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STERIC EFFECTS IN BICYCLIC RING SYSTEMS. III. EVALUATION OF TORSIONAL STRAIN IN BASE-CATALYZED DEUTERIUM EXCHANGE OF KETONES AND HYDROBORATION OF OLEFINS[1]

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It was proposed[2] in 1967 that the exo selectivity exhibited in many different reactions by various norbornyl derivatives could be ascribed at least in part to the torsional strain arising from eclipsing interactions with bridgehead substituents. The theory is quite plausible and has been used in the interpretation of a variety of data,[3] but independent experimental tests have failed[4] to produce confirmatory evidence for its importance. This communication reports further tests utilizing larger substituents to magnify the torsional strains, but leads to the conclusion that torsional effects in such systems are either minor or are obscured by other factors.

Since one of the principal cases on which the torsional theory was originally proposed was base-catalyzed deuterium exchange of camphor it seemed appropriate to make a test using the recently developed technique for measuring the rates of such reactions.[5] The torsional strain arising from a substituent in the 4-position of the enolate of a norcamphor derivative is illustrated in a side view (Fig. I). The transition state for exo attack by the electrophile (D_2O) has R_3 moved away from an eclipsing interaction with R_4, whereas endo attack moves R_3 into an eclipsing interaction; thus increased torsional strain should increase the rate of exo substitution and decrease endo substitution. Similarly exo abstraction from the ketone would be favored and endo disfavored. Hydroboration was another example included in the original proposal, and has the advantage of possessing two eclipsing interactions and should display a more pronounced effect.

For R_3=R_4=H the maximum energy of the interaction would approximate the corresponding barrier in ethane, 0.98 kcal,[6] but for R_3=H,R_4=Me it would approximate the methyl-hydrogen eclipsing barrier, 1.43 kcal.[7] The difference of 0.45 kcal should be experimentally observable. Accordingly the base-catalyzed deuterium exchange of camphor (**1**) and 4-methylcamphor (**2**) and the hydroboration of 7,7-dimethylnorborene (**3**) and 1,4,7,7-tetramethyl-

Figure I. Torsional Strain in Bicycloheptanone Enolates

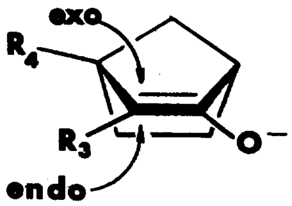

Figure II. Relative Rates of NaOD-Catalyzed Deuterium Exchange of Ketones at 25° in 2:1 Dioxane:D_2O[a]

[a] Rates were measured as in ref. 5 utilizing mass spectrometry, and are relative to endo exchange in norcamphor.

Figure III. Stereochemistry of Hydroboration of Substituted Norbornenes in THF.[b]

[b] Results on 3 from ref. 8: as noted therein the fraction of exo attack increases with increasing borane concentration. These results are for 10% excess.

norbornene (**4**),[9] were compared (Figures II and III).

The differences in *exo* rates between **1** and **2**, and the *endo* rates in **1** and **2**, are small but are genuine, as they were obtained by a competitive technique with both ketones in the same solution followed by separation by gas chromatography. Both rate trends are opposite the prediction of torsional theory. The hydroboration results show a modest enhancement of *exo* substitution with larger bridgehead substituents as predicted by torsional theory, but comparison of derivatives with a single bridgehead methyl have been reported[8] that show no difference (**3** vs. 1,7,7-trimethylnorbornene) or slightly decreased *exo* attack (norbornene vs. 1-methylnorbornene). Thus only small and apparently random variations are observed in the *exo* selectivity in these compounds with bridgehead methyl substituents, and no confirmatory evidence for the occurrence of torsional effects is revealed by this test.

It has already been reported[4a] for solvolysis reactions that methyl substitution at the 1 and 2 positions does not enhance *exo/endo* rate ratios, even though the eclipsing interaction in these cases should be quite large. Similarly it has been found independently[4b] that the bridgehead methyl in 4,6,6-trimethylnorcamphor does not enhance *exo* base-catalyzed deuterium exchange over the rate in norcamphor.

The failure of the substituent effect approach to confirm the occurrence of the torsional effect may mean that it is minimal or nonexistent in these reactions. A possible explanation would be that the ground states are already so near the maximum in the potential energy curve that torsional strain decreases on either *exo* or *endo* attack. Alternatively the change in geometry at the transition state may be so small that there is little increase in strain.[10] On the other hand the effect could be obscured by other factors, such as direct steric interference by the substituents and inductive effects. Rates studies on borohydride reduction of 1-methyl substituted bicyclic ketones[11] show that rate differences by factors of as much as 10 result (ascribed mainly to steric effects[11]) but that these operate equally on *exo* and *endo* attack. A more subtle effect is that any substituent will distort the geometry of norbornyl ring[12], and thus may alter the reactivity in unpredictable ways. Such changes in geometry would change the magnitude of the torsional effect, and render hazardous the prediction of reactivities based on this effect without accurate descriptions of the geometries of the molecules actually under investigation.

By contrast the same substituent test in the cyclohexyl series has shown significant contributions from torsional effects in oxymercuration[13a], but not in hydroboration and epoxidation.[13b]

In summary, the substitutent test does not confirm a major role for the torsional effect in norbornyl systems. Apparently, it will be impossible to assign the contribution due to torsional effects in norbornyl derivatives until the geometries of the reactants and transition states are known with greater accuracy.

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