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DYNAMIC ISOTOPE DILUTION KINETIC STUDY OF THE THERMAL CONVERSIONS OF BICYCLO[3.2.0]HEPT-2-ENE TO BICYCLO[2.2.1]HEPT-2-ENE AND TO CYCLOPENTADIENE AND ETHENE

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ABSTRACT

Mixtures of bicyclo[3.2.0]hept-2-ene and bicyclo[2.2.1]hept-2-ene, with one isomer labeled with two deuterium atoms, were isomerized in the gas phase at 276 °C. By following the concentration ratios of d_0 and d_2 versions of bicyclo[2.2.1]hept-2-ene as functions of time one finds that the partitioning of bicyclo[3.2.0]hept-2-ene between the primary products bicyclo[2.2.1]hept-2-ene and cyclopentadiene plus ethene is 2 : 1. This and earlier stereochemical results permit the calculation of the partitioning of the [3.2.0] olefin between the orbital symmetry allowed [1,3] carbon shift-with-inversion product and several forbidden or non-concerted reaction channels (approximately 1 : 1) and the stereochemistry of the ethene-d_2 formed from *exo, exo*-[6,7-$^2H_2$]bicyclo[3.2.0]hept-2-ene directly (1 : 1 E : Z).

INTRODUCTION

The unimolecular gas-phase reactions of bicyclo[3.2.0]hept-2-ene (**1**) were investigated over the temperature range 307–353 °C by Cocks and Frey in 1971.[1] The overall decomposition of **1** was kinetically first order at initial reactant pressures above 2 Torr; product mixtures were found to contain norbornene, cyclopentadiene plus ethene, and five other products (Scheme 1). Three of the five were identified as methylcyclohexa-1,3-dienes by comparison of GC retention times with those of authentic samples on four different columns. The other two products had similar retention times to those of *trans,trans*-hepta-1,3,5-triene and '*cis*-hepta-1,3,5-triene.'

Kinetic data were analyzed in terms of three primary reactions (Scheme 1): olefin **1** reacts through [1,3] carbon migration of C-7 from C-1 to C-3 to form bicyclo[2.2.1]hept-2-ene (norbornene; **2**), cleavage of the C-1—C-7 and C-5—C-6 bonds to give cyclopentadiene (**3**) and ethene, and fragmentation of the cyclobutane unit in the alternative sense, with cleavage of C-1—C-5 and C-6—C-7 to yield hepta-1,3Z,6-triene (**4**). Both norbornene and the heptatriene reacted further under the reaction conditions to give cyclopentadiene and ethene, respectively, through a retro-Diels–Alder process, and a mixture of the five isomers found in the product mixture.[1]

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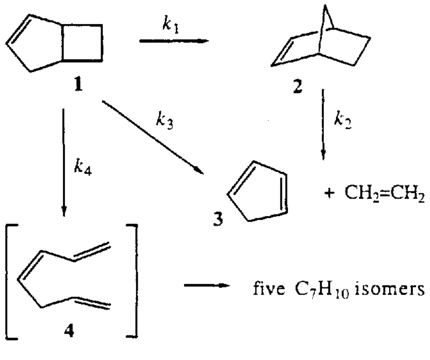


Scheme 1

This kinetic study showed that $(k_1 + k_3) \gg k_4$ and that k_1 and k_3 were of similar magnitude. The provisional character of this last inference was emphasized repeatedly: 'rate constants for individual processes are subject to large errors;' 'the calculated values for k_1 are ... subject to large errors;' 'most of the experimental inaccuracies occur in splitting the sum $(k_1 + k_3)$ into its component rate constants;' 'our values for $(k_1 + k_3)$ are reliable but ... the individual values are suspect.'[1]

The fundamental circumstance which impeded the deduction of reliable values for k_1 and k_3 is that fact that $k_2 \gg k_1$. For the kinetic situation outlined in Scheme 1, the concentration of **2** as a function of time is as given in equation (1), and is always very small when $k_2 \gg k_1$.

$$[\mathbf{2}(t)] = k_1(k_2 - k_0)^{-1}\{\exp(-k_0t) - \exp(-k_2t)\}[\mathbf{2}(0)] \qquad (1)$$

Here k_0 is the rate constant for disappearance of **1**; $k_0 = k_1 + k_3 + k_4$.

To measure a reliable value of k_1 one must measure $[\mathbf{2}(t)]$ accurately, which is a difficult task when **2** is always a minor component in a complex reaction mixture. When $[\mathbf{2}(t)]$ is very small, small absolute errors in measuring it are large relative errors, leading to large errors in estimates of k_1.

Several facets of the thermal chemistry of bicyclo[3.2.0]hept-2-ene as delineated by Cocks and Frey[1] attracted our attention. It is one of the simplest bicyclic olefins giving a [1,3] carbon sigmatropic migration product through a suprafacial process,[2] and thus with only two stereochemical options; it offers a direct competition between a possibly allowed and concerted [1,3] shift with inversion and cyclobutane cycloreversion pathways, which are generally considered to be stepwise, diradical-mediated reactions;[3] and it presents some daunting challenges to experimentalists concerned with detailed definitions of stereochemistry and reaction rates for specific individual paths.

One of these challenges has just been faced by two groups concerned with the stereochemistry of the [1,3] shift reactions, **1** to **2**.[4,5] Using deuterium-labeling techniques, the isomerization was shown to proceed with predominant but not exclusive inversion at the migrating carbon.

1-d_2

2-d_2

Another challenge, definition of the relative importance of the four possible stereochemical paths open for the conversion **1** to **4**, seems beyond the grasp of currently available techniques and strategies. Here we address two others, the kinetic partitioning between k_1 and k_3 and the stereochemistry of the reaction **1**-d_2 to **3** plus [1,2-$^2H_2$]ethene.

RESULTS

Dynamic isotope dilution method

A dynamic isotope dilution approach was employed to secure a reliable measure of k_1. This experimental technique seemed well suited and practicable for our objectives. It is, however, not so commonly utilized as to require no explanation, yet the logic, mathematical analysis and experimental tactics involved are easily understood.

If two reactions, the thermal decomposition of olefin **1** (Scheme 1) and the Diels–Alder retroadditon of **2**-d_2, took place simultaneously in a gas-phase kinetics bulb, the labeled norbornene-d_2 could be viewed as an internal time-dependent (hence 'dynamic') standard; [**2**-$d_2(t)$] could be calculated at any time if [**2**-$d_2(0)$] and the rate constant for disappearance of **2**-d_2 were known. Measurements of [**2**(t)]/[**2**-$d_2(t)$] by mass spectrometry could then give **2**(t) and lead to values for k_1 and k_3. This approach would avoid analytical situations where two concentrations of very different magnitudes must be determined simultaneously by the same experimental method, inevitably leading to comparable absolute errors for both and large relative errors for the low-concentration component.

Mathematical treatment of this kinetic situation is straigthforward. Rate constants k_j ($j = 0$–4) have been defined above (Scheme 1). Let k_j' be the corresponding rate constants for reactions involving d_2-labeled substrates **1**-d_2 and **2**-d_2. If **1** and **2**-d_2 are heated simultaneously, Equations (1) and (2) apply.

$$[\mathbf{2}\text{-}d_2(t)] = \{\exp(-k_2't)\}[\mathbf{2}\text{-}d_2(0)] \tag{2}$$

Let α represent the molar ratio of [3.2.0] substrate to isotopically different norbonene at $t = 0$; then the experimentally accessible [**2**(t)]/[**2**-$d_2(t)$] ratio is a constant times a simple function of independently measurable or already known rate constants and α [Equation (3)].

$$[\mathbf{2}(t)]/[\mathbf{2}\text{-}d_2(t)] = k_1(k_2 - k_0)^{-1}\{\exp(k_2' - k_0)t - \exp(k_2' - k_2)t\}\alpha \tag{3}$$

A simple linear correlation of the experimentally observable concentration ratio for the isotopically distinct norbornene compounds in reaction mixtures against the given function of rate constants and time, and the initial concentration ratio α, will have a slope equal to $k_1(k_2 - k_0)^{-1}$.

For an inverse labelling experiment, that is, one with **1**-d_2 and **2** as starting materials, equation (4) would apply.

$$[\mathbf{2}\text{-}\mathbf{d}_2(t)]/[\mathbf{2}(t)] = k_1'(k_2' - k_0')^{-1}\{\exp(k_2 - k_0')t - \exp(k_2 - k_2')t\}\alpha \tag{4}$$

If secondary deuterium kinetic isotope effects were negligible, then equations (3) and (4) would reduce to equation (5); both regular and inverse dynamic isotope dilution experimental data should correlate in simple linear fashion with $\{\exp[k_2 - k_0)t] - 1\}\alpha$.

$$\{[\mathbf{2}(t)] \text{ from } \mathbf{1}(0)\}/[\mathbf{2}(t) \text{ from } \mathbf{2}(0)\} = k_1(k_2 - k_0)^{-1}\{\exp[(k_2 - k_0)t] - 1\}\alpha \tag{5}$$

Syntheses

Bicyclo[3.2.0]hept-2-ene (**1**) was secured through a selective reduction of bicyclo[3.2.0]hepta-2,6-diene[6] with diimide.[7] Reductions of bicyclo[3.2.0]hepta-2,6-diene and norbornadiene with dideuteriodiimide afforded the d_2-labelled substrate **1-d_2** and dynamic standard **2-d_2**. These compounds were easily isolated from the respective reaction mixtures and purified by preparative gas chromotography.

Gas-phase isomerizations

A 1-l Pyrex kinetics bulb was designed and fabricated to permit the withdrawal of small samples of a gasesous reaction mixture during kinetic runs with the aid of a gas-tight valved syringe. When a sample had been secured, the syringe valve was closed, the sampling needle was replaced with one suitable for injection into a gas chromatograph inlet and the relative concentrations of a reactant versus octane as an internal standard or of a d_0- versus d_2-hydrocarbon were determined by GC–MS analyses in the selected ion monitoring mode.

A mixture of **1**, **1-d_2**, octane and 2-methylpentane, serving as a bath gas to bring the initial pressure to about 45 Torr, was heated at 275·7 °C; the first-order rate constant k_0 for the overall disappearance of bicyclo[3.2.0]hept-2-ene calculated from the seven kinetic points taken over a 37-h period (1·5 half-lives) was $8\cdot2\times10^{-6}$ s^{-1}. For the competitive decomposition of **1** and **1-d_2**, logarithms plots of $[\mathbf{1}\text{-}d_2(t)]/[\mathbf{1}(t)]$ data obtained by GC–MS against time led to a value for $k_0 - k_0'$ of 6×10^{-7} s^{-1}; k_0', then, is $7\cdot6\times10^{-6}$ s^{-1}. The composite of secondary deuterium isotope effects for all decomposition modes of the [3.2.0] olefin is accordingly $k_0/k_0' = 1\cdot08$, a reasonable[8] though not too precisely defined value.

Two kinetic runs at 276·2 and 276·0 °C for the Diels–Alder retrogression of norbornene (**2**) were run with octane as internal standard and 2-methylpentane as a bath gas.[9] The reactions were run to 3·6 and 4·2 half-lives, and gave k_2 values of 2·81 and $2\cdot82\times10^{-4}$ s^{-1}, respectively. A competitive run with **2** and **2-d_2** at 275·7 °C gave $k_2 - k_2' = 6\cdot3\times10^{-6}$ s^{-1}; k_2', then, at 276·0 °C is $2\cdot76\times10^{-4}$ s^{-1} and $k_2/k_2' = 1\cdot02$.

From these four experimentally defined first-order rate constants (k_0, k_0', k_2 and k_2'), the differences required for calculations based on Equations (3) and (4) are $k_2' - k_0 = 2\cdot68\times10^{-4}$, $k_2' - k_2 = -6\times10^{-6}$, $k_2 - k_0' = 2\cdot74\times10^{-4}$ and $k_2 - k_2' = 6\times10^{-6}$ (all in units of s^{-1}).

Dynamic isotopic dilution kinetic runs

Four independent dynamic isotopic dilution kinetic runs were conducted, one using **1** and **2-d_2** as starting materials and three using the inverse labeling option. The data are presented in Table 1.

The first run based on the concurrent reactions of **1** and **1-d_2** was analyzed with the aid of equation (3). The linear correlation between observed $[\mathbf{2}(t)]/[\mathbf{2}\text{-}d_2(t)]$ along the ordinate and $\{\exp(k_2' - k_0)t - \exp(k_2' - k_2)t\}\alpha$ values along the abscissa, required by equation (3), was observed. Standard least-squares linear regression analysis gave intercept, −0·024, slope $1\cdot72\times10^{-2}$ and $r = 0\cdot999$ (5 points).

The three runs based on the 'inverse labeling' option, with **1-d_2** and **2** as co-reactants, were treated together since the correlation of equation (4) predicts that data from runs with different $[\mathbf{1}\text{-}d_2(0)/[\mathbf{2}(0)]$ ratios will fall on the same straight line. That expectation was confirmed (Figure 1). Linear regression gave intercept −0·031, slope $1\cdot67\times10^{-2}$ and $r = 0\cdot999$ (13 points).

Table 1. Norbornene from bicyclo[3.2.0.]hept-2-ene to isotopically distinct norbornene internal standard at 276 °C

Run 1: $\alpha = 7{\cdot}30^a$		Run 2: $\alpha = 2{\cdot}97^b$		Run 3: $\alpha = 3{\cdot}394^b$		Run 4: $\alpha = 4{\cdot}93^b$	
t^c	$[\mathbf{2}(t)]/[\mathbf{2}\text{-}d_2(t)]$	t	$[\mathbf{2}\text{-}d_2(t)]/[\mathbf{2}(t)]$	t	$[\mathbf{2}\text{-}d_2(t)]/[\mathbf{2}(t)]$	t	$[\mathbf{2}\text{-}d_2(t)]/[\mathbf{2}(t)]$
1·54	0·048	4·03	0·078	3·99	0·094	2·73	0·065
2·54	0·096	5·33	0·132	5·24	0·156	3·77	0·121
3·61	0·187	6·40	0·203	7·25	0·362	4·75	0·193
4·71	0·285	7·71	0·325			5·88	0·318
6·89	0·654	9·06	0·511				
		10·59	0·827				

[a] $\alpha = [\mathbf{1}(0)]/[\mathbf{2}\text{-}d_2(0)]$.
[b] $\alpha = [\mathbf{1}\text{-}d_2(0)]/[\mathbf{2}(0)]$.
[c] time ($\times 10^{-3}$), s.

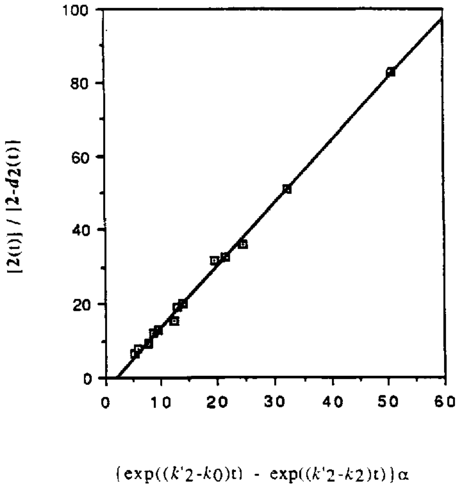


Figure 1. Dynamic isotopic dilution plot for runs 2, 3 and 4 (Table 1) correlated with equation (4)

When all 18 data sets in Table 1 were correlated by the function given in equation (5), with neglect of secondary isotope effects, both regular and inverse labeling data fell on the same line, with intercept $-0{\cdot}029$, slope $1{\cdot}66 \times 10^{-2}$ and $r = 0{\cdot}999$ (Figure 2).

DISCUSSION

While 'static' isotope dilution experiments have long been utilized to secure information which would be hard to gain by other means,[10] the 'dynamic' isotope dilution kinetic method employed here has been exercised much less frequently. Notable recent successes with this kinetic method have been achieved by Zimmerman and co-workers[11] as they clarified the significance of possible intermediates in complex photochemical reactions.

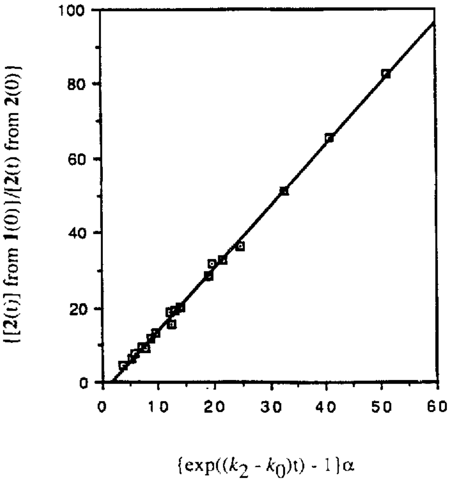


Figure 2. Dynamic isotope dilution plot for normal and inverse labelling runs 1, 2, 3 and 4 (Table 1) correlated with equation (5)

According to the kinetic analysis which they used, adapted to our kinetic situation and notational conventions, and when $[2(0)] = 0$ and $k_2 = k_2'$, equation (6) relates the observable quantities to rate constants.

$$\ln\{[\mathbf{2}\text{-}d_2(0)][\mathbf{1}(t)] - [\mathbf{2}\text{-}d_2(t)][\mathbf{1}(0)]\}/\{[\mathbf{2}\text{-}d_2(t)][\mathbf{2}(t)]\} = k_2t + \ln[(k_2 - k_0)/k_1] \quad (6)$$

Hence a plot of the function of concentrations on the left against time should correlate with time, in a simple linear fashion with slope equal to k_2 and intercept equal to $\ln[(k_2 - k_0)/k_1]$. In this work, the alternative derivation seemed more convenient and appropriate. For a linear plot based on equation (3) the unknown being estimated, $k_1(k_2 - k_0)^{-1}$, is derived from a slope, while the correlation of equation (6) gives $\ln[(k_2 - k_0)/k_1]$ as an intercept, extrapolated from experimental points secured at reaction times substantially greater than zero. Especially when relative few kinetic points are available for analysis, the extrapolation to an intercept as in equation (6) seems more vulnerable to error than the correlations of equations (3) and (4). The data analysis of equation (6) may be used to advantage in certain situations, however, such as when k_2 is not known from independent experiments and all concentrations called for in equation (6) may be determined.

A standard estimation of 95% confidence intervals for the intercepts and slopes[12] for the linear correlations of Figures 1 and 2 shows that the intercepts are not significantly different from zero, nor are the slopes significantly different from one another. For the second correlation, the slope is $(1{\cdot}67 \pm 0{\cdot}04) \times 10^{-2}$.

In addition to the likely error in these correlations associated with scatter in data from GC–MS determinations of the relative concentrations of labeled and unlabeled norbornenes, the final value of the slope from the correlation will depend on uncertainties in α values and, very critically, in the rate constants used in the exponential terms. For equation (5), for instance, propagation of error considerations[13] leads to the conclusion that, since the partial derivative of $\exp[(k_2 - k_0)t] - 1$ with respect to $k_2 - k_0$ is $t\{\exp(k_2 - k_0)t\}$, the contribution from uncertainty in $k_2 - k_0$ to the total variance in the slope of the correlation plot will increase rapidly with time. One thus has conflicting considerations to balance: data at long times will tend to give higher correlation coefficients, but any error in $k_2 - k_0$ will contribute more and more to the overall variance of the calculated slope.

The important point to keep in mind is that the relatively narrow estimates of uncertainty in slope obtained with the correlations of equations (4) and (5) do not include uncertainties stemming from a lack of total accuracy in the rate constants used to calculate the exponential functions on the right-hand side of the equations. Inaccurate values of these rate constants may give linear plots, but the calculated slope values will not provide reliable estimates of k_1. Aware of this, measurements of k_2, k_2', k_0 and k_0' were made in the same kinetic bulb and with the same digital platinum resistance thermometer used in the isotope dilution experiments, and data as gathered in Table 1 were secured emphasizing times within two half-lives for the cycloreversion of the internal standard.

Three-way kinetic partitioning of 1-d_2

The detailed kinetic study of Cocks and Frey[1] gives $k_1 + k_3 = 0{\cdot}87\, k_0$ at 276 °C, a value consistent with our own observations. We assume that this proportionality will be reasonably valid for **1**-d_2 also: $k_1' + k_3' = 0{\cdot}87\, k_0'$. Hence $k_1' + k_3' = 6{\cdot}6 \times 10^{-6}$, $k_1' = 1{\cdot}67 \times 10^{-2}$, $k_2' - k_0' = 4{\cdot}5 \times 10^{-6}$, $k_3' = 2{\cdot}1 \times 10^{-6}$ and $k_4' = 1{\cdot}0 \times 10^{-6}$ (all in units of s^{-1}).

Stereochemistry of direct formation of [1,2-$^2H_2$]ethene from 1-d_2

Total [1,2-$^2H_2$]ethene generated from **1**-d_2 at 276 °C is a 33 : 67 mixture of Z and E isomers (33 ± 2% Z).[4] The stereochemistry of ethene-d_2 formed by way of an intermediate norbornene-d_2 is governed by k_i' and k_r', since the Diels–Alder retrogression occurs with clean preservation of stereochemistry. ([1,2-$^2H_2$]ethene from **2-d₂**, analysed by FT-IR, was of Z stereochemistry; no E isomer was detected.[14]) Stereochemical work with **1**-d_2 at 276 °C has shown[4] that the two stereochemical components of k_1 are in the proportion $k_i' : k_r' = 76 : 24$. Simple arithmetic then leads to the estimates that 16% of the ethene-d_2 generated is the Z isomer and 52% is the E isomer formed by way of norbornene-d_2 isomers. The stereochemistry of ethene production by the direct k_3' path is then 17 : 15 Z : E. Given the experimental uncertainties in the estimation of ethene-d_2 stereochemistry by FT-IR spectroscopy and of the stereochemistry of the isomerization from **1**-d_2 to norbornene-d_2 isomers,[4] the very small apparent preference for (Z)-ethene-d_2 production in the direct k_3' fragmentation is not meaningful: the E and Z isomers are formed at equal rates.

Five-way kinetic partitioning of [6,7-$^2H_2$]bicyclo[3.2.0]hept-2-ene

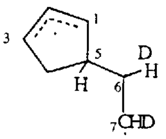
From the value of k_1' now available, $k_i' = 3{\cdot}4 \times 10^{-6}$ and $k_r' = 1{\cdot}1 \times 10^{-6}\ s^{-1}$. Hence five distinct rearrangement and fragmentation modes for **1**-d_2 have now been assessed at 276 °C; in order of relative importance, and as a percent of the overall rate constant $k_0' = k_i' + k_r' + k_3' + k_4'$, they are $k_i' = 45\%$, $k_3' = 28\%$, equally divided between (E)- and (Z)-ethene-d_2-producing variants, $k_r' = 14\%$ and $k_4' = 13\%$.

CONCLUSIONS

The complexities inherent in the multiple thermal reactions of **1**-d_2 pose severe difficulties to experimental investigations and equally serious problems of interpretation. The delineation of relative importance of the five discrete modes of reaction attempted here or, more accurately, or four discrete modes and one composite mode (k_4', having four possible stereochemical variants participating to unknown extents), depends on experimental evidence derived from reaction kinetics,[1] analyses of stereochemistry for intermediate norbornene-d_2 and ethene-d_2 isomers[4] and dynamic isotope dilution kinetic studies. Each experimental result involves some uncertainty and, when combined, the breakdown of relative rate constants summarized above is subject to some imprecision.

Two conclusions follow from this realization. First, continued efforts toward more precise ways of gaining primary data are needed, in this case and of course in other investigations of thermal reactions of comparable complexity. Part of this potential for improvement may be realized through better synthetic methods for preparing precisely defined isotopically labeled molecules for study, and part through improved analytical techniques. It seems likely, for example, that tunable diode laser spectroscopy applied to analyses of [1,2-$^2H_2$]ethene isomers will give substantially more precise results than can be attained by FT-IR spectroscopy.[15]

Second, any interpretation of the relative rates deduced must focus on the general pattern observed. A rationale purporting to derive each relative rate constant to the nearest 1% would be more than the data could support. Acknowledging this limitation, the data nonetheless show several clear results: at 276 °C, the $k_i' : k_3'$ balance is about 68 : 32, or 2 : 1, and the ethene-d_2 generated in the direct k_3' path is a 1 : 1 mixture of stereoisomers. A diradical (**5**) leading directly from **1**-d_2 to **3** and CHD=CHD formed by rotation about C-5—C-6 toward H—C-5 as the C-1—C-7 bond breaks, and which lives long enough for rotation about C-6—C-7 to permit stereorandom ethene-d_2 formation, is the most obvious mechanistic rationale for this result. This diradical intermediate does not reclose at C-1, as bicyclo[3.2.0]hept-2-ene-d_2 recovered from reaction mixtures shows no loss of stereochemical integrity.[4,5] Whether diradical **5** always fragments or sometimes closes at C-3 to give norbornene-d_2 isomers is not deducible from the data available.



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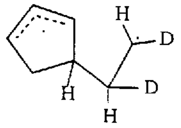

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If **5** always fragments, then k_3' relates to its formation, and loss of stereochemistry on the same direct route (k_i') may be ascribed to another diradical (**6**), formed from **1**-d_2 with rotation about the C-5—C-6 bond away from H—C-5, and which partitions between inversion and retention products. Alternatively, some combination of an allowed [1,3] carbon sigmatropic shift with inversion component and a stereochemistry-compromising kinetically-competitive alternative path may be involved.

If, on the other hand, the k_r' component of the [1,3] shift derives from **5**, then so would an equal component of the k_i' product; the allowed path would be associated with a rate constant $k_i' - k_r' = 2{\cdot}3 \times 10^{-6}\ s^{-1}$ (30% of k_0') and the rate constant for the formation of **5** would be $2k_r' + k_3' = 4{\cdot}3 \times 10^{-6}\ s^{-1}$. Even this extreme point of view leaves the stereochemically allowed [1,3] shift reaction as a major component, and of similar magnitude as the alternative non-allowed isomerizations and fragmentations.

At a higher temperature (312 °C), Klärner *et al.*[5] observed 11% retention stereochemistry in norbonene-d_2 products from **1**-d_2 and 18 ± 4% (*Z*)-[$^2H_2$]ethene from direct and indirect paths. Assuming that ethene-d_2 formed by way of k_3' again consists of 1 : 1 $Z:E$, then one may estimate by simple calculation the $k_1':k_3'$ balance, i.e. k_1' is 82% of $k_1' + k_3'$. This deduction from the assumption suggests that the $k'_1:k'_3$ ratio increases with increasing temperature, or the $(k_i' - k_r'):(2k_r' + k_3')$ ratio increases with increasing temperature. The second interpretation views the increase in stereoselectivity in the [1,3] carbon migration at the higher temperature as the consequence of a change in the $(k_i' - k_r'):(2k_r' + k_3')$ balance, rather than as a more selective partitioning of diradical **6**. The allowed [1,3] shift would then have a higher activation energy that the cleavage of **1-d_2** to form diradical **5**.

After a 17-year hiatus,[1] a return to this fundamental problem in reaction kinetics and stereochemistry[16] has begun to yield some relevant information and make plain the complexities of the reactions involved.[4,5] Clearly, though, more detailed experimental work employing a variety of techniques will be required over a range of temperatures before the full complexities of the thermal chemistry of **1** and **1-d_2** will be unraveled and better understood, and current uncertainties and speculations are sorted out.

EXPERIMENTAL

Octane (Gold Label, 99+ %) and 2-methylpentane (99+ %) were used as received from Aldrich Chemical Company. Norbornene (**2**) (Aldrich), distilled through a 10-cm glass Vigreux column, had b.p. 95–96 °C.

Gas chromatographic–mass spectometric (GC–MS) analyses were performed with Hewlett-Packard (HP) 5890, 5970B and 9836 instruments and computer. The GC–MS data were acquired with injection port and transfer line temperatures of 160 °C, a carrier gas (helium) flow-rate of 0·6 ml min^{-1} and an oven temperature program of 30 °C held for 6·5 min, then increased at 15 °C min^{-1} to 100 °C. Data acquisition was executed in the selected ion monitoring mode.

Analytical GC analyses were carried out with a 25 m × 0·2 mm i.d. cross-linked 5% phenylmethylsilicone fused-silica capillary column (column A) and a 25 m × 0·2 mm i.d. cross-linked methylsilicone capillary column (column B) connected to a single injection port using a 0·4-mm two-hole Supeltex M-2A Ferrule (Supelco, 2-2467). The carrier gas was helium at a flow-rate of 1 ml min^{-1}; a detector temperature of 300 °C, injector temperature of 160 °C, oven temperature of 45 °C and HP 3390A and 3392A reporting integrators were used. Preparative GC separations were accomplished with a 300 cm × 0·6 cm i.d. 20% β,β'-oxydipropionitrile on Chromosorp P column at 40 °C and a Varian Aerograph A90-P3 instrument with helium as the carrier gas.

Proton NMR spectra were obtained for $CDCl_3$ solutions with Me_4Si at δ 0·0 ppm as internal reference on a General Electric QE 300-MHz or GN 500-MHz instrument, interfaced to a VAX 8650 data system. Gas-tight syringes used for introducing a sample into the kinetics bulb were obtained from Dynatech Precision Sampling Corp. (Series A-2, 5·0, 2·0 and 0·5 ml). Dilute solutions of hydrocarbon products were concentrated by careful distillation using either a Nester/Faust spinning-band apparatus equipped with a 70-cm Teflon band or a B/R Instrument Corp. Model 800 micro spinning-band apparatus equipped with an 20-cm Teflon band.

Bicyclo[3.2.0]hept-2-ene (1)

A yellow suspension of 114 mg of potassium azodicarboxylate (0·59 mmol), 50 mg of bicyclo[3.2.0]hepta-2,6-diene[6] (0·54 mmol) and 0·5 ml of methanol was stirred at room temperature under a nitrogen atmosphere. A solution of 37·2 μl of glacial acetic acid

(0·65 mmol) and 0·2 ml of methanol was added slowly by syringe over 2 h. The reaction mixture was then stirred for 18 h; the yellow color faded and a white precipitate appeared. The mixture was cooled in an ice-bath and added to a cold mixture of water and pentane. The layers were separated and the aqueous portion was extracted three times with pentane. The pentane extract was washed with water, saturated $NaHCO_3$ and brine and then dried over $MgSO_4$. The resulting solution was filtered and concentrated by distillation. Capillary GC analysis gave the following retention times on column A (column B, % yield): unreacted bicyclo[3.2.0]hepta-2,6-diene, 4·21 min (3·84 min, 5%); **1**, 5·00 min (4·60 min, 89%); bicyclo[3.2.0]heptane, 5·65 min (5·25 min, 6%). Preparative GC afforded pure **1**: ^{1}H NMR, d 5·77–5·79 (d, 2H), 3·21 (bs, 1H), 2·86–2·89 (quintet, 1H), 2·49–2·54 (dd, 1H), 2·29–2·32 (quintet, 1H), 2·11–2·17 (m, 2H), 1·64–1·70 (quintet, 2H).[17] GC–MS analysis, *m*/*z* (relative intensity): 95 (0·3), 94 (M^+, 3·7), 91 (7·1), 79 (27·1), 77 (16·5), 67 (6·8), 66 (100), 40 (6·9), 39 (22·8).

[6,7-$^2H_2$] Bicyclo[3.2.0]hept-2-ene(1-d_2)

This was prepared in an analogous reaction from 40 mg of bicyclo[3.2.0]hepta-2,6-diene (0·43 mmol), 114·6 mg of potassium azodicarboxylate (0·59 mmol), 37·5 ml of acetic acid-d_1 (Norrel, 99 atom-% ^{2}H, 0·65 mmol) and 0·7 ml of methanol-d_1 (Aldrich, 99·5+ atom-% ^{2}H). Capillary GC analysis of the concentrated product mixture gave the following retention times on column A (column B, % yield): for unreacted starting diene, 4·17 min (3·81 min, 5%); **1**-d_2, 4·97 min (4·59 min, 90%); bicyclo[3.2.0]heptane-2,3,6,7-d_4, 5·54 min (5·16 min, 5%). For **1**-d_2: ^{1}H NMR, d 5·77–5·79 (d, 2H), 3·20 (bs, 1H), 2·85–2·87 (m, 1H), 2·49–2·54 (dd, 1H), 2·30 (m, 0·17H), 2·11–2·15 (m, 1·17H), 1·62–1·67 (t, 1·66H). GC–MS analysis, *m*/*z* (relative intensity): 97 (0·3), 96 (M^+, 3·6), 93 (3·8), 81 (12·5), 80 (15·2), 67 (9·4), 66 (100), 40 (11·6), 39 (14·5).

[5,6-$^2H_2$]Norbornene

This was prepared through a dideuteriodiimide reduction of norbornadiene (7·0 g, 76 mmol) using 11·65 g of potassium azodicarboxylate (60 mmol), 4·03 g of acetic acid-d_1 and 15 ml of methanol-d_1. Capillary GC analysis of the crude product mixture gave the following retention times on column A (column B, % yield): for unreacted norbornadiene, 3·72 min (3·37 min, 54%), **2**-d_2, 4·03 min (3·69 min, 28%); [2,3,5,6-$^2H_4$]norbornane, 4.78 min (4·40 min, 18%); For GC-purified **2**-d_2: ^{1}H NMR, d 5·99 (s, 2H), 2·84 (s, 2H), 1·54 (bs, 0·25H), 1·30–1·31 (m, 1H), 1·06–1·08 (m, 1H), 0·93 (bs, 1·75H). GC–MS analysis, *m*/*z*(relative intensity), 97 (0·9), 96 (M^+, 11·9), 80 (7·5), 78 (6·7), 67 (10·0), 66 (100), 40 (16·9).

Mass spectral analyses

The mass spectral analyses were based on relative *m*/*z* M and $M+2$ ion intensities and the appropriate relationship [equation (7)][18] to convert observed $(M+2)/M$ ratios to the corresponding concentrations ratios; here *d*0 and *d*2 as subscripts refer to ion ratios determined with authentic d_0 and d_2 reference compounds. There was no observable $M+2$ ion for **1**; for **2** the $(M+2)/M$ ratio was 0.002. For **1**-d_2 and **2**-d_2, $M/(M+2)$ ratios were 2·816 and 0·047.

$$[C_7H_8D_2]/[C_7H_{10}] = \{[(M+2)/M] - [(M+2)/M]_{d0}\}/\{1 - [(M+2)/M][M/(M+2)]_{d2}\} \tag{7}$$

Kinetic bulb

A 1-l Pyrex bulb was fitted with a 20 cm × 6 mm i.d. Pyrex stem, an Ace Flickit Teflon stopcock (8200–05), Ace threaded adaptor (5037–03) containing a Hamilton septum (76010) and Ace nylon bushing (65037–12), and a QG Corp. Teflon stopcock leading to a vacuum line. The bulb was situated in a spherical cavity within an aluminium block fitted with thermostatically controlled heating cartridges (Wellman EC2081). Half of the heating cartridges were connectged directly to a Superior Metric Powerstat while the remainder were regulated by a Bayley Instrument Model 253 Precision Temperature Controller. The temperature of the aluminium block close to the bulb was monitored with an HP 2802A digital thermometer. The pyrolysis bulb was conditioned by heating cyclohexene (distilled) at 276 °C and 50 Torr for 48 h.

Rate constants for the decomposition of bicyclo[3.2.0]hept-2-ene (k_0) and [6,7-$^2H_2$]bicyclo[3.2.0]hept-2-ene (k_0')

The initial pyrolysis mixture contained 29·6 mg of **1** (0·31 mmol), 32·9 mg of **1**-d_2 (0·34 mmol), 11·0 mg of octane (0·10 mmol) and 57·5 mg of 2-methylpentane (0·67 mol). The mixture was injected into the evacuated kinetics bulb at 275·7 °C. The pressure in the bulb after introduction of the mixture was calculated to be 49 Torr. The mixture was sampled with a gas-tight syringe and analyzed by GC–MS. Seven sets of m/z 94, 96 (for bicyclo[3.2.0]hept-2-enes) and 114 (for octane) ion intensities were obtained over 37 h (1·5 half-lives). After correcting the m/z intensities for a component derived from **1**-d_2, the natural logarithms of the corrected 94/114 ion intensity ratios versus time were subjected to least-squares analysis to give $8{\cdot}2 \times 10^{-6}\,s^{-1}$ for the rate constant k_0 ($r = 0{\cdot}98$). (Calculation based on the activation parameters reported by Cocks and Frey[1] give $k_1 + k_3 = 8{\cdot}8 \times 10^{-6}\,s^{-1}$ at 276 °C.) A logarithmic plot of [**1**-$d_2(t)$]/[**1**(t)] versus time (six points) gave $k_0 - k_0' = 6 \times 10^{-7}\,s^{-1}$.

Kinetics of retrogression for norbornene (2) and [5,6-$^2H_2$]norbornene (2-d_2)

In a typical experiment, 17 mg of **2**, 25 mg of octane, and 83 mg of 2-methylpentane were injected into the evacuated kinetics bulb at 276·6 °C. The mixture was sampled with a gas-tight syringe and analyzed by GC–MS five times over 3·6 half-lives. A first-order kinetic plot for norbornene relative to octane as internal standard gave $2{\cdot}8 \times 10^{-4}\,s^{-1}$ for the Diels–Alder retroaddition of **2**. A duplicate run (276·0 °C, six points, over 4·2 half-lives) gave $2{\cdot}81 \times 10^{-4}\,s^{-1}$. A mixture of **2**, **2**-d_2, octane and 2-methylpentane at 275·7 °C was followed in a similar manner (ten points, 4 half-lives); the rate constants derived were $k_2 = 2{\cdot}78 \times 10^{-4}$ and $k_2 - k_2' = 6{\cdot}3 \times 10^{-6}\,s^{-1}$.

Dynamic isotopic dilution experiments

In a typical kinetic run, 30·0 mg of **1**-d_2 (0·31 mmol), 9·9 mg of **2** (0·11 mmol), 12·5 mg of octane (0·11 mmol) and 71·0 mg of 2-methylpentane (0·82 mmol) were combined. Analysis by capillary GC indicated a [**1**-d_2(0)]/[**2**(0)] ratio of 2·97. The mixture was injected into the evacuated ($3{\cdot}5 \times 10^{-5}$ Torr) kinetics bulb at 276·0 ± 0·2 °C. The reaction mixture was sampled with a gas-tight syringe fitted with a 0·028 × 16 in needle (custom made by Supelco) at various times. The long needle was replaced with a shorter needle (0·028 × 2 in) (Supelco 2-2299) and the sample was injected directly into the GC–MS system for analysis. Observed concentration ratios for **2** and **2**-d_2 for all four dynamic isotopic dilution runs are recorded in Table 1.

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REFERENCES

1. A. T. Cocks and H. M. Frey, *J. Chem. Soc. A* 2564 (1971).
2. R. H. Newman-Evans and B. K. Carpenter, *J. Am. Chem. Soc.* **106**, 7994 (1984); P. N. Skancke, K. Yamashita and K. Morokuma, *J. Am. Chem. Soc.* **109**, 4157 (1987); G. D. Andrews and J. E. Baldwin, *J. Am. Chem. Soc.* **99**, 4853 (1977).
3. T. A. Micka, *PhD Dissertation*, University of Oregon (1980); *Diss. Abstr. B.* **41**, 1780 (1980).
4. J. E. Baldwin and K. D. Belfield, *J. Am. Chem. Soc.* **110**, 296 (1988).
5. F.-G. Klärner, R. Drewes and D. Hasselmann, *J. Am. Chem. Soc.* **110**, 297 (1988).
6. J. E. Baldwin and K. D. Belfield, *J. Org. Chem.* **52**, 4772 (1987).
7. N. H. Werstiuk, *Can. J. Chem.* **53**, 26 (1975).
8. J. J. Gajewski, in *Isotopes in Organic Chemistry*, edited by E. Buncel and C. C. Lee, Vol. 7, pp. 115–175. Elsevier, Amsterdam (1987).
9. W. C. Herndon, W. B. Cooper and M. J. Chambers, *J. Phys. Chem.* **68**, 2016 (1964); B. C. Roquitte, *J. Phys. Chem.* **69**, 1351 (1965); R. Walsh and J. M. Wells, *J. Chem. Soc., Perkin Trans. 2* 52 (1976).
10. M. B. Neiman and D. Gal, *The Kinetic Isotope Method and Its Application*. Elsevier, New York (1971).
11. H. E. Zimmerman and D. R. Diehl, *J. Am. Chem. Soc.* **101**, 1841 (1979); H. E. Zimmerman, C. W. Carpenter and A. M. Weber, *J. Am. Chem. Soc.* **107**, 1073 (1985); H. E. Zimmerman and J. M. Nuss, *J. Org. Chem.* **51**, 4604 (1986).
12. T. E. Kurtz, *Basic Statistics*, pp. 278–279 and 312. Prentice-Hall, Englewood Cliffs, NJ (1963).
13. C. L. Perrin, *Mathematics for Chemists*, p. 159. Wiley–Interscience, New York (1970).
14. B. L. Crawford, Jr, J. E. Lancaster and R. G. Inskeep, *J. Chem. Phys.* **21**, 678 (1953).
15. D. K. Lewis, D. A. Glenar, B. L. Kalra, J. E. Baldwin and S. J. Cianciosi, *J. Am. Chem. Soc.* **109**, 7225 (1987).
16. A. Fernandez, *J. Chem. Phys.* **82**, 3123 (1985).
17. W. J. Leigh and R. Srinivasan, *J. Org. Chem.* **48**, 3970 (1983).
18. P. S. Engel, W.-K. Chae, S. A. Baughman, G. E. Marschke, E. S. Lewis, J. W. Timberlake and A. E. Luedtke, *J. Am. Chem. Soc.* **105**, 5030 (1983); H. Kwart and K. A. Wilk, *J. Org. Chem.* **50**, 817 (1985).