time identical with that for the material described above. At least eight additional minor products were also detected.

**B. With Aqueous Acid.** A mixture of 1.22 g of epoxide **17** and 25 ml of 4% sulfuric acid was stirred at 0° for 90 min under an atmosphere of nitrogen and then saturated with sodium chloride and extracted with ether. Drying of the resulting ether extracts over saturated sodium chloride solution followed by anhydrous sodium sulfate and subsequent removal of the solvent by distillation gave 1.40 g of colorless wet crystals which was chromatographed on 45 g of silica gel. Elution with 1:3 ether–benzene gave 665 mg (53% yield) of **(+)-3α,4β-carandiol (19)** as a colorless oil which was further purified by short-path distillation at 103–104° (0.2 mm), $[\alpha]^{25}{}_{5461}$ +87° (*c* 1.25); nmr spectrum: $\tau$ 6.50 (m, 1, CH–4), 8.82 (s, 3, $CH_3$-10), 8.94 and 8.98 (2s, 6, $CH_3$-8 and -9), and 9.34 (m, 2, CH-1 and -6); lit.[7a] mp 30°, $[\alpha]^{20}D$ +84.15° (*c* 6, chloroform).

Further elution with 1:1 ether–benzene gave 318 mg (26% yield) of **(+)-3β,4β-carandiol (18)**; colorless needles from ethyl acetate, mp 138.5–139.5°; $[\alpha]^{25}D$ +64° (*c* 1.49); lit.[7a] mp 137°, $[\alpha]^{20}D$ +61.25° (*c* 4).

**C. With Methanolic Acid.** A solution containing 341 mg of epoxide **17** in 15 ml of 4% methanolic sulfuric acid was stirred at 0° for 90 min under an atmosphere of nitrogen. The resulting mixture was diluted with saturated sodium chloride solution and extracted with ether. The combined ether extracts were washed with saturated sodium bicarbonate solution and dried over saturated sodium chloride solution followed by anhydrous sodium sulfate. Removal of the solvent by distillation gave 450 mg of a colorless liquid which was chromatographed on 20 g of silica gel. Elution with 1:19 ether–benzene gave 283 mg (70% yield) of **(−)-3α-methoxy-4β-caranol (27)**, mp 57.5–63°. Sublimation gave long colorless needles, mp 63.5–64.5°; $[\alpha]^{25}{}_{5461}$ −69° (*c* 1.25); $\lambda_{max}^{CH_2Cl_2}$ 2.75 $\mu$; nmr spectrum: $\tau$ 6.20 (t, 1, CH–4), 6.60 (s, 3, $-OCH_3$), 8.72 and 8.80 (2s, 9, $CH_3$–8, –9, and –10), and 9.2 (m, 2, CH–1 and –6); *m/e* 184, 152, 137, 134, 125, 123, and 119.

*Anal.* Calcd for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94. Found: C, 71.4; H, 11.0.

Elution with 1:3 ether–benzene gave 41 mg (10% yield) of **(+)-4β-methoxy-3β-caranol (28)** as a colorless liquid which was further purified by short-path distillation at 82° (0.5 mm); $\lambda_{max}$ 2.90 $\mu$; $[\alpha]^{27}D$ +53° (*c* 1.74); nmr spectrum: $\tau$ 5.96 (t, 1, CH–4), 6.90 (s, 3, $-OCH_3$), and 8.86, 8.92, and 8.98 (3s, $CH_3$–8, –9, and –10); *m/e* 166, 152, 151, 150, 137, 135, 134, 132, and 123.

*Anal.* Calcd for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94. Found: C, 71.8; H, 10.9.

**(+)-3α-Methoxy-4-caranone (29).** Titration of a solution of 75 mg of alcohol **27** in 5 ml of acetone with 1 molar equiv of 2.67 *M* chromic acid solution[20] gave, on isolation, 75 mg of ketone **29** as a pale yellow liquid. Further purification by gas chromatography followed by short-path distillation at 88–89° (3.5 mm) gave a colorless liquid, $\lambda_{max}$ 5.80 $\mu$; $[\alpha]^{27}D$ +21° (*c* 2.08); nmr spectrum: $\tau$ 6.70 (s, 3, $CH_3O-$), 8.74 (s, 3, $CH_3$–3), and 8.83 and 9.04 (2s, 6, $CH_3$-9 and -8); *m/e* 182, 153, 150, 148, 139, 135, 122. This material exhibited spectral and gas chromatographic behavior quite distinct from that of a specimen of (+)-3β-methoxy-4-caranone.[15b]

*Anal.* Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96 Found: C, 72.6; H, 10.1.

**Acknowledgment.** The able technical assistance of Messrs. T. R. Walker and H. J. Krauss is gratefully acknowledged.

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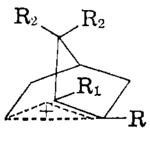
# The Rates of Methoxyl Exchange of Camphor and Norcamphor Dimethyl Ketals in Methanol-$d_4$

**T. G. Traylor and Charles L. Perrin**

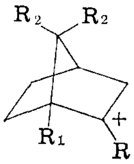
*Contribution from the Department of Chemistry, Revelle College, University of California, San Diego, La Jolla, California 92038.* *Received February 14, 1966*

**Abstract:** In methanol-$d_4$, methoxyl exchange in camphor and norcamphor dimethyl ketals (III) proceeds through the *classical* 2-methoxybicyclo[2.2.1]heptyl-2 cations (IV). The *exo*/*endo* rate ratios for ionization to IV and for reaction of IV with solvent to give labeled III are identical. The observed *exo*/*endo* ratios are 0.10 for camphor dimethyl ketal (IIIb) and 16 for norcamphor dimethyl ketal (IIIa). Reaction of the cations (IV) with hydrides gives *exo*/*endo* rate ratios very close to those for the exchange reaction (0.13 and 20). These results define the behavior of *classical* bicycloheptyl systems and provide a basis for estimating the importance of steric effects and anchimeric assistance in other bicycloheptyl systems. In particular we conclude that bicyclo[2.2.1]heptyl-2 cations having no 2-substituent are not classical.

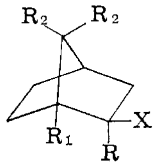
Considerable interest and controversy have arisen over the structure of 2-bicyclo[2.2.1]heptyl cations.[1,2] The large *exo*/*endo* rate ratios in solvolysis and the high stereospecificity for formation of *exo* products have been interpreted[1,3] as evidence for neighboring group participation, leading to bridged ions IB.



IB



IC



II

It has also been suggested[2b] that if this interpretation is correct, substitution of methyl, phenyl, or *p*-anisyl groups at the 2-position (II, R = Me, $C_6H_5$, *p*-Me-$OC_6H_4$) should lead to stabilization of the classical ion IC relative to the bridged ion IB; such stabilization should diminish the necessity for participation and

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(1) (a) S. Winstein, E. Clippinger, R. Howe, and E. Vogelfanger, *J. Am. Chem. Soc.*, 87, 376 (1965); (b) A. Colter, E. C. Friedrich, N. J. Holness, and S. Winstein, *ibid.*, 87, 378 (1965); (c) R. Howe, E. C. Friedrich, and S. Winstein, *ibid.*, 87, 379 (1965); (d) S. Winstein, *ibid.*, 87, 381 (1965); (e) S. Winstein, A. H. Lewin, and K. C. Pande, *ibid.*, 85, 2324 (1963).

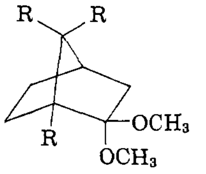
(2) (a) H. C. Brown, F. C. Chloupek, and M.-H. Rei, *ibid.*, **86**, 1246 (1964); (b) *ibid.*, **86**, 1247 (1964); (c) *ibid.*, **86**, 1248 (1964); (d) H. C. Brown and H. M. Bell, *ibid.*, **86**, 5003 (1964); (e) *ibid.*, **86**, 5006 (1964); (f) *ibid.*, **86**, 5007 (1964); (g) H. C. Brown and M.-H. Rei, *ibid.*, **86**, 5004 (1964); (h) *ibid.*, **86**, 5008 (1964); (i) H. C. Brown and H. M. Bell, *ibid.*, **85**, 2324 (1963).

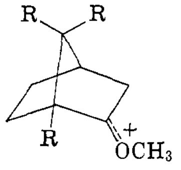
(3) For a historical summary of this concept see J. A. Berson, "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 3.

thereby decrease both the *exo/endo* rate ratio and the *exo/endo* product ratio. "Under this condition, the characteristics now associated with the nonclassical structure of the norbornyl cation should reveal a marked decrease with the increasing classical nature of the cation, vanishing in a truly classical norbornyl cation derivative."[2b] Roberts[4] has made a similar suggestion. Because the expected diminutions were not observed, it was concluded[2b,c,e,h] that the kinetic and stereochemical phenomena in 2-bicycloheptyl systems require neither the postulated neighboring carbon participation nor the intermediate bridged ion IB. The solvolytic behavior of such systems was therefore ascribed to steric effects which produce an inherent preference for *exo* reaction.[5]

It has been argued in return[9] that the 2-methyl, 2-phenyl, and 2-*p*-anisyl substituents introduce new steric effects, etc., which weaken the interpretation of the results obtained. Schleyer[10] has estimated the steric effect on $k_{exo}/k_{endo}$ for solvolysis of 2-alkyl- and 2-aryl-substituted norbornyl derivatives and has concluded that the results reported by Brown, *et al.*,[2] are not inconsistent with bridged ions. While we admit that such steric effects occur, we would agree with Brown and Rei[2h] that quantitative estimates of these effects are subject to large errors.

In order to extend the approach of Brown, *et al.*, to a truly classical bicycloheptyl cation without introducing appreciable steric effects, we have studied the kinetics of methoxyl exchange in camphor dimethyl ketal (IIIb) and norcamphor dimethyl ketal (IIIa).[11] These reactions are equivalent to solvolyses leading to the highly stabilized[12] 2-methoxybicycloheptyl cations (IV). The justification for the use of IV as a model for a "classical" bicycloheptyl cation is given in the Discussion.


IIIa, R = H
b, R = Me

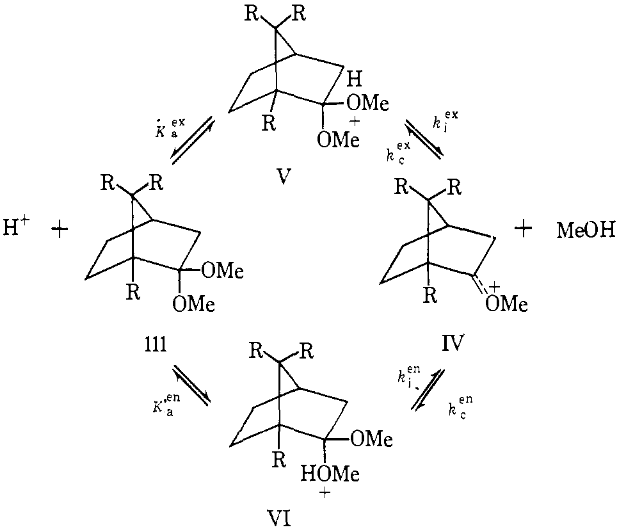

IVa, R = H
b, R = Me

According to the bridged-ion view,[1] the "classical" cation IV should behave like the corresponding ketone[1c] and not show such a marked preference for formation by *exo* ionization or disappearance by *exo* attack. The other view[2] predicts that the usually large preference for reaction at the *exo* position should persist in the ionization of III and in nucleophilic attack on IV.

The results of this study define the behavior of classical bicycloheptyl ions, from which the magnitude of steric effects and anchimeric assistance in less stabilized bicycloheptyl systems can be estimated. In addition, our observations afford additional means for a decision between the two interpretations presented above.

## Results

**Kinetic Studies.** Ketal hydrolysis ordinarily shows specific acid catalysis,[14a,b] and its mechanism is well understood.[14b,15] Carbonium ion formation is the rate-limiting step, and it has been shown that the mechanism does not change on going from water to aqueous methanol,[16] except that in anhydrous methanol, only exchange can occur, without hydrolysis. Therefore we can be confident that the mechanism of each individual step in the over-all exchange process is



Since there is only a single reactant (III) and a single product (IV), we need be concerned with only two possible transition states, and their relative free energies. The transition state for loss of the *exo* methanol from conjugate acid V must be identical with the transition state for *exo* capture of methanol by the intermediate carbonium ion IV, and *mutatis mutandis*, for *endo* ionization and capture (VI $\rightleftarrows$ IV, through another transition state, VI*). Therefore, according to the principle of microscopic reversibility, $\Delta F^*_{endo} - \Delta F^*_{exo} = RT \ln (k_i^{ex}K_a^{en}/k_i^{en}K_a^{ex}) = RT \ln (k_c^{ex}/k_c^{en})$, *i.e.*, the *exo/endo* capture rate ratio must be identical with the *exo/endo* (pseudo-first-order) ionization rate ratio! This is a unique feature which considerably simplifies the over-all kinetic scheme. If we neglect minor isotope effects, we may write this scheme in terms of pseudo-first-order rate constants for ionization, $k_{ex}$ and $k_{en}$ (below). Here the microscopic reversibility has been taken into account, but not the macroscopic reversibility, which introduces further complexity. The reasoning leading

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(4) J. D. Roberts, quoted by C. J. Collins, Z. K. Cheema, R. G. Werth, and B. M. Benjamin, *J. Am. Chem. Soc.*, 86, 4913 (1964).

(5) This preference, independent of phenyl substitution, is also observed in the 3 → 2 hydride migrations which occur in both the 3-methyl-2-norbornyl cations[6] and the 2-phenyl-3-*exo*-hydroxy-2-norbornyl cation,[7] and in the 3 → 2 methyl migration in a camphyl cation.[8]

(6) J. A. Berson, J. H. Hammons, A. W. McRowe, R. G. Bergman, A. Remanick, and D. Houston, *J. Am. Chem. Soc.*, 87, 3248 (1965).

(7) C. J. Collins, Z. K. Cheema, R. G. Werth, and B. M. Benjamin, *ibid.*, 86, 4913 (1964).

(8) A. M. T. Finch, Jr., and W. R. Vaughan, *ibid.*, 87, 5520 (1965).

(9) See footnote 12 of ref 1d.

(10) P. von R. Schleyer, "Symposium on Linear Free Energy Correlations," preprint, U. S. Army Research Office, Durham, N. C., 1964.

(11) Throughout this paper, the a series refers to bicycloheptyl (R = H) and the b series to 1,7,7-trimethyl bicycloheptyl (R = Me).

(12) The observation[13] that methoxymethyl chloride undergoes S$_N$1 solvolysis ~$10^{13}$ times as fast as does *n*-propyl chloride attests to the extraordinary ability of $\alpha$-methoxyl to stabilize carbonium ions.

(13) P. Ballinger, P. B. D. de la Mare, G. Kohnstam, and B. M. Prestt, *J. Chem. Soc.*, 3641 (1955).

(14) (a) M. M. Kreevoy, C. R. Morgan, and R. W. Taft, Jr., *J. Am. Chem. Soc.*, 82, 3064 (1960); (b) M. M. Kreevoy and R. W. Taft, Jr., *ibid.*, 77, 3146 (1955); (c) *ibid.*, 77, 5590 (1955).

(15) L. L. Schaleger and F. A. Long, *Advan. Phys. Org. Chem.*, 1, 1 (1963).

(16) A. M. Wenthe and E. H. Cordes, *J. Am. Chem. Soc.*, 87, 3173 (1965).

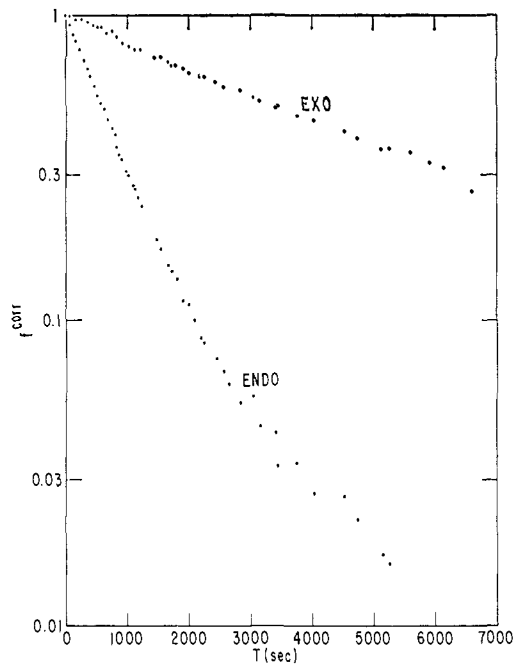
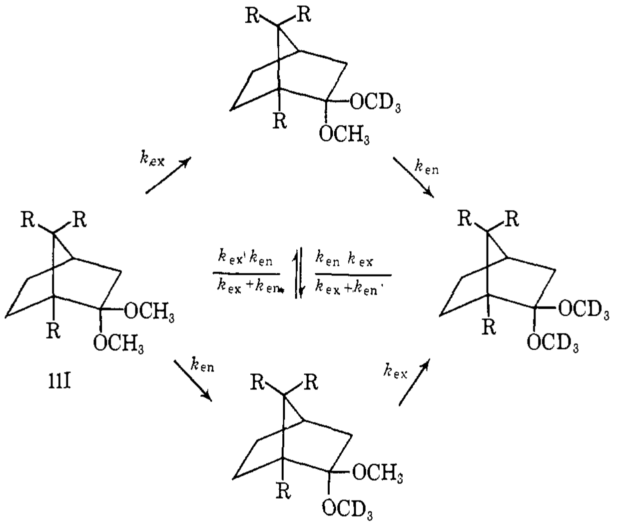


Figure 1. Kinetics of disappearance of *exo*- and *endo*-$OCH_3$ of camphor dimethyl ketal in methanol-$d_4$, temperature 31.8°.

to this scheme, and to the term which corrects for the macroscopic reversibility, is given in the Appendix.



These kinetic equations may be solved[17] explicitly for $f_{ex}$ and $f_{en}$, the fraction (relative to initial values) of *exo* and *endo* methoxyl protons, respectively, remaining at a given time. These are the experimentally observed quantities.

However, the kinetics are complicated by the reversibility of these reactions. Since the kinetics are followed by nmr, an appreciable mole fraction (about 0.05) of substrate must be present, so that the pool of $D_3COD$ is not infinite. Therefore, the form of a correction term, involving $f_H$, the current fraction (experimentally observed) of $H_3COD$ in the solvent, was derived (see Appendix) and applied to the experimental data.

$$f_{ex}^{corr} = \frac{f_{ex}^{expt} - f_H}{1 + f_H} = \frac{k_{ex}(k_{ex} - k_{en})}{k_{ex}^2 + k_{en}^2} \exp[-(k_{ex} + k_{en})t] + \frac{k_{en}(k_{ex} + k_{en})}{k_{ex}^2 + k_{en}^2} \exp\left[-2\frac{k_{ex}k_{en}}{k_{ex} + k_{en}}t\right] \quad (1)$$

$$f_{en}^{corr} = \frac{f_{en}^{expt} - f_H}{1 + f_H} = \frac{k_{en}(k_{en} - k_{ex})}{k_{ex}^2 + k_{en}^2} \exp\left[-(k_{ex} + k_{en})t\right] + \frac{k_{ex}(k_{ex} + k_{en})}{k_{ex}^2 + k_{en}^2} \exp\left[-2\frac{k_{ex}k_{en}}{k_{ex} + k_{en}}t\right] \quad (2)$$

The logarithms of the corrected quantities were plotted against time, and the ratio, $k_{ex}/k_{en}$, was determined from the slopes. A typical kinetic run is shown in Figure 1.[18] The results of six kinetic runs are listed in Table I, according to the nmr peak assignments which are documented below.

**Assignment of Configuration of Methoxyl Groups.** We have assigned the methoxyl which exchanges more rapidly in norcamphor dimethyl ketal (IIIa) the *exo* configuration and that which exchanges more rapidly in camphor dimethyl ketal (IIIb) the *endo* configuration on the basis of the reduction reactions described below.

**Reduction of Camphor and Norcamphor Dimethyl Ketals with Lithium Aluminum Hydride.** Camphor dimethyl ketal (IIIb) was reduced with $AlCl_3$–$LiAlH_4$ by the method of Eliel, *et al.*,[19] and the crude product examined in three ways. The infrared spectrum was almost identical with that of isobornyl methyl ether (VIIb) and indicated a trace of bornyl methyl ether (VIIIb). By comparison of its gas–liquid chromatogram and its nmr spectrum with those of similar mixtures of authentic ethers, it was possible to estimate the product ratio to be 90 ± 1% isobornyl methyl ether (VIIb) and 10 ± 1% bornyl methyl ether (VIIIb).

A similar reduction of norcamphor dimethyl ketal produced a mixture of 95% *endo* norbornyl methyl ether (VIIIa) and 5% *exo* norbornyl methyl ether (VIIa).

While it must be admitted that catalysis of ketal reduction by $AlCl_3$-like species in ether is not strictly comparable to catalysis of methoxyl exchange by carboxylic acids in methanol, it is reasonable to assume that the reductions also proceed through the 2-methoxybicycloheptyl cations (IV). However, the pertinent feature of these reductions is not the mode of action of the Lewis acid present, but the fact that the $AlH_4^-$-like species attacks cation IVa predominantly on its *exo* side and attacks cation IVb predominantly on its *endo* side.

**Reduction of 2-Methoxy-2-bicycloheptyl Cations IVa and IVb with Lithium Borohydride.** Borohydride ion has been used to trap solvolytically generated carbonium ions in order to infer the stereochemistry of the reactions of these carbonium ions with other nucleophiles.[1e,2e,f,i] We have therefore prepared the carbonium ions IVa and IVb and subsequently reduced them with lithium borohydride.

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[17] D. M. Yost, *J. Am. Chem. Soc.*, **86**, 4739 (1964); F. A. Matsen and J. L. Franklin, *ibid.*, **72**, 3337 (1950).

[18] Although the ratio of the slopes in Figure 1 is 0.16, the correct value for the ratio of the rate constants is 0.08. This factor of two arises from the form of the exponent of the second term of eq 1, which is the dominant term at long reaction times.

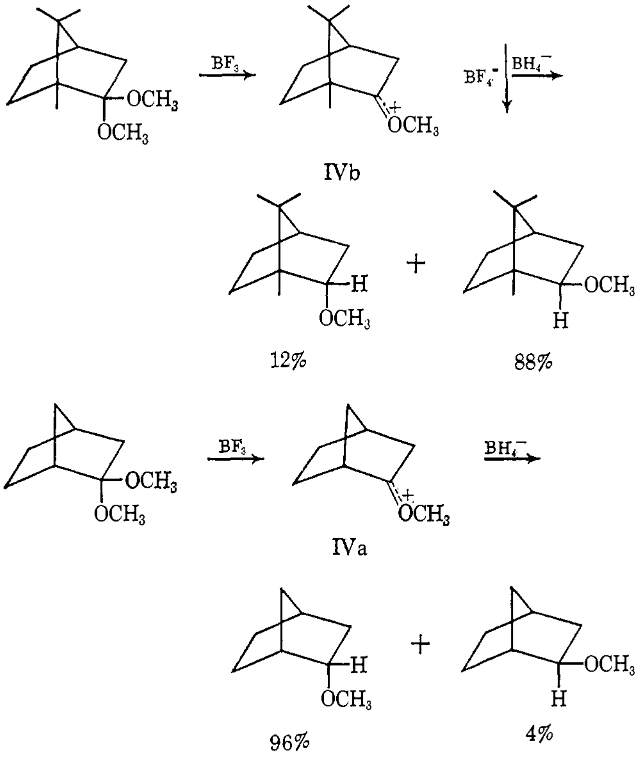
[19] E. L. Eliel, V. G. Badding, and M. N. Rerick, *J. Am. Chem. Soc.*, **84**, 2371 (1962); E. L. Eliel and D. Nasipuri, *J. Org. Chem.*, **30**, 3809 (1965).

Table I

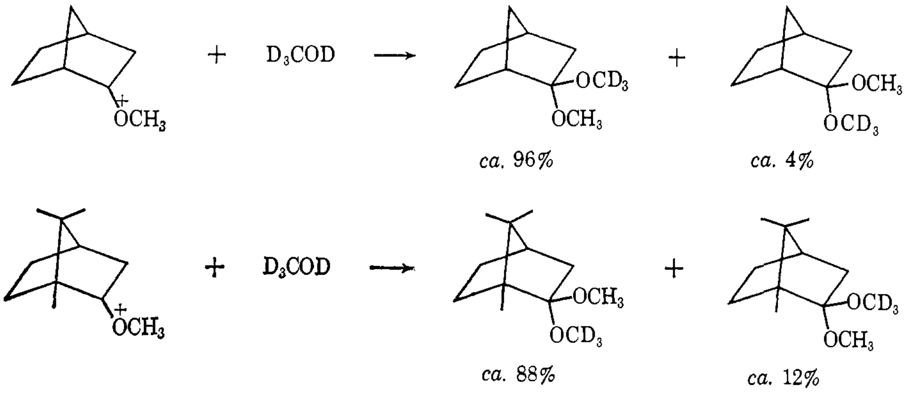
| Ketal | Acid | Solvent | $k_{ex}/k_{en}$ | $k_{en}$, sec$^{-1}$ |
|---|---|---|---|---|
| IIIb | Acetic (9 $\mu$l) | $D_3COD$ (0.3 ml) | 0.10[a] | $1.0 \times 10^{-4}$[b] |
| IIIb | Acetic (20 $\mu$l) | $D_3COD$[c] (0.3 ml) | 0.09[d] | $1.5 \times 10^{-4}$[b] |
| IIIb | *p*-Cyanobenzoic (10 mg) | $D_3COD$[c] (0.4 ml) | 0.08[a] | $12 \times 10^{-4}$[b] |
| IIIb | Acetic (10 $\mu$l) | 97% *i*-PrOH–3% $H_2O$ | 1.0[e] | |
| IIIa | *p*-Cyanobenzoic (10.0 mg) | $D_3COD$[c] (0.4 ml) | 16[a] | $5.1 \times 10^{-5}$ |
| IIIa and IIIb | *p*-Cyanobenzoic (10.5 mg) | $D_3COD$[c] (0.4 ml) | 4[a] | $(k_{en}^{IIIb}/k_{ex}^{IIIa})$[f] |

[a] From peak heights. [b] Variations in these rate constants are due to variations in acidity. [c] Distilled from $CaH_2$. [d] From integrated peak areas. [e] Hydrolysis; no isopropyl ketal was formed. [f] In this mixture the more rapidly exchanging methoxyl in camphor dimethyl ketal exchanged four times as fast as the more rapidly exchanging methoxyl in norcamphor dimethyl ketal. This direct measure of the relative reactivity of the two ketals is considered more reliable than that obtained from reactions in separate solutions.

Scheme I



Scheme II



When boron trifluoride etherate was added to an ether solution of camphor dimethyl ketal, a colorless precipitate formed immediately. This precipitate, which proved to be the fluoroborate salt of IVb, was treated in suspension with excess lithium borohydride and afforded a mixture of ethers (88% *exo*, 12% *endo*) nearly identical with the mixture obtained by the lithium aluminum hydride reduction described above.

When boron trifluoride etherate was added to norcamphor dimethyl ketal, no precipitate was formed. However, the double methoxyl peak in the nmr disappeared and was replaced by a broad singlet. Treating this solution with a solution of lithium borohydride in ether afforded a high yield of norbornyl methyl ethers containing about 95–97% of the *endo* isomer (identical with the mixture obtained by $LiAlH_4$ reduction).

These results are summarized in Scheme I.

Again, we find that hydride adds predominantly to the *exo* side of IVa and predominantly to the *endo* side of IVb. Reductions of these stabilized carbonium ions are remarkably similar to reductions of ketones[20] in their stereochemistry, as might be expected.

Since the stereochemistry of reactions of carbonium ions with borohydride is nearly the same as with other nucleophiles,[1e,2e,l] we may conclude from the results of our reductions that similar *exo*/*endo* product ratios will be observed with methanol (see, *e.g.*, Scheme II), and by microscopic reversibility, the *exo*/*endo* rate ratios for ionization must be identical with the corresponding product ratios.

We therefore make the assignments of nmr peaks observed in methanol-$d_4$ shown in Figure 1. The relative rates of disappearance of these peaks are shown in parentheses. Thus, for both ionization and product

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[20] (a) D. S. Noyce and D. B. Denney, *J. Am. Chem. Soc.*, **72**, 5743 (1950); (b) C. H. DePuy and P. R. Story, *ibid.*, **82**, 627 (1960); (c) in $LiAlH_4$ reductions of methylated norbornanones, "Nur wenn das Brücken-C-atom 7 in *cis*-Stellung zur funktionnellen Gruppe eine Methylgruppe trägt ensteht in ebenso hoher Ausbeute der *exo*-Alkohol": S. Beckmann, *Bull. Soc. Chim. France*, 1319 (1960); (d) J. A. Berson, "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 3, Table III.

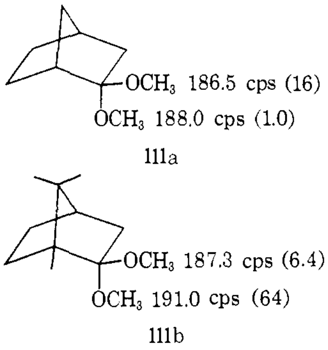

Figure 1.

formation, $k_{exo}/k_{endo} = 16$ for IIIa and IVa and 0.10 for IIIb and IVb. Support for these values rests upon our assignments, based on the comparison with $k_{exo}/k_{endo} =$ 20 for IVa and 0.12 for IVb from reduction reactions. If we made the reverse assignment for (*e.g.*) IIIa (*i.e.*, $k_{exo}/k_{endo} = 1/16$), this would require that the steric requirements of borohydride and methanol differ in their *exo/endo* selectivity toward the carbonium ion IVa by a factor of $16 \times 20 = 320$. It is therefore quite doubtful that the above assignment is incorrect.

## Discussion

**Assumptions.** The relevance of our ketal exchange results to the problem of *exo/endo* reactivities in other 2-bicycloheptyl systems depends upon the justification of four assumptions: (1) That relative rates of methoxyl exchange in these ketals reflect the solvolytic behavior of 2-methoxy-2-bicycloheptyl cations (IV). Clearly the *exo/endo* ratios observed in the exchange reactions are identical both with those for capture of methanol by the intermediate ions (IV) and with the ratios of pseudo-first-order rate constants for formation of ion IV from III. But ether basicities generally show slight dependence upon steric effects,[21] so that we may assume the basicities of the *exo* and *endo* oxygens in the ketals to be the same. If so, the observed *exo/endo* ratios also represent relative rates of ionization of methanol from protonated ethers V and VI to form cation IV. This assumption is not required for our conclusions, since we are interested only in steric effects in the two transition states. Nevertheless, it is the ionization of methanol from the conjugate acids V and VI which bears the closest resemblance to S$_N$1 solvolyses.

(2) That 2-methoxy-2-bicycloheptyl cations (IV) cannot be bridged. However, Wenthe and Cordes[16] have discussed the effect of methoxyl substitution on carbonium ion stability. They have shown that the first methoxyl increases carbonium ion stability by several kcal/mole, whereas the second and third methoxyls have almost negligible effect. If a methoxyl group will not add stabilization to an $\alpha$-alkoxy carbonium ion, then we may safely conclude that "nonclassical delocalization" will not increase the stability of such ions. Thus 2-methoxy-2-bicycloheptyl cations (IV) can derive no stabilization from neighboring group participation. The relative insensitivity[14] of ketal solvolyses to structure corroborates this conclusion. Therefore, the exchange reactions of these ketals provide models for a consideration of the stereochemical behavior of "classical" bicycloheptyl cations.

(3) A third assumption—that our assignments of the nmr peaks are correct—is not entirely necessary for our conclusions concerning bridging. Thus, if camphor dimethyl ketal exchanges with a $k_{exo}/k_{endo} = 10$ instead of 0.1, we would still be led to the same conclusions because either number is to be compared to $10^5$ for other bornyl systems.

However, if we are not justified in extrapolating the results of the hydride reductions in order to assign the stereochemistry of the ketal exchanges, the following discussion could just as well have been based upon the unambiguous stereochemistry of the reductions. There would still remain two questions: (1) Why does solvolysis of isobornyl chloride lead to only *exo* alcohols, whereas cation IVb shows an *exo/endo* ratio of 0.13 in its reactions with hydrides? (2) Why does solvolysis of norbornyl derivatives lead exclusively to *exo* product, whereas cation IVa shows an *exo/endo* ratio of only 20 in its reactions with hydrides? We have chosen to consider the results of the exchange reactions, rather than the results of the reductions, because the former are more accurate and because in the former, the principle of microscopic reversibility permits extending results to the ionization reactions.

(4) We also assume, without presenting any justification, that our results concerning steric effects in reactions of these stabilized carbonium ions may be extrapolated to predict steric properties of other secondary carbonium ions. In the following discussion we assume all four of these postulates.

**Comparison of Stereochemistry in Stabilized and Unstabilized Bicycloheptyl Cations.** Both the present study and the recently reported study by Gassman and Marshall[22] propose that electron removal at C$_1$ or electron donation at C$_2$ sufficient to prevent any anchimeric assistance can be introduced without the accompanying steric effects discussed above. The results of both studies on both solvolysis and product stereochemistry are compared with results in unstabilized bicycloheptyl systems and camphors in Table II.

The most striking result in Table II is the change of $k_{exo}/k_{endo}$ in the bornyl–isobornyl derivative solvolyses from $10^5$ for 2-hydrogen to $10^{-1}$ for 2-methoxyl substitution. It is quite clear that the presence of the 2-methoxyl substituent inhibits participation, as do 7-oxo and, to a lesser extent, 2-*p*-anisyl substitution. This leads to the inescapable conclusion that some special phenomenon is encountered in the solvolyses of isobornyl chloride and *exo*-norbornyl tosylate, as has often been suggested. We therefore interpret these data as strong evidence that *classical* 2-bicycloheptyl ions *do* behave like the corresponding ketones and show small $k_{ex}/k_{en}$ ratios, and, as a corollary, we conclude that simple 2-bicycloheptyl cations are not classical.

**Steric Hindrance to Ionization.** Brown[2c] has suggested that the *exo/endo* rate ratio in norbornyl systems derives from steric hindrance to the departure of the *endo* leaving group. We have now documented this type of steric hindrance and can estimate its importance.

In our completely reversible system the ionization transition state VIa* is higher in energy than Va*.

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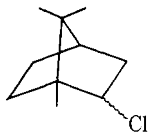
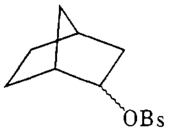
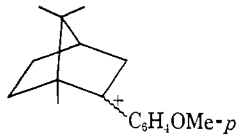
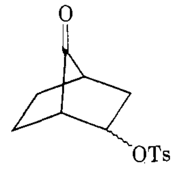
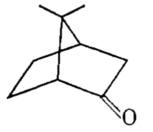
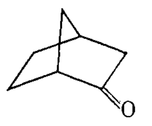
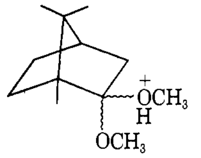
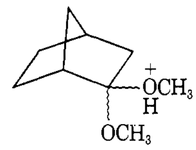
[21] E. M. Arnett, *Progr. Phys. Org. Chem.*, 1, 223 (1963), Table XXIa.

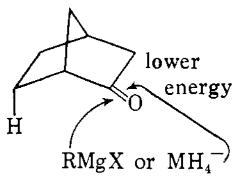
[22] P. G. Gassman and J. Marshall, *J. Am. Chem. Soc.*, **87**, 4648 (1965).

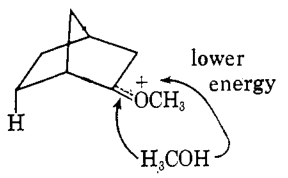
**Table II**

| | | | | |
|---|---|---|---|---|
| Structure |  |  |  |  |
| $k_{ex}/k_{en}$ (ionization) | $10^5$[a] | 1600[b] | | 0.2[c] |
| $k_{ex}/k_{en}$ (product) | $>2x10^3$[d] | $>5x10^3$[e] | 6.7($NaBH_4$)[f] | 2[c] |
| Structure |  |  |  |  |
| $k_{ex}/k_{en}$ (ionization) | ... | ... | 0.1[g] | 16[g] |
| $k_{ex}/k_{en}$ (product) | 0.1 ($LiAlH_4$)[d] | 9($LiAlH_4$)[d] | 0.1,[g] 0.13,[h] 0.13[i] | 16,[g] 20,[h] 24[i] |

[a] Reference 23. [b] Polarimetric ratio, ref 1b. Titrimetric ratio = 350, ref 24. [c] Reference 22. [d] Reference 1c. [e] Reference 1a. [f] Reference 2f. [g] This work, exchange. [h] This work, $LiAlH_4$–$AlCl_3$ reduction of ketals. [i] This work, $LiBH_4$ reductions of carbonium ions IVa and IVb.

In additions to ketones, this higher energy transition state is always attributed[1c] to a greater steric hindrance to *endo* attack.





But if *endo* attack is sterically decelerated relative to *exo* attack, then, by microscopic reversibility, there must also be greater steric hindrance to *endo* departure of methanol in our ketal exchanges![25] Thus, out of a total (polarimetric) $k_{exo}/k_{endo}$ factor[1b] of 1600 in norbornyl tosylate solvolyses, about[26] a factor of 16 may be attributed to steric hindrance to ionization.

Since the faster (*endo*) methoxyl of IIIb is four times as fast in exchanging as is the faster (*exo*) methoxyl of IIIa (Table I), we must conclude that strain is relieved in the IIIb transition state.[29] But there must be less relief of steric strain in the transition state for exchange of *exo* methoxyl of IIIb than in that of its *endo* methoxyl. This effect is equivalent to a steric hindrance to ionization of the *exo* methanol of Vb (R = Me), due to the *syn*-$C_7$ methyl group.

**Estimation of the Anchimeric Assistance in *exo*-2-Bicycloheptyl Systems.** We may use our 2-methoxybicycloheptyl systems as standards for estimating the extent of anchimeric assistance, according to the method of Winstein and Grunwald.[30] This assistance is measured by $k_\Delta/k_s$, the ratio of the rate of anchimerically assisted solvolysis to the rate of unassisted solvolysis, and this quantity may be evaluated by correcting the observed *exo/endo* solvolysis ratio for the *exo/endo* steric factor obtained from the ketal exchange studies and for energy differences in the reactants.

For example, in the norbornyl system, the results of the ketal exchanges indicate a 16:1 preference for *exo* reaction due to steric effects in the transition states. On the other hand, if the energy difference between *exo* and *endo* reactants in solvolysis (1.2 kcal/mole in the acetates[28]) were lost on going to the transition state, *endo*-norbornyl derivatives should react about six times as rapidly as *exo*. These corrections are in opposite directions, so that the extent of anchimeric assistance is estimated as $1600 \times {}^{6}/_{16} = 600$. To obtain the estimates of $k_\Delta/k_s$ listed in Table III, we have divided the observed *exo/endo* ratios by $^{16}/_{6}$ for those systems without a *syn*-$C_7$ methyl group[20c] and by $^{4}/_{10}$ for those systems with a *syn*-$C_7$ methyl group.[31]

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(23) F. Brown, E. D. Hughes, C. K. Ingold, and J. F. Smith, *Nature*, 168, 65 (1951).

(24) S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, 71, 2953 (1949).

(25) It is attractive to propose that the 6-*endo* hydrogen pushes the *endo* methoxyl and thereby facilitates departure of the *exo* methanol. However, it is difficult to apply this idea to the reverse reaction: How can interference of the 6-*endo* hydrogen also facilitate *exo* capture of methanol? Whatever factor is responsible for the transition state energy difference in the addition reactions must also be responsible in the ionization reactions.

(26) In the absence of quantitative evaluation of the relative steric requirements of methanol and tosylate leaving groups, we assume that our measure of steric effects involving methanol may be applied directly to estimate steric effects in tosylate solvolyses: steric *A* factors for acetoxy, methoxy, and tosyloxy substituents in cyclohexane systems are nearly identical.[27] Also, acid-catalyzed acetate exchange in norbornyl acetate proceeds with *exo/endo* ratios comparable to those in tosylate solvolysis.[28] On the other hand, there is no guarantee that the transition states for these two types of reaction occur at the same position along the reaction coordinates.

(27) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, Table 8-6.

(28) H. L. Goering and C. B. Schewene, *J. Am. Chem. Soc.*, 87, 3516 (1965).

(29) Kreevoy, Morgan, and Taft[14] have observed up to tenfold accelerations in hydrolyses of sterically hindered ketals and acetals. A more striking example of steric acceleration of ionization is the 64-fold acceleration of the *endo* methoxyl of IIIb relative to that of IIIa. Since such an effect is not observed in solvolyses, the steric effects in the *endo* transition states VIa* and VIb* should be comparable. The 64-fold acceleration may then be attributed to steric differences in the reactants, IIIa and IIIb. In reactant tosylates the *endo*-6-hydrogen–*endo*-oxygen repulsion accounts for a rate factor of 6, and the *syn*-$C_7$-methyl-*exo*-oxygen repulsion accounts for a factor of about 4; the remainder of the factor of 64 is attributed to a buttressing effect. Such corrections must be applied below to account for reactant energy differences in tosylate solvolyses.

(30) S. Winstein, E. Grunwald, and L. L. Ingraham, *J. Am. Chem. Soc.*, 70, 821 (1948); S. Winstein and E. Grunwald, *ibid.*, 70, 828 (1948).

(31) We have guessed the difference between the energies of borneol and isoborneol to be at least 0.8 kcal/mole, based on the observations that sodium reductions of apocamphor, camphor, and 4-methylcamphor yield principally the thermodynamically more stable *endo* alcohols (ref 3, p 127).

**Table III**

| 2-Bicycloheptyl system (II, R = H) | Solvolysis $k_{ex}/k_{en}$ | $k_\Delta/k_s$[a] |
|---|---|---|
| Norbornyl (II, $R_1 = R_2 = H$) | 1,600[b] | 600 |
| 1-Methylnorbornyl (II, $R_1$ = Me, $R_2$ = H) | 12,500[c] | 4,000 |
| Apobornyl (II, $R_1$ = H, $R_2$ = Me) | 4,100[b] | ~10,000 |
| Bornyl (II, $R_1 = R_2$ = Me) | 100,000[d] | ~200,000[d] |

[a] These corrected values may be in error to the extent that methanol and tosylate differ in size.[26] [b] Reference 1b. [c] Reference 32. [d] Reference 23.

It is clear from Table III that (within the limits of our crude estimates) $k_\Delta/k_s$ is comparable to the observed $k_{exo}/k_{endo}$ and that most of the magnitudes of the high *exo*/*endo* ratios observed in these solvolyses must be attributed to anchimeric assistance, presumably leading to IB. Steric effects are *not* large enough to account for such ratios.

**Internal Steric Effects.** There is another kind of steric effect in this and in other systems, which is not related to the controversy concerning bridged ions because it is consistent with either view.

Since the 7-methyl groups in the apobornyl and bornyl systems do not contribute significant electronic stabilization to the bridged ion, much of the energy change giving the $k_\Delta/k_s$ in these systems must result from relief of steric strain. This relief of strain is not due simply to removal of leaving group interaction because no such large effect was observed in ketal solvolyses. We therefore propose that internal strain in the bicycloheptyl system is relieved by lengthening the 1–6 bond.[33] This picture differs only slightly from the bridged ion concept in emphasis—the driving force for *exo* solvolysis is ascribed to strain relief rather than increased $C_6$–$C_2$ bonding.[36] We feel that this is the reason occurrence of sp$^3$-carbon-bridged ions is confined to strained systems.

This steric exaltation of anchimeric assistance is similar to that which causes β,β,β-triphenylethyl tosylate to solvolyze faster than β,β-diphenylethyl tosylate even though both compounds solvolyze with rearrangement.[37] In these, as in isobornyl chloride solvolysis, the reactions undoubtedly proceed through a bridged transition state.

## Experimental Section[38]

**Synthesis.** Camphor dimethyl ketal (IIIb) was prepared from *dl*-camphor by the method of Arbusov:[39] bp 110° (28 mm), $n^{22}$D 1.4656, $d^{25}$ 0.9784, no carbonyl absorption in infrared, nmr in Table IV. *Anal.* Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.19. Found: C, 71.99; H, 10.88. Isobornyl methyl ether (VIIb) was prepared by the method of Bertram and Walbaum:[40] $n^{22}$D 1.4620 (lit.[41] $n^{20}$D 1.4625). Bornyl methyl ether (VIIIb) was prepared from methyl iodide and potassium *dl*-bornyloxide in xylene, according to the procedure of Meerwein and Gérard:[41] bp 74–75° (12 mm), $n^{22}$D 1.4615 (lit.[42] $n^{23.4}$D 1.4624).

Norcamphor dimethyl ketal (IIIa), prepared as above (using gaseous HCl instead of sulfuric acid), had bp 73° (20 mm), $d^{25}$ 0.99, no carbonyl absorption in infrared, and had the reasonable nmr shown in Table IV. *Anal.* Calcd for $C_9H_{16}O_2$: C, 69.18; H, 10.32. Found: C, 69.11; H, 10.20. *exo*-Norbornyl methyl ether (VIIa) was prepared by acid-catalyzed addition of methanol to norbornene.[43] *Anal.* Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.32; H, 10.87. Infrared and nmr spectra (Table IV) are consistent with the assigned structure. *endo*-Norbornyl methyl ether (VIIIa) was prepared by treating the corresponding norborneol mixture with sodium hydride and methyl iodide in ether. The norborneol mixture was obtained by reduction of norcamphor (Aldrich) with lithium aluminum hydride in ether.[20b] The infrared and nmr spectra are consistent with the *endo* assignment of the major constituent.

Methanol-$d_4$ (99 atom % D) was obtained from Merck Sharp and Dohme of Canada, Ltd., and was used in one run without purification. Material (5 g) used in other runs was allowed to stand 20 hr over about 0.1 g of calcium hydride and distilled in a vacuum line, then sealed in a syringe cap ampoule. The significant kinetic behavior of IIIb was not changed by this purification.

**Kinetics.** Samples of the ketals (0.100 ml) and the solvent were syringed into a dried nmr tube and capped, and the nmr spectrum was taken. No reaction occurred. The catalyzing acid was either syringed with a microsyringe or added as a solid, the tube shaken to dissolve the acid, and the methoxyl region repeatedly scanned either in the spectrum or integral mode.[44] Both methods gave similar results, although measurement of peak heights was found to be more convenient.

During the course of the exchange reaction, the two methoxyl peaks decreased in intensity, *at different rates*, and a peak due to methanol appeared and increased with time. The height of each peak was recorded with time and "normalized" so that the total absorption of all three peaks was unity; this procedure eliminates error due to variation in peak heights resulting from changes in field homogeneity.

The relative rate constants were determined from the variations in peak height as described in the Appendix. Results are listed in Table I.

After most of the ketal methoxyls had exchanged, a complete spectrum was taken. A comparison of the spectrum with that of the starting material indicated that the ketal structure was still present. In one case the completely exchanged ketal (from IIIb) (trifluoroacetic acid was used to bring about rapid exchange) was reisolated after neutralizing the solution and shown to be at least 75% ketal and to contain some camphor by its infrared spectrum.

**Nuclear Magnetic Resonance Spectra.** The spectra of all compounds studied are indicated in Table IV.

**Reduction of Camphor Dimethyl Ketal with Lithium Aluminum Hydride–Aluminum Chloride.** The ketal (IIIb) (0.88 ml, 0.0043 mole) was reduced by the method of Eliel, *et al.*[19] Evaporation

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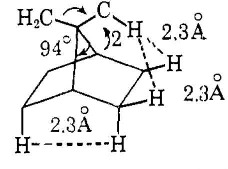
(32) P. von R. Schleyer and D. C. Kleinfelter, quoted by J. A. Berson, "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 3, Table VIIA.

(33) The reason the bornyl system has so much more internal strain than does the norbornyl systems is readily apparent from the structure of bis-1-apocamphyl.[34]



The $C_7$ methyls are forced together by the *exo* hydrogens of the $C_2$–$C_3$ and $C_5$–$C_6$ wings; both angle and H–H repulsion strains are thereby introduced. These strains and the $C_1C_7C_4$ angle strain[35] can be relieved by lengthening of the $C_1C_6$ bond.

(34) L. Sieker, R. A. Alden, J. Kraut, and T. G. Traylor, unpublished X-ray data.

(35) As suggested by S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, 74, 1154 (1952), footnote 15.

(36) This is not to claim that partial $C_6$–$C_2$ bonding does not occur; indeed, it is the possibility of such bonding that permits lengthening of the $C_6$–$C_1$ bond and the consequent relief of strain.

(37) H. C. Brown, R. Bernheimer, and K. J. Morgan, *J. Am. Chem. Soc.*, 87, 1280 (1965).

(38) Analyses are by Huffman Laboratories, Inc., Wheatridge, Colo. Nmr spectra were taken on Varian HR-60 and A-60 instruments; temperatures of the probes were 32° and were constant to about ±0.3°.

(39) A. Arbusov, *J. Russ. Phys. Chem.*, 40, 637 (1908); *Chem. Zentr.*, II, 1340 (1908); see also ref 14.

(40) J. Bertram and H. Walbaum, *J. Prakt. Chem.*, [2] 49, 9 (1894); through Beilstein, H VI 89.

(41) H. Meerwein and L. Gérard, *Ann.*, 435, 184 (1923).

(42) H. Baubigny, *Z. Chem.*, 299 (1868); *Ann. Chim.*, [4] 19, 221 (1870); through Beilstein, H VI 78.

(43) S. J. Cristol, W. K. Seifert, D. W. Johnson, and J. B. Jurale, *J. Am. Chem. Soc.*, 84, 3918 (1962).

(44) Wenthe and Cordes[16] have applied this kinetic technique to the study of other ketal and ortho ester hydrolyses.

Table IV. Nuclear Magnetic Resonance Spectra Taken at 60 Mc

| Compound | Solvent | Absorptions, multiplicity, and integral[a,b] |
|---|---|---|
| Isobornyl methyl ether (VIIb) | None, $D_3COD$ | 48.5 (s, 3), 53.0 (s, 3), 57 (s, 3), 30–100 (m, 3), 101 (s, 4), 180 (d, 1), 192.2 (s, 3) |
| Bornyl methyl ether (VIIIb) | None, $D_3COD$ | 51.0 (s, 9), 60–130 (m, 7), 197.0 (s, 3) |
| Camphor | $CCl_4$ | 50.0 (s, 3), 51 (s, 3), 57.8 (s, 3), 85 (s, 1.5), 111 (s, 1), 35–130 (m, 7) |
|  | MeOH | 49.0, 52.0, 58.0, 85, 111, 35–130 |
| Camphor dimethyl ketal (IIIb) | $CD_3OD$ | 50.0 (s, 3), 54.5 (s, 3), 57.5 (s, 3), 50–150 (m, 7), 187.3 (s, 3), 191.0 (s, 3) |
| Norcamphor dimethyl ketal (IIIa) | $CH_3OH$ or $CD_3OD$ | 70–120 (m, 8.3), 140 (m, 2), 186.5 (s, 3), 188.0 (s, 3) |
| *exo*-Norbornyl methyl ether (VIIa) | $C_6H_6$, $D_3COD$ | 45 (broad), 55 (broad), 78 (broad), 125 (broad), 193.7 (singlet) |
| *endo*-Norbornyl methyl ether (VIIIa) | $C_6H_6$, $D_3COD$ | 68–138 (m, 10), 193.3[c] (s, 3.3), 210 (m, 1) |
| $H_3COD$ | $D_3COD$ | 199.6 |

[a] Positions are given in cps downfield from tetramethylsilane. Multiplicities and relative areas for each absorption are given in the parentheses which follow the position. [b] Although absolute accuracies of the methoxyl proton positions of III, VII, and VIII are only ±1 cps, the relative positions were more accurately determined in mixtures of these compounds. [c] The very small peak at 193.7 cps due to VIIa impurity is omitted. See preparation.

of the ether solution yielded 0.542 g (75%) of a product whose infrared spectrum was almost identical with that of isobornyl methyl ether. A glpc analysis on Ucon Polar 50-HB-2000 at 75° (incomplete separation) indicated about 10% bornyl methyl ether. Comparison of the 197- and 192-cps peaks in the nmr of the product revealed 11% bornyl methyl ether and 89% isobornyl methyl ether.

**Reduction of Norcamphor Dimethyl Ketal with Lithium Aluminum Hydride–Aluminum Chloride.** The ketal (IIIa) (0.99 g) was reduced in three separate experiments by the method described above. Yields of the methyl ether product were 0.4 g (50%) and 0.65 g (80%) in two runs. According to methoxyl areas in the nmr, the ratio of *exo*-norbornyl ether to its *endo* isomer was 19:1. This analytical technique was checked by adding known amounts of the *exo* ether and comparing methoxyl areas. Although the difficulty we experienced in attempting separation of this mixture by glpc would lead us to believe that loss during evaporation of ethyl ether would not fractionate the *exo–endo* mixture, we carried out one reduction (0.99 g of ketal) in the presence of 0.15 ml of *exo*-norbornyl methyl ether. The product (0.79 g) contained 18% *exo* ether by nmr analysis. This is consistent with an *exo*/*endo* ketal reduction product ratio of 19:1.

**Preparation of 2-Methoxy-1,7,7-trimethylbicyclo[2.2.1]heptyl-2-fluoroborate (IVb, $BF_4^-$).** A flask having a fritted glass inlet at the bottom and equipped for filtration under nitrogen was charged with 25 ml of absolute ether which was held above the frit and stirred by a rapid flow of nitrogen. To this solvent was added (at room temperature) 5.0 ml (40 mmoles) of distilled boron trifluoride etherate, then 9.0 ml (45 mmoles) of camphor dimethyl ketal. The precipitate which separated immediately was filtered by reversing the direction of nitrogen flow, washed twice with dry ether, and dried under vacuum for 3 hr, yield 6.4 g (70% based on available $BF_4^-$). *Anal.* Calcd for $C_{11}H_{19}OBF_4$: C, 52.00; H, 7.54; methoxyl, 12.20. Found: 51.14, 51.39; H, 7.50; methoxyl, 11.7. The solid is insoluble in $CCl_4$ or ether, but soluble in tetrahydrofuran. Treating this salt with water produced camphor, as indicated by its infrared spectrum. In methanol containing excess sodium methoxide, the ketal is regenerated. These properties are similar to those of the previously reported 2-ethoxy-2-cation fluoroborate prepared by treating camphor with triethyloxonium fluoroborate.[45]

**Reduction of IVb Fluoroborate with Lithium Borohydride.** The above procedure was repeated with 4.0 ml of camphor dimethyl ketal and 2.50 ml of boron trifluoride etherate in 25 ml of ether. The resulting suspension was treated, with stirring, with 0.54 g of 83% pure lithium borohydride in 10 ml of ether. The precipitate dissolved, and the solution was treated with cold water, then dilute acid. The ether layer was separated, dried over sodium sulfate, then over magnesium sulfate, and evaporated at aspirator pressure at 30°, yield 2.64 g (78%). The infrared spectrum was identical with that of the product from the lithium aluminum hydride–aluminum chloride reduction. Furthermore, the nmr spectra of these two product mixtures were identical even with the ratios of methoxyl peaks at 197.0 and 192.2 cps. Thus, this reduction also produced 88% *exo* ether and 12% *endo* ether.

**Reduction of IVa Fluoroborate with Lithium Borohydride.** When norcamphor dimethyl ketal (IIIa) was treated with boron trifluoride etherate in ether, there was no precipitate. However, the formation of a salt was evidenced by the disappearance of the methoxyl peaks at 186.5 and 188.0 cps and the appearance of a new broad singlet at 187 cps in the nmr.

As in the procedure for reduction of IVb fluoroborate, 0.6 ml (3.84 mmoles) of norcamphor dimethyl ketal in 6.0 ml of ether was treated with 0.48 ml (3.85 mmoles) of boron trifluoride etherate. After about 5 min, 0.15 g of lithium borohydride in 4 ml of ether was added at 0° and the mixture stirred for 15 min at 25°. Hydrolysis and isolation as described above afforded 0.36 g (75% yield) of ethers. The infrared spectrum was identical at every peak with that of the mixture obtained by the lithium aluminum hydride–aluminum chloride reduction procedure described above. In addition, a comparison of peak heights at 193.7 (*exo*) and 193.3 (*endo*) cps in the nmr indicated 4% *exo* and 96% *endo* norbornyl methyl ether. This is also identical with the product mixture from the lithium aluminum hydride–aluminum chloride reduction within the limits of the method.

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## Appendix

The reasoning leading to the over-all reaction scheme is as follows. (1) Ionization of camphor dimethyl ketal (III) to ion IV proceeds with pseudo-first-order rate constant, ($k_{ex} + k_{en}$), since both the *exo* and *endo* methoxyls are capable of leaving. But only the fraction, $k_{ex}/(k_{ex} + k_{en})$, of the ions (IV) capture $D_3COD$ to form camphor dimethyl ketal-*exo*-$d_3$ (III-*exo*-$d_3$) and only the fraction, $k_{en}/(k_{ex} + k_{en})$, of the ions (IV) capture $D_3COD$ to form III-*endo*-$d_3$. (2) The rate constants for ionization of *exo*- and *endo*-$OCH_3$ from the two possible isomers (III-$d_3$) are $k_{ex}$ and $k_{en}$, respectively. In both cases, the resultant intermediate ions (IV-$d_3$) must add $D_3COD$ to form camphor dimethyl ketal-$d_6$ (III-$d_6$), even though the addition

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[45] H. Meerwein, G. Hinz, P. Hofmann, E. Kroning, and E. Pfeil, *J. Prakt. Chem.* 147, 257 (1937)

may be either *exo* or *endo*. (3) The rate constants for ionization of *exo*- and *endo*-$OCD_3$ from the two possible isomers (III-$d_3$) are $k_{ex}$ and $k_{en}$, respectively. But only the fraction, $k_{en}/(k_{ex} + k_{en})$ or $k_{ex}/(k_{ex} + k_{en})$, respectively, of the resultant ions (IV) capture $D_3COD$ in such fashion as to effect conversion of one isomer into the other.

For solving the linear differential equations implied by these kinetics, a matrix method[17] is especially convenient, since it can readily be extended to correct for reversibility. Let $\mathbf{C}$ be a column matrix whose elements are the concentrations of the four chemical species, as a function of time, $t$, let $\dot{\mathbf{C}}$ be a column matrix whose elements are the time derivatives of these concentrations, and let $\mathbf{C}_0$ be $\mathbf{C}$ at time zero. The four differential equations may be abbreviated as a single matrix equation, $\dot{\mathbf{C}} = \mathbf{KC}$, where $\mathbf{K}$ is a $4 \times 4$ matrix of appropriate rate constants. The solution is given by $\mathbf{C} = \mathbf{X}\exp(\Lambda t)\mathbf{X}^{-1}\mathbf{C}_0$, where $\mathbf{X}$ is a $4 \times 4$ matrix whose columns are the eigenvectors of $\mathbf{K}$, $\mathbf{X}^{-1}$ is its inverse, and $\exp(\Lambda t)$ is a diagonal matrix whose diagonal elements are the exponentials of $t$ times the eigenvalues of $\mathbf{K}$. Thus it is possible to solve for the total concentrations of *exo* and *endo* methoxyls as a function of time.

To take account of the incursion of reversibility, the rate constants for reactions replacing $OCH_3$ by $OCD_3$ must be multiplied by $f_D$, the fraction of $D_3COD$ in the solvent. Also, rate constants for the reverse reactions must be introduced, and these will involve instead $f_H$, the fraction of $H_3COD$ in the solvent. As a result, the rate constant matrix is no longer $\mathbf{K}$, but $\mathbf{K} + f_H\mathbf{K}'$.

Since $f_H$ increases as the exchange reaction proceeds, a second-order component is introduced into the kinetics. These kinetics could not be solved analytically, but the effect of reversibility was considered as a small correction. Perturbation theory was used to determine the first-order correction to the eigenvector matrix, $\mathbf{X}$ (the first- and second-order corrections to the eigenvalues vanish), to obtain the form of a correction term to be applied to the experimental data, so that they could be related to the rate constants as shown in eq 1 and 2. Further details are available on request.

# The Mechanism of the Photochemical Valence Tautomerization of 2,3-Diphenylindenone Oxide. IV. Evidence for Vibrationally Excited Ground-State Intermediates[1a]

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**Abstract:** It has been shown that 2,3-diphenylindenone oxide (I) and its valence tautomer (II) are photochemically interconverted. Sensitization, quenching, and quantum yield measurements permit a quantitative analysis of the fate of each of the excited states of I. It is shown that the rate of crossing from the excited states to the ground state of I is much greater than in unreactive ketones. These data together with other evidence that tends to exclude interconversions of any of the electronically excited states of I with electronically excited states of II strongly suggest that both the forward and reverse reactions proceed through vibrationally excited ground states of the two tautomers. Vibrationally excited ground-state molecules are thought to arise during crossing from electronically excited states, and the data suggest that the vibrational energy is not randomly distributed immediately after crossing but is concentrated at the reaction site. In developing these arguments most of the side products of these reactions have been identified and data bearing on the mechanisms of their formation are described. A particularly interesting sequence of steps has been established for the formation of *cis*- and *trans*-3-ethoxy-2-hydroxy-2,3-diphenylindanones (VIII and IX) during irradiation of I in alcohol.

In recent years there has been considerable controversy concerning the mechanism of the photochemical rearrangements of unsaturated epoxy and cyclopropyl ketones.[2] While hypothetical dipolar intermediates derived by cleavage of the three-membered ring have been employed with substantial success in rationalizing the products of the reactions,[2,3] the question of the mechanism of formation of these intermediates and the nature of the electronic state (excited or ground) of the intermediates at the time of their formation remains a matter of conjecture.[4] The recent observations that 2,3-diphenylindenone oxide (I)[1a,5] and the related tri- and tetraphenyl-2,3-epoxycyclopent-4-en-1-ones (III, R = H and Ph, respectively)[6,7]

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[1] (a) A preliminary report of this work has appeared previously: E. F. Ullman and W. A. Henderson, Jr., *J. Am. Chem. Soc.*, **86**, 5050 (1964); (b) to whom inquiries should be addressed at Synvar Research Institute, Palo Alto, Calif.

[2] For reviews of these reactions see (a) O. Jeger, K. Schaffner, and H. Wehrli, *Pure Appl. Chem.*, **9**, 555 (1964); (b) H. E. Zimmerman, *Advan. Photochem.*, 1, 183 (1963); (c) O. L. Chapman, *ibid.*, 1, 323 (1963).

[3] See *inter alia* (a) D. H. R. Barton and G. Quinkert, *J. Chem. Soc.*, 1 (1960); (b) H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, 83, 4486 (1961); (c) P. J. Kropp, *Tetrahedron*, 21, 2183 (1965); (d) B. Nann, H. Wehrli, K. Schaffner, and O. Jeger, *Helv. Chem. Acta*, **48**, 1680 (1965); (e) O. L. Chapman and L. F. Englert, *J. Am. Chem. Soc.*, **85**, 3028 (1963).

[4] See discussions by G. S. Hammond and N. J. Turro, *Science*, **142**, 1541 (1963), and J. Saltiel, *Surv. Progr. Chem.*, **2**, 293 (1964).

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[6] E. F. Ullman, *ibid.*, **85**, 3529 (1963).

[7] J. M. Dunston and P. Yates, *Tetrahedron Letters*, 505 (1964).