warm to 25°, and quenched with 2 equiv of dimethyl disulfide. Aqueous acid work-up gave an essentially quantitative yield of the α-methylthio ester with no detectable sulfenylation α to the ketone. This material was carried on in the usual manner (Table I, entry 7) to give a 90% overall yield of the conjugated ester.

When simple ketone enolates (generated as in the case of ester enolates) were quenched at 25° with a 15% excess of diphenyl disulfide,[5b,10] the corresponding α-phenylsulfenyl ketones (Table I, entries 6b and 8) were isolated in high yield. For α-methylene ketones a ratio of ketone:amide based:isulfide of 1:2:1.1 was required. Surprisingly, after oxidation to the sulfoxide as previously, facile elimination occurred at 50° either neat or in carbon tetrachloride solution. The fact that benzenesulfenic acid should be a better leaving group than methylsulfenic acid accounts for this 70° temperature lowering for elimination of the aryl *vs.* alkyl sulfoxides.[3e]

The method is quite mild as the compatibility with *tert*-butyl esters (Table I), acetals,[11] allylic alcohols,[11] and epoxides[11] demonstrates. The fact that all intermediates in the sequence are stable, easily isolable compounds allows for the possibility of other structural modification prior to thermolysis. The commercial availability and ease of handling of dimethyl and diphenyl disulfides and the ability of dimethyl disulfide to sulfenylate in a chemospecific[12] reaction further illustrates the synthetic potential of the above reaction sequence.

Acknowledgment. We wish to thank the National Science Foundation and the National Institutes of Health (General Medical Sciences) for their generous support of our programs.

(10) *Cf.* T. Fujisawa, K. Hata, and T. Kojima, *Chem. Lett.*, 278 (1973).

(11) T. N. Salzmann and B. M. Trost, unpublished results.

(12) The term chemospecific is introduced to define a reaction which is specific for a given structural unit even in the presence of other functionality that might have appeared to be as or more reactive. For example, the ability to brominate α to a ketone in the presence of a double bond (or *vice versa*) would also constitute a chemospecific reaction.

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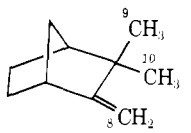
An Analysis of the Acid-Catalyzed Racemization of (−)-Camphene-^{13}C. Is *endo*-Methyl Migration Necessary?[1]

Sir:

In a recent ^{13}C nmr study[2] of the racemization of camphene-*8*-^{13}C (1.71 *M* camphene, 6.59 *M* pyruvic acid in acetonitrile at 137–138°), during which the extent of isotopic labeling in all three methyls was determined after partial racemization, the authors claim to have detected a small fraction of 3,2-*endo*-methyl shift. We doubted this conclusion, since 3,2-endo shifts in bicyclo-



camphene and numbering system

[2.2.1]heptyl compounds are, in general, inhibited.[3,4] In addition, these authors[2] reported that their results were compatible with three competing racemization processes, one of which (k_1) was *endo*-methyl migration, and then stated "the assignment of zero values to α does not give a good agreement of experimental mole fractions of X/X_0 with the predicted value." In their[2] notation, α is the fraction proceeding with *endo*-methyl migration and X/X_0 signifies the mole fractions (above normal abundance) of ^{13}C at C_8 after reaction times of 1.5 and 3.0 hr.

The mathematical method employed[2] seemed to us to be unnecessarily cumbersome. In addition the authors,[2] after calculating the fractions of reaction proceeding through the three competing processes from their individual experimental runs, averaged these fractions "to give single experimental values" from which theoretical curves for these "experimental" values *vs.* time were computed. Thus the individual fits for each of the four experimental runs were not compared with and then without *endo*-methyl migration, but rather the fit was determined with the synthetically averaged values.

The average of the four derived α values calculated by Vaughan, Stothers, and coworkers[2] is 0.026, from which we determine a standard deviation[5] of ±0.023 and a 95% confidence level[5] of about ±0.046, a value greater than the presumed fraction (α = 0.026) of *endo*-methyl migration. If we consider that there are only four observations, then the limits of error would be even greater.

For all of the above-mentioned reasons, we reanalyzed the data[2] using a more direct method, and demonstrate unequivocally and beyond any doubt that these data are fit equally well by a mechanism in which k_1 is omitted. Thus, by Occam's razor,[6] we conclude that endo migration of methyl should not be included in the mechanism.

There is at least one other way to treat their data.[2] We replaced their scheme[7] with the model shown in Scheme I, in which the appropriate intermediates are also considered. In our model A is (−)-camphene-*8*-^{13}C, B is (+)-camphene-*9*-^{13}C, C is (−)-camphene-*10*-^{13}C, D is (+)-camphene-*10*-^{13}C, E is (−)-camphene-*9*-^{13}C, F is (+)-camphene-*8*-^{13}C, a–f are the protonated forms of A–F; k_1 is the racemization process 3,2-*endo*-Me, k_2 is the racemization process Wagner–Meerwein, 6,2-hydride shift Wagner–Meerwein, k_3 is the racemiza-

(1) Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

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

(3) C. J. Collins, Z. K. Cheema, R. G. Werth, and B. M. Benjamin, *ibid.*, **86**, 4913 (1964); P. von R. Schleyer, *ibid.*, **89**, 701 (1965). There are only two documented cases of 3,2 endo hydride migration: A. W. Bushell and P. Wilder, Jr., *ibid.*, **89**, 5720 (1967); P. Wilder, Jr., and W. C. Hsieh, *J. Org. Chem.*, **36**, 2552 (1971).

(4) See also C. J. Collins and C. K. Johnson, *J. Amer. Chem. Soc.*, **95**, 4766 (1973).

(5) See, for example, D. J. Finney, "Experimental Design and Its Statistical Basis," University of Chicago Press, Chicago, Ill., 1955, p 35.

(6) "Pluralitas non est ponenda sine necessitate," a dictum posed by the Franciscan philosopher, William Ockham (or Occam, c. 1280–1349). "Encyclopedia Britannica," Vol. 16, Wm. Benton, Publisher, London, 1966, p 858.

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

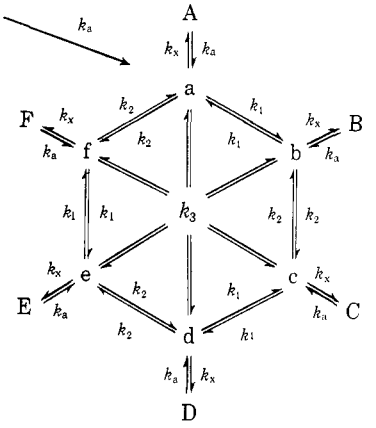
Table I. Comparison of the Observed[2] ^{13}C Distributions on Racemization of (−)-Camphor-8-^{13}C with Those Calculated Using Eq 1–5, Neglecting 3,2-*endo*-Methyl Migration (k_1)

Time, hr		Mole fractions			
		Obsd		Calcd	
1.5	$m_a + m_f$ (C_8)	0.858 ± 0.01[b]	0.874 ± 0.01[c]	0.869[f,g]	0.875[h,g]
	$m_b + m_e$ (C_9)	0.020 ± 0.002	0.017 ± 0.002	0.017	0.016
	$m_c + m_d$ (C_{10})	0.123 ± 0.007	0.109 ± 0.007	0.114	0.110
	$m_b + m_d + m_f$[a]	0.124 ± 0.012		0.132	0.128
3.0	$m_a + m_f$ (C_8)	0.770 ± 0.008[d]	0.766 ± 0.008[e]	0.767[i]	0.778[i]
	$m_b + m_e$ (C_9)	0.028 ± 0.004	0.032 ± 0.005	0.031	0.028
	$m_c + m_d$ (C_{10})	0.202 ± 0.009	0.202 ± 0.009	0.202	0.194
	$m_b + m_d + m_f$[a]	0.215 ± 0.021		0.235	0.227

[a] Fraction of inversion.[10] [b] Experiment 16.[2] [c] Experiment 17.[2] [d] Experiment 18.[2] [e] Experiment 19.[2] [f] $k_2/k_x = 0.179$; $k_3/k_x = 0.998$.[10] [g] Mole fraction of unreacted (−)-camphene-^{13}C: 0.623. [h] $k_2/k_x = 0.171$; $k_3/k_x = 0.875$. [i] Mole fraction unreacted (−)-camphene-^{13}C: 0.329.

Scheme I

1 mol of (−)-camphene-8-^{13}C
(plus x mol of (−)-camphene-8-^{13}C
which do not react)



tion process 3,2-*exo*-Me, k_a is the rate constant for protonation of camphene, and k_x is the rate constant for deprotonation of camphene. From the experimental data[8] the sums of the mole fractions of ^{13}C in C_8 ($m_a + m_f$), C_9 ($m_b + m_e$), and C_{10} ($m_c + m_d$) after 1.5 and 3.0 hr of reaction time are available. For each mole of (−)-camphene-8-^{13}C which has entered into the reaction after any period of time, it is possible to demonstrate[9] the following relations

$$Ym_b' = k_1m_a' + k_2m_c' + k_3m_e' \quad (1)$$

$$Ym_c' = k_1m_d' + k_2m_b' + k_3m_f' \quad (2)$$

$$Ym_d' = k_1m_c' + k_2m_e' + k_3m_a' \quad (3)$$

$$Ym_e' = k_1m_f' + k_2m_d' + k_3m_b' \quad (4)$$

$$Ym_f' = k_1m_e' + k_2m_a' + k_3m_c' \quad (5)$$

in which $Y = k_1 + k_2 + k_3 + k_x$ and $\Sigma m_i' = 1$. Since k_a is the rate constant for the slow step, it is so much smaller than all the other k's, that the terms containing k_a in the numerator are also insignificant and have been dropped. The mole fractions m_a'–m_f' are related to m_a–m_f in the following way: $(x + m_a')/(1 + x) = m_a$; $m_b'/(1 + x) = m_b$, etc., in which x is the moles of (−)-camphene-8-^{13}C which did not enter into the reaction after the given period of time.

Using standard computer techniques, we solved eq 1–5 for those values of x and k_1/k_x, k_2/k_x, and k_3/k_x which are consistent with the experimentally determined[2] ^{13}C fractions at C_8, C_9, and C_{10}, and with the calculated[10] fractions of inversion at 1.5 and 3.0 hr, respectively. We found that there is a range of values for the three ratios k_1/k_x, k_2/k_x, and k_3/k_x which are reasonably compatible with all four experimental runs. The results,[2] in fact, seem to be quite insensitive to k_1 over a range of contribution by k_1 to the racemizing process of 0–8%. The fit is best when $k_1 = 0$ (that is, leaving *endo*-methyl migration out of the model entirely). For all four experiments of Vaughan and coworkers[2] there are values for k_2/k_x and k_3/k_x which will duplicate the data within experimental error. The range of values (k_2/k_x 0.171–0.179; k_3/k_x 0.875–0.988) which allows us to recalculate the appropriate mole fractions for all four runs with the best overall agreement is shown, together with the results calculated therefrom, in Table I.

Thus the data of Vaughan, *et al.*,[2] can be explained with only two racemizing processes (k_2 and k_3), and offer no evidence whatsoever for *endo*-methyl (k_1) migration.

(8) Tables I and II, p 1267 of ref 2.

(9) B. M. Benjamin and C. J. Collins, *J. Amer. Chem. Soc.*, 78, 4329 (1956), discuss the area theorem of J. Z. Hearon which was used in the derivations.

(10) Using $k_{rac} = 5.2 \pm 0.43 \times 10^{-5}$ sec^{-1} as reported by Vaughan, *et al.*,[2] we calculated the fractions of inversion ($m_b + m_d + m_f$) at 1.5 and at 3.0 hr to be 0.124 and 0.215, respectively. The error reported[2] in the rate constant is ±8.3%; the error in these fractions of inversion is certainly greater. Stothers, Vaughan, *et al.*, (ref 2, p 1266) comment on the "lack of precision"... "inherent in the nature of the experimental technique." We estimate a lower limit for the error in the fraction of inversion as ±10%.

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Carbon Scrambling in $C_5H_5^+$, $C_5H_6^+$, and $C_7H_7^+$ Produced by Electron Impact

Sir:

Electron impact decomposition of benzene to extrude a C_2H_2 fragment has been shown[1] to occur with extensive scrambling of both the hydrogen and carbon atoms prior to the extrusion.

We report here on the electron impact fragmentations of cycloheptatriene, cyclopentadiene, and norbornadiene, all doubly labeled with vicinal ^{13}C atoms, to

(1) (a) C. G. McDonald and J. Shannon, *Aust. J. Chem.*, **15**, 771 (1962); (b) K. R. Jennings, *Z. Naturforsch. A*, **22**, 454 (1967); (c) J. H. Beynon, R. M. Caprioli, W. O. Perry, and W. E. Baitinger, *J. Amer. Chem. Soc.*, **94**, 6828 (1972); (d) R. J. Dickinson and D. Williams, *J. Chem. Soc. B*, 249 (1971); (e) I. Horman, A. N. H. Yeo, and D. H. Williams, *J. Amer. Chem. Soc.*, **92**, 2131 (1970).