Camphene. IV. Interconversions of Three Homocamphenes[1,2]

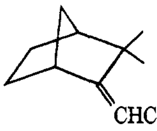
Wyman R. Vaughan*[3] and David M. Teegarden[4]

Contribution from the Department of Chemistry, University of Connecticut, Storrs, Connecticut 06268, University of Michigan, Ann Arbor, Michigan 48104, and the University of Wisconsin—Platteville, Platteville, Wisconsin 53818.
Received January 22, 1974

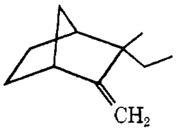
Abstract: The preparations of 8-, 9- and 10-homocamphene are described. and their interconversions in acetonitrile–pyruvic acid have been studied and compared with camphene racemization mechanisms. The kinetics of the various processes, which are interrupted before secondary rearrangements become a problem, indicate that each isomer is transformed into its products *via* simultaneous (competitive) reactions.

When the present research was first undertaken, its purpose was to investigate primarily the effect of substitution at the 8 position of camphene, *i.e.*, on the methylene carbon. The earliest systematic study of this problem was carried out in 1942[5] and its results appeared strongly to suggest that various optically active, 8-substituted camphenes racemized in acidic media without experiencing any isomerizations attributable to alkyl migrations of the type experienced by 1-substituted camphenes and then generally called Nametkin rearrangements.[6a] At the time, the Wagner–Meerwein rearrangement was well established[6b] for the camphene system, but of itself could not account for the racemization of either camphene or 8-substituted camphenes. Some years later, however, the fact of 6,2-hydride migration was demonstrated for norbornyl cations,[7] and a combination of such a rearrangement with a prior and subsequent Wagner–Meerwein rearrangement can in fact account for racemization of an 8-substituted camphene. That no Nametkin rearrangements were observed[5] was attributed by Roberts[8] to the possibility that 8-substituted camphenes may be appreciably more stable thermodynamically than their 9- or 10-substituted isomers.

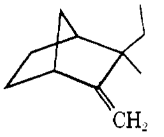
In the intervening years carbon-14 tracer studies[8–10] firmly established the participation of both Nametkin (hereinafter designated N) and Wagner–Meerwein/6,2-hydride/Wagner–Meerwein (hereinafter designated WMH) mechanisms in the racemization of camphene itself, and the fact of both an *exo*- and an *endo-N*-methyl shift was brought to light, albeit with too much weight assigned to the endo-N process.[10] More recently a previously discounted fourth racemization mechanism involving tricyclene formation was suggested,[11a] and most recently this has been confirmed[2] along with a drastic downward revision of the amount of endo-N rearrangement, which brings the behavior of camphene into line with the experimental generalization that endo-3,2 shifts by substituents other than hydrogen are inhibited.[11b] Thus in a study of the behavior of 8-methylcamphene (**1**) its potential rearrangement *via* any or all of four mechanisms into 10-methylcamphene (**2**) and 9-methylcamphene (**3**) must be considered: six distinguishable isomerization reactions and three racemization reactions. Tricyclene formation, as one of the four mechanisms, has the same structural and stereochemical consequences as the WMH mechanism and kinetically can be determined only if its rate of formation and/or reconversion to camphene is demonstrable, and its intervention proven by isolation.



1



2



3

Synthesis

Compounds **2** and **3** are epimeric at C-3 and their syntheses involve the epimeric 2-norbornanones as intermediates (**2a**, **2b**; **3a**, **3b**), these being available by way of Corey's highly stereoselective alkylations of 2-norbornanone.[12] Conversion of the 3,3-dialkyl-2-norbornanones (**2b** and **3b**) to **2** and **3** involved Corey's modified Wittig procedure;[13] and the expected configuration of **3** was confirmed by comparison with spectrographic data for **3** prepared independently.[14] Both epimeric methylcamphenes were shown to be isomerically pure by glpc.

---

(1) Abstracted from the Ph.D. dissertation of D. M. T., The University of Michigan, 1972. Much of the experimental work was carried out at The University of Wisconsin—Platteville.

(2) Paper III: C. W. David, B. W. Everling, R. J. Kilian, J. B. Stothers, and W. R. Vaughan, *J. Amer. Chem. Soc.*, **95**, 1265 (1973).

(3) Address correspondence to this author at the University of Connecticut.

(4) Fellowship support for this work for D. M. T. is gratefully acknowledged to the Union Carbide Corporation, the Uniroyal Foundation, and the donors of the Paul Bagley Fellowship.

(5) J. J. Ritter and G. Vlases, Jr., *J. Amer. Chem. Soc.*, **64**, 583 (1942).

(6) (a) S. Nemetkin and L. Brussoff, *Justus Liebigs Ann. Chem.*, **459**, 144 (1927); (b) H. Meerwein and F. Montfort, *ibid.*, **435**, 207 (1924).

(7) (a) J. D. Roberts and C. C. Lee, *J. Amer. Chem. Soc.*, **73**, 5009 (1951); (b) J. D. Roberts, C. C. Lee, and W. H. Saunders, *ibid.*, **76**, 4501 (1954).

(8) J. D. Roberts and J. A. Yancey, *J. Amer. Chem. Soc.*, **75**, 3165 (1953).

(9) W. R. Vaughan and R. Perry, Jr., *J. Amer. Chem. Soc.*, **75**, 3168 (1953).

(10) W. R. Vaughan, C. T. Goetschel, M. H. Goodrow, and C. L. Warren, *J. Amer. Chem. Soc.*, **85**, 2282 (1963).

(11) (a) P. Hirsjarvi, K. Heinonen, and L. Pirila, *Suom. Kemistilehti B*, **37**, 77 (1964). (b) Although inhibition of endo-3,2-shifts appears to be generally observed, specific exceptions have been noted, *e.g.*, A. W. Bushell and P. Wilder, Jr., *J. Amer. Chem. Soc.*, **89**, 5721 (1967), and more recently S. Rengaraju and K. D. Berlin, *Tetrahedron*, **27**, 2399 (1971); **28**, 2882 (1972).

(12) E. J. Corey, R. Hartmann, and P. A. Vatakencherry, *J. Amer. Chem. Soc.*, **84**, 2611 (1962).

(13) R. Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, **28**, 1128 (1963).

(14) W. R. Vaughan, J. Wolinsky, R. R. Dueltgen, S. Grey, and F. S. Seichter, *J. Org. Chem.*, **35**, 400 (1970).

Preparation of **1** from 3,3-dimethyl-2-norbornanone (camphenilone) *via* the appropriate Wittig reaction failed as a practicable procedure as did the obvious Grignard approach which resulted in nearly quantitative reduction of camphenilone by ethylmagnesium bromide. However, replacement of ethylmagnesium bromide by ethyllithium led to a good yield of the expected tertiary alcohol which was smoothly dehydrated without any rearrangement by means of thionyl chloride to give **1** free of its structural iosmers. The kinetic runs afforded **1** as a single isomer.

Kinetic Procedures

The choice of reaction medium (acetonitrile–pyruvic acid) was dictated by previous experience with this system[8,10] and the wish to be able to compare rate data with that of concurrent work on camphene itself.[2] In early runs it became apparent that unusual care had to be taken to ensure the purity of both solvent and catalyst by redistillation immediately prior to use and to employ a somewhat lower temperature (138 ± 0.2°) than previously[8,10] if irreproducible data were to be avoided.

Another factor of comparable importance to reproducibility was the total quantity of the reacting system for each run. The use of 0.0336 mol of pyruvic acid/mol of acetonitrile with 1.10 ± 0.03 *M* olefin (total weight ~0.05 g) proved to be a workable compromise between an amount of recoverable olefin suitable for glpc analyses and a total volume small enough to permit relatively rapid thermal equilibrium with the heating bath to be established. But even so, the data for comparatively short times are not as reliable as for longer time intervals.

The range of times was from 0 to 420 min, approximately an hour longer than the half-life of the most reactive compound (**2**) beyond which data became less reproducible. For each data point a small sealed glass tube was immersed in a temperature-controlled oil bath, and the reaction was quenched at the appropriate time by immersion in ice–water. The recovered isomer mixtures were analyzed at least twice for each data point by glpc, the peak areas being determined by planimetry. Data are summarized in Tables I–III. Previous experience with camphene[2,10] showed that volatile products (*i.e.*, camphene) can be recovered in high yield after rearrangement, and glpc curves for **1**, **2**, and **3** show approximately the same amount of total olefin at 0 and at 420 min. Therefore no internal standard was deemed necessary. The conceivable intervention of pyruvate esters was never considered a problem.[2,8,10] Choice of this system in the present and previous work[2,10] was dictated by a desire for direct comparison of pseudo-first-order rate constants with those obtained for camphene.[2]

Table I. Reactant and Product Mole Fractions for Isomerization of **1**

	Mole fractions[a]			
		Products		
Time, min	Reactant **1**	**2**	**3**	**4**
0	1.0	0	0	0
30	0.99	0.01	0	0
60	0.99	0.01	0	0
90	0.99	0.01	0	0
180	0.98	0.02	0	0
300	0.97	0.03	0	0
420	0.96	0.04	0	0

[a] Calculated values from least-squares plot.

Table II. Reactant and Product Mole Fractions for Isomerization of **2**

	Mole fractions[a]			
		Products		
Time, min	Reactant **2**	**1**	**3**	**4**
0	1.0	0	0	0
30	1.0	0	0	0
90	0.88	0.10	0.02	0.01
150	0.76	0.20	0.03	0.02
240	0.61	0.24	0.07	0.07
300	0.53	0.29	0.09	0.09
420	0.40	0.38	0.13	0.10

[a] Calculated values from least-squares plot.

Table III. Reactant and Product Mole Fractions for Isomerization of **3**

	Mole fractions[a]			
		Products		
Time, min	Reactant **3**	**1**	**2**	**4**
0	1.0	0	0	0
30	1.0	0	0	0
60	1.0	0	0	0
90	0.96	0.02	0.003	0.01
120	0.95	0.02	0.01	0.02
150	0.93	0.02	0.02	0.04
180	0.92	0.02	0.03	0.03
240	0.89	0.03	0.03	0.05
300	0.86	0.04	0.05	0.06
360	0.83	0.05	0.05	0.07
420	0.80	0.06	0.05	0.09

[a] Calculated values from least-squares plot.

During the isomerization of both **2** and **3**, a new compound (**4**) appeared and was collected by glpc. Its nmr spectrum[15a] showed the presence of two methyl singlets and no absorption attributable to vinyl hydrogen. Of the two most likely compounds, both methyltricyclenes (by analogy with camphene[2]), the meso isomer is excluded since it would necessarily exhibit but one methyl singlet (six equivalent protons). Consequently **4** most likely is 2,3-dimethyl-3-ethyltricyclo[2.2.1.0^{2,6}]heptane or *asym*-methyltricyclene. High-resolution mass spectrometry[15b] established the molecular formula of **4** as $C_{11}H_{18}$ (calcd, 150.1408500; found, 150.1408536), and the fragmentation pattern from the mass spectrometer[15b] closely resembles that for compounds **1**, **2**, and **3**, but even more striking resemblance of the fragmentation pattern for **4** to that of tricyclene itself[1] was observed. Thus one may confidently accept the proposed structure of **4** as correct. The minute amounts produced precluded independent study of its reactions.

The choice of 420 min as the longest time for acquisition of kinetic data was dictated by two considerations: the need to avoid secondary rearrangements which

---

(15) (a) Certain of the nmr spectra were recorded by Dr. Robert Romanet, Chemistry Department, University of Rochester, to whom the authors express appreciation. (b) The authors are indebted to Professor Robert B. Fairweather of The University of Connecticut Department of Chemistry for these mass-spectrometric data. Support for this work in the form of a National Science Foundation instrument grant (NSF GP-18332) to the University of Connecticut is gratefully acknowledged.

Table IV. Calculation of Individual Rate Constants

	From ([product] *vs.* $1 - e^{-kt}$) plot		From partitioning ratios	
Product	Slope	k, sec^{-1}	Ratio	k, sec^{-1}
Reaction of Olefin **1** [$k_1 = k_{12} = 1.29 \pm 0.10 \times 10^{-6}$ sec^{-1}]				
Reaction of Olefin **2** [$k_2 = 3.62 \pm 0.38 \times 10^{-5}$ sec^{-1}]				
1	0.640	k_{21}, $2.1 \pm 0.3 \times 10^{-5}$	0.62	k_{21}, $2.2 \pm 0.3 \times 10^{-5}$
3	0.233	k_{23}, $7.7 \pm 0.9 \times 10^{-6}$	0.20	k_{23}, $7.1 \pm 0.8 \times 10^{-6}$
4	0.200	k_{24}, $6.6 \pm 0.7 \times 10^{-6}$	0.18	k_{24}, $6.5 \pm 0.7 \times 10^{-6}$
Reaction of Olefin **3** [$k_3 = (9.25 \pm 0.58) \times 10^{-6}$ sec^{-1}]				
1	0.326	k_{31}, $2.7 \pm 0.3 \times 10^{-6}$	0.28	k_{31}, $2.6 \pm 0.3 \times 10^{-6}$
2	0.321	k_{32}, $2.7 \pm 0.3 \times 10^{-6}$	0.27	k_{32}, $2.5 \pm 0.4 \times 10^{-6}$
4	0.486	k_{34}, $4.1 \pm 0.4 \times 10^{-6}$	0.45	k_{34}, $4.2 \pm 0.4 \times 10^{-6}$

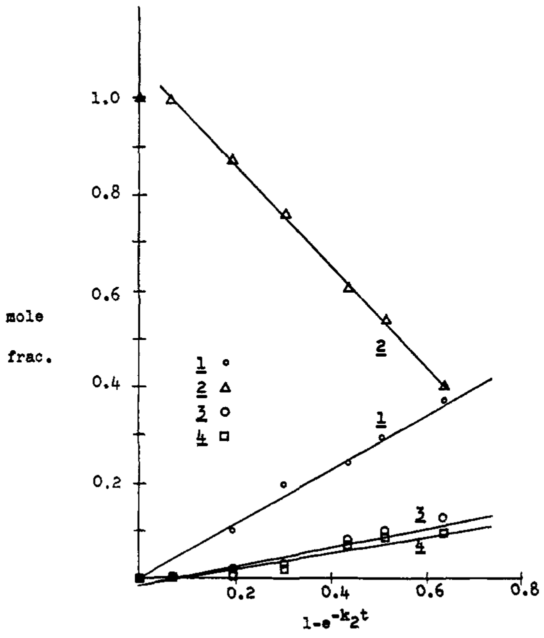


Figure 1. Plot of olefin mole fraction *vs.* $1 - e^{-kt}$ for compound **2**.

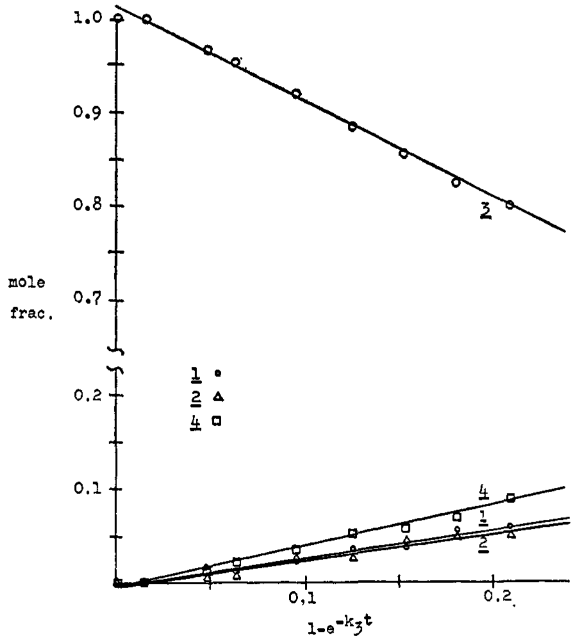


Figure 2. Plot of olefin mole fraction *vs.* $1 - e^{-kt}$ for compound **3**.

would enormously complicate the kinetic problem, and the instability of the solvent–catalyst system at longer periods when the decomposition of pyruvic acid can be demonstrated. Over this time interval the usual tests for reaction order confirm the expected pseudo-first-order kinetics[16] for the isomerization of the starting olefin in each case; *and* at the same time appropriate analyses of the kinetic data show that in *each case* the products of isomerization are produced in competitive (concurrent) pseudo-first-order reactions, no product being obtained indirectly (by a consecutive series of reactions).[17] The significant data for **2** and **3** are displayed in Figures 1 and 2.

The individual rate constants can be calculated directly in two ways: from the partitioning ratios and by taking advantage of the linearity of the [product] *vs.* $[1 - e^{-kt}]$ plots.

The former method applied to **3** → **1** gives

$$N_1/\sum N \text{ products} = k_{31}/(k_{31} + k_{32} + k_{34})$$

$$k_3 = k_{31} + k_{32} + k_{34}$$

whence

$$k_{31} = (N_1/\sum N \text{ products})k_3$$

The latter method uses a least-squares analysis of the appropriate data which affords a reasonably good straight line for the function

$$[\mathbf{1}] = (k_{31}[\mathbf{3}]_0/k_3)(1 - e^{-k_3t})$$

whence

$$k_{31} = \text{slope}(k_3/[\mathbf{3}]_0)$$

The individual rate constants calculated by both methods are displayed in Table IV.

The relationship between the individual specific rates (*e.g.*, k_{12}) and the "real" specific rates for the rearrangement steps (*e.g.*, $k_{1\text{i}-2\text{i}}$) is obvious

$$k_{12} = k_{1\text{i}-2\text{i}}K_\text{a}[\text{HP}]/[\text{P}^-]$$

wherein

$$K_\text{a} = [\mathbf{1}\text{i}][\text{P}^-]/[\mathbf{1}][\text{HP}]$$

and HP is pyruvic acid with P⁻ being pyruvate ion. Proton transfers are assumed to be rapid steps with the interconversion of organic cations being slow.

Discussion

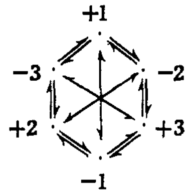
In the introductory portion of this paper it was pointed out that there are at least nine distinct reactions which must be considered in a comprehensive study of

---

[16] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism: A Study of Homogeneous Chemical Reactions," 2nd ed, Wiley, New York, N. Y., 1961, p 12.

[17] Reference 16, pp 166–169.

the isomerization of 8-methylcamphene (**1**). Fortunately appreciable simplification can be effected by working only with racemic **1**, **2**, and **3**; *i.e.*, racemization of each structural isomer need not be considered. Thus the hexagonal array



in which any compound can be transformed into either of its neighbors (with configurational inversion) or into its enantiomer (directly across the hexagon) may be reduced to a trigonal array, with the added proviso that a potential fourth component, **4**, constitutes a competitive route for the interconversion of **2** and **3** (note that the actual rearranging species are the protonated olefins: *cf.* Figure 3). Without explicit study of the isomerization of **4**, which would furnish the two additional rate constants, k_{42} and k_{43}, there are in principle eight determinable (approximately) rate constants (Table V): k_{12}, k_{13}; k_{21}, k_{23}, k_{24}; k_{31}, k_{32}, k_{34}. In practice, the failure to detect any **3** during the isomerization of **1** made the determination of k_{13} impossible. Since this process involves an endo-N rearrangement (methyl), failure to detect it was not surprising. What was surprising was the detection of a significant amount of the reverse processs (k_{31}) as one of three *concurrent* isomerizations of **3** (*i.e.*, **1** is produced directly from **3** and *not via* **2**).

$$\begin{tikzcd}
\mathbf{3} \arrow[r, shift left] \arrow[d, shift left] \arrow[dr] & \mathbf{1} \arrow[l, shift left] \arrow[d, shift left] \\
\mathbf{4} \arrow[r, shift left] \arrow[u, shift left] & \mathbf{2} \arrow[l, shift left] \arrow[u, shift left] \arrow[ul]
\end{tikzcd}$$

Table V. Comparative Rate and Equilibrium Constants

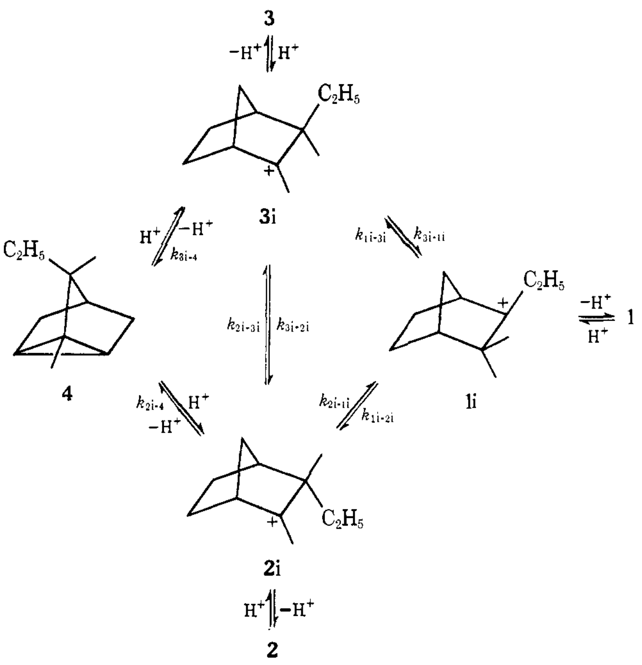
Mechanism	Type of rearrangement	$k \times 10^6$, sec^{-1}	Camphene equiv $k \times 10^6$, sec^{-1}	Equilibrium constants
$1 \rightarrow 2$	Exo-N	1.3	28	0.062
$1 \rightarrow 3$	Endo-N	∼0	1.4	∼1
$2 \rightarrow 1$	Exo-N	21	28	16
$2 \rightarrow 3$	WMH	7.4	21	2.7
$2 \rightarrow 4$	T[a]	6.6	1.8	1.6[b]
$3 \rightarrow 1$	Endo-N	2.7	1.4	Very large
$3 \rightarrow 2$	WMH	2.7	21	0.37
$3 \rightarrow 4$	T[a]	4.1	1.8	0.62[b]

[a] Tricyclene formation. [b] For the reaction $2 \rightarrow 3$ *via* **4**.

In the discussion which follows it is assumed that the reactions are rapid compared to cation rearrangements

$$\text{olefin} + \text{HP} \rightleftharpoons \text{cation}^+ + \text{P}^-$$

and that they have comparable equilibrium constants (*cf.* Figure 3). Without such assumptions any estimate of relative reactivities and/or stabilities is beyond the scope of present experimental data. The apparent rate constants and derived equilibrium constants (Table V) are consistent both with the previously observed enhanced stability of 8-substituted camphenes[4,8] and intuitive steric considerations. Therefore we believe our assumptions are reasonably valid.



Reaction	Mode
1i ⇌ 2i	3,2-*exo*-methyl shift
1i ⇌ 3i	3,2-*endo*-methyl shift
2i ⇌ 3i	Wagner-Meerwein/6,2-hydride rearrangements

Figure 3.

The relative thermodynamic stabilities of the isomeric methylcamphenes (and inferentially of the related carbonium ions) are reflected in the approximate equilibrium constants for the conversion of **2** to each of the other isomers. But it is not possible to fit camphene itself into such a scale. However, it is possible to compare rate constants for the various rearrangement types (Table V), not only for forward and reverse reactions among the methylcamphenes but also with the corresponding rate constants for camphene. And such comparisons lead at once to the conclusion that **1** is not only the most stable of the three isomeric methylcamphenes, as suggested by Roberts[8] of 8-substituted camphenes in general, but also that **1** is very much more stable toward methyl shifts than camphene itself in which somewhat more than half of camphene racemization is attributable to methyl shifts.[2] Furthermore **2**, for which all of the rearrangements experienced by camphene except endo-N (very minor for camphene) are observed, is rather less reactive than camphene. The general order of reactivity is camphene > **2** > **3** > **1**, and the only mechanisms in which camphene appears to be less reactive than either **2** or **3** are tricyclene (mechanism T, Table V) formation and **3** → **1** (endo-N). Perhaps this reactivity sequence may be attributed to a greater degree of order in the transition states for camphene racemization (*e.g.*, symmetry) as compared with those leading from the methylcamphenes; assuredly it is not to be attributed to greater relief of steric strains in camphene.

The most obvious steric effect of the additional methyl group in **2** and **3** is the introduction of greater potential nonbonded interactions of the methyl hydrogens with the 5-endo hydrogen in **2** and the 7-syn hydrogen in **3**. When strain is mentioned hereinafter, it refers to the appropriate nonbonded interactions. These strains will be relatively unchanged (on cation formation) in the C-2 cations derived from **2** and **3**, for these cations most likely possess the geometry normally associated with classical tertiary cations as suggested for 2-ethyl- and 2-methylnorbornyl cations by Olah.[18-20] From the relative thermodynamic stabilities of **2** and **3**, one infers that the effects of strain are more pronounced in **2**.

From the data in Table V it is obvious that any *structural* isomerization of **1** affords thermodynamically less stable products. Thus the cation from **1** (which necessarily possesses more nonbonded interactions than the corresponding camphene cation, both probably having classical cation geometry[18-20]) has additional strain; but this is evidently not sufficient to decrease its thermodynamic stability significantly relative to the cations from **2** and **3**. The net result is a pronounced preference for WMH rearrangement of **1**, detectable only if one uses optically active **1** or analogs thereof.[5]

Although the exothermicity of reactions **2** → **1** and **3** → **1** is probably insufficient for rigorous application of the Hammond hypothesis,[21] it is not unreasonable to suggest that the transition states will be subject to strains (see above) affecting the geometry of carbon 3: *endo*-ethyl (**2**) forcing the *exo*-methyl back toward the bridge, and the *exo*-ethyl forcing the *endo*-methyl more toward the underside of the norbornane cage. As in the case of camphene itself both cations—and the transition states which resemble them—will have a vacant p orbital at carbon 2, perpendicular to the plane defined by carbons 1, 2, and 3; and the exo and endo sp^3 orbitals of carbon 3 will be respectively more or less parallel to the vacant p orbital.[2] If one assumes that the geometry in the camphene cation is essentially ideal for *exo*-methyl migration (*i.e.*, formation of the lowest energy transition state), any pressure (*e.g.*, from strains arising from an *endo*-ethyl group on carbon 3) tending to move the *exo*-methyl back toward the bridge will result in geometry less than ideal for transition state formation (and consequent methyl migration); and conversely any strain tending to move an *endo*-methyl group down toward the underside of the cage, relative to its location in the camphene cation, will bring the endo sp^3 orbital of carbon 3 more nearly parallel to the vacant p orbital of carbon 2—thus improving the conditions for *endo*-methyl migration over those in camphene.

The rate constants, k_{21} and k_{31}, compared to those for corresponding camphene behavior suggest that this is indeed the consequence of the extra methyl group in **2** and **3** and their respective cations: attached to carbon 9, *endo*-methyl migration is enhanced, and to carbon 10, *exo*-methyl migration is somewhat suppressed. These phenomena are not inconsistent with a lesser thermodynamic stability of **2** (and its cation) relative to **3** (and its cation) which, of course, is a consequence of the greater total strain in **2** than in **3** (for $K_{23} = 2.7$). However, data in Table V imply that $K_{31} > K_{21}$ whereas the reverse must be true. The apparent contradiction arises from failure to observe **1** → **3** under the reaction conditions used, presumably owing to too high an activation energy. For fulfillment of the condition, $K_{21} > K_{31}$, the minimum value for k_{13} must be $>1.7 \times 10^{-7}$ sec^{-1} (*i.e.*, $K_{13} \neq 0$ if $k_{13} > 0$).

In camphene the WMH racemization constitutes 41% of the entire process[2] and possesses a rate constant approximately three times that for the corresponding process in **2** and seven times that for the corresponding process in **3**. However, WMH is usually pictured as three discrete rearrangements: Wagner–Meerwein or skeletal, 6,2-hydride shift, and again Wagner–Meerwein. In addition, the same structural and stereochemical consequences obtain if the conversion of **2** to **3** (or its reverse) occurs *via* cyclene (**4**) formation and opening, which in camphene is a very minor participant in the racemization process. Since the same compound, **4**, is formed by the same mechanistic process of cyclization by loss of the appropriate proton from the cations of **2** and **3**, it is not surprising that **4** is formed more rapidly from the thermodynamically less stable system which owes its greater energy content to greater strains than those in **3**. The presence of these greater strains in both **2** and **3**, as compared to camphene, should in fact enhance the cyclization process to **4** and compared to tricyclene itself even though **4** may itself contain greater strains than does tricyclene, unless these are enough greater seriously to destabilize **4** relative to tricyclene. For the conversion of camphene to tricyclene the estimated equilibrium constant is 0.12, and one may thus infer that **4** is very likely less stable thermodynamically than either **2** or **3**.

Now the evidence of Table V indicates that the WMH pathway is somewhat better than the route *via* **4** for the **2**–**3** interconversion, but, as noted, not nearly so much better as in the case of camphene. And the probability that the conversion of **4** to both **2** and **3** is exothermic suggests that both transition states resemble **4** more than they do **2** or **3**. Furthermore, at some stage of the WMH pathway it seems very likely that there is also a transition state which has some of the characteristics of **2** while structurally resembling **4**. And if **4** is more strained than tricyclene, this hypothetical transition state must also be effectively more energetic than the corresponding one in camphene—from the rate data enough so as to suppress the WMH process appreciably. It may be inferred that this transition state occurs during the 6,2-hydride migration when the actual epimerization occurs and the locus of strain is transferred. In camphene this state would be symmetrical and lacking any such strain-induced barrier.

Finally it is interesting to note that no *meso*-methyltricyclene was detected in the present work, only the (presumably) less stable *asym*-methyltricyclene (**4**). Such a cyclene would necessarily arise from bridging of the **1** cation, but apparently it is inhibited. This poses a presently unanswerable question: if the **1** cation is less stable than the camphene cation, as suggested above, why does it not bridge in sufficient amount to be readily detected, since its less stable isomer (**2**) is produced in amounts sufficient for kinetic analysis? It would seem that one must postulate the intermediacy of *meso*-methyltricyclene as part of a competitive pathway to the WMH racemization of **1** which is not observable under the conditions of the present studies involving only the racemic forms of **1**, **2**, and **3**.

---

(18) G. A. Olah, J. R. DeMember, C. Y. Lui, and A. M. White, *J. Amer. Chem. Soc.*, **91**, 3958 (1969).

(19) G. A. Olah, A. M. White, J. R. DeMember, A. Commeyras, and C. Y. Lui, *J. Amer. Chem. Soc.*, **92**, 4627 (1970).

(20) G. A. Olah, J. R. DeMember, C. Y. Lui, and R. D. Porter, *J. Amer. Chem. Soc.*, **93**, 1442 (1971).

(21) G. S. Hammond, *J. Amer. Chem. Soc.*, **77**, 334 (1955).

In conclusion it seems appropriate and wholly relevant to the findings of this investigation to quote Berson's cautionary statement[22] that "any evaluation of 'invariance' or 'insensitivity' is on weak grounds if based upon a set of experimental data all of which show 'complete' preference for one path over another. Wide variations in actual sensitivity may hide beneath an apparent 'insensitivity' which is attributable to nothing more than choice of systems that *all* have selectivities so high that they lie at the extreme edge of the available experimental techniques and thus cannot be ranked."

Our choice of system and conditions was made deliberately to avoid the complicating factors of *exo*- and *endo*-ethyl migration as well as one of the associated WMH rearrangements. But one can scarcely suggest that any or all of these processes fail to occur because they were not observed.

If one assumes[23] on whatever grounds that the rate constant for *endo*-methyl migration in camphene is mathematically zero, the corollary argument (that *no* *endo*-3,2-methyl shift occurs in camphene because the data[2] are compatible with this point of view[23]) is no more convincing than would be the conclusion that *exo*-ethyl migration does not occur in the present system because it was not observed. Obviously it cannot be observed under the given reaction conditions. Indeed the unexpected observance of an *endo*-3,2-methyl shift (k_{31}) in the present work is more readily acceptable in terms of a twofold enhancement, attributable to the new methyl group (Table V), of an already existing *endo*-3,2-methyl shift in camphene[2] ($\sim 1.4 \times 10^{-6}$ sec^{-1} increasing to $\sim 2.7 \times 10^{-6}$ sec^{-1}) than almost infinitely large enhancement (*e.g.*, zero increasing to 2.7×10^{-6} sec^{-1}). Equally significant is a comparison of the *exo*/*endo*-3,2-methyl shift ratios for camphene (~20:1) and for k_{21}/k_{31} (~8:1). Any effect of an ethyl group *vs.* a methyl group, whatever its origin, is not expected to be appreciable; and therefore, the change in ratio from ~20:1 to ~8:1 for *exo*-methyl (camphene) *vs.* *exo*-ethyl (**3**) is more readily acceptable than 100–1000:1 (zero *endo*-3,2-methyl shift in camphene) to 8:1 (**3**). Thus it would appear reasonable to accept the conclusion previously proposed:[2] the existence of an *endo*-3,2-methyl shift in camphene, while very small, is very likely not zero under the conditions used.

Experimental Section

Melting points were taken in a stirred oil bath and are uncorrected, as are boiling points. Elemental analyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich. Infrared spectra were obtained with a Perkin-Elmer Model 21 (sample as thin film) or a Perkin-Elmer Model 137 (sample in solution) spectrophotometer. Nuclear magnetic resonance spectra were obtained with Varian Associates Models A-60 and/or T-60 spectrometer,[15a] with carbon tetrachloride solvent. Chemical shifts are expressed in parts per million downfield from internal tetramethylsilane (δ 0). The 100-MHz spectra were taken on a Varian Associates Model HA-100 instrument.[24] Mass spectra were obtained with an Associated Electrical Industries, Ltd., MS-9 double focusing, high-resolution spectrometer at an ionizing voltage of 70 eV.[15b] Gas chromatographic analyses were performed either on an F&M Model 500 programmed-temperature instrument equipped with Disc integrator (columns A and B) or on a Varian Aerograph Model 90-P chromatograph (column C). In the latter case, relative peak areas were determined by planimetry. Gas chromatographic columns consisted of 0.25-in. i.d. stainless steel, as follows: (A) 6-ft, 10% silicone rubber (SE-30) on Chromosorb P; helium flow rate 40 ml/min; column temperature 100–175°; (B) 6-ft, 10% polyester (LAC-446) on Chromosorb P; flow rate 40 ml/min; temperature 100–175°; (C) 12-ft, 5% Carbowax 1500 on Gas Chrom RA; flow rate 60–70 ml/min; temperature 62°.[25] Thin-layer chromatography adsorbent was Brinkmann silica gel GF$_{254}$ on 3×15 cm glass plates or microslides. Development was with 90% hexane–10% diethyl ether.

3,3-Dimethyl-2-ethyl-2-norbornanol (1a). A. With Ethylmagnesium Bromide. To a stirring, refluxing suspension of ethylmagnesium bromide in diethyl ether, prepared *in situ* with 44.2 g of ethyl bromide (0.41 mol) and 9.97 g of magnesium (0.41 g-atom), was added dropwise 7.18 g of camphenilone (0.052 mol) dissolved in 50 ml of anhydrous diethyl ether over a period of 30 min. Following the addition, the reaction mixture was refluxed for an additional hr.

The cooled mixture was treated dropwise with a saturated ammonium chloride solution[26] until the reaction mixture became clear. After settling, the ether solution was decanted from the white solid, which was then washed twice with fresh solvent. The ether phases were combined, the ether was removed, and the residue was distilled, affording a mixture of two alcohols (**1a** and **1b**), the desired tertiary alcohol being the minor product.

The major product, 3,3-dimethyl-2-norbornanol (**1b**), was characterized by its nmr spectrum, including two three-proton singlets at 0.82 and 0.95 ppm and two one-proton multiplets at 3.50 and 3.56 ppm, the latter resulting from the exo and endo hydrogens bonded to carbon 2.

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 76.90; H, 11.50.

B. With Ethyllithium. An ice-cold ether solution of ethyllithium (2 g of lithium shot, 15.1 g of freshly distilled ethyl bromide, and 135 ml of anhydrous diethyl ether) was filtered through glass wool in a nitrogen atmosphere into a 300-ml, three-necked, round-bottomed flask fitted with dropping funnel, reflux condenser, and mechanical stirrer. Then a solution of 3.84 g of 3,3-dimethyl-2-norbornanone (0.028 mol) in 25 ml of diethyl ether was added dropwise to the stirring ethyllithium solution at a rate to maintain gentle reflux (approximately 45 min). This reaction mixture was then stirred at room temperature for 48 hr under slight positive pressure of nitrogen.

This reaction mixture was hydrolyzed by adding dropwise a saturated ammonium chloride solution until the white mass settled to the bottom of the flask. After 30 min the clear ether layer was decanted and the residue washed with two portions of fresh ether. The combined ether layers, which were dried over anhydrous magnesium sulfate, were concentrated, and the concentrate was distilled, affording 3.69 g of low melting product with a boiling point of 90.0–90.5° (8 mm) (0.22 mol, 79% yield; lit.[27] bp 89–93° (7 mm)).

In the nmr spectrum the *gem*-dimethyl protons appeared as singlets at 0.93 and 0.88 ppm, while the ethyl CH$_3$ hydrogens appeared as a triplet (J = 7.0 Hz) centered at 0.88 ppm. The OH group exhibited a strong, broad peak in the infrared spectrum at 3500 cm^{-1}.

Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.47; H, 11.90.

3,3-Dimethyl-2-ethylidenenorbornane (1). Thionyl chloride (20 ml, 0.3 mol, bp 74.5–75.5°) was added to a mixture of 12.9 g of 3,3-dimethyl-2-ethyl-2-norbornanol (**1a**; 0.077 mol) and 60 ml of pyridine (freshly distilled from potassium hydroxide) in a 100-ml round-bottomed flask. Following stirring at room temperature for 10 hr, 40 ml of water was added cautiously to the reaction mixture, which was then extracted with three portions of diethyl ether. After being washed with dilute hydrochloric acid, dilute base, and finally water, and being dried over anhydrous magnesium sulfate, the ether layer was concentrated and the residue distilled, the

---

[22] J. A. Berson, J. H. Hammons, A. W. McRowe, R. G. Bergman, A. Remanick, and D. Houston, *J. Amer. Chem. Soc.*, **89**, 2590 (1967).

[23] C. J. Collins and M. H. Lietzke, *J. Amer. Chem. Soc.*, **95**, 6842 (1973).

[24] The 100-MHz spectra were graciously recorded by Mr. Frank Parker, Department of Chemistry, University of Michigan.

[25] The advice of Professor Julian Johnson (Department of Chemistry, University of Connecticut) and consultation, preparation, and testing of the column by Mr. R. F. Kruppa (Applied Science Laboratories, Inc., State College, Pa.) are gratefully acknowledged.

[26] L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 419.

[27] C. A. Stone, M. L. Torchiana, K. L. Meckelnburg, J. Stavorski, M. Sletzinger, G. A. Stein, W. V. Ruyle, D. F. Reinhold, W. A. Gaines, H. Arnold, and K. Pfister III, *J. Med. Pharm. Chem.*, **5**, 665 (1962).

portion boiling between 63.5 and 66.0° (14 mm) being collected as product, 6.9 g (0.046 mol, 60% yield).

Anal. Calcd for $C_{11}H_{18}$: C, 87.94; H, 12.07. Found: C, 87.80; H, 11.98.

Chromatographic analysis (gas and thin layer) and the nmr spectrum indicate that the product is a mixture of the two geometrical isomers in a ratio of approximately 4:1. These isomers were separated by liquid chromatography on silica gel containing 23% silver nitrate, giving the following results.

Minor Component. The nmr spectrum of this compound consisted of a one-proton quartet centered at 5.10 ppm (J = 7.0 Hz), a sharp three-proton doublet at 1.59 ppm (J = 7.0), and two three-proton singlets at 1.18 and 1.13 ppm.

Major Component. In the nmr, the one-proton quartet appears at 4.90 ppm (J = 6.8 Hz), the sharp three-proton doublet at 1.57 ppm (J = 6.8 Hz), and the three-proton singlets at 0.99 and 0.96 ppm. The infrared spectrum included a medium-strength stretching band at 1636 cm^{-1}. The mass spectrum of this major component has significant peaks at m/e 150 (parent peak), 135 (base peak), 121, 107, and 93.

3-Ethyl-2-norbornanone (2a). In a typical experiment, 15.5 g of 2-norbornanone (Aldrich, mp 88–90°, 0.14 mol) dissoved in approximately 40 ml of anhydrous diethyl ether was placed in a three-necked, 3-l., round-bottomed flask fitted with an efficient reflux condenser with a calcium sulfate drying tube, mechanical stirrer, and inlet tube. After the system had been purged with dry nitrogen gas, triphenylmethylsodium solution was transferred under nitrogen pressure into the stirring ketone solution until the bright red color of slight excess of the alkylsodium persisted. After the mixture was stirred for 2 or 3 min, the flask was submerged in ice while 260 g of ethyl iodide (Fisher Certified Reagent; 1.7 mol; 12-fold excess) dissolved in an equal volume of diethyl ether was added, slowly at first until the vigorous reaction subsided. When all of the alkylating agent had been added, the ice bath was removed, and the reaction mixture stirred at room temperature, still in a nitrogen atmosphere, for 4–5 hr.

Following decantation from the solid residues, the crude reaction mixture was steam-distilled until the distillate was clear and almost odorless. Then the layers of the steam distillate were separated, the upper aqueous layer was washed three times with diethyl ether, and the washings were combined with the lower organic layer, washed with a saturated sodium chloride solution, and dried over anhydrous magnesium sulfate. After removal of the drying agent by filtration, and of the ether and excess ethyl iodide by distillation, the concentrate was distilled, giving 6.6 g of a mixture of starting material and product in a 1:1.3 ratio, as determined by gas chromatography. This distillate was further purified by means of a spinning band column, the product boiling at 82–84° (13 mm). The methyl protons absorbed in the nmr as a triplet centered at 1.02 ppm (J = 4.9 Hz), while the carbonyl group absorbed in the infrared at 1747 cm^{-1}.

Anal. Calcd for $C_9H_{14}O$: C, 78.22; H, 10.21. Found: C, 78.04; H, 10.29.

3-*endo*-Ethyl-3-*exo*-methyl-2-norbornanone (2b). In the alkylation apparatus, a solution of 1.95 g of 3-ethyl-2-norbornanone (**2a**; 97% pure, 0.014 mol) and 10 ml of diethyl ether was stirred with a slight excess of triphenylmethylsodium solution for 2 min, after which 24.2 g of methyl iodide (Eastman; 0.17 mol) in diethyl ether was added. Gas chromatographic analysis of the concentrated solution resulting from work-up indicated a 1:1 mixture of starting ketone and product. Realkylation of this mixture reduced the amount of 3-ethyl-2-norbornanone to 30%.

In another set of reactions, 16.1 g of 3-ethyl-2-norbornanone (0.117 mol) yielded, after two alkylations, 10.5 g of 87% pure product (0.060 mol, 56% conversion based on recovered starting material) with a boiling point of 98.5–99.0° (21 mm).

Final purification of the alkylated ketone was accomplished by preparative gas chromatography on an 8 ft × $^3/_8$ in. i.d., stainless steel column containing 15% SE-30 on Chromosorb W (45–60 mesh) at 150°.

The infrared spectrum included a band at 1743 cm^{-1}, and in the nmr two methyl hydrogen absorptions appeared, a singlet at 0.95 ppm, and a triplet at 0.92 ppm (J = 6.0 Hz).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.89; H, 10.49.

3-*endo*-Ethyl-3-*exo*-methyl-2-methylenenorbornane (2). Sodium hydride (4.3 g of a 50% dispersion; *ca.* 0.08 mol) was placed in a dry, nitrogen-filled 300-ml round-bottomed flask and washed three times with anhydrous petroleum ether. After the last of the volatile solvent was flushed from the system with more dry nitrogen, 60 ml of dimethyl sulfoxide (stored over Linde type 4A molecular sieve and distilled from calcium hydride, bp 55–56° (4 mm)) was added and the system stirred at 65° for 45 min. While the resulting white mixture was cooled in ice, 23.6 g of methyltriphenylphosphonium bromide (Aldrich, mp 230–232°, 0.065 mol) suspended in 100 ml of dry dimethyl sulfoxide was added, and this intensely red mixture allowed to warm to room temperature.

Next, the ketone, 7.94 g of 3-*endo*-ethyl-3-*exo*-methyl-2-norbornanone (**2b**; 0.052 mol), dissolved in 40 ml of dimethyl sulfoxide, was added to the above ylide mixture and the system stirred for 24 hr. After the reaction mixture was poured into approximately 100 g of ice–water and this extracted three times with ether, the ether layer was washed with water and dried over anhydrous magnesium sulfate. When the ether solution was concentrated, a precipitate formed, which was removed by filtration. The filtrate was distilled, boiling between 65.5 and 66.0° (11 mm).

The nmr spectrum consisted of two sharp one-proton singlets at 4.69 and 4.44 ppm, a sharp three-proton singlet at 0.97 ppm, and a three-proton triplet at 0.88 ppm (J = 6.8 Hz). Olefinic peaks in the infrared spectrum included 1656, 1422, and 872 cm^{-1}. Strong mass spectrum peaks were m/e 150 (parent peak), 135, 121 (base peak), 93, and 79.

Anal. Calcd for $C_{11}H_{18}$: C, 87.94; H, 12.07. Found: C, 87.86; H, 12.06.

3-*exo*-Ethyl-3-*endo*-methyl-2-norbornanone (3b). Following the general alkylation procedure described for the ethylation of 2-norbornanone, 10.0 g of 3-methyl-2-norbornanone (**3a**;[12] 0.081 mol) in 100 ml of anhydrous diethyl ether was treated with a slight excess of triphenylmethylsodium solution, followed by the addition of 250 ml of ethyl iodide (3.1 mol) dissolved in 250 ml of diethyl ether. Following normal work-up, including steam distillation, separation, drying, and concentration of the organic portion of the steam distillate, the residue was distilled, giving 5.6 g of the product (0.037 mol, 55% conversion based on recovery of 1.6 g starting material) boiling between 95 and 96° (18 mm). Nmr peaks [methyl singlet at 0.90 ppm and methyl triplet centered at 0.86 ppm (J = 6.4 Hz)] and infrared absorption (strong carbonyl stretch at 1740 cm^{-1}) compared reasonably well with those reported by Wolinsky.[14]

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 79.04; H, 10.69.

3-*exo*-Ethyl-3-*endo*-methyl-2-methylenenorbornane (3). To prepare the ylide, 3.8 g of sodium hydride (7.8 g of a 50% dispersion, 0.16 mol) was stirred with 75 ml of dimethyl sulfoxide in a 500-ml round-bottomed flask in a nitrogen atmosphere for 1 hr at 65°. After the mixture had been cooled in an ice bath, 54.4 g of methyltriphenylphosphonium bromide (0.15 mol) dissolved in 125 ml of dimethyl sulfoxide was added, forming a red suspension.

When the methylenetriphenylphosphorane mixture had warmed to room temperature, 5.8 g of 3-*exo*-ethyl-3-*endo*-methyl-2-norbornanone (**3b**; 0.038 mol) dissolved in 40 ml of dimethyl sulfoxide was added, and the mixture was stirred and heated (50°) in a nitrogen atmosphere for 72 hr. (After 69 hr the concentration of ketone in the reaction mixture was very small.)

The cooled reaction mixture was then poured into about 100 g of ice–water, accompanied by a vigorous reaction, and the aqueous mixture was extracted with four 100-ml portions of *n*-pentane. The combined pentane extracts were then washed with 200 ml of water and 200 ml of saturated sodium chloride solution, and dried overnight with magnesium sulfate. After filtration, the pentane solution was concentrated and the residue distilled, resulting in 3.42 g of product boiling between 74 and 76° (19 mm) (60% yield).

Absorption in the nmr included two sharp one-proton singlets at 4.73 and 4.44 ppm, and a sharp singlet at 1.00 ppm (lit.[14]: 4.72, 4.42, and 1.00, respectively). Infrared peaks include 3100, 1660, 1422, and 872 cm^{-1} (lit.[14] peaks at 1661 and 885 cm^{-1}). Abundant peaks in the mass spectrum are m/e 150 (parent peak), 135, 122, 121 (base peak), 107, and 93.

Anal. Calcd for $C_{11}H_{18}$: C, 87.94; H, 12.07. Found: C, 88.08; H, 12.02.

Kinetic Procedures. The controlled-temperature bath consisted of a 2-l. insulated beaker containing mineral oil, mechanical stirrer, calibrated thermometer (−2 to 202° in 0.2°), and two coiled resistance heaters, one of which was regulated by an Instruments for Research and Industry "Therm-O-Watch" electronic controller. Temperature precision is estimated as ±0.2°.

The olefins were purified before the runs by collection from the gas chromatograph. Immediately prior to a run, the acetonitrile was distilled from phosphorus pentoxide, bp 79.8–80.0°; $n^{20.0}\mathrm{D}$

1.3442 (lit.[28] bp 81.6°, $n^{20}\text{D}$ 1.34423). Likewise, pyruvic acid was purified just before use by distillation at reduced pressure, bp 71.2–72.2° (22 mm), $n^{20}\text{D}$ 1.4272 (lit.[29] bp 75–80° (25 mm), $n^{20}\text{D}$ 1.4280).

Samples tubes (4 mm i.d. Pyrex) were charged with 0.0109 ± 0.0003 g of olefin (7.26×10^{-5} mol), 0.0026 ± 0.0001 g of pyruvic acid (3.0×10^{-5} mol), and 0.0355 ± 0.005 g of acetonitrile. Olefin concentration at the reaction temperature was 1.10 ± 0.03 *M*. After the tubes were sealed to a length of approximately 5 cm, they were placed in the oil bath (time = 0).

At measured intervals, the reactions were quenched by plunging the tubes in ice–water. After 50 μl of CCl_4 was added to each tube to effect solution, the contents were analyzed by gas chromatography (column C).

Analysis of Errors. The gas chromatographic response (thermal conductivity) to the three isomeric olefins was considered uniform and was linear with the sample sizes used. The peak areas, determined by planimetry, were reproducible to less than 1% for all peaks except the minor ones, which were subject to significantly greater error. The precision of peak area measurements of duplicate injections of the same sample was less than 2% for major peaks.

Each of the olefins (**1**–**3**) was collected individually from the gas chromatograph and analyzed for decomposition during chromatographic analysis. The nuclear magnetic resonance spectra and gas chromatograms of the collected samples were identical with those of the original compounds. Likewise, the chromatogram of a known mixture of the olefins in pyruvic acid–acetonitrile, dissolved in carbon tetrachloride, prepared for calibration purposes, indicated that no detectable isomerization was taking place in the gas chromatograph.

To estimate the error in the values of the slopes generated by the least-squares analyses (and thus the error in the observed rate constants), the standard deviation of the slope, σ, was estimated by

$$\sigma = \left[\frac{n}{n\sum X_i^2 - (\sum X_i)^2}\,\frac{\sum d_i^2}{n-2}\right]^{1/2}$$

with *n*, the number of experimental points; X_i, the *i*th *X* (time) value; and d_i, the difference for the *i*th point between the calculated value for log [olefin] and the observed value. The "Student *t* distribution" was used to obtain the 95% confidence interval.

---

[28] G. D. van Epps and E. E. Reid, *J. Amer. Chem. Soc.*, **38**, 2130 (1916).

[29] V. V. Tschelinzeff and W. N. Schmidt, *Ber.*, **62**, 2211 (1929).

Progressive Specific Hydrogen Rearrangements Quenched by Molecular Ion Fragmentation in 2-Methylpropene. Mass Spectral Serendipity[1]

P. J. Derrick*[2a] **and A. L. Burlingame**[2b]

Contribution from the Space Sciences Laboratory, University of California, Berkeley, California 94720. *Received September 7, 1972*

Abstract: The loss of a methyl radical from 2-methylpropene, 2-methylpropene-*1,1*-d_2, and 2-methyl-d_3-propene-*3,3,3*-d_3 has been studied at times from 10^{-11} to 10^{-6} sec following field ionization (FI). Considerable rearrangement of the H and D in the deuterated species occurs prior to fragmentation even at times as short as a few $\times 10^{-11}$ sec. The rearrangement leads to almost complete H–D randomization prior to fragmentation at 7×10^{-10} sec. The observed H–D randomization may be rationalized in terms of successive isomerizations *via* 1,3 allylic hydrogen shifts. The electron impact (EI) mass spectra of 2-methylpropene, 2-methylpropene-*1,1*-d_2, and 2-methyl-d_3-propene-*3,3,3*-d_3 have been measured at high and low ionizing energies and are discussed in relation to the FI results.

It is recognized that the unimolecular reaction systems set up by gas-phase ionization of alkenes are typically extremely complex.[3] The mass spectra of isotopically labeled species show that extensive molecular rearrangement leading to randomization of the labels tends to occur either prior to or as an integral part of fragmentation.[4–7] The nature of the rearrangement processes remains, however, largely a matter of conjecture, even for the smallest molecules such as propenes and butenes. It has been proposed that the processes leading to hydrogen randomization in the propene ion involve only 1,3 shifts.[6b,c] Other workers have suggested that both 1,2 and 1,3 shifts are operative.[6d] Yet again it has been suggested that randomization in propene, butene, and pentene radical-ions is predominantly due to 1,2-hydrogen shifts.[6e] 1,3-Allylic hydrogen shifts have been envisaged to occur in the $\Delta^{4(8)}$-menthene[7] and methylcyclohexene[8] radical-ions. McLafferty, *et al.*,[9] have proposed that closely analogous 1,3-hydrogen shifts occur in the enolic $C_3H_6O\cdot^+$ ion. Conversely, however, it has been suggested[10] that whereas 1,2-, 1,4-, and 1,5-hydrogen shifts are in general facile unimolecular reactions of radical-cations, 1,3-

---

[1] The work was performed in collaboration with Dr. A. M. Falick who is also responsible for the computation of lifetimes. See J.-P. Pfeifer, A. M. Falick, and A. L. Burlingame, *Int. J. Mass Spectrom. Ion Phys.*, 11, 345 (1973).

[2] (a) Present address: Department of Chemistry, University College, University of London, London WC1H OAJ, England; (b) John Simon Guggenheim Memorial Fellow, 1970–1972.

[3] See H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967.

[4] W. A. Bryce and P. Kebarle, *Can. J. Chem.*, **34**, 1249 (1956).

[5] J. H. Beynon, "Mass Spectrometry and Its Application to Organic Compounds," Elsevier, Amsterdam, 1960, pp 262–263.

[6] (a) G. K. Helmkamp and N. Schnautz, *J. Org. Chem.*, **24**, 529 (1959); (b) H. H. Voge, C. D. Wagner, and D. P. Stevenson, *J. Catal.*, **2**, 58 (1963); (c) W. H. McFadden, *J. Phys. Chem.*, **67**, 1074 (1963); (d) S. R. Smith, R. Schor, and W. P. Norris, *ibid.*, **69**, 1615 (1965); (e) B. J. Millard and D. F. Shaw, *J. Chem. Soc. B*, 664 (1966).

[7] D. S. Weinberg and C. Djerassi, *J. Org. Chem.*, **31**, 115 (1966).

[8] T. H. Kinstle and R. E. Stark, *J. Org. Chem.*, **32**, 1318 (1967).

[9] F. W. McLafferty, D. J. McAdoo, J. S. Smith, and R. Kornfield, *J. Amer. Chem. Soc.*, **93**, 3720 (1971).

[10] M. T. Bowers, D. H. Aue, and D. D. Elleman, *J. Amer. Chem. Soc.*, **94**, 4255 (1972).