Table I. Dimerization of Butadiene[a]

Expt	Catalyst, mmol	Ar, psig	N_2, psig	CO_2, psig	Temp, °C	Convn, %	Product yields,[b] %: 1,3,7-OT	4-VCH	1,5-COD	"Others"
1	None			400	120	14	0	100		
2	$(Ph_3P)_3Pt$, 0.5		400		120	18	4	96		
3	$(Ph_3P)_3Pt$, 0.5			400	120	30	68	32		
4	None	400			110	10	0	100		
5	$(Ph_3P)_3Pt$, 0.5	400			110	15	4	96		
6	$(Ph_3P)_3Pt$, 0.5			400	110	21	75	25		
7	$(Ph_3P)_3Pt$, 0.5		400		95	6	3	97		
8	$(Ph_3P)_3Pt$, 0.5			400	95	12	80	20		
9	$(Ph_3P)_3Pt$, 0.5			300 (+100 air)	120	13	20	80		
10	$(Ph_3P)_2(CO_3)Pt$, 0.65			>400	120		17	75		8
11	$(Ph_3P)_2(CO_3)Pt$, 0.65 + Ph_3P, 2.7			>400	120		>68	<32		
12	$(Ph_3P)_2(CO_3)Pt$, 0.65 + Ph_3P, 2.7				120		<32	>68		
13	$(Ph_3P)_4Ni$, 0.45		400		120	71		17	66	17
14	$(Ph_3P)_4Ni$, 0.43			400	120	17		93	7	
15	$[(PhO)_3P]_4Ni$, 0.43				120	87	1	14	82	3
16	$[(PhO)_3P]_4Ni$, 0.43			>400	120	<42		90	8	2

[a] Autoclave (80 ml) experiments. Butadiene, ~16 g (300 mmol); time, 17 hr; solvent, 30 ml of benzene. In expt 12 and 15 the pressure was autogenic, *i.e.*, the autoclave was flushed with nitrogen at atmospheric pressure and then heated. In expt 10, 11, and 16 the gas was introduced into the autoclave to 400 psig and the system subsequently heated; in all other experiments the autoclave was heated to the desired temperature and then the gas was introduced so that the total pressure was 400 psig. [b] Yields are based on converted butadiene. 1,3,7-OT is *trans*-1,3,7-octatriene; 4-VCH is 4-vinyl-1-cyclohexene; 1,5-COD is 1,5-cyclooctadiene; "others" consisted of unidentified butadiene dimers and/or trimers.

present, $(Ph_3P)_3Pt$ is converted to $(Ph_3P)_2(CO_3)Pt$.[3] In the presence of independently synthesized $(Ph_3P)_2(CO_3)Pt$, mainly 4-vinyl-1-cyclohexene was produced from butadiene (expt 10). Interestingly, $(Ph_3P)_2(CO_3)Pt$ with a controlled excess of Ph_3P (~4 mol/mol of catalyst) present does promote the formation of mainly *trans*-1,3,7-octatriene, provided that carbon dioxide is present (expt 11 and 12). Independently, it was demonstrated that the excess Ph_3P converts the carbonato complex to $(Ph_3P)_3Pt$: $(Ph_3P)_2(CO_3)Pt$ + excess $Ph_3P \rightarrow (Ph_3P)_3Pt + Ph_3PO + CO_2$. Although 400 psig of carbon dioxide was generally employed in the above experiments, 15–30 psig was sufficient to show a significant influence on the product composition.

Results similar to those described above for $(Ph_3P)_3Pt$ were obtained with $(Ph_3P)_4Pd$[4] as the catalyst. The conversion of butadiene increased and *trans*-1,3,7-octatriene became the predominant product when carbon dioxide was introduced.

Carbon dioxide also influences the $(Ph_3P)_4Ni$- and $[(PhO)_3P]_4Ni$-catalyzed dimerization of butadiene. In the absence of carbon dioxide, 1,5-cyclooctadiene is the predominant product[5] (expt 13 and 15), whereas in the presence of carbon dioxide (expt 14 and 16) mainly 4-vinyl-1-cyclohexene is formed. Since with carbon dioxide present the conversion of butadiene is reduced (compare expt 13 and 14) to that level anticipated for thermal dimerization only (expt 1), it appears that the carbon dioxide is almost completely inhibiting the 1,5-cyclooctadiene-producing activity of the nickel catalysts.

At the moment we are unable to propose a reliable mechanism to explain the effects of carbon dioxide. If metal–carbon dioxide complexes are formed *in situ*, they must be rather unstable since all attempts at isolation were unsuccessful. The above results, however, should be of general interest to anyone studying metal catalysis since carbon dioxide is frequently present in reaction systems and catalyst properties may be influenced.

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(3) C. J. Nyman, C. E. Wymore, and G. Wilkinson, *Chem. Commun.*, 407 (1967); F. Cariati, R. Mason, G. B. Robertson, and R. Ugo, *ibid.*, 408 (1967).

(4) L. Malatesta and M. Angoletta, *J. Chem. Soc.*, 1186 (1957).

(5) G. Wilke, *et al.*, *Angew. Chem.*, **75**, 10 (1963); *Angew. Chem. Intern. Ed. Engl.*, **2**, 105 (1963).

(6) To whom correspondence should be addressed.

Methoxy and Nitro Substituent Effects and Anchimeric Assistance in Solvolysis of Tertiary 2-Methyl-2-benzonorbornenyl *p*-Nitrobenzoates[1]

Sir:

As an indirect criterion for carbon participation in solvolysis of secondary *exo*-2-norbornyl derivatives, Brown has employed the expected rapid attenuation of the *exo*/*endo* rate ratio as a 2-substituent is added and then made increasingly more electron releasing.[2a] This is based on the reasonable supposition that an electron-releasing group will be more rate enhancing for the anchimerically unassisted *endo* derivative than the anchimerically assisted *exo* epimer. However, such substituent effects can be treacherous, since substituents can introduce various steric problems. How treacherous the indirect criterion is has been illustrated by its application by Brown and Tritle to 2-benzonorbornenyl solvolysis.[2b] By introducing methyl and phenyl substituents at C-2 they found that the *exo*/*endo* rate ratio changed from 7500[3a,c] for hydrogen to 6500

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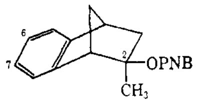
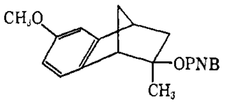
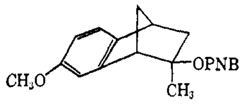
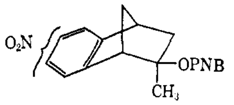
(1) Supported in part by the National Science Foundation.

(2) (a) H. C. Brown, *Chem. Brit.*, 199 (1966); *Chem. Eng. News*, **45**, No. 7, 87 (1967); (b) H. C. Brown and G. L. Tritle, *J. Amer. Chem. Soc.*, **88**, 1320 (1966).

(3) (a) P. D. Bartlett and W. P. Giddings, *ibid.*, **82**, 1240 (1960); (b) W. P. Giddings and J. Dirlam, *ibid.*, **85**, 3900 (1963); (c) H. Tanida,

Table I. Summary of Solvolysis Rates in 50% Aqueous Acetone

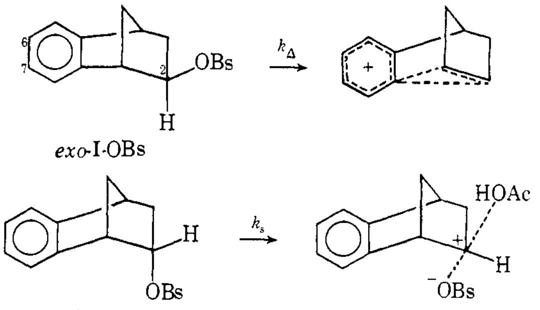
Compd	Structure	Temp, °C	10^6k, sec^{-1} ^{a}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	Relative rates, 125°
exo-III-OPNB		125.0	224 ± 6^b			1^c
		100.0	19.0 ± 0.2^b	28.3 ± 1.3	−4.6 ± 3.5	
exo-IV-OPNB *homo-para*		125.0	3470^d			16
		100.0	320 ± 5			
		75.0	21.1 ± 0.5	27.3 ± 1.0	−1.7 ± 2.9	
exo-V-OPNB *homo-meta*		125.0	165 ± 3			0.74
		100.0	13.3 ± 0.2	29.0 ± 0.9	−3.7 ± 2.4	
exo-VI-OPNB		125.0	5.60 ± 0.18			0.025

^{a} Mean value of two determinations. ^{b} Similar values were previously reported by Brown and Tritle.[2b] ^{c} The *exo/endo* rate ratio for this system was estimated by Brown and Tritle[2] to be 6500. For the *endo* isomer they obtained a rate constant of 4.0×10^{-6} sec^{-1} at 150°. ^{d} Calculated from the rate constants at lower temperatures.

for methyl to 4300 for phenyl. They remarked, "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." They further concluded, "The results are clearly more consistent with the steric explanation than that based on carbon participation."[2b]

Subsequently, considerable work was reported by three different groups[4] concerning methoxy substituent effects and by one group[4c] concerning nitro effects in acetolysis of secondary 2-benzonorbornenyl derivatives. While substituent effects are small for the *endo* derivatives, they are large for the *exo* epimers. In fact, the data for acetolysis of substituted *exo*-2-benzonorbornenyl brosylate (*exo*-I-OBs) derivatives give a relatively good $\rho\sigma^+$ line,[4d,5] with ρ −3.3 at 77.6° The results show conclusively that acetolysis of *exo*-I-OBs and *endo*-I-OBs is best interpreted with anchimerically assisted ionization (k_Δ) of the *exo*-I-OBs due to carbon participation and anchimerically unassisted ionization (k_s) of the epimeric *endo*-I-OBs.[3a,b]

While it was evident that Brown and Tritle's indirect method of testing for anchimeric assistance in the secondary derivatives had failed, it was still not clear where ionization changes from anchimerically assisted (k_Δ) to essentially unassisted (k_s), as 2-*R* groups are added. Aryl substituent effects in the tertiary cases are helpful in this connection, and we now report methoxy and nitro substituent effects in solvolysis of the 2-methyl-2-benzonorbornenyl *p*-nitrobenzoates and discuss their implication.



exo-I-OBs

endo-I-OBs

2-Methylenebenzonorbornene[2b,6] was prepared from 2-benzonorbornenone[3a] using the Corey modification[7] of the Wittig reaction. Oxymercuration–demercuration[8] of the olefin gave 2-methyl-*exo*-2-benzonorbornenol, methyl singlet at τ 9.04, mp 86–88° (lit.[2b] 88.8–89.5°), *p*-nitrobenzoate (*exo*-III-OPNB) mp 111–113° (lit.[2b] 112–114°). Similar reactions with 6- and 7-methoxy-2-benzonorbornenone[4a] led to *homo-para* and *homo-meta* liquid *exo* alcohols, *homo-para p*-nitrobenzoate (*exo*-IV-OPNB)[9] mp 188.5–190°, *homo-meta p*-nitrobenzoate (*exo*-V-OPNB)[9] mp 163.5–165°. Both alcohol isomers showed nmr methyl absorptions at τ 9.05. Addition of methylmagnesium iodide to 6-methoxy-2-benzonorbornenone yielded the *homo-para endo* alcohol, a colorless liquid with a methyl singlet at τ 8.56.

Treatment of 2-methyl-*exo*-2-benzonorbornenol with acetic anhydride in pyridine led to the *exo* acetate, mp 48–50°. Nitration of the tertiary acetate with fuming

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K. Tori, and K. Kitahonoki, *J. Amer. Chem. Soc.*, **89**, 3212 (1967), footnote 27. These authors quote a corrected *exo/endo* rate ratio of 15,000 in the acetolysis of 2-benzonorbornenyl brosylates pointed out to them by Brown and Tritle, instead of 7500 originally reported by Bartlett and Giddings.[3a]

(4) (a) D. V. Braddon, G. A. Wiley, J. Dirlam, and S. Winstein, *ibid.*, **90**, 1901 (1968); (b) H. Tanida, H. Ishitobi, and T. Irie, *ibid.*, **90**, 2688 (1968); (c) H. C. Brown and G. L. Tritle, *ibid.*, **90**, 2689 (1968); (d) H. Tanida, H. Ishitobi, T. Irie, and T. Tsushima, *ibid.*, **91**, 4512 (1969).

(5) (a) We mentioned previously[4a] a ρ of −2.8 based only on the unsubstituted and *p*-MeO points; (b) an even better linear free-energy correlation exists between log *k* for *exo*-I-OBs derivatives and log *k* for the neophyl analog.[5c] The slope of the least-squares line is 1.12, this line reproducing four points (6-OCH$_3$, 7-OCH$_3$, H, and 6- and 7-NO$_2$) with a mean deviation of 0.01 log unit. (c) A. Diaz and S. Winstein, *J. Amer. Chem. Soc.*, **91**, 4300 (1969), and references cited therein.

(6) D. J. Sandman and K. Mislow, *ibid.*, **91**, 645 (1969).

(7) R. Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, **28**, 1129 (1963).

(8) H. C. Brown and W. J. Hammar, *J. Amer. Chem. Soc.*, **89**, 1524 (1967).

(9) Satisfactory carbon and hydrogen analyses were obtained for the new compounds mentioned.

nitric acid in acetic acid and acetic anhydride at *ca.* 5° yielded a mixture of *homo-para* and *homo-meta* nitroacetates,[10a] mp 109–112°. Hydrolysis of the acetate mixture with dilute hydrochloric acid in methanol led to the *exo* alcohols, a yellow liquid with a methyl singlet at τ 8.97, *p*-nitrobenzoate (*exo*-VI-OPNB)[10b] mp 192–196° dec.

The *p*-nitrobenzoates of the tertiary alcohols were solvolyzed in 50% aqueous acetone. The data are summarized in Table I. The products and yields are summarized in Table II.

Table II. Products and Yields[a]

Compd	% *exo* alcohol in ROH[b]	% exocyclic olefin	% unknown compd
exo-III-OPNB	>99.6	29	<0.3
exo-IV-OPNB	>99.9	5	<0.3
exo-V-OPNB	>99.5	42	<0.3
exo-VI-OPNB	95.3[c]	51	13

[a] The compounds were solvolyzed at 125° in 50% aqueous acetone (ROPNB 0.011 *M*) containing 0.017 *M* NaOAc. [b] Control experiments showed the *endo* alcohols to be fully stable under these conditions. [c] An authentic sample of the *endo* alcohol was not available. A glpc peak was assigned the *endo* alcohol on the basis of relative retention times found for the other *endo* alcohols.

Theory and previous experience with the secondary 2-benzonorbornenyl system[4] lead one to expect rate enhancement by a *homo-p*-methoxy and slight rate retardation by a *homo-m*-methoxy group in the anchimerically assisted solvolysis (k_Δ). Substantial rate retardation would be expected for deactivating substituents, such as the nitro group. On the other hand, such substituent effects should be very small for anchimerically unassisted solvolysis. As is clear from Table I, the *homo-p*-methoxy group is substantially accelerating, *homo-m*-methoxy is slightly retarding, while *homo-p-* and *homo-m*-nitro are substantially retarding in solvolysis of the tertiary *exo* derivatives.

The factor of 16 at 125° (extrapolated value 25 at 25°), by which the *homo-p*-methoxy group accelerates the tertiary *exo* system, compares favorably with the factor of 150 at 25°, which was previously found in the secondary derivative.[4a] The nitro group retards the tertiary *exo* system by a factor of 40 at 125°. A plot of the present rate data against σ^+ is shown in Figure 1, where a ρ of -1.9 is obtained[11] at 125°. As can be expected, the ρ is smaller in magnitude than it is for the secondary *exo*-I system. However, it is much too large for k_s, and it shows that anchimerically assisted ionization (k_Δ) is very dominant in solvolysis of the tertiary *exo* system.

While the addition of the 2-methyl substituent must be decreasing the k_Δ/k_s ratio in solvolysis of the tertiary *exo* derivatives, it is obvious that this decrease is only moderate. It certainly is not sufficient to render anchimerically unassisted solvolysis (k_s) dominant, as is sometimes assumed, *a priori.* The effect of a 2-phenyl substituent in the 2-benzonorbornenyl system is reported in a following communication.[12]

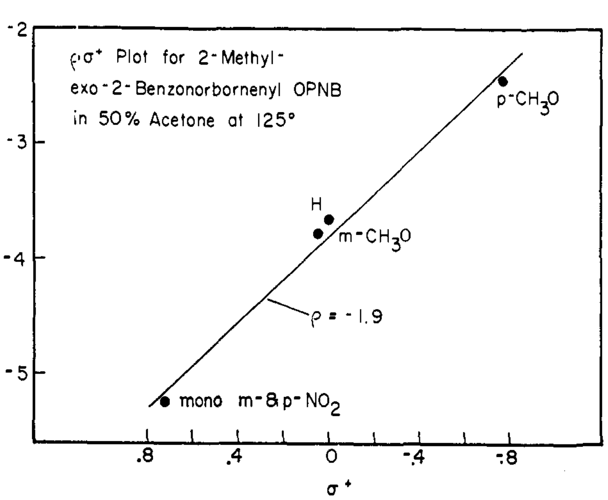

Figure 1. Methoxy and nitro substituent effects and anchimeric assistance in solvolysis of 2-methyl-2-benzonorbornenyl *p*-nitrobenzoates.

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[10] (a) The nmr spectrum showed that two protons in the aromatic region were appreciably more deshielded than the third proton, in agreement with the introduction of the nitro group β to the norbornyl ring fusion; (b) although the two *exo* isomers could not be separated, this was not felt to be a very serious problem, since a *p*-NO$_2$ and *m*-NO$_2$ group have similar σ^+ values, $+0.777$ and $+0.662$, respectively.

[11] An even better linear free-energy correlation exists between log *k* for the tertiary *exo* derivatives and log *k* for neophyl OTs[5c] in AcOH at 75°. The slope of the least-squares line is 0.55, this line reproducing four points with a mean deviation of 0.06 log unit.

[12] J. P. Dirlam and S. Winstein, *J. Amer. Chem. Soc.*, **91**, 5907 (1969).

[13] National Science Foundation Trainee, 1965–1969.

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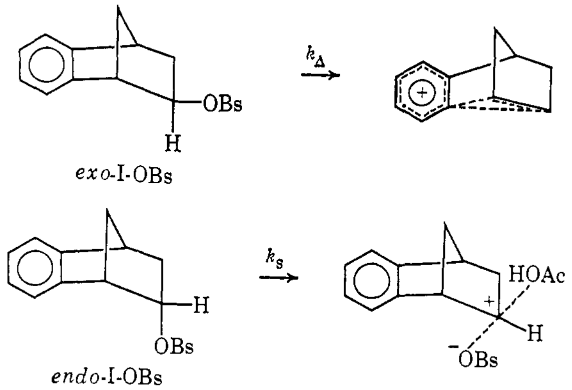
Methoxy Substituent Effects in Solvolysis of 2-Phenyl-2-benzonorbornenyl *p*-Nitrobenzoates[1,2]

Sir:

In solvolysis of *exo*-2-benzonorbornenyl bromobenzenesulfonate (*exo*-I-OBs) ionization is strongly anchimerically assisted (k_Δ), whereas ionization of the *endo* epimer (*endo*-I-OBs) is anchimerically unassisted (k_s).[3a,b] Substituent effects in the benzo group of the



exo-I-OBs

endo-I-OBs

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[1] Supported in part by the National Science Foundation.

[2] Reported by S. Winstein at the 21st National Organic Chemistry Symposium of the American Chemical Society, Salt Lake City, Utah, June 15–19, 1969.

[3] (a) P. D. Bartlett and W. P. Giddings, *J. Amer. Chem. Soc.*, **82**, 1240 (1960); (b) W. P. Giddings and J. Dirlam, *ibid.*, **85**, 3900 (1963); (c) H. Tanida, K. Tori, and K. Kitahonoki, *ibid.*, **89**, 3212 (1967), ref 27. The *exo/endo* rate ratio in the acetolysis of 2-benzonorbornenyl brosylates is corrected from 7500 to 15,000.