produce organometallics which yield mainly unlabeled hydrocarbons on deuterolysis; this suggests that π-type complexes are formed. In contrast, the high deuterium incorporation in the hydrocarbons from the deuterolysis of the organoaluminum compounds indicates σ-type carbon–metal bonds.

Aluminum atoms react similarly with propyne and 2-butyne, mainly by addition to make 1,2-dialuminoalkenes. Partial protolysis of this product by unreacted propyne accounts for the deuteration pattern of the propyne and allene on deuterolysis with deuterium oxide. A combination of mass spectral cracking patterns and infrared data show that the propene product has vinyl but no methyl deuterium. The propyne has some deuterium at the methyl and some at the ethynyl positions. This labeling and the formation of allene-d_1 can be explained if $AlCH_2C{\equiv}CH$ is present in addition to the $CH_3C{\equiv}CAl$.

Table II. Products of Deuterolysis of Organoaluminum Compounds from Propyne and Aluminum Atoms (1.25 mmol)

Product	Yield, mmol	%					
		d_0	d_1	d_2	d_3	d_4	d_5
Propene	1.07	3	43	53	1	0	0
Propyne	0.63	35	61	4	0	0	
Allene	0.075	1	83	16	0	0	
Propane	0.030	2	5	33	36	20	4
Hydrogen	0.034	0	11	89			
Methane	0.055			Not determined			

The reaction of 2-butyne is cleaner, the only products being *cis*- and *trans*-2-butenes in a 2:1 ratio.

Benzene does not appear to react with aluminum atoms; a negligible amount of volatile product is recovered on hydrolysis of the residue. The small amount of benzene recovered (20%) is d_0.

Reactions of aluminum atoms with other substrates will be reported later.

Acknowledgment. The financial support of the Air Force Office of Scientific Research (1983) is acknowledged with gratitude. L. R. Wolf thanks the National Science Foundation for a Graduate Fellowship.

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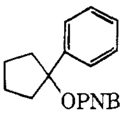
Received July 24, 1971

Effect of a Homoallylic Double Bond on the Rates of Solvolysis of 1-Phenylcyclopentyl and 2-Phenyl-2-norbornanyl *p*-Nitrobenzoates. Evidence for the Absence of π Participation as a Factor in the High Exo:Endo Rate Ratio in the 2-Phenyl-2-norbornenyl System

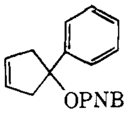
Sir:

The introduction of a homoallylic double bond into 1-phenylcyclopentyl and *exo*- and *endo*-2-phenyl-2-norbornanyl *p*-nitrobenzoates causes modest rate retardations of comparable magnitudes. It is considered that π participation cannot be significant in the rate of solvolysis of 2-phenyl-2-*exo*-norbornenyl *p*-nitrobenzoate, so that the observed high exo:endo rate ratio must arise from other factors, presumably steric hindrance to ionization in the endo isomer.[1]

The rate of solvolysis in 80% acetone of 1-phenylcyclopentyl *p*-nitrobenzoate (I) is retarded by a factor of 3.3 by the introduction of a homoallylic double bond (II). Clearly, participation by the homoallylic double bond in II cannot be significant.[2] The small rate retardation which is observed is in the direction anticipated for the inductive effect of the double bond on the rate of solvolysis.[3]



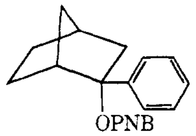
I



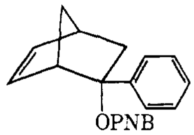
II

$k_{\text{rel}}^{25°}$ 1.0 1.0/3.3

This conclusion is supported by the behavior of the 2-phenyl-2-*endo*-norbornenyl *p*-nitrobenzoate (IV). This derivative solvolyzes 8.8 times slower than the saturated analog, 2-phenyl-2-*endo*-norbornyl *p*-nitrobenzoate (III). Participation is believed not to be a significant factor in the solvolysis of *endo*-norbornyl derivatives. Consequently, here also the modest rate retardation is presumably a reflection of the unfavorable inductive influence of the double bond.



III

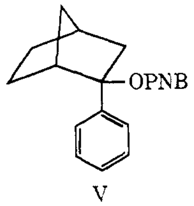


IV

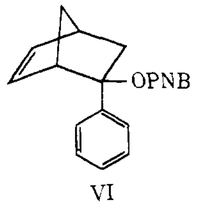
$k_{\text{rel}}^{25°}$ 1.0 1.0/8.8

In the corresponding exo isomers, the possibility of participation must be considered. However, in the saturated derivative, 2-phenyl-2-*exo*-norbornyl *p*-nitrobenzoate (V), evidence has been offered that it must solvolyze without significant σ participation.[4] Indeed, a detailed nmr study of the 2-phenyl-2-norbornyl cation led to the conclusion that the data supported a classical formulation.[5]

Consequently, the observation that the rate of solvolysis of 2-phenyl-2-*exo*-norbornenyl *p*-nitrobenzoate (VI) solvolyzes at a rate 6.2 times slower than the saturated derivative V reveals that the effect of the double bond on the exo isomer is almost identical with the effect of the double bond on the endo isomer. Clearly,



V



VI

$k_{\text{rel}}^{25°}$ 1.0 1.0/6.2

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[1] E. N. Peters and H. C. Brown, *J. Amer. Chem. Soc.*, **94**, 5899 (1972).

[2] It has been concluded that the cyclopentyl system has an unfavorable planar geometry for π participation: P. D. Bartlett and M. R. Rice, *J. Org. Chem.*, **28**, 3351 (1963).

[3] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed, Cornell University Press, Ithaca, N. Y., 1969, Chapter II.

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[5] D. G. Farnum and G. Mehta, *ibid.*, **91**, 3256 (1969).

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	Endo	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}.

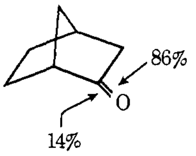
π participation in this system cannot be a significant factor in the rate of solvolysis of VI.

The experimental data are summarized in Table I.

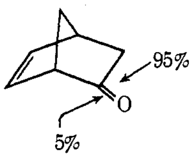
The exo:endo rate ratio of 2-phenyl-2-norbornyl (V/III) is 143. There is no evidence of σ participation in the exo isomer. Indeed, it is generally accepted that neighboring group participation should be negligible in systems containing such a stabilized tertiary benzylic cationic center.[6] Consequently, 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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(13) Proctor and Gamble Fellow in Chemistry, 1970–1971.

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Received August 2, 1972

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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