

none.² Equilibrium was approached from both sides at several temperatures with several equilibrations run at each temperature. The composition of the mixtures was determined by vapor phase chromatography (v.p.c.) through an 8-ft. Ucon column which resulted in the complete separation of the *cis*- and *trans*- β -decalones. A number of side products were also formed during the equilibration. Some of these, presumably alcohols, proved difficult to separate from the ketones by v.p.c. These substances were, however, conveniently removed by treating the sample with concentrated sulfuric acid for a short time, pouring the mixture into water, and extracting with ether.² That this did not affect the equilibrium composition was shown by the fact that a known mixture of I and II was recovered unchanged from the sulfuric acid treatment. The other side products were identified as *cis*- and *trans*-decalin, tetralin, and naphthalene by comparison of their v.p.c. retention times with that of authentic samples. Prolonged heating of the ketone mixture over Pd greatly increased the amount of these side products which were formed but did not change the relative amounts of I and II which were present at equilibrium. The decalone composition for the entire equilibration procedure was reproducible to within $\pm 0.4\%$. The equilibration data are listed in Table I.

TABLE I

Temp., °K.	%I	K	F, kcal./mole
493	24.52 \pm 0.43	3.08 \pm 0.03	-1.10
523	22.71 \pm 0.26	3.40 \pm 0.05	-1.27
573	19.05 \pm 0.23	4.25 \pm 0.07	-1.65
531 ^a		3.52	-1.33 \pm 0.02

^a Temperature used in the calculation of ΔH and ΔS .³ K, at this temperature, was determined graphically.

A plot of $\ln K$ vs. $1/T$ indicated that the enthalpy change for the reaction was not linear with temperature. The thermodynamic data for the *cis* \rightleftharpoons *trans* equilibration, $\Delta H_{531} = +2.25 \pm 0.24$ kcal./mole and $\Delta S_{531} = 6.74 \pm 0.45$ e.u., were evaluated using the method described by Douglas and Crockford.³ *This entropy change is the highest we have found recorded for any cis-trans isomerization.* In fact it is about five to ten times larger than the usual ΔS observed for such reactions. It represents one of the few instances in such equilibrations in which the ΔS is of such a magnitude as to cause a difference in sign between the ΔF and ΔH of the reaction.⁴

The enthalpy change for *cis* \rightleftharpoons *trans* decalin equilibration is -2.72 ± 0.20 kcal./mole.⁵ Subtracting the ΔH for the decalone equilibration from this value results in an energy assignment for the 3-alkyl ketone effect of 4.97 kcal./mole, a value which is clearly inconsistent with the empirical correlations initially proposed. By use of a similar comparison of the enthalpy changes for the *trans* \rightleftharpoons *cis* isomerizations of 1,3-dimethylcyclohexane and 3,5-dimethylcyclohexanone, Allinger and Freiberg have reported the magnitude of the 3-alkyl ketone effect to be no larger than 0.6 kcal./mole,² a value more in agreement with theoretical con-

siderations. However, the ΔH for the 3,5-dimethylcyclohexanone isomerization was calculated from a ΔF determined from equilibration data obtained at only one temperature and an entropy change (-1.4 e.u.) based on an entropy of mixing term which bears no relationship to the equilibration. This assumption, that the entropy of mixing approximates the entropy of isomerization, invalidates the entire argument.

This fact, in conjunction with the data presented for the decalone isomerization, raises doubts not only about the validity of the assignment made for the magnitude of the 3-alkyl ketone effect but also about the soundness of the experimental method used to obtain this information.

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Secondary α -Deuterium Isotope Effects in Acetolyses of *endo*- and *exo*-Norbornyl and 2-(Δ^3 -Cyclopentenyl)ethyl Arenesulfonates

Sir:

Recently, Brown and co-workers¹ reported some kinetic data which suggest doubts on certain mechanistic interpretations of solvolysis based on the nonclassical norbornyl cation. Some of the conclusions based on relative rates were necessarily indirect, these authors themselves pointed out that results from tertiary cations cannot be extrapolated to the norbornyl system, and comparisons between bicyclic and cyclopentyl systems may be complicated by solvent participation. We wish to report the secondary α -deuterium kinetic isotope effects observed in the acetolyses of *endo*- and *exo*-norbornyl-2-*d* *p*-bromobenzenesulfonates (I-*d* and II-*d*, respectively) and 2-(Δ^3 -cyclopentenyl)-ethyl-1,1-*d*₂ *p*-nitrobenzenesulfonate² (III-*d*₂). The relative magnitudes of these isotope effects may shed further light on the mechanisms of these solvolyses.

endo-Norboreneol-2-*d* was obtained from reduction of norcamphor with lithium aluminum deuteride. After conversion to I-*d*, the presence of any minor amount of *exo* isomer, II-*d*, was removed by selective solvolysis in aqueous acetone.³ Treatment of I-*d* with dry tetramethylammonium acetate in acetone⁴ gave *exo*-norbornyl-2-*d* acetate which was reduced with lithium aluminum hydride and then converted to II-*d*.⁵ From 4-bromocyclopentene,⁶ using the malonic ester synthe-

(1) H. C. Brown, F. J. Chloupek, and M.-H. Rei, *J. Am. Chem. Soc.*, **86**, 1246, 1247, 1248 (1964).

(2) R. G. Lawton, *ibid.*, **83**, 2399 (1961); P. D. Bartlett and S. Bank, *ibid.*, **83**, 2591 (1961); P. D. Bartlett, *Ann.*, **653**, 45 (1962).

(3) J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, **76**, 4501 (1954).

(4) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey, and S. Suzuki, *ibid.*, **80**, 2326 (1958).

(5) The correctness of this assignment is confirmed by n.m.r. II-*d* prepared in this way gave no detectable absorption for any C-2 proton. On the other hand, the *endo* isomer I showed n.m.r. absorption of an *exo*-proton at C-2 and after its conversion to II by this method the spectrum showed the presence of only an *endo*-proton at C-2, corresponding to pure *exo* isomer II. (For some of the spectra, see E. W. C. Wong and C. C. Lee, *Can. J. Chem.*, **42**, 1245 (1964).)

(6) M. R. Rice, Ph.D. Thesis, Harvard University, 1957; P. D. Bartlett and M. R. Rice, *J. Org. Chem.*, **28**, 3351 (1963).

(3) T. B. Douglas and H. D. Crockford, *J. Am. Chem. Soc.*, **57**, 97 (1935).

(4) See, for instance, the various isomerization data reported by Allinger, as well as R. M. Gascoigne, *J. Chem. Soc.*, 876 (1958). A sign inversion between the ΔF and ΔH for the isomerization of *cis*- and *trans*-cyclohexene is reported by A. C. Cope, P. T. Moore, and W. R. Moore, *J. Am. Chem. Soc.*, **81**, 3153 (1959).

(5) N. L. Allinger and J. L. Coke, *ibid.*, **81**, 4080 (1959).

sis, Δ^3 -cyclopentenylacetic acid was obtained. The latter was treated with lithium aluminum deuteride to give 2-(Δ^3 -cyclopentenyl)ethanol-1,1- d_2 which was, in turn, converted to III- d_2 . Analyses⁷ showed that I- d , II- d , and III- d_2 contained, respectively, 0.94, 0.94, and 1.94 D atoms per molecule.

Rates of acetolysis were determined at a number of temperatures. In order to minimize possible errors in the isotope effects due to variations between experiments, at each temperature, corresponding protio and deuterio compounds were solvolyzed simultaneously. First-order specific rate constants were derived from least squares plots of the experimental data, with the aid of a digital computer. The 95% confidence limits (standard deviations $\times 1.96$) were better than $\pm 1\%$ for practically all of the k values. The isotope effects, as measured by k_H/k_D , are given in Table I.

TABLE I
KINETIC ISOTOPE EFFECTS IN ACETOLYSES
AT VARIOUS TEMPERATURES

I and I- d		II and II- d		III and III- d_2	
Temp., °C.	k_H/k_D	Temp., °C.	k_H/k_D	Temp., °C.	k_H/k_D
50.07	1.203	20.00	1.131	40.50	1.148
50.07	1.204	20.00	1.119	50.20	1.139
55.18	1.197	24.85	1.108	60.65	1.129
60.65	1.172	30.02	1.111	60.65	1.135
65.14	1.181	35.00	1.101		
70.00	1.201				
$\Delta\Delta H^*$, cal./mole	128 \pm 272	240 \pm 174	150 \pm 67		
$\Delta\Delta S^*$, e.u.	0.004 \pm 0.002	0.59 \pm 0.01	0.19 \pm 0.01		

It is seen that k_H/k_D is almost independent of temperature, though the trend appears to indicate somewhat lower isotope effects at higher temperatures. Following the treatment of Leffek, Robertson, and Sugamori,⁸ $\log(k_H/k_D)$ were plotted against reciprocals of absolute temperature by the least-squares method. From the slopes and intercepts, $\Delta\Delta H^*$ ($\Delta H_D^* - \Delta H_H^*$) and $\Delta\Delta S^*$ ($\Delta S_D^* - \Delta S_H^*$) were calculated and included in Table I.

The results clearly show higher k_H/k_D for the *endo*- than the *exo*-norbornyl system. Extrapolation of the kinetic data for II and II- d to 50° gave a k_H/k_D of 1.07 for the *exo* system as compared to a k_H/k_D of 1.20 for the *endo* isomer at the same temperature. According to the treatment of Streitwieser,^{4,9} participation of a neighboring group in the rate-determining step of a carbonium ion reaction, an essential feature leading to a nonclassical intermediate, would produce a decrease in the magnitude of the α -deuterium kinetic isotope effect. The present results thus would appear to be mutually compatible supporting evidence either for Streitwieser's treatment or for the nonclassical norbornyl cation in the acetolysis of *exo*-norbornyl *p*-bromobenzenesulfonate.

However, the over-all isotope effect observed for the *exo*-norbornyl system might be complicated by the possibility of internal return.¹⁰ Such a process could lead to scrambling of the D atom in the *exo-p*-bromobenzenesulfonate being solvolyzed. For example, return from norbornonium *p*-bromobenzenesulfonate ion pair would give rise to a mixture of II- d and *exo*-norbornyl-1- d *p*-bromobenzenesulfonate. To ascertain how such returns might influence the net isotope effect observed for II and II- d will require further investigations.

The acetolysis of III gave *exo*-norbornyl acetate in very high yield,² indicating a limiting carbonium ion reaction. The observed k_H/k_D for III and III- d_2 of about 1.14 for two α -deuterium atoms is much less than the expected value of about 15% rate retardation per deuterium atom.⁹ For this system, complication by D scrambling in III- d_2 during solvolysis is less likely than in II- d . Although no internal return studies have been made, a possible product of return during acetolysis of III is *exo*-norbornyl *p*-nitrobenzenesulfonate, which would solvolyze much faster than III. If such a return were to occur to a significant extent, deviations in the kinetics might be expected during the course of a reaction; but this was not observed. The relatively low k_H/k_D of 1.14 for III and III- d_2 , or 1.07 per D atom, however, could again be explained by Streitwieser's hypothesis, a decrease in the α -deuterium kinetic isotope effect being attributed to the participation of the Δ^3 -double bond in the rate-determining step to give a nonclassical norbornyl cation.

In Streitwieser's treatment,⁴ the assumptions made led to the conclusion that difference in rate as a result of α -deuterium substitution is predominantly due to changes in zero-point energy. From the present results on the effects of temperature, the confidence limits for the evaluated $\Delta\Delta H^*$ and $\Delta\Delta S^*$ are quite large; nevertheless, they are of comparable magnitude to the "standard errors" reported by Leffek and co-workers.⁸ To the extent that the present values of $\Delta\Delta H^*$ and $\Delta\Delta S^*$ may be regarded as having some statistical significance, one may conclude that apparently $\Delta\Delta H^*$ contributes more than $T\Delta\Delta S^*$ to $\Delta\Delta F^*$, which would be consistent with the assumption that α -deuterium isotope effects in these solvolyses may be largely due to differences in zero-point energy.

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