Evidence for Intermolecular Radical–Olefin Addition as the General Mechanism for Aliphatic Free-Radical Rearrangement

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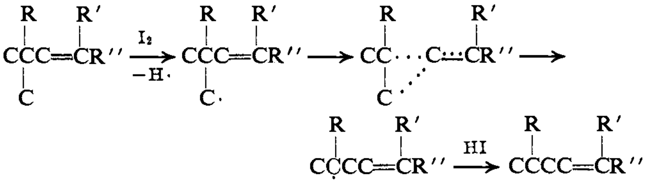
Abstract: Two mechanisms, (1) radical–olefin addition followed by β elimination and (2) 1,2-vinyl group migration, have been invoked to explain a number of thermal hydrocarbon free-radical rearrangements. Using 3,3-dimethyl-1-butene as the reactant, it is shown that of these two paths the addition mechanism alone can account for the thermal reaction in which 2-methyl-2-pentene is formed. The vinyl migration product is formed in the iodine reaction and is due to the interference resulting from the scavenging action of the halogen on free-radical chain carriers. Other olefins also give products predictable by the addition mechanism.

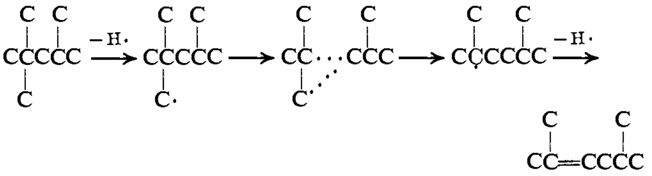
Although reported examples of thermal aliphatic free-radical rearrangements are few, their number is continuously increasing with the variety of reaction systems and molecular structures being studied.[2] Of the references given, three involve hydrocarbon oxidation reactions,[2a,b,e] for which special considerations prevail. Thus, in two of these cases, rearrangement is believed to occur *via* oxygenated free radicals.[2b,e]

Two mechanisms have been invoked to account for the aliphatic reactions.[2c,d,f] In a study of the high-temperature reaction of iodine with aliphatic hydrocarbons, it was proposed that rearrangement occurs by *intramolecular 1,2-vinyl group migration*, resulting in CH_2 insertion.[2f]



R, R′, R″ = CH_3 or H

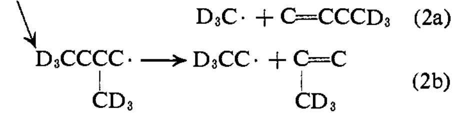
Rust and Collamer[2a] explain the presence of 2,5-dimethylhexene product in the oxidation of 2,2,4-trimethylpentane by a similar mechanism.



In this case, carbon insertion occurs by 1,2-alkyl rather than 1,2-vinyl migration. In light of the work by Slaugh and co-workers, it is probable that dehydrogenation to 2,4,4-trimethyl-2-pentene occurs, followed by rearrangement of the olefin.

Bryce, *et al.*, were the first to postulate the intermolecular *free-radical–olefin addition* mechanism to explain the free-radical rearrangements observed in the thermal decompositions of 1-butene and 1-butene-4-d_3.[3]

$$D_3CCC{=}C \longrightarrow D_3C\cdot + \cdot CC{=}C \qquad (1)$$



$$D_3C\cdot + D_3CCC{=}C \longrightarrow D_3CC\dot{C}CCD_3 \longrightarrow D_3C\cdot + C{=}CCCD_3 \qquad (2a)$$

$$D_3C\cdot + D_3CCC{=}C \longrightarrow D_3CC\underset{\substack{|\\ CD_3}}{C}C\cdot \longrightarrow D_3CC\cdot + \underset{\substack{|\\ CD_3}}{C}{=}C \qquad (2b)$$

$$D_3C\cdot + D_3CCC{=}C \longrightarrow D_3CH + D_3C\underset{\cdot}{C}C{=}C \qquad (3)$$

Evidence for the role of a methyl intermediate was obtained by sensitization with $(CH_3)_2Hg$ to provide a source of methyl radicals which accelerated formation of all products found in the unsensitized reaction; deuterium distribution in the reaction of 1-butene-4-d_3 was similar in both cases. Evidence for reaction 2a comes from undeuterated butene found in the sensitized reaction with 1-butene-4-d_3; that for 2b is deduced from the appearance of $C{=}CCD_3$ in the product of that reaction. Hydrogen abstraction, step 3, is indicated by CD_3H formation, which was found as the largest component of the deuterated methane products.

The work presented in this paper on the thermal reaction of 3,3-dimethyl-1-butene (3,3-DMB^{2-}) and other branched C_6 alkenes offers strong evidence that radical–olefin addition is the favored path for the high-temperature thermal rearrangement of aliphatic hydrocarbons, in the absence of interfering reactions.

Experimental Section

Apparatus and Procedure. A Vycor tube with separate inlets for inert diluent gas and liquid feed was placed inside a heated brass block. The heat of the block was controlled by West "Gardsmen." The block was wired in five separate sections to ensure minimum temperature differences along the length of the reactor. Gas was conventionally metered with a Fisher-Porter flow meter and liquid by syringe using a constant-rate syringe drive (JKM Instrument Co., Model S-1, obtainable from Fisher Scientific Co.).

A Perkin-Elmer 154 DG capillary column gas chromatograph equipped with flame ionization detector was connected to the exit of the reactor tube. The total gas stream passed through a six-port gas-sampling valve which could be diverted to the gas chromatograph when desired. Compound identification was based on calibration with authentic materials and gas chromatography time-of-flight mass spectrometric analyses, to confirm identification. In all cases, a squalane column was used.

Materials. All hydrocarbons except 4-M-1-C_5^{2-} were purchased from Columbia Organic Chemicals, Inc.; 4-M-1-C_5^{2-} was obtained from Phillips Petroleum Co. The materials were dried over $MgSO_4$ for 1 week and used directly. Purity of materials was the highest

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[1] To whom inquiries should be addressed at Esso Research and Engineering Co., Government Research Laboratory, Linden, N. J.

[2] (a) F. F. Rust and D. O. Collamer, *J. Am. Chem. Soc.*, **76**, 1055 (1954); (b) S. Sato and R. J. Cvetanović, *Can. J. Chem.*, **37**, 953 (1959), and earlier references by R. J. C.; (c) J. A. Berson, C. J. Olsen, and J. S. Walia, *J. Am. Chem. Soc.*, **82**, 5000 (1960); (d) W. A. Bryce and M. S. Hardman, *Can. J. Chem.*, **40**, 1031 (1962), and ref 4–6 therein; (e) D. L. Trimm and C. F. Cullis, *J. Chem. Soc.*, 1430 (1963); (f) L. H. Slaugh, R. D. Mullineaux, and J. H. Raley, *J. Am. Chem. Soc.*, **85**, 3180 (1963); (g) L. H. Slaugh, *ibid.*, **87**, 1522 (1965).

[3] W. A. Bryce and P. Kebarle, *Trans. Faraday Soc.*, **54** 1660 (1958).

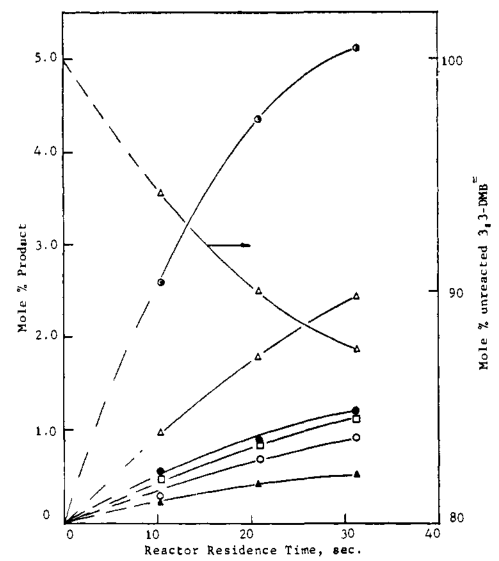


Figure 1. 3,3-Dimethyl-1-butene pyrolysis (Vycor tube volume 52 cc), 510°, 1 atm absolute, concentration 1.68×10^{-3} *M:* △, C_1; ▲, $C_3{}^{2-}$; ●, i-$C_4{}^{2-}$; ○, 2-M-2-$C_4{}^{2-}$; □, 2-M-2-$C_4{}^{4-}$; ⊙, 2-M-2-$C_5{}^{2-}$.

obtainable (~99%; only 2,3-DM-2-$C_4{}^{2-}$ was 96.4% pure and appropriate corrections were made).

Results

The major products obtained in the flow reactor study of 3,3-DMB^{2-} pyrolysis are shown in Figure 1 and Table II as a function of reaction time. The C_6-olefin product consisted almost entirely of 2-methyl-2-pentene (2-M-2-$C_5{}^{2-}$).

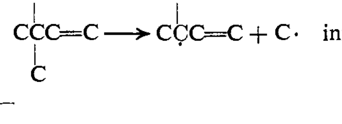
In Figure 2 a log–log plot of the rate of product formation *vs.* reactant concentration yields a straight line. The slope of this plot is 0.94, *i.e.*, the reaction is approximately first-order. Reaction rates were calculated from the equation $r = F\Delta X/V$, where F = feed rate, moles/hr, ΔX = fractional conversion to product (2-M-2-$C_5{}^{2-}$), and V = reactor volume, l, which is valid at low conversions.

Possible heterogeneous effects were checked by packing the Vycor reactor with quartz beads. Thus, while the surface:volume ratio was increased 5.8-fold, the volume was half of the empty tube. At identical residence times, conversion was unchanged.

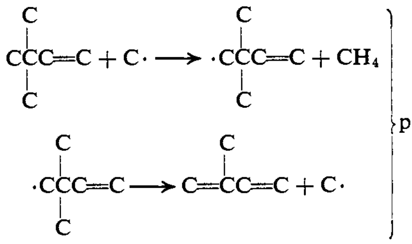
These results show the absence of gross surface effects, although a combination of wall initiation *and* termination cannot be ruled out. Over-all, the thermal rearrangement of 3,3-DMB^{2-} to 2-methyl-2-pentene appears to be a nearly first-order homogeneous reaction.[4]

Discussion

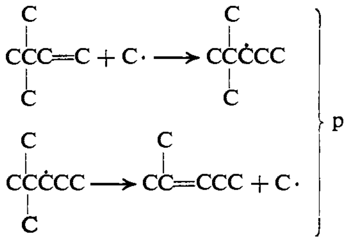
The following free-radical chain reaction mechanism would account for the products found.



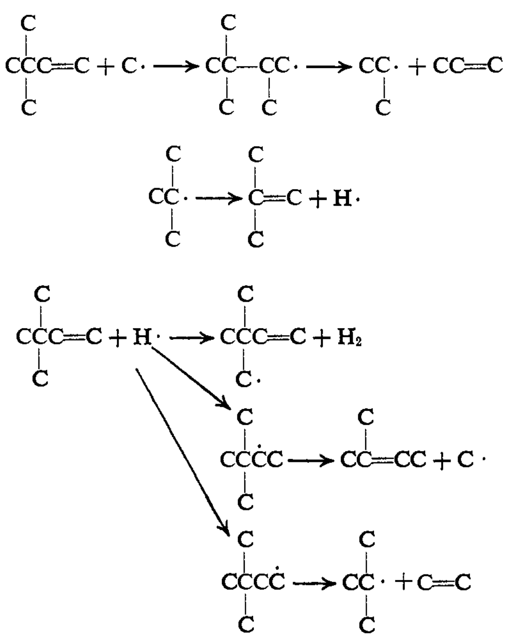
initiation

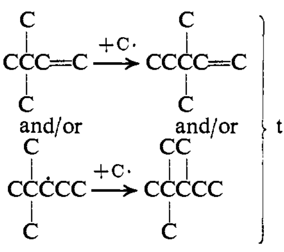


propagation (4)



propagation (5)





(6a)

termination

(6b)

The experimental results show propagation steps 4 and 5 to be of chief significance. Chain termination *via* the recombination of methyl radicals is considered negligible, on the basis of the small amount of C_2 products. The proposed termination steps 6 are supported by a gas chromatographic peak corresponding to one of the predicted products, 3,3-dimethyl-1-pentene. Also, a reaction initiated by unimolecular decomposition and terminated by bimolecular β-μ (decomposable + nondecomposable) radical recombination is known to obey over-all first-order kinetics,[5] as in the present case.

The propagation steps possess a common feature wherein a radical chain carrier adds to a double bond or it abstracts hydrogen. The resulting radical loses an

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(4) An independent study showed the Vycor glass to have slight acidic properties which was manifested in the formation of minor amounts of rearranged products, such as 2,3-DM-$C_4{}^{2-}$ from 3,3-DMB^{2-}, and 2-M-$C_5{}^{2-}$ from 4-M-1-$C_5{}^{2-}$ (see Table II).

(5) E. W. R. Steacie, "Atomic and Free Radical Reactions," 2nd ed, Reinhold Publishing Corp., New York, N. Y., 1954, p 105.

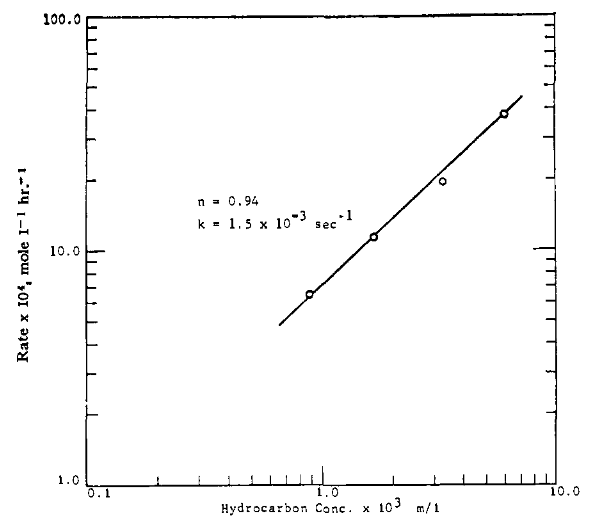
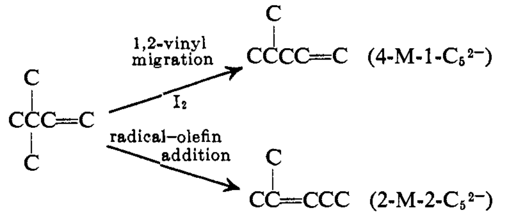


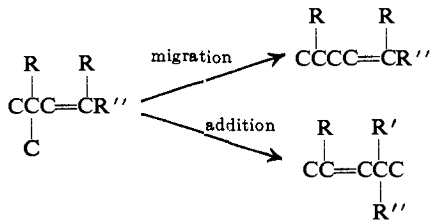
Figure 2. 3,3-DMB^{2-} pyrolysis, 510°, 1 atm absolute. Rate refers to 2-M-2-C$_5$$^{2-}$ production.

aliphatic radical by β elimination. Bryce, *et al.*, as mentioned previously, proposed this scheme to explain the results found in the decomposition of butene[3] sensitized by $(CH_3)_2Hg$.

It has been mentioned that aliphatic free-radical rearrangements have been accounted for in terms of 1,2-vinyl group migration.[2f,g] Evidence was presented to show that (1) unsaturation is a prerequisite for rearrangement, since 2,2-dimethylpropane does not rearrange to the 2-methylbutyl structure; and (2) methyl group migration does not occur. The choice between mechanistic alternatives for a reaction is facilitated when a different product follows for each. The 3,3-DMB^{2-} rearrangement offers a clear illustration.



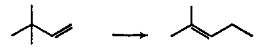
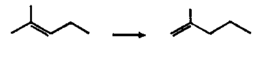
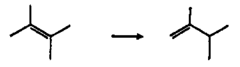
More generally



R, R′, R″ = CH_3 or H

The mechanism of radical–olefin addition followed by β elimination explains the formation of the observed product, 2-M-2-C$_5$$^{2-}$. *1,2-Vinyl migration would lead to 4-M-1-C$_5$$^{2-}$, which was not observed* (under the experimental conditions, 0.002 mole % was detectable). The possibility of a consecutive reaction, 3,3-DMB^{2-} → 4-M-1-C$_5$$^{2-}$ → 2-M-2-C$_5$$^{2-}$, can be eliminated. Thermal double-bond isomerization is known to be quite slow. The values of rate constants and values for n (rate equations $r = k[C]^n$ could be used for all cases) obtained at 510° for a number of double-bond isomerizations of C_6 olefins as well as the 3,3-DMB^{2-} rearrangement are presented in Table I. Calculations show that such indirect reaction could lead to no more than 0.001 of the observed conversion to 2-M-2-C$_5$$^{2-}$. In the absence of iodine, the thermal reaction, proceeding *via* radical–olefin addition, stands out clearly. The only C_6 olefin formed of the 2-methylpentene structure is 2-methyl-2-pentene. Absence of the other isomers shows that double-bond isomerization is negligible.

Table I. Thermal Rearrangement of C_6 Olefins[a]

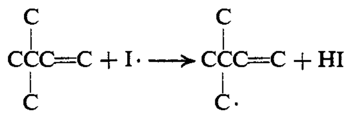
Reaction	$k \times 10^3$, sec^{-1} [b]	n
	1.5	0.94
	2.7	0.94
	1.4	0.92
	0.28	0.90

[a] Reaction conditions: 510°, 1 atm absolute, N_2 diluent; Vycor tube flow study. [b] Rate constant precise to approximately 12%. [c] Rate constant refers to *cis*- and *trans*-4-M-2-C$_5$$^{2-}$.

The vinyl migration-predicted product, 4-M-1-C$_5$$^{2-}$, was not reported as a product for the reaction in which it is expected, *i.e.*, high-temperature reaction of 3,3-DMB^{2-} with iodine. Instead, 2-methylpentanes and 2-methylpentadienes were found. According to Slaugh, *et al.*, double-bond shift from 4-M-1-C$_5$$^{2-}$ to more stable isomers and dehydrogenation occurs in the presence of iodine. The same undoubtedly occurred with 2-methylbutane which would rearrange as 3-methyl-1-butene to give 1-pentane; both 1- and 2-pentanes were found. Slaugh, *et al.*, also reported such secondary reactions in their study of C_5 to C_8 olefins with iodine, so that the observed products were not those directly predicted by the vinyl migration mechanism.

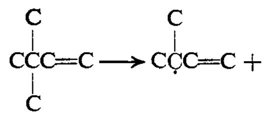
The presence of iodine will interfere with radical–olefin addition by making an alternative reaction path highly competitive, or even predominant. With iodine the reaction initiation steps are

$$I_2 \longrightarrow 2I\cdot$$



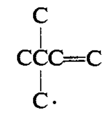
$$\mathrm{C\overset{C}{\underset{C}{C}}C{=}C + I\cdot \longrightarrow C\overset{C}{\underset{C\cdot}{C}}C{=}C + HI}$$

as compared to the initiation



$$\mathrm{C\overset{C}{\underset{C}{C}}C{=}C \longrightarrow C\overset{C}{\underset{\cdot}{C}}C{=}C + C\cdot}$$

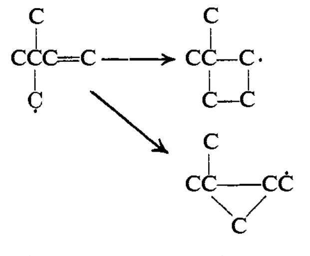
which occurs both in the presence and absence of iodine. To sustain the radical–olefin addition, methyl radicals must be present. It may be expected that their concentration will fall sharply because of the reaction with I_2 (or I·), so that the only remaining species of importance will be



$$\mathrm{C\overset{C}{\underset{C\cdot}{C}}C{=}C}$$

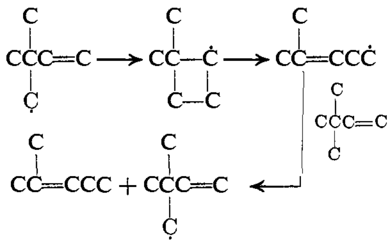
when iodine is present and 1,2-vinyl migration will occur. It will also occur at low temperatures where the methyl and/or hydrogen chain carriers will not be normally generated. Thus, the 2-cyclopentenylmethyl radical derived from the peroxyacetate underwent the expected 1,2-vinyl migration to yield the 4-cyclohexenyl radical in solution at 140°.[2g]

Other possible reaction mechanisms which may be postulated to account for the observed products would involve *intramolecular* addition reactions.[6] For example, in the case of 3,3-DMB^{2-}, intramolecular addition would lead to cyclobutane or cyclopropane intermediates.



Such small-ring intermediate radicals would be highly strained and hence their formation is expected to be energetically unfavored. The path involving the cyclopropane intermediate would differ from the vinyl-migration mechanism only if the radical abstracted hydrogen to form 1,1,2-trimethylcyclopropane. Based on the known reactions of cyclopropane and its alkyl derivatives, the thermal decomposition of this intermediate would not lead to the product distribution observed for 3,3-DMB^{2-}.

The main objections to the mechanism involving the 1,1-dimethylcyclobutyl intermediate are ring strain and the necessity for the alkenyl radical produced to propagate the reaction chain *via* hydrogen abstraction.



Experimental evidence is not available for arriving at a definite conclusion regarding the possible contribution of cyclic intermediates to the formation of the observed reaction products. On the other hand, the evidence obtained by Bryce and Kebarle[3] on the role of intermolecular methyl radical–double-bond addition reactions provides strong support for the addition/β elimination mechanism as the favored reaction path.

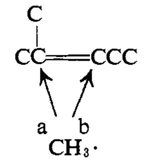
Free-radical addition to the double bond of the remaining olefins in Table I and/or abstraction from an allylic carbon, both followed by β elimination, leads to predicted product distributions in agreement with those found, shown in Table II. In each case, double-bond isomerization, involving hydrogen-atom addition and elimination, is a major reaction. The other products are seen to be quite specific for each parent olefin. This is indicative of the role of nonrandom attack on the hydrocarbon molecule.

Table II. Thermal Reactions of Olefins[a]

Products	3,3-DMB^{2-}	2-M-2-C$_5$$^{2-}$	2,3-DM-2-C$_4$$^{2-}$	4-M-1-C$_5$$^{2-}$
C_1	0.99[d]	0.68	*g*	
C_2, C_2^{2-} [b]		0.36		0.31
C_3, C_3^{2-} [b]	0.24			2.06
i-C_4^{2-}, 1-C_4^{2-} [b]	0.56	0.10		0.49
2-M-1,3-C_4^{4-}	0.48	0.79		0.08
3,3-DMB^{2-}		0.01[f]		
2-M-2-C_4^{2-}	0.31	0.19	0.03	
1,3-C_5^{4-}				0.15
2-M-2-C_5^{2-}	2.59			0.12
2,3-DM-1-C_4^{2-}	0.12		1.69	
2-M-1-C_5^{2-}		3.31		0.12
4-M-2-C_5^{2-}				0.52
M-1,3-C_5^{4-} [c]	0.22	0.36	*h*	0.02
3,3-DM-1-C_5^{2-}	0.03[e]			
2,3-DM-1,3-C_4^{4-}			0.10	

[a] Reaction conditions: 510°, 1 atm absolute pressure. [b] The members of the pair were not resolvable. [c] A mixture of *trans*-2-2-M-1,3-C_5^{4-} and 4-M-1,3-C_5^{4-}. [d] Products expressed in mole % of hydrocarbon feed. [e] Identification is not positive. [f] Identity of C_6 olefin positively established by time-of-flight mass spectrometry. [g] C_1 detected. [h] Unknown gas chromatography peaks were obtained, one of which could be the proposed 3-methyl-1,2-butadiene.

In the case of 2-M-2-C_5^{2-}, all of the reaction products formed in sufficient quantities can be accounted for by $CH_3\cdot$ addition followed by β elimination (for *i*-C_4^{2-}, H addition and subsequent β elimination are required). The fact that the yield of 3,3-DM-1-C_4^{2-} is low is a reflection of competition for $CH_3\cdot$ addition at two sites.



Stability considerations of the resulting secondary and tertiary free radicals favor path b over path a. Path b leads to the observed reaction products: C_1; C_2/C_2^{2-}; 1-C_4^{2-}/*i*-C_4^{2-}; 2-M-1,3-C_4^{4-}; 2-M-2-C_4^{2-}; and M-1,3-C_5^{4-}. These factors provide additional evidence for radical addition followed by β elimination as the general mechanism in such reactions.

Acknowledgment. The authors wish to express their appreciation to the Esso Research and Engineering Company for permission to publish this work.

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[6] The referees of this paper are acknowledged for suggesting the possibility of intramolecular addition reactions.