3-methyl-4-pentenal, the rates of formation of 3-methyl-1-butene and 1-pentene are given by eq 24 and 25. The ratio of rates is pro-

$$d[R_u\text{-H}]/dt = k_{4u}[R_u\text{CHO}][R_u\cdot] \quad (24)$$

$$d[R_r\text{-H}]/dt = k_{6u}[R_u\text{CHO}][R_r\cdot] \quad (25)$$

vided by eq 26. Application of the assumptions stated

$$d[R_u\text{-H}]/d[R_r\text{-H}] = k_{4u}[R_u\cdot]/k_{6u}[R_r\cdot] \quad (26)$$

above and the steady-state approximation⁵² to eq 21–23 yields expressions for the steady-state concentrations of $R_b^t\cdot$, $R_b^c\cdot$, and $R_r\cdot$ (eq 27–29). Simple

$$[R_b^t\cdot] = (k_2^t[R_u\cdot] + k_{-3}^t[R_r\cdot]) / (k_3^t + k_{-2}^t) \quad (27)$$

$$[R_b^c\cdot] = (k_2^c[R_u\cdot] + k_{-3}^c[R_r\cdot]) / (k_3^c + k_{-2}^c) \quad (28)$$

$$[R_r\cdot] = (k_3^t[R_b^t\cdot] + k_3^c[R_b^c\cdot]) / (k_{-3}^t + k_{-3}^c + k_{6u}[R_u\text{CHO}]) \quad (29)$$

manipulation of eq 27–29 affords $[R_u\cdot]/[R_r\cdot]$ (eq 30)

$$[R_u\cdot]/[R_r\cdot] = N_u/D_u \quad (30)$$

where

$$N_u = k_{-3}^t(k_3^c + k_{-2}^c) \{ k_{-2}^t(k_{-3}^t + k_{-3}^c) + k_{6u}(k_3^t + k_{-2}^t)[R_u\text{CHO}] \} + k_{-3}^c(k_3^t + k_{-2}^t) \{ k_{-2}^c(k_{-3}^t + k_{-3}^c) + k_{6u}(k_3^c + k_{-2}^c)[R_u\text{CHO}] \}$$

and

$$D_u = (k_{-3}^t + k_{-3}^c) \{ k_3^t k_2^t (k_3^c + k_{-2}^c) + k_3^c k_2^c (k_3^t + k_{-2}^t) \}$$

If $[R_u\cdot]/[R_r\cdot]$ is placed in eq 26 and the resulting equation integrated, an expression for $R_u\text{-H}/R_r\text{-H}$ is obtained (eq 31). Starting from 2-methyl-4-pentenal,

$$R_u\text{-H}/R_r\text{-H} = k_{4u}N_u/k_{6u}D_u \quad (31)$$

$R_r\text{-H}/R_u\text{-H}$ is given by eq 32

$$R_r\text{-H}/R_u\text{-H} = k_{6r}N_r/k_{4r}D_r \quad (32)$$

(52) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1962, p 172.

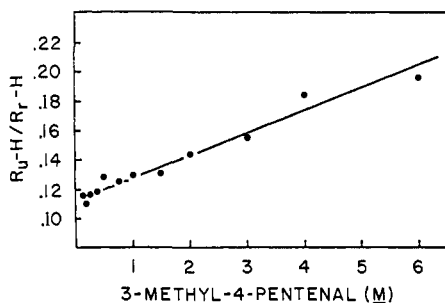


Figure 2. Plot of the ratio of 3-methyl-1-butene, R_{u-H} , to 1-pentene, R_{r-H} , vs. the 3-methyl-4-pentenal concentration.

where

$$N_r = k_2^t(k_3^c + k_{-2}^c)\{k_3^t(k_2^t + k_2^c) + k_{4r}(k_3^t + k_{2-}^t)[R_r\text{CHO}]\} + k_2^c(k_3^t + k_{-2}^t)\{k_3^c(k_2^t + k_2^c) + k_{4r}(k_3^c + k_{-2}^c)[R_r\text{CHO}]\}$$

and

$$D_r = (k_2^t + k_2^c)\{k_{-3}^t k_{-2}^t(k_3^c + k_{-2}^c) + k_{-3}^c k_{-2}^c(k_3^t + k_{-2}^t)\}$$

Equations 31 and 32 are too cumbersome to be used directly in the discussion of the relationship of initial aldehyde concentration to olefin ratios, but they are particularly useful as starting points for examining approximate mechanistic models. One obvious approximation which should be considered is the limiting case where all of the rate constants for the various reactions of R_b^t are equal to the rate constants for the corresponding reactions of R_b^c . In such a case, eq 31 and 32 reduce to eq 33 and 34. Several lines of reasoning suggest that eq 33 and 34 might be reason-

$$R_u-H/R_r-H = \{2k_{4u}k_{-3}k_{-2} + k_{6u}k_{4u}(k_3 + k_{-2})[R_u\text{CHO}]\}/2k_{6u}k_3k_2 \quad (33)$$

$$R_r-H/R_u-H = \{2k_{6r}k_3k_2 + k_{6r}k_{4r}(k_3 + k_{-2})[R_r\text{CHO}]\}/2k_{4r}k_{-3}k_{-2} \quad (34)$$

ably good approximations. To begin with, it is known that at least some rearrangement takes place through both R_b^t and R_b^c , for both *trans*- and *cis*-1,2-dimethylcyclopropane are reaction products. An extrapolation of the thermochemical data of Flowers and Frey⁵³ indicates that the free energy difference between *trans*- and *cis*-1,2-dimethylcyclopropane at 130° is small (*trans* favored by about 0.2 kcal/mole, gas phase). It is, therefore, likely that k_2^t is similar in magnitude to k_2^c and that k_{-3}^t approximates k_{-3}^c . Although a number of other *trans* and *cis* rate constant relationships could be commented on at length, it is doubtful whether any meaningful conclusions could be drawn from such discussions. A working plan has been adopted below whereby it is assumed that eq 33 and 34 determine the olefin ratios. Several consequences of allowing the chemistries of R_b^t and R_b^c to be different are pointed out separately.

In Figure 2 the ratio of 3-methyl-1-butene to 1-pentene is plotted vs. the initial 3-methyl-4-pentenal concentration. The data fit a straight line satisfactorily, which it should if eq 33 holds. In terms of

(53) M. C. Flowers and H. M. Frey, *Proc. Roy. Soc. (London)*, **A257**, 122 (1960).

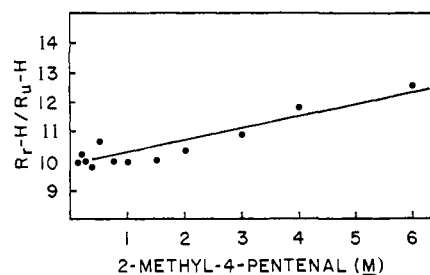


Figure 3. Plot of the ratio of 1-pentene, R_{r-H} , to 3-methyl-1-butene, R_{u-H} , vs. the 2-methyl-4-pentenal concentration.

eq 33 the slope, m_u , and ordinate intercept, I_u , are given by eq 35 and 36. From Figure 2, m_u and I_u

$$m_u = k_{4u}(k_3 + k_{-2})/2k_3k_2 = 0.017 \quad (35)$$

$$I_u = k_{4u}k_{-3}k_{-2}/k_{6u}k_3k_2 = 0.11 \quad (36)$$

are 0.017 and 0.11. R_r-H/R_u-H is plotted against the concentration of 2-methyl-4-pentenal in Figure 3. If a straight line is drawn through the data, it is found that the fit of the points at low concentrations is less satisfactory than in Figure 2. It should be noted, however, that it is in this concentration range that olefin ratio reproducibility is poorest. The slope, m_r , and intercept, I_r , of this plot are given by eq 37 and 38 and are 0.42 and 9.9, respectively.

$$m_r = k_{6r}(k_3 + k_{-2})/2k_{-3}k_{-2} = 0.42 \quad (37)$$

$$I_r = k_{6r}k_3k_2/k_{4r}k_{-3}k_{-2} = 9.9 \quad (38)$$

Two relationships can be derived directly from the slopes and intercepts in Figure 2 and 3. If m_r is divided by the product of m_u and I_r , k_{4r}/k_{4u} is obtained (this ratio is 2.5:1). The product of m_r and I_u divided by m_u gives $k_{6r}/k_{6u} = 2.7$. In view of the magnitude of these ratios, it is somewhat surprising that R_r is only slightly more selective than R_u toward the two aldehydes. Equations 36 and 38 reveal that the olefin ratios at low aldehyde concentrations are controlled by the ratio of chain-transfer rate constants and the equilibrium constant for the interconversion of R_u and R_r , $k_3k_2/k_{-3}k_{-2}$. Since the equilibrium constant is the same for both systems, the k_6/k_4 ratios in the two systems are responsible for any difference in limiting olefin ratios.

The rearrangement of R_u to R_r converts a primary radical into a secondary radical. This transformation should be exothermic by 4 kcal/mole.⁵⁴ A 4 kcal/mole energy difference at 130° corresponds to an equilibrium constant of 150. If $k_3k_2/k_{-3}k_{-2}$ is 150, then from eq 36 and 38, k_{4u}/k_{6u} and k_{4r}/k_{6r} are 16.5 and 15, which are reasonable qualitative relationships for chain-transfer rate constants for primary and secondary radicals with common substrates.

Some of the most potentially interesting information concerning homoallylic rearrangements is tied up in m_u and m_r . It would be desirable, for example, to

(54) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 50. It is assumed that the entropy change in going from R_u to R_r is not the predominant factor in determining the over-all free energy change. A comparison of the thermodynamic parameters for 3-methyl-1-butene and 1-pentene in the gas phase supports this assumption (Selected Values of Properties of Hydrocarbons and Related Compounds, American Petroleum Institute Research Project 44).

obtain rate constant ratios k_2/k_{4u} and k_{-3}/k_{6r} , which are contained in m_u and m_r , in order to explore the effect of structure variation on reactivity. To be able to do this, it is necessary to know the relative magnitudes of k_3 and k_{-2} , the rate constants which partition R_b^t and R_b^c to R_u and R_r . The fact that R_b^t-H and R_b^c-H constituted less than 1% of the decarbonylation products from either 3-methyl- or 2-methyl-4-pentenal in all likelihood indicates that R_b^t and R_b^c possess shorter lifetimes (in this regard *vide infra*) and are present in lower steady-state concentrations than R_u and R_r . If R_b^t and R_b^c lie in shallow energy wells along the reaction coordinate, it follows that k_3 and k_{-2} cannot differ by orders of magnitude. If it is assumed that $k_3 = k_{-2}$, then k_2/k_{4u} is 59 (eq 35) and k_{-3}/k_{6r} is 2.4 (eq 37). In addition, $k_2 = 150k_{-3}$ for a $k_3k_2/k_{-3}k_{-2}$ value of 150. Consider next the effect of assigning modestly different values to k_3 and k_{-2} . Rate constant k_3 is probably greater than k_{-2} , since ring opening to R_r is more exothermic than to R_u . Assuming that $k_3 = 2k_{-2}$, which corresponds to a relative free energy of activation of about 0.5 kcal/mole at 130°, k_2/k_{4u} and k_{-3}/k_{6r} become 44 and 3.6, respectively. Although it has been necessary to assume a k_3 to k_{-2} relationship in the discussion presented here, interpretation of rearrangement data by the above procedure looks promising, for it appears possible to measure k_3/k_{-2} experimentally.⁵⁵

It has been assumed up to this point that all of the rate constants in the *cis* series equal those in the *trans* series. A contrasting approximation would be one in which the free energy of R_b^c is much greater than that of R_b^t , forcing all rearrangement to take place through R_b^t . If $k_2^t \gg k_2^c$ and $k_{-3}^t \gg k_{-3}^c$, eq 31 and 32 reduce to equations similar to eq 33 and 34 except that the twos do not appear in the numerators and denominators.

A second point worth noting concerns ring-opening rate constants k_3 and k_{-2} . It is conceivable that the $k_3^c > k_3^t$ and $k_{-2}^c > k_{-2}^t$, owing mainly to a small difference in ground-state energies between R_b^c and R_b^t . The influence of such rate constant differences on eq 33 and 34 should not be great, however. This can be seen by letting $k_3^c = fk_3^t$ and $k_{-2}^c = fk_{-2}^t$, where f is some constant. Under such circumstances eq 31 and 32 reduce to eq 33 and 34.

One aspect of the mechanism proposed in Figure 1 which should have further experimental support is the intervention of cyclopropylcarbinyl radicals in the rearrangement process. An interesting order of magnitude calculation of the maximum expected half-lives of R_b^t and R_b^c can be made in the following way. Any given R_b^t or R_b^c has three reaction pathways available to it, reaction with aldehyde to form dimethylcyclopropane, formation of R_u , and formation of R_r . The latter two pathways predominate. An expression for $(R_r-H + R_u-H)/(R_b^t-H + R_b^c-H)$ for 3-methyl-4-pentenal (eq 39) can be derived following the procedures outlined in the derivation

(55) The scheme in Figure 1 can be entered through R_b^t and R_b^c as well as through R_u or R_r . A detailed consideration of the kinetic equations resulting from entry from R_b^t and R_b^c indicates that it should be possible to obtain an estimate of k_3/k_{-2} by studying the decarbonylations of the isomeric (2-methylcyclopropyl)acetaldehydes. Moreover, it may be possible to probe certain k^t and k^c relationships with these aldehydes.

$$\frac{R_r-H + R_u-H}{R_b^t-H + R_b^c-H} = \frac{2k_{6u}k_3k_2 + 2k_{4u}k_{-3}k_{-2} + k_{4u}k_{4u}(k_3 + k_{-2})[R_uCHO]}{2k_{5u}k_2(2k_{-3} + k_{6u}[R_uCHO])} \quad (39)$$

of eq 33 and 34. $(R_r-H + R_u-H)/(R_b^t-H + R_b^c-H)$ is approximately 100:1 for 0.5 M 3-methyl-4-pentenal (Table III). Assuming $k_2/k_{4u} = 59$, $k_{-3}/k_{6u} = 6.5$, $k_{4u}/k_{6u} = 16.5$, and $k_{5u} = 10^3-10^5$ l./mole sec,⁵⁶ then $k_3 = k_{-2} \sim 10^6-10^8$ /sec. This corresponds to an R_b^c half-life of about $10^{-6}-10^{-8}$ sec. Any experimental probe which is employed to gain further evidence for the existence of R_b^t and R_b^c as reaction intermediates must be able to operate on this general time scale to be effective.

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 routinely recorded 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. Chemical shifts are reported as parts per million displacements from tetramethylsilane as an internal standard. The infrared spectra were obtained on a Perkin-Elmer Model 137 Infrared 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 carried out on an F & M Scientific Model 609 flame-ionization gas chromatograph equipped with a Minneapolis-Honeywell recorder (Model Y153-999) fitted with a Disc Instruments integrator. Limited quantities of reaction products were collected with the aid of a Model 609FD fraction delivery system. 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% diisodecyl phthalate (DIDP); 20% 1,2,3-(2-cyanoethoxy)propane (TCEP); 20% Carbowax 20M (CAWX); 30% propylene glycol-silver nitrate (PGSN). Microanalyses were obtained from Midwest Microlab, Inc., Indianapolis, Ind. 46226.

Specially Purified Materials. A. Crotyl alcohol (Aldrich) was redistilled, bp 118°. It was found that the purity of crotyl alcohol varies considerably from vendor to vendor.

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

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

D. Ethyl vinyl ether (Eastman) was distilled, bp 35°, from sodium immediately prior to use.

E. 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-4-pentenal was prepared by the thermal rearrangement of crotyl vinyl ether, which was obtained following the general transesterification method B of Watanabe and Conlon.³³ Crotyl alcohol (41.3 g, 0.57 mole) was refluxed with 7.9 g of recrystallized mercuric acetate for 8 hr at 36° in ethyl vinyl ether (303.7 g, 4.20 moles). The reaction mixture was washed with ten 170-ml portions of 5% sodium carbonate solution. This extensive washing was found to be a useful modification of the usual procedure³⁷ where starting alcohol and vinyl ether product are normally separated by fractional distillation. The washed products were dried over 45 g of anhydrous magnesium sulfate. About 1 g of

(56) (a) R. E. Dodd, *J. Chem. Soc.*, 878 (1952). (b) Values of E and $\log A$ for the reactions of several primary alkyl radicals with aldehydes are listed in ref 15, p 117.

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

diphenylamine was added and the excess ethyl vinyl ether removed by distillation. Crude crotyl vinyl ether (26.5 g) was collected, bp 97–103°. The ether was heated in a sealed Pyrex ampoule for 90 min, yielding 26.0 g (0.265 mole, 46%) of crude 3-methyl-4-pentenal. High purity 3-methyl-4-pentenal was obtained by preparative vpc. Chromatographed, vacuum-transferred material, bp 118–119° (739 mm) (lit.³² bp 116°), 2,4-dinitrophenylhydrazone,⁸⁸ mp 91–92° (lit.³² mp 90.5°), was used for the decarbonylation studies.

Ethyl Propenyl Ether. Propionaldehyde (58.08 g, 1.00 mole) and absolute ethanol (46.07 g, 1.00 mole) were mixed at 0°. Dry hydrogen chloride gas was passed slowly through the solution in a manner that prevented excessive mixing of the organic layer with the aqueous layer which was being formed. The formation of ethyl 1-chloropropyl ether was conveniently monitored by nmr. Upon completion of the reaction (1.25 hr), the organic layer was separated and dried over calcium chloride and distilled at a reduced pressure (about 200 mm). The crude ethyl 1-chloropropyl ether (100.12 g, 85% yield) which was obtained was used in the preparation of ethyl propenyl ether without further purification.

Ethyl 1-chloropropyl ether (100.12 g, 0.846 mole) was added at a slow, steady rate to pyridine (118.5 g, 1.69 moles). After the addition was completed, the reaction products were distilled. Material boiling 50–110° was collected, washed with 5% sodium carbonate solution, and dried over anhydrous calcium chloride. Redistillation of the ethyl propenyl ether gave 40.0 g (46.5% over-all yield) of product, bp 70° (lit.⁸⁹ bp 69.1–69.4°).

2-Methyl-4-pentenal. A solution of ethyl propenyl ether (210.5 g, 2.45 moles), allyl alcohol (71.20 g, 1.23 moles), mercuric acetate (17.6 g, 0.055 mole), and 0.6 g of acetic acid was refluxed for 18 hr at 74°. Allyl alcohol and ethanol were removed from the reaction products by extensive washing with 5% sodium carbonate solution. The ethers were dried over anhydrous calcium chloride. About 0.5 g of diphenylamine was added to the products and unreacted ethyl propenyl ether was removed by distillation. An nmr spectrum of the crude allyl propenyl ether revealed that some of the ether had already rearranged to 2-methyl-4-pentenal.

Transesterification employing ethyl propenyl ether did not take place as smoothly as similar procedures with ethyl vinyl ether. The possibility of utilizing either acetic acid or mineral acid catalysis was explored. In these studies the exchange reaction was conveniently monitored at various time intervals in the following manner. A small portion of reaction products was washed extensively with 5% sodium carbonate solution to remove the allyl and ethyl alcohols and was dried over anhydrous calcium chloride. The ratio of ethyl propenyl ether to allyl propenyl ether was determined by nmr analysis by comparing propenyl methyl proton absorption, which is common to both compounds, with the methylene proton absorption of the ethyl propenyl ether. This ratio was 1.81 at the conclusion of the reaction reported above. Several attempts to catalyze the transesterification with mineral acids were unsuccessful. Acetic acid seemed to help. The conditions employed for the reaction above do not represent those suggested by an extensive investigation but were merely found to work. Spectral data indicated that a significant quantity of propionaldehyde allyl ether acetal was formed as a by-product.

The crude allyl propenyl ether was sealed in a Pyrex ampoule and heated at 150° for 1 hr. The 2-methyl-4-pentenal which was obtained was purified by simple distillation followed by preparative vpc, yielding 18.6 g (15.4% over-all yield) of aldehyde, bp 118°, n_{D}^{25} 1.4192.

Anal. Calcd for $C_8H_{10}O$: C, 72.43; H, 10.27. Found: C, 72.57, 72.43; H, 10.00, 9.97.

The 2,4-dinitrophenylhydrazone, mp 102–102.5°, of 2-methyl-4-pentenal was prepared.⁸⁸

Anal. Calcd for $C_{12}H_{14}N_4O_4$: C, 51.79; H, 5.07; N, 20.14. Found: C, 52.16, 52.14; H, 5.32, 5.44; N, 20.03, 19.73.

2-Methyl-4-pentenal had characteristic aldehyde infrared absorption bands (neat film) at 2720 and 1725 cm^{-1} . The terminal olefin absorbed at 1642 cm^{-1} . The nmr spectrum was highly indicative of the aldehyde's structure and integrated well. The nmr consisted of a doublet (7 cps, 3.00 protons) extending from 1.7 to 2.8, complex absorption (3.00 protons) extending from 4.7 to 5.2 (terminal olefinic protons), complex absorption (1.00 proton)

extending from 5.4 to 6.2 (remaining vinyl proton), and a doublet (1 cps, 0.96 proton) at 9.55 (aldehydic proton).

Decarbonylation of 3-Methyl-4-pentenal. 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 gas buret was added 2.86 g of redistilled diphenyl ether and 1.97 g (0.0201 mole) of 3-methyl-4-pentenal. The reaction flask was placed in an oil bath maintained at 129.6° and allowed to come to thermal equilibrium. Di-*t*-butyl peroxide (0.74 cc, 0.004 mole) was added employing a syringe. After a short induction period, carbon monoxide was evolved. The reaction was arrested after 359 min when the rate of carbon monoxide evolution had dropped to 0.2 cc/min. A total of 191 cc (43%) of carbon monoxide had formed. The volatile components which had collected in the cold trap were combined with the residual material in the reaction flask. The reaction products were examined by vpc (DIDP column, 25°). The virtually exclusive, low-boiling reaction products, as identified by their vpc retention times, were 3-methyl-1-butene, 1-pentene, acetone, and *t*-butyl alcohol. The ratio of 1-pentene to 3-methyl-1-butene was 10.8:1. The low-boiling components were separated from the solvent by simple distillation.

1-Pentene was isolated by vpc (DIDP column, 25°). The infrared and nmr spectra of the 1-pentene so isolated were superimposable upon those of an authentic sample. Unreacted 3-methyl-4-pentenal was isolated (DIDP column, 100°) and was found to have infrared and nmr spectra identical with those of the starting aldehyde.

Reaction Products Stability. A solution containing 0.445 g (3.90 mmoles) of redistilled *n*-heptaldehyde, 0.219 g (1.35 mmoles) of di-*t*-butyl peroxide, and 0.063 g (0.899 mmole) of 3-methyl-1-butene was made up to a 1.0-ml volume with chlorobenzene. The solution was sealed in an ampoule, heated for 45 min at 129.6°, cooled in ice water, and stored in the refrigerator until it was analyzed. The reaction products were analyzed employing the DIDP column (35°). Less than 1% conversion of 3-methyl-1-butene to 1-pentene was noted.

A solution containing 0.458 g (4.01 mmoles) of *n*-heptaldehyde, 0.219 g (1.35 mmoles) of di-*t*-butyl peroxide, and 0.055 g (0.784 mmole) of 1-pentene was made up to a 1.0-ml volume with chlorobenzene. Reaction and analysis procedures were similar to those used for 3-methyl-1-butene. No 3-methyl-1-butene was detected.

Olefin ratios were determined for various initial aldehyde concentrations employing the following procedure. Chlorobenzene solutions which were 4.0 and 3.0 *M* in aldehyde were diluted to one-half concentration in successive steps down to 0.125 and 0.094 *M* solutions, respectively. Each of the parent solutions also contained 20 mole % of di-*t*-butyl peroxide. One milliliter of each of the solutions that were prepared was sealed into ampoules which were fabricated from 10 × 75 mm Pyrex test tubes. There was approximately 1 ml of free space above each solution. The sealed ampoules were placed in a thermostated silicone oil bath maintained at (129.6 ± 0.1°). Temperature regulation was achieved using an H-B Instrument Co. Red Top thermoregulator in conjunction with an American Instrument Co. electronic relay (4-5301). The trimming heater that the relay controlled was a light bulb. One-half of the light bulb, the side facing the ampoules, was covered with aluminum foil. The aldehyde solutions were heated for varying lengths of time, depending upon their concentrations. The reaction periods employed were: neat aldehyde (6 *M*), 3.0 *M*, 20 min; 2 *M*, 1.5 *M*, 30 min; 1.0 *M*, 0.75 *M*, 45 min; 0.50 *M*, 0.38 *M*, 90 min; 0.25–0.094 *M*, 120 min. Decarbonylation was arrested by cooling the ampoules in ice water. The ampoules were stored at –20° until they were analyzed. The extent of decarbonylation in all solutions was less than 10% (Tables III and V). It was shown that the ratio of olefins does not vary significantly during the reaction periods which were used. To illustrate, 0.12 *M* solutions of 3-methyl-4-pentenal that were heated for periods of 30, 60, 90, and 120 min had 1-pentene to 3-methyl-1-butene ratios of 9.7 ± 0.3, 10.3 ± 0.3, 9.6 ± 0.4, and 9.7 ± 0.2, respectively.

1-Pentene to 3-methyl-1-butene ratios were determined by vpc. The DIDP (25–50°) column was generally used for analyses, although the TCEP (25°) column gave identical results. Separation of 1-pentene and 3-methyl-1-butene was better on the former column. The detector responses of the two olefins were the same within experimental error, so that the integrated peak areas could be compared directly. The reproducibility of olefin ratios was influenced by a number of factors. Aldehyde purity appears to be quite important. Good reproducibility was achieved, however,

(58) 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., 1958, p 219.

(59) M. G. Voronkov, *Zh. Obshch. Khim.*, 20, 2060 (1950); *Chem. Abstr.*, 45, 5608a (1951).

