Table I. Rates of Solvolysis of 2-Phenyl-2-norbornenyl *p*-Nitrobenzoates and Related Derivatives in 80% Acetone at 25.0°

Compd[a]	$k_1 \times 10^6$, sec^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	ΔS, eu	Rel rate at 25°: Exo	Rel rate at 25°: Endo	Rel rate at 25°: Exo/endo
I[b]	2.60[c]	23.7	−4.8	1.0		
II[d]	0.798[c]	24.0	−6.1	1.0/3.3		
III[e]	0.053	25.0	−7.7		1.0	
IV[f]	6.03×10^{-3}[c]	26.3	−7.9		1.0/8.8	
V[e]	7.56[c]	23.6	−2.8	1.0		143
VI[g]	1.22[c]	24.7	−2.7	1.0/6.2		202

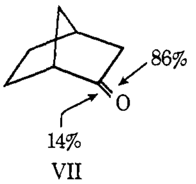
[a] All new compounds gave spectral and microanalytical data consistent with the proposed structure. [b] $k^{75} = 926 \times 10^{-6}$ sec^{-1}, $k^{50} = 61.6 \times 10^{-6}$ sec^{-1}. [c] Calculated from data at other temperatures. [d] Mp 90.5–91.4°; ROH bp 76–78° (2.6 mm); $k^{75} = 307 \times 10^{-6}$ sec^{-1}, $k^{50} = 19.7 \times 10^{-6}$ sec^{-1}. [e] Reference 4. [f] Mp 117.0–118.5°; $k^{100} = 55.5 \times 10^{-6}$ sec^{-1}, $k^{75} = 4.10 \times 10^{-6}$ sec^{-1}. [g] Mp 99.0–101.5°; ROH mp 66.3–67.0°; $k^{75} = 570 \times 10^{-6}$ sec^{-1}, $k^{50} = 33.7 \times 10^{-6}$ sec^{-1}.

π participation in this system cannot be a significant factor in the rate of solvolysis of VI.

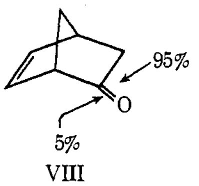
The experimental data are summarized in Table I. The exo:endo rate ratio of 2-phenyl-2-norbornyl (V/III) is 143. There is no evidence of σ participation in the exo isomer. Indeed, it is generally accepted that neighboring group participation should be negligible in systems containing such a stabilized tertiary benzylic cationic center.[6] Consequently, the high exo:endo rate ratio has been attributed not to an enhanced exo rate, but to a retarded endo rate.[4,7] It has been suggested that steric hindrance to ionization, arising from the interference of the 6-endo hydrogen with the departing anion, is responsible.[7]

The exo:endo rate ratio for the unsaturated system (VI/IV) is 202. The evidence here presented is that the rate of the exo isomer is not enhanced by π participation. The question arises as to whether it is possible to account for the high exo:endo rate ratio in terms of steric hindrance to ionization, in view of the absence of an endo 6-hydrogen atom. Such an interpretation would require that the π cloud of the double bond in the rigid bicyclic system must be capable of resisting the departure of the anion in much the same manner as the endo 6-hydrogen in the saturated derivative.[1,7]

That this proposal is not unreasonable is indicated by the observation that the stereoselectivity of the reduction of dehydronorcamphor (VIII) is even greater than that of norcamphor (VII).[8] The results on the reduction of bicyclo[2.2.2]octanone and bicyclo[2.2.2]octenone also support the proposal. Indeed, a number of norbornene derivatives undergo reactions with predominant exo attack of the reagent. Among these reactions may be mentioned hydroboration[9] and carbenation[10] of norbornadiene, the reaction of methylmagnesium iodide and dimethylsulfonium methylide with dehydronorcamphor,[11] and deuterium exchange in dehydronorcamphor.[12]



VII



VIII

The stereoselectivity for exo attack in the noncarbonium ion reactions listed above must be the result of a more difficult attack from the endo direction. Therefore, the endo environment, with the π cloud of the 5,6-double bond, must be more hindered than the exo face. In view of the lack of evidence for π participation in the 2-phenyldehydronorbornenyl derivatives examined in the present study, the high exo:endo ratio must likewise be attributed to the differences in the steric invironment, favoring solvolysis of the exo isomer.

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(6) (a) C. A. Bunton, "Nucleophilic Substitution at a Saturated Carbon Atom," Elsevier, Elmsford, N. Y., 1963; also see C. A. Bunton and G. O'Connor, *Chem. Ind. (London)*, 1182 (1965); (b) G. D. Sargent, *Quart. Rev., Chem. Soc.*, **20**, 301 (1965).

(7) (a) H. C. Brown, "Boranes in Organic Chemistry," Cornell University Press, Ithaca, N. Y., in press, Chapters 9, 10, and 11; (b) H. C. Brown, F. J. Chloupek, and M.-H. Rei, *J. Amer. Chem. Soc.*, **86**, 1248 (1964).

(8) H. C. Brown and J. Muzzio, *ibid.*, **88**, 2811 (1966).

(9) G. Zweifel, K. Nagase, and H. C. Brown, *ibid.*, **84**, 183, 190 (1962).

(10) H. E. Simmons and R. D. Smith, *ibid.*, **80**, 5323 (1958); **81**, 4256 (1959).

(11) R. S. Bly, C. M. DuBose, and G. B. Konizer, *J. Org. Chem.*, **33**, 2188 (1968).

(12) T. T. Tidwell, *J. Amer. Chem. Soc.*, **92**, 1448 (1970).

(13) Proctor and Gamble Fellow in Chemistry, 1970–1971.

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Nitro Group Migrations during Aromatic Nitration

Sir:

Intramolecular migrations of the nitro group during aromatic nitration can have important consequences on isomer proportions and rates of nitration. Studies of nitration of *o*-xylene in H_2SO_4 solutions provide a clear example.

Coombes and Russell reported that the ratio of 3-nitro-*o*-xylene to 4-nitro-*o*-xylene changed smoothly from about 0.5 to 1.5 when *o*-xylene was nitrated in H_2SO_4 solutions ranging from 50 to 70%.[1] The isomer ratio appeared constant above and below this acidity range. While changes in isomer proportion could be related to changes in the nature of the electrophile,[2,3] this possibility is apparently excluded by the data.[1] None of the alternative explanations considered could be established.

It is possible to give a fairly direct account of these changes in isomer proportion if one grants that formation of the 1,2-dimethyl-1-nitrocyclohexadienyl cation (1) is competitive with formation of the isomeric cy-

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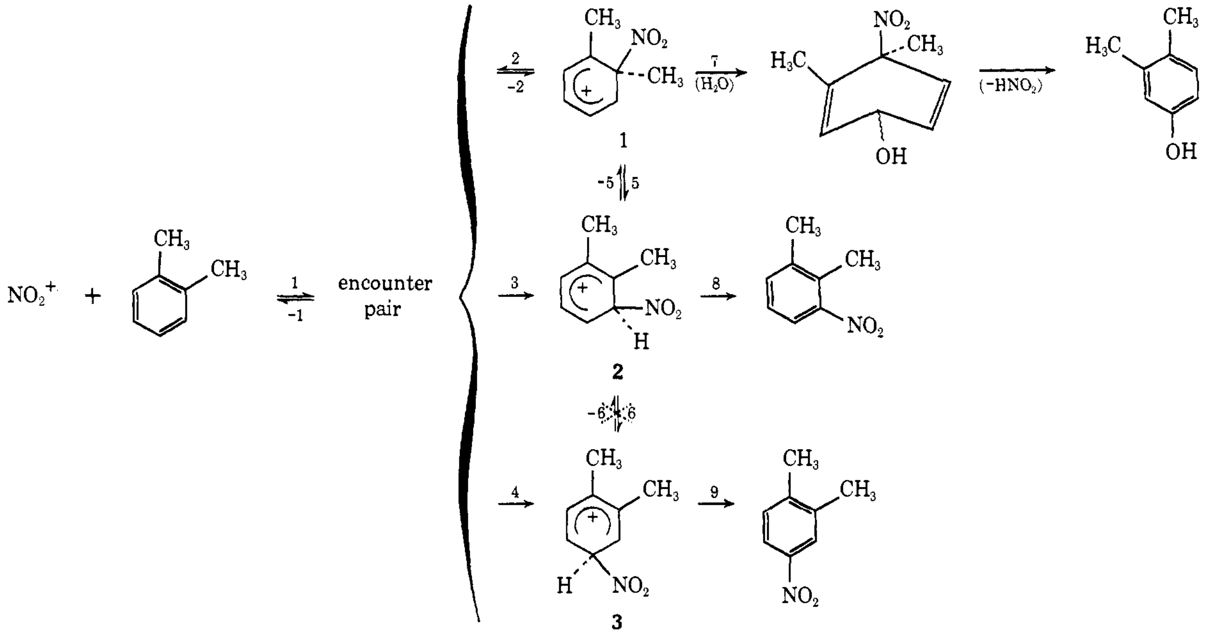
(1) R. J. Coombes and L. W. Russell, *J. Chem. Soc. B*, 2443 (1971).

(2) (a) C. W. F. Kort and H. Cerfontain, *Recl. Trav. Chim. Pays-Bas*, **87**, 24 (1968); (b) A. J. Prinsen and H. Cerfontain, *ibid.*, **88**, 833 (1969).

(3) J. G. Hoggett, R. B. Moodie, J. R. Penton, and K. Schofield, "Nitration and Aromatic Reactivity," Cambridge University Press, Cambridge, England, 1971.

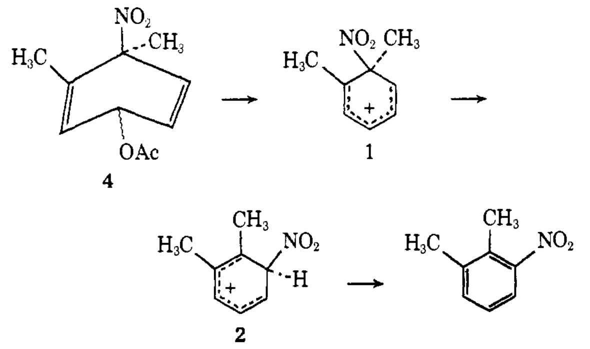
Scheme I



clohexadienyl cations, Scheme I. Excluding methyl migrations,[4] one can identify three major reaction pathways of **1**: return to reactants (or encounter pair), intramolecular migration of the nitro group, and nucleophilic attack by solvent. Thus the isomer ratio change observed could be characteristic of a change in dominant reaction path of **1**. A change is readily associated with the decrease in water activity with increasing H_2SO_4 concentration; nucleophilic capture (step 7) might dominate at 50% H_2SO_4, but rearrangement (step 5) might dominate above about 70% H_2SO_4.

To test this scheme (Scheme I), two lines of investigation seemed obligatory. A clear demonstration of intramolecular migration of the nitro group was required. In addition, a reinvestigation of the material balance in nitration of *o*-xylene was necessary, since the scheme implies formation of phenolic product at low acid concentrations.

An ideal test of intramolecular rearrangement involves preparation of the ion **1** by a route unlikely to yield either **2** or **3** as first-formed products. The availability of 3,4-dimethyl-4-nitrocyclohexa-2,5-dienyl acetate (**4**) provided a solvolytic approach, eq 1. Solvolysis of **4** in aqueous systems is known to yield 4-acetoxy-*o*-xylene.[5] We anticipated, however, that the mode of solvolysis would change in concentrated sulfuric acid systems to one involving alkyl–oxygen cleavage.



(1)

If **1** is formed by solvolysis of **4**, 3-nitro-*o*-xylene should be the major product in H_2SO_4 solutions greater than 70%, but the yield of this solvolysis product should fall off rapidly as the H_2SO_4 concentration decreases.

Our expectations were confirmed. Solvolysis of the higher melting isomer of **4** in 85.1, 70.2, 59.9, and 49.3% H_2SO_4 gave 3-nitro-*o*-xylene in 93, 80, 15, and 2% yields, respectively. No 4-nitro-*o*-xylene ($\ngtr 0.5\%$) was detected.

The dienyl acetate **4** was isolated from the product mixture obtained upon treatment of *o*-xylene with nitric acid in acetic anhydride.[5] Solvolyses carried out using this crude product mixture are collected in Table I. The pattern of results is analogous to that observed in the solvolysis of the isolated dienyl acetate.

Table I. Product Distribution from Reaction of *o*-Xylene with Nitric Acid in Acetic Anhydride before and after Solvolysis

	Mol %			
		After solvolysis[b] at 25°		
Products	Before solvolysis[a]	H_2O	50% H_2SO_4	70% H_2SO_4
3-Nitro-*o*-xylene	14	14.8	15.3	58.0
4	57			
4-Acetoxy-*o*-xylene		54.3	3.2	
4-Nitro-*o*-xylene	29	31.0	31.4	33.0
Rel yield, %[c]		(100)	50	91
3-Nitro/4-nitro	0.47	0.48	0.49	1.75

[a] Nmr analysis. [b] Glpc analysis. [c] *p*-Nitrotoluene used as an internal standard.

These solvolysis studies provide the required demonstration of rearrangement of **1** by a 1,2-nitro group shift and show how the extent of this rearrangement can

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[4] One might predict that the nitro group would be a better leaving group than methyl; see C. L. Perrin, *J. Org. Chem.*, **36**, 420 (1971). No evidence of the suspected methyl migration product, 2,6-dimethylnitrobenzene, has been found in any of the nitration and solvolytic studies reported here, *vide infra*.

[5] D. J. Blackstock, J. R. Creney, A Fischer, M. P. Hartshorn, K. E. Richards, J. Vaughan, and G. J. Wright, *Tetrahedron Lett.*, 2793 (1970), and references cited herein.

be altered by solvent acid concentration. The absence of significant amounts of 4-nitro-*o*-xylene under any conditions of solvolysis of **4** rules out multistep rearrangements passing through ion **2**. In addition, this result implies that reversion of ion **1** to xylene (or encounter pair) is unimportant. Thus, addition–elimination products are required for a material balance.

One can estimate from the overall change in nitro-*o*-xylene isomer ratios that about 40% of the substitution proceeds *via* the σ complex **1**.[6] For nitration at 60% H_2SO_4, this implies that about 66% of the products are nitro-*o*-xylenes; the remainder should be found as 3,4-dimethylphenol or products stemming from nitration and sulfonation of 3,4-dimethylphenol. When *o*-xylene was nitrated in 60% H_2SO_4, following the conditions reported by Coombes and Russell,[1] the following product distribution was obtained by gas chromatographic analysis: 3-nitro-*o*-xylene, 29%; 4-nitro-*o*-xylene, 38%; and mono- and dinitro-3,4-dimethylphenols, 33%.[7]

Perrin has discussed the potential importance of aromatic electrophilic attack at the substituent position (*ipso* attack).[8] Results reported here show how such processes can modify the yield and distribution of product in the superficially straightforward nitration of *o*-xylene. One can envision analogous situations arising in a number of polyalkylbenzene systems. The need to carefully consider *ipso* attack whenever one attempts to rationalize product or rate data in aromatic substitution reactions seems clear.

Acknowledgment. We thank Dr. John Penton for drawing our attention to this problem and for a number of valuable discussions. The interest, encouragement, and facilities made available by Professor H. Zollinger are gratefully acknowledged.

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(6) This estimate is based on the assumption that the percentage of ion 3 formed is independent of acidity and that the nitration products formed in 70% H_2SO_4 represent a complete material balance.

(7) Coombes and Russell reported variable amounts of uncharacterized "highly polar oxidation product of *o*-xylene, particularly at lower acidities." [1]

(8) C. L. Perrin and G. A. Skinner, *J. Amer. Chem. Soc.*, **93**, 3389 (1971).

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Synthesis of a Zwitterion *nido*-Carborane from 1,6-Dicarba-*closo*-hexaborane(6) and Trimethylamine

Sir:

We wish to report a new carborane obtained as a dipolar ion, 5-$(CH_3)_3N^+$-[2,4-$C_2B_4H_6^-$], from the reaction of 1,6-dicarba-*closo*-hexaborane(6) with trimethylamine. From available evidence a pyramidal structure is suggested with the nitrogen bonded to a boron atom in the pentagonal base, Figure 1.

The reaction of 1,6-$C_2B_4H_6$ (5.98 mmol) with $(CH_3)_3N$ (15.20 mmol) was conducted in a sealed glass vessel. After 1 day at room temperature a white crystalline material began to form on the walls of the container.

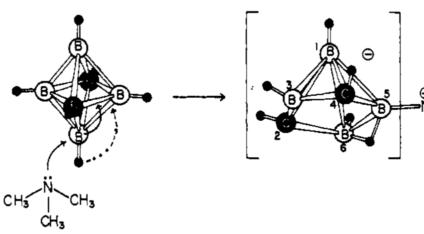

Figure 1. Reaction of 1,6-$C_2B_4H_6$ with trimethylamine to give 5-$(CH_3)_3N^+$-[2,4-$C_2B_4H_6^-$] (proposed overall mechanism).

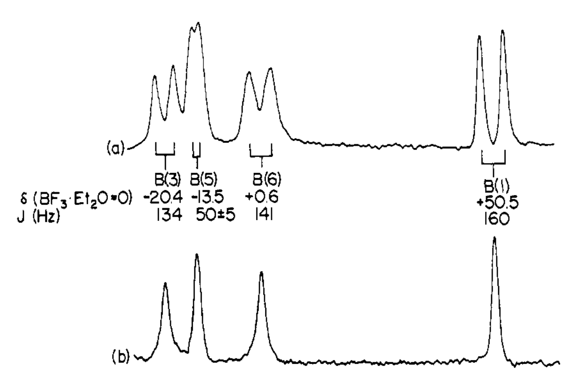

Figure 2. Boron-11 nmr of 5-$(CH_3)_3N^+$-[2,4-$C_2B_4H_6^-$] at 32.1 MHz: (a) undecoupled, (b) proton noise decoupled.

The contents of the vessel were allowed to stand with stirring for 10 additional days after which time any unreacted volatile starting materials were separated and measured. Both $(CH_3)_3N$ (10.52 mmol) and 1,6-$C_2B_4H_6$ (1.27 mmol) were recovered indicating that the reaction had proceeded to nearly 80% completion to give a compound with a 1:1 ratio of 1,6-$C_2B_4H_6$ and $(CH_3)_3N$. The new compound is a thermally stable white solid that does not appear to dissociate at ambient temperatures. It is soluble in polar solvents such as monoglyme and *N*,*N*-dimethylformamide but insoluble in carbon disulfide, chloroform, and trimethylamine. This suggests that the new product has ionic or partial ionic character, for every previously known parent carborane has reasonable solubility in a nonpolar solvent such as a carbon disulfide.

The boron-11 nmr of the new material is composed of four equal intensity doublets (Figure 2), three of which have coupling constants large enough to indicate B–H_{terminal} groups.[1] The separation of peaks in the fourth doublet δ -13.5 ($J = 50 \pm 5$ Hz) is much too small for terminal-hydrogen coupling but is not unusual for bridge-hydrogen to boron splitting.[1] Since this boron has no terminal hydrogen, it is proposed that this atom is the site of attachment to the -$N(CH_3)_3$, a group which would not be expected to cause further observable splitting. One of the three B–H_{terminal} doublets, δ $+50.6$, is located at very high field strongly suggesting an apical environment within the framework of a pyramid.[1,2] The other low-field resonances are in the region expected for borons located at the base of this pyramid.

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(1) G. R. Eaton and W. N. Lipscomb, "NMR Studies of Boron Hydrides and Related Compounds," W. A. Benjamin, New York, N. Y., 1969.

(2) T. Onak and J. Spielman, *J. Magn. Resonance*, **3**, 122 (1970), and references cited therein.