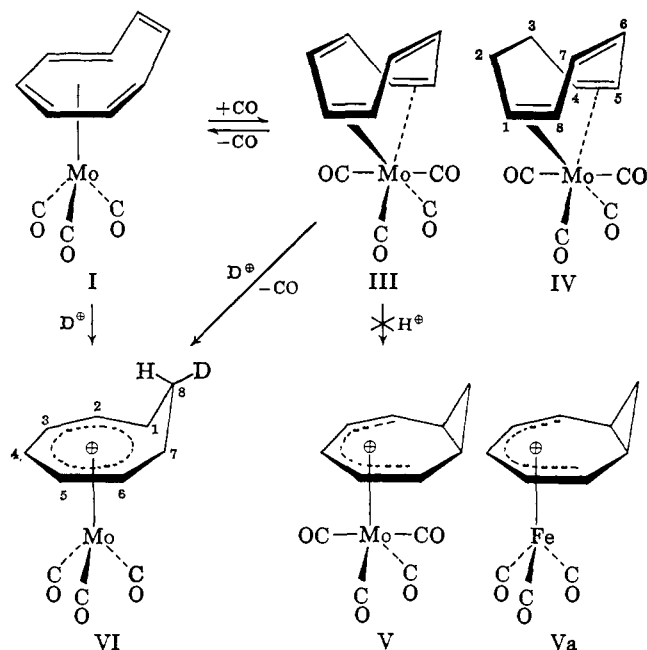


deuterium, the only C-8 proton visible in the nmr spectrum being the high-field "inside" one at τ 10.20. This is the identical stereospecificity previously observed³ in protonation of I.



A deep red solution of $C_8H_8Mo(CO)_3$ ³ (1.8 g) in hexane (180 ml) is subjected to CO at atmospheric pressure, with shaking, for 4 min;¹¹ the color changes to bright orange and the excess CO is swept away with nitrogen. Fine yellow needles of $C_8H_8Mo(CO)_4$ (III), obtained by slow cooling, are washed onto a fritted filter and sucked dry under nitrogen; yield, 1.3 g, or 65% based on starting complex. The compound may be recrystallized in hexane, but as rapidly as possible due to disproportionation which occurs in solution.

Anal. Calcd for $C_{12}H_8MoO_4$: C, 46.15; H, 2.58; Mo, 30.75. Found: C, 46.39; H, 2.73; Mo, 30.88.

Fresh solutions of III show two sharp lines in the nmr, τ 4.46 and 5.80, characteristic of the tub conformation of this olefin in its complexes.⁹ III shows four medium to strong bands in the carbonyl stretching region as may be expected for a *cis*-disubstituted octahedral metal carbonyl: 2049 (m), 1969 (m), 1959 (m), and 1902 (s) cm^{-1} (Beckman IR 4, LiF prism, cyclohexane solution).

Yellow crystals of 1,3,5- $C_8H_{10}Mo(CO)_4$ (IV) are prepared in a manner entirely analogous to III from 1,3,5- $C_8H_{10}Mo(CO)_3$ ¹² (infrared ν_{CO} 2044 (m), 1962 (s), 1950 (m), and 1907 (s) cm^{-1}).

Anal. Calcd for $C_{12}H_{10}MoO_4$: C, 45.86; H, 3.21; Mo, 30.55. Found: C, 45.61; H, 3.33; Mo, 30.43.

The nmr spectrum of IV consists of three singlets, relative intensities 2:4:4, at τ 4.05 ($H_{6,7}$), 5.06 ($H_{1,4,5,8}$), and 7.16 (methylene $H_{2,3}$), respectively. This can be

(11) Further CO insertion, which occurs readily, leads to complete displacement of olefin and formation of hexacarbonyl.

(12) Prepared in 16% yield by the method of Fischer, *et al.*,⁴ or in higher yield (41%) by reaction of the olefin with the diglyme complex of $Mo(CO)_3$ analogous to the preparation of I.³ The nmr spectrum was identical with the one reported by R. B. King, *Inorg. Chem.*, **2**, 807 (1963).

accounted for only by the structure shown for IV.¹³

(13) Bonding of the metal to 1,3-olefinic sites of either the cyclooctatriene or the tautomeric bicyclo[4.2.0]octadiene-2,4 may be excluded with certainty. In the first of these two possibilities a very complex spectrum would be expected since all the protons are different. In the second case, five separate proton signals are expected, as found⁶ for this group in $C_8H_{10}Fe(CO)_3$.

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Received January 3, 1966

exo-endo Rate Ratios in the Solvolysis of Tertiary 2-Benznorbornenyl *p*-Nitrobenzoates. Evidence for the Absence of Significant Carbon Participation as a Factor in the *exo-endo* Rate Ratios

Sir:

The high *exo-endo* rate ratio exhibited by norbornyl brosylate, 350,^{1a} and the high stereospecificity exhibited by the product, >99.9% *exo*,^{1b,2} have been attributed to carbon participation in the transition state followed by the formation of a bridged norbornyl cation which substitutes almost exclusively *exo*. The two phenomena have previously been considered to provide independent confirmatory evidence for carbon participation. However, a careful examination of the energy diagram published by Goering and Schewene² makes it clear that these two characteristics are not independent, but are closely related. It follows from the principle of microscopic reversibility that in the symmetrical system which was the subject of their study the norbornyl intermediate, in reacting with the solvent, must pass over the same two transition states that are involved in the solvolysis of the reactants (Figure 1).

It follows that the factor responsible for the difference in energy between the *exo* and *endo* transition states must likewise be responsible for the stereoselectivity leading to the almost exclusive formation of the *exo* product. The amount of bridging that may or may not be present in the free ion is not directly involved in the stereoselectivity of the substitution. It is the amount of bridging in the *exo* transition state, or whatever the factor responsible for the difference in stability of the two transition states, that will control the distribution of the norbornyl cation between *exo* and *endo* products.

The authors discussed their results in terms of stabilization of the *exo* transition state by carbon bridging.² However, the diagram is equally compatible with the alternative proposal that the *endo* transition state is destabilized by steric interactions between the departing group and the projecting ethylene bridge^{3,4} (Figure 1). It follows that an understanding of the factors involved in the high *exo-endo* rate ratios exhibited by norbornyl derivatives should help resolve the problem of the structure of the norbornyl cation.

The 2-benznorbornenyl derivatives⁵ appear to offer

(1) (a) S. Winstein, *et al.*, *J. Am. Chem. Soc.*, **74**, 1127 (1952); (b) *ibid.*, **87**, 376 (1965).

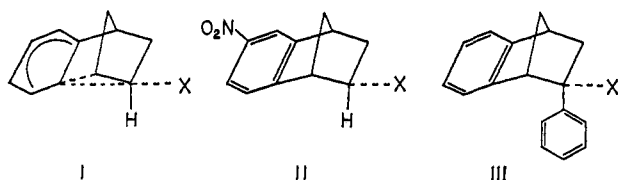
(2) H. L. Goering and C. B. Schewene, *ibid.*, **87**, 3516 (1965).

(3) H. C. Brown, F. J. Chloupek, and M.-H. Rei, *ibid.*, **86**, 1248 (1964).

(4) It is important to recognize that up to the present time no experimental data have been reported to provide independent confirmation for the postulated presence of participation and accompanying charge delocalization in a norbornyl system not undergoing rearrangement to a more stable structure.

(5) (a) P. D. Bartlett and W. P. Giddings, *J. Am. Chem. Soc.*, **82**, 1240 (1960); (b) W. P. Giddings and J. Dirlam, *ibid.*, **85**, 3900 (1963).

many advantages for such a study. The *exo-endo* rate ratio is 7500,^{6a} much higher than in the norbornyl case. If this *exo-endo* rate ratio is the result of carbon participation in the transition state (I), as proposed,⁵ both the amount of participation and the magnitude of the rate ratio would be expected to drop sharply as deactivating substituents are introduced into the aromatic ring (II), or as the cationic center is made more and more stable by the introduction of methyl and phenyl substituents (III), providing steric factors do not interfere.



On the other hand, if the *exo-endo* rate ratio arises from the unusual steric requirements of the rigid bicyclic system, as we have proposed,³ the *exo-endo* rate ratio would not be expected to be altered significantly by such modifications.

Accordingly, we undertook these tests of the alternative proposals. In the present communication we report our observations on tertiary benznorbornenyl derivatives. The effect of introducing both activating and deactivating substituents in the benzene ring on the *exo-endo* rate ratio is currently under investigation.

Addition of phenylmagnesium bromide to 2-benznorbornenone^{5a} produced *p*-phenyl-*endo*-benznorbornenol, mp 85.2–86.5°, *p*-nitrobenzoate mp 124.5–

Table I. Rates of Solvolysis and *exo-endo* Rate Ratios for Secondary and Tertiary 2-Benznorbornenyl Derivatives^d

Substituents		Solvent	Temp, °C	Rate constants $k_1 \times 10^6$ sec ⁻¹	<i>exo-endo</i> rate ratio at 25°
<i>endo</i> -2	<i>exo</i> -2				
H	OBs	HOAc	25	7.47	7500
OBs	H	HOAc	25	0.001 ^a	
H	OTs	EtOH	75	247	
			50	14.0	
			25	0.497 ^a	6400
OTs	H	EtOH	150	62.6	
			125	8.15	
			25	0.04775 ^a	
Ph	OPNB	80% Me ₂ CO	100	1160	
			75	110	
			25	0.305 ^a	4300
OPNB	Ph	80% Me ₂ CO	125	24.2	
			100	1.90	
			25	0.04716 ^a	
Me	OPNB	80% Me ₂ CO ^c	125	8.97	
			100	0.748	
			25	0.04359 ^a	6500
OPNB	Me	80% Me ₂ CO ^c	150	0.165	
			25	0.0555 ^{a,b}	

^a Calculated from the rate constants at higher temperatures. ^b Estimated from the rate constant at 150° assuming entropy of activation of -4.1 (that observed for the *exo* derivative). ^c Because of the slowness of the solvolysis, these rates were run in 50% aqueous acetone and converted to 80% by use of the factor, 24.2, determined experimentally. ^d All compounds exhibited analytical data and nmr spectra in agreement with the assigned structures.

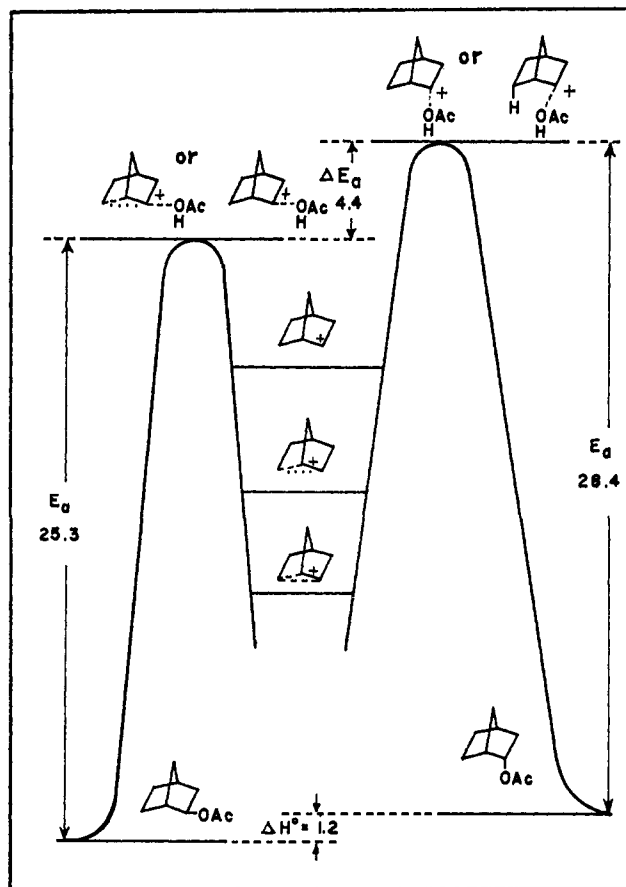


Figure 1. Modified Goering-Schewene energy diagram for the acid-catalyzed acetolysis of *exo*- and *endo*-norbornyl acetates demonstrating how the norbornyl cation (shown in three possible structures—classical unbridged, unsymmetrical partially bridged, or symmetrical fully bridged) must pass over the same two transition states involved in its formation.

126.0°. Hydrogen chloride yielded 2-phenyl-*exo*-benznorbornenyl chloride, mp 76.0–77.5°. Hydrolysis of the chloride produced 2-phenyl-*exo*-benznorbornenol, mp 112.8–113.4°, *p*-nitrobenzoate mp 186–188° dec. Addition of methylmagnesium iodide to the ketone yielded 2-methyl-*endo*-benznorbornenol, mp 60.5–62.0°, *p*-nitrobenzoate mp 77.5–79.0°. This tertiary alcohol was unusually inert toward hydrogen chloride, and vigorous conditions yielded a mixture of secondary and tertiary chlorides. Accordingly, the Wittig reaction was used to produce 2-methylenebenznorbornene, bp 75–77° (2 mm), n_D^{20} 1.3632; the latter was epoxidized (not isolated) and converted with lithium aluminum hydride to 2-methyl-*exo*-benznorbornenol, mp 88.8–89.5°, *p*-nitrobenzoate mp 112–114°.

exo- (mp 55.0–56.5°) and *endo*-benznorbornenyl tosylate (mp 93.0–94.5°) were prepared and solvolyzed in ethanol to ascertain whether the *exo-endo* rate ratio was sensitive to the solvent. The *p*-nitrobenzoates of the tertiary alcohols were solvolyzed in 80% aqueous acetone. The data are summarized in Table I.

The large difference in the reactivities of the *exo* and *endo* isomers necessitated measuring the rates at different temperatures and extrapolating the data down to a single temperature, 25°, used for the comparison. Naturally, such an extrapolation introduces some uncertainty in the resulting values. However, within this

unavoidable experimental uncertainty, it is evident that the four *exo-endo* rate ratios are essentially constant. Certainly, there is no change in the *exo-endo* rate ratio of the magnitude one might have predicted for the major decrease in carbon participation which should have accompanied the introduction of a highly stable tertiary benzylic carbonium center at position 2.

The results are clearly more consistent with the steric explanation than that based on carbon participation. However, we prefer to establish the effect of substituents in the aromatic ring before reaching a final decision.

(6) Purdue Research Foundation Fellow.

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Stereochemistry of the Grignard Reagents from *exo-* and *endo-*Norbornyl Chlorides

Sir:

Sauers and Kwiatkowski¹ have recently proposed that the Grignard reagent prepared from *exo*-norbornyl bromide was a rapidly equilibrating mixture of *exo* and *endo* isomers. This postulate was based on the observation that carbonation of the reagent from the *exo*-norbornyl bromide gave a mixture of *exo* and *endo* acids whose ratio depends on the temperature of carbonation. In order to study the nature of the norbornyl Grignard reagent we have examined the proton nmr spectra of the Grignard reagents prepared from both *exo-* and *endo-*norbornyl chlorides as a function of temperature.²

The *exo*-norbornyl chloride was prepared by the addition of hydrogen chloride to norbornene³ while the *endo*-norbornyl chloride was prepared by catalytic hydrogenation of a 10:90 mixture of *exo-* and *endo-*5-chloro-2-norbornenes⁴ and then solvolysis of the resulting mixture of chlorides in 80% ethanol-water to remove the *exo* isomer. The Grignard reagents were prepared from triply sublimed magnesium⁵ in nmr tubes which had been adapted so that a small rubber serum bottle cap allowed: first, the evacuation of the tube containing the magnesium, and then the addition of the ethyl ether, halide, and an internal standard.⁶ After the Grignard had been prepared the tubes were centrifuged so that the excess magnesium and traces of magnesium hydroxide would be trapped in the inside of the serum cap. The spectra were recorded on a Varian A-60 variable temperature nmr spectrometer.

The spectra of the Grignard reagents were identical whether prepared from the *exo* or *endo* chlorides. At 25°, two high-field multiplets were observed, one at τ 9.88 and the other at τ 10.32. If one assigns the low-

field multiplet to the hydrogen on the carbon bearing the magnesium atom in the *endo* configuration and the higher field multiplet to the corresponding proton on the *exo* Grignard reagent by analogy with other *exo-endo* pairs of norbornyl compounds, then the difference in position for the *exo* proton of *endo*-norbornyl chloride and the *exo* proton of *endo*-norbornyl Grignard is 4.06 ppm. The difference for the *endo* proton of *exo*-norbornyl chloride and the *endo* proton of *exo*-norbornyl Grignard is 4.14 ppm. This difference in effective magnetic shielding is consistent with the value of 4.19 ppm we have observed in going from ethyl chloride to the corresponding ethyl Grignard reagent, lending support to our assignments. The difference in position of the two norbornyl Grignard high-field multiplets, 0.44 ppm, is also consistent with the corresponding difference for a large number of *exo-endo* pairs of norbornyl compounds, 0.40 to 0.48 ppm.

The integration of the area under each of the high-field multiplets was essentially independent of the temperature, -40 to +80°. The average integration for several different samples of the Grignard reagent prepared from the *endo*-norbornyl chloride indicated 54% *endo* and 46% *exo* norbornyl Grignard. A similar average for the reagent prepared from the *exo* chloride indicated a composition of 53% *endo*- and 47% *exo*-norbornyl Grignard reagents. The addition of up to $\frac{3}{4}$ mole of water or carbon dioxide per mole of Grignard did not affect the high-field proton splitting pattern or the relative integrations of these peaks but did lower the absolute area of each. If we accept Sauers' proposal, to explain the varying ratios of products, that carbon dioxide reacts faster with the *exo*-norbornyl Grignard than with the *endo*, then these reagents must reequilibrate before the nmr spectrum is taken after the addition of the water or carbon dioxide. On this basis, the isomerization at room temperature must be relatively rapid on a laboratory time scale, 0.5 hr.

The high-field, τ 10.32, multiplet assigned to the *endo* proton of the *exo*-norbornyl Grignard reagent is very similar to the multiplet of the corresponding proton of *exo*-norbornyl chloride. This τ 10.32 multiplet is the X portion of an AA'MX system. First-order analysis^{7,8} yielded the nonzero coupling constants for the spin-spin interactions of $J_{AX} = 9.6$, $J_{A'X} = 7.5$, $J_{MX} = 2.3$ cps. The lower field, τ 9.88, multiplet assigned to the *exo* proton of the *endo*-norbornyl Grignard reagent appears more complex, as does the *exo* proton of *endo*-norbornyl chloride. First-order analysis indicated that this nine-line multiplet (intensities 1,2,2,2,2,2,2,1) is the X portion of an ABMNX system where the coupling constants are $J_{AX} = 13.2$, $J_{BX} = 6.6$, $J_{MX} = 3.3$, and $J_{NX} = 3.3$ cps.

Not only are the relative intensities of the two high-field multiplets constant when the temperature is varied, but there was no indication of broadening of the multiplets as the temperature was lowered or raised. This can be interpreted as evidence that the *exo* and *endo* forms of the Grignard reagent are not rapidly isomerizing on an nmr time scale. This is in agreement with Roberts' conclusions for secondary Gri-

(1) R. R. Sauers and G. T. Kwiatkowski, *J. Org. Chem.*, **27**, 4049 (1962).

(2) E. A. Hill has recently published a related study (*ibid.*, **31**, 20 (1966)).

(3) L. Schmerling, *J. Am. Chem. Soc.*, **68**, 195 (1946).

(4) J. D. Roberts, W. Bennett, and R. Armstrong, *ibid.*, **72**, 3329 (1950).

(5) We are grateful to the Dow Chemical Co. for a generous gift of triply sublimed magnesium used in these investigations.

(6) The τ values were calculated using the methyl proton of toluene at τ 7.67 as the internal standard inasmuch as tetramethylsilane interfered with the measurements.

(7) P. L. Corio, *Chem. Rev.*, **60**, 363 (1960).

(8) Coupling constants were measured on a Varian HA-100 spectrometer. We are indebted to Dr. D. Hollis for running these spectra.