To 12 ml of a cooled stirred solution of 48% HBr in H_2O was added first about 10 g of concentrated H_2SO_4 and then 7.3 ml (~0.1 mol) of the isopropyl alcohol/water azeotrope. The solution was heated to reflux for 6 hr and then distilled to give a fraction with a bp 59–62° (shown to be isopropyl bromide by comparison of nmr and glpc retention time with a commercial sample). Conversion of the bromide to the iodide was accomplished by refluxing a mixture of 10 g of isopropyl bromide in 200 ml of acetone with 30 g of sodium iodide. After 72 hr the solution was filtered and again 30 g of sodium iodide added. An additional 24 hours of refluxing yielded a mixture in which about 95% of the bromide had been converted to the iodide.

A solution of 20 g (0.27 mol) of *N-tert*-butylamine and 10 g (0.06 mol) of isopropyl iodide was refluxed for 24 hr after which the mixture was cooled and 50 ml of 2 *M* NaOH was added dropwise. The solution was then saturated wih sodium chloride and the top amine layer separated and distilled. An impure fraction (bp 75–83°) was shown to contain the *N-tert*-butyl-*N*-isopropylamine and final purification of this compound was achieved by collection on a 20% SE-30 glpc column.

A solution of 2 g (0.014 mol) of methyl iodide and 1.8 g (0.024 mol) of *N-tert*-butyl-*N*-isopropylamine was sealed in a glass reaction bomb and heated to 60° for 12 hr. The product mixture was added to 10 ml of H_2O and this cooled solution (0°C) was then saturated with KOH. The top amine layer was analyzed on a 20% SE-30 column and *N-tert*-butyl-*N*-methyl-*N*-isopropylamine collected: nmr peaks at δ 2.10 (3 H singlet, methyl), 1.04 (9 H singlet, *tert*-butyl), 0.95 (6 H, doublet, J = 7.0 Hz, methyl) and 3.23 (1 H, septet, J = 7.0 Hz, methine hydrogen).

Anal. Calcd for $C_8H_{19}N$: C, 74.34; H, 14.82; N, 10.84. Found: C, 74.28; H, 14.55; N, 10.97.

***N-tert*-Butyl-*N*-methyl-*N*-(isopropyl-d_7)amine (8)** was prepared in exactly the same fashion as *N-tert*-butyl-*N*-methyl-*N*-isopropylamine above except that acetone-d_6 and lithium aluminum deuteride were employed. For **8**: ^{1}H nmr peaks (CCl_4) at δ 2.10 (3 H singlet, N-methyl) and 1.07 (9H singlet, *tert*-butyl).

***N-tert*-Butyl-*N*-(2,2,2-trideuterioethyl)-*N*-(isopropyl-d_7)amine (9)** was prepared in the same manner as *N-tert*-butyl-*N*-methyl-*N*-isopropylamine using 2 g (0.016 mol) of the *N-tert*-butyl-*N*-(isopropyl-d_7)amine and 1 g (0.006 mol) of ethyl-d_5 iodide: nmr peaks at 2.51 (2 H singlet, methylene protons) and 1.10 (9 H singlet, *tert*-butyl protons).

***N-tert*-Butylaziridine** was prepared by the method of Bottini and Roberts.[21]

Acknowledgment. We are grateful to the National Science Foundation (Grant No. GP-18197) for support.

(21) A. T. Bottini and J. D. Roberts, *J. Amer. Chem. Soc.*, **80**, 5203 (1958).

Effect of α Substitution on the Solvolysis of Bicyclo[3.1.1]heptyl-6 and Bicyclo[3.2.0]heptyl-6 Derivatives[1]

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Abstract: The effects of α-methyl, α-phenyl, and α-*p*-anisyl substitution on the rates and products of solvolysis of bicyclo[3.1.1]heptyl-6 and bicyclo[3.2.0]heptyl-6 3,5-dinitrobenzoates have been determined. Methyl substitution led to a marked rate increase for the less reactive isomers and only a small increase for the more reactive isomers. It did not have a major effect on the products of the solvolysis of the latter compounds. Phenyl and *p*-anisyl substitution was far more effective in localizing charge and led in part to unrearranged solvolysis products. The nature of the cyclobutyl cation is considered in the light of these results.

We have previously reported on the solvolyses of bicyclo[3.1.1]heptyl-6 and bicyclo[2.1.1]hexyl-5 derivatives.[3,4] In each case the endo derivative was much more reactive (10^6–10^7) than the exo isomer and rearranged products were formed. It appeared that rearrangement occurred during the ionization step and that the high rate acceleration resulted from the driving force for rearrangement.

It seemed possible to confirm this conclusion and to obtain an estimate of the driving force for rearrangement by examining the effect of α substitution. The introduction of a charge stabilizing substituent should result in localization of charge and a decreased tendency for rearrangement. The endo/exo rate ratio should correspondingly be reduced.

The preparation of the 6-methylbicyclo[3.1.1]heptan-6-ols as well as the related 6-methylbicyclo[3.2.0]heptan-6-ols has been reported in another connection.[5] The alcohols were converted to dinitrobenzoates, and the rates of solvolysis were determined in 80% acetone. The kinetic data are summarized in Table I and the product distribution is recorded in Table II. Relative rate factors are summarized in Table III.

Methyl substitution at a secondary center usually leads to a rate increase on the order 2×10^4.[6] The k_{CH_3}/k_H ratio observed with the less reactive *exo*-bicyclo[3.1.1]heptyl-6 dinitrobenzoate (5×10^5) is larger by a factor of 10. On the other hand, the endo isomer gave a k_{CH_3}/k_H ratio of only 20. Thus, the exo compound appears normal in its behavior leading to an unrearranged classical ion in the rate-determining step. The higher than normal k_{CH_3}/k_H ratio is probably a reflection of the difficulty of forming the cyclobutyl cation in the absence of a means of stabilization. Thus, the k_{CH_3}/k_H ratio has been found to increase to 5×10^7 for the acetolysis of 7-norbornyl tosylates.[7] In the case of

(1) This investigation was supported by Public Health Grant GM-12800 from the National Institute of General Medical Sciences.
(2) Taken from part of the Ph.D. Thesis of Wan-fang Chen, 1971.
(3) K. B. Wiberg, R. A. Fenoglio, V. Z. Williams, Jr., and R. W. Ubersax, *J. Amer. Chem. Soc.*, **92**, 568 (1970).
(4) K. B. Wiberg and B. A. Hess, Jr., *J. Amer. Chem. Soc.*, **89**, 3015 (1967).
(5) K. B. Wiberg and W.-f. Chen, *J. Org. Chem.*, **37**, 3235 (1972).
(6) E. F. Cox, M. C. Caserio, M. S. Silver, and J. D. Roberts, *J. Amer. Chem. Soc.*, **83**, 2719 (1961).
(7) H. Tanida, Y. Hata, S. Ikegami, and H. Ishitobi, *J. Amer. Chem. Soc.*, **89**, 2928 (1967).

Table I. Rates of Solvolysis of α-Methyl-Substituted Derivatives in 80% Acetone

3,5-Dinitrobenzoate	T, °C	k, sec^{-1}	Internal return, %	$\Delta H^{\neq}$	$\Delta S^{\neq}$	$k_{rel}(100°)$
6-Methyl-*endo*-bicyclo[3.1.1]heptyl-6	99.67	1.75×10^{-4}	16.5	26.2	−6	960
	99.46	1.70×10^{-4}				
	78.06	$(1.85 \pm 0.01) \times 10^{-5}$				
	100.0[a]	1.80×10^{-4}				
6-Methyl-*exo*-bicyclo[3.1.1]heptyl-6	139.91	5.24×10^{-5}	16	28.6	−10	5.9
	140.09	$(5.09 \pm 0.07) \times 10^{-5}$				
	157.5	$(2.20 \pm 0.02) \times 10^{-5}$				
	100.0[a]	1.10×10^{-6}				
6-Methyl-*endo*-bicyclo[3.2.0]heptyl-6	120.2	$(2.72 \pm 0.02) \times 10^{-5}$	14	27.8	−9	20.4
	140.1	$(1.63 \pm 0.03) \times 10^{-4}$				
	100.0[a]	3.82×10^{-6}				
6-Methyl-*exo*-bicyclo[3.2.0]heptyl-6	138.7	$(2.16 \pm 0.02) \times 10^{-5}$	16	31.7	−4	1.83
	152.9	$(8.12 \pm 0.09) \times 10^{-5}$				
	100.0[a]	3.42×10^{-7}				
1-Methylcyclohexyl-1	99.95	$(1.51 \pm 0.01) \times 10^{-5}$	0	30.8	+1	81.5
	119.7	$(1.28 \pm 0.01) \times 10^{-4}$				
	100.0[a]	1.53×10^{-5}				
1-Methylcyclobutyl-1	160.0	5.78×10^{-5}	0	29.7	−10	(1.0)
	140.0	1.02×10^{-5}				
	100.0[a]	1.87×10^{-7}				
tert-Butyl	100.0	1.55×10^{-5}	0	28.3	−5	79.5
cis-1-Methylbicyclo[4.1.0]heptyl-2	85.86	5.13×10^{-4}	2	24.9	−5	1060
	75.61	$(1.78 \pm 0.02) \times 10^{-4}$				
	66.21	6.43×10^{-5}				
	100.0[a]	1.98 ± 10^{-3}				
trans-1-Methylbicyclo[4.1.0]heptyl-2	77.55	$(4.86 \pm 0.03) \times 10^{-4}$	1.5	26.0	−2	1680
	70.00	1.89×10^{-4}				
	64.95	1.18×10^{-4}				
	100.0[a]	5.01×10^{-3}				
Cyclohexyl-1	150.0	2.5×10^{-7}				
	100.0[c]	2.1×10^{-9}				
Cyclobutyl-1	150.0[b]	1.2×10^{-6}				
	100.0[c]	1.0×10^{-8}				

[a] Extrapolated values. [b] Unpublished results, T. Nakahira, this laboratory. [c] Estimated values based on $\Delta H^{\neq} \approx 30$ kcal/mol.

Table II. Products of the Solvolysis of α-Methyl-Substituted Derivatives

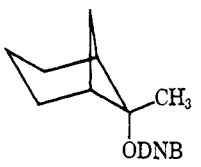
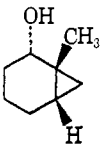
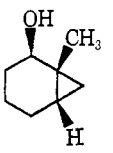
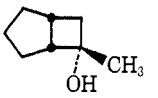
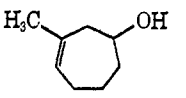
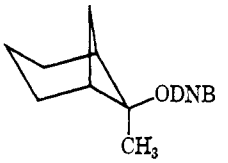
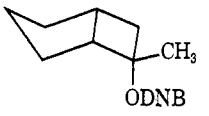
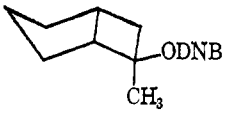
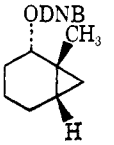
	100° 12hr	 53%	 19%	 1%	 27%	olefins
	160° 12hr	37%	12%	4%	35%	12%
	140° 12hr	46%	15%	9%	26%	4%
	160° 12hr	47%	15%	6%	23%	9%
	85° 4hr	60%	21%	2%	17%	
	85° 4hr	59%	20%	2%	20%	

Table III. Relative Rate Comparisons for Methyl Substitution

Compd	k_{CH_3}/k_H	$k/k_{cyclobutyl}$	k_{endo}/k_{exo}
endo-Bicyclo[3.1.1]-heptyl-6	20	1×10^3 (H)[4] 960 (CH_3)	4×10^6 (H) 160 (CH_3)
exo-Bicyclo[3.1.1]-heptyl-6	5×10^5	2×10^{-4} (H)[4] 6 (CH_3)	
endo-Bicyclo[3.2.0]-heptyl-6	20	20 (H)[8] 20 (CH_3)	500 (H) 11 (CH_3)
exo-Bicyclo[3.2.0]-heptyl-6	700	0.04 (H)[8] 1.8 (CH_3)	
Cyclobutyl	20[a]	(1)	
Cyclohexyl	7×10^3 [b]	5 (H) 80 (CH_3)	

[a] The k_{CH_3}/k_H ratio increases to 600 when the mesylates are solvolyzed in glacial acetic acid: unpublished results, J. Hiatt, this laboratory; *cf.* K. B. Wiberg and G. L. Nelson, *J. Amer. Chem. Soc.*, presented for publication. [b] This is a minimum value because the slow observed rate of solvolysis of cyclohexyl 3,5-dinitrobenzoate may contain a component of carbonyl–oxygen bond cleavage.

the endo compound, the driving force for rearrangement is decreased as a result of methyl substitution leading to a low methyl/hydrogen rate ratio.

The rates of solvolysis relative to the correspondingly substituted cyclobutyl and cyclohexyl derivatives are also of interest. The *endo*-bicyclo[3.1.1]heptyl-6 tosylate is 1×10^3 more reactive than cyclobutyl tosylate, and with methyl substitution the rate ratio decreases only to 960. Thus, the bicyclo[3.1.1]heptyl system and cyclobutyl both react at an accelerated rate. This can also be seen in the observation that cyclobutyl 3,5-dinitrobenzoate is five times as reactive as cyclohexyl, but 1-methylcyclobutyl 3,5-dinitrobenzoate is only 1/80 as reactive as 1-methylcyclohexyl 3,5-dinitrobenzoate.

The *exo*-bicyclo[3.1.1]heptyl-6 3,5-dinitrobenzoate is 10^4 less reactive than cyclobutyl dinitrobenzoate and 10^3 less reactive than cyclohexyl. With methyl substitution it becomes six times as reactive as methylcyclohexyl. Thus, this exo isomer appears to be a good model for an unassisted ionization of a cyclobutyl derivative. The low reactivity as compared to cyclohexyl results from the small angle at the reaction site leading to a large strain increase on going to a trigonal center.[8]

The results are in good agreement with the description of these reactions which was developed earlier.[9] Only the endo isomer has the geometry necessary for a concerted rearrangement to another ion. The exo isomer has no such path and thus ionizes to an unrearranged classical ion which then is able to react further.

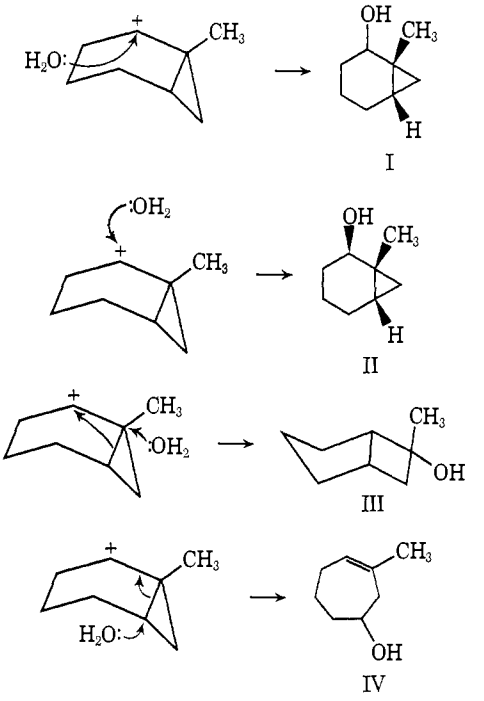
The products are also in accord with this description. Both isomers lead to rearranged products in about the same proportion. Thus, both species pass through the same ion(s) on the way to products.

The bicyclo[3.2.0]heptyl-6 dinitrobenzoates behave in the same general fashion. The endo isomer has the geometry required for a concerted rearrangement and therefore it gives a decrease in the k_{endo}/k_{exo} ratio on methyl substitution. The rate effect for α-methyl substitution is essentially the same as for *endo*-bicyclo[3.1.1]heptyl-6 and cyclobutyl derivatives, suggesting that all three behave in essentially the same fashion.

(8) H. C. Brown and G. Ham, *J. Amer. Chem. Soc.*, 78, 2735 (1956).
(9) K. B. Wiberg and J. G. Pfeiffer, *J. Amer. Chem. Soc.*, 92, 553 (1970).

The product ratio is quite similar to that obtained from the bicyclo[3.1.1]heptyl derivatives, and the 1-methylbicyclo[4.1.0]heptyl-2 dinitrobenzoates also give similar product mixtures. The simplest assumption is that the 1-methylbicyclo[4.1.0]heptyl-1 cation is formed in each of these cases and is the source of all the products (Scheme I). This would help account for

Scheme I



the observation that only one of the two isomers of III is formed. The other isomer would require attack by water from a sterically less favorable position below the ring junction. The results clearly indicate that an α-methyl group does not localize the charge sufficiently to repress rearrangement.

Further charge localization may be effected by using phenyl or *p*-anisyl as a substituent. The endo alcohols were easily prepared by the reaction of the ketones with the corresponding Grignard reagent. The alcohols were converted into 3,5-dinitrobenzoates and rates of solvolysis were determined giving the data in Table IV. The products are summarized in Table V, and Table VI gives the relative rates of reaction. The exo alcohols could not readily be prepared. However, *exo*-6-*p*-anisylbicyclo[3.2.0]heptan-6-ol was a product of the solvolysis of the *endo*-dinitrobenzoate. It could be isolated in sufficient quantity to permit conversion to the dinitrobenzoates and a study of the kinetics and products of solvolysis.

Even with a phenyl substituent, the *endo*-bicyclo[3.1.1]heptyl derivative leads only to rearranged products. Correspondingly, it gives smaller k_{Ph}/k_{CH_3} and k_{CH_3OPh}/k_{Ph} ratios than the bicyclo[3.2.0]heptyl derivatives. This must be a reflection of the relatively large strain relief in the rearrangement of a bicyclo[3.1.1]heptyl cation to a bicyclo[3.2.0]heptyl cation. The three phenyl-substituted compounds which were examined gave the same products in essentially the same ratio.

It may be noted that whereas 6-methyl-*endo*-bicyclo[3.1.1]heptyl-6 3,5-dinitrobenzoate gave only the endo

Table IV. Rates of Solvolysis of α-Phenyl and α-Anisyl Derivatives

3,5-Dinitrobenzoate	T, °C	k, sec^{-1}	Internal return, %	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	k_{rel}
6-Phenyl-*endo*-bicyclo[3.1.1]heptyl-6	87.06	$(1.55 \pm 0.03) \times 10^{-4}$	9	26.2	−4	1.58[b]
	67.66	$(1.82 \pm 0.05) \times 10^{-5}$				
	100.0[a]	5.72×10^{-4}				
6-Phenyl-*endo*-bicyclo[3.2.0]heptyl-6	101.35	$(3.22 \pm 0.03) \times 10^{-4}$	9	27.2	−2	0.76[b]
	84.05	$(5.22 \pm 0.02) \times 10^{-4}$				
	100.0[a]	2.77×10^{-4}				
1-Phenyl-*cis*-bicyclo[4.1.0]heptyl-2	101.35	$(3.25 \pm 0.02) \times 10^{-4}$	11	26.9	−3	0.8[b]
	84.05	$(5.39 \pm 0.02) \times 10^{-5}$				
	100.0[a]	2.83×10^{-4}				
1-Phenylcyclobutyl	84.7	$(7.47 \pm 0.01) \times 10^{-5}$	0	26.7	−3	(1.0)[b]
	99.95	$(3.61 \pm 0.01) \times 10^{-4}$				
	100.0[a]	3.61×10^{-4}				
1-Phenylcyclohexyl	53.6	$(9.57 \pm 0.03) \times 10^{-6}$	0	27.9	+4	6.2[b]
	67.9	$(6.05 \pm 0.03) \times 10^{-5}$				
	100.0[a]	2.27×10^{-3}				
6-Anisyl-*endo*-bicyclo[3.1.1]heptyl-6	19.89	$(2.02 \pm 0.01) \times 10^{-5}$	0	22.8	−2	0.2[c]
	35.47	$(1.54 \pm 0.01) \times 10^{-4}$				
	25.0[a]	4.08×10^{-5}				
6-Anisyl-*endo*-bicyclo[3.2.0]heptyl-6	19.95	$(4.13 \pm 0.02) \times 10^{-5}$	0	21.3	−6	0.39[c]
	34.76	$(2.53 \pm 0.01) \times 10^{-4}$				
	25.0[a]	7.86×10^{-5}				
6-Anisyl-*exo*-bicyclo[3.2.0]heptyl-6	0.00	$(3.69 \pm 0.12) \times 10^{-5}$	0	20.9	−2	5.0[c]
	14.5	$(2.71 \pm 0.03) \times 10^{-4}$				
	25.0	1.02 ± 10^{-3}				
1-Anisylcyclobutyl	5.15	$(1.19 \pm 0.01) \times 10^{-5}$	0	23.0	+2	(1.0)[c]
	25.0	$(2.04 \pm 0.03) \times 10^{-4}$				
1-Anisylcyclohexyl	0.00	$(4.74 \pm 0.14) \times 10^{-5}$	0	20.0	−5	5.6[c]
	14.5	$(3.21 \pm 0.02) \times 10^{-4}$				
	25.0[a]	1.15×10^{-3}				

[a] Calculated rate constant. [b] Based on 1-phenylcyclobutyl as 1.0, 100°. [c] Based on 1-anisylcyclobutyl as 1.0, 25°.

Table V. Products of Solvolysis of α-Aryl-Substituted Derivatives

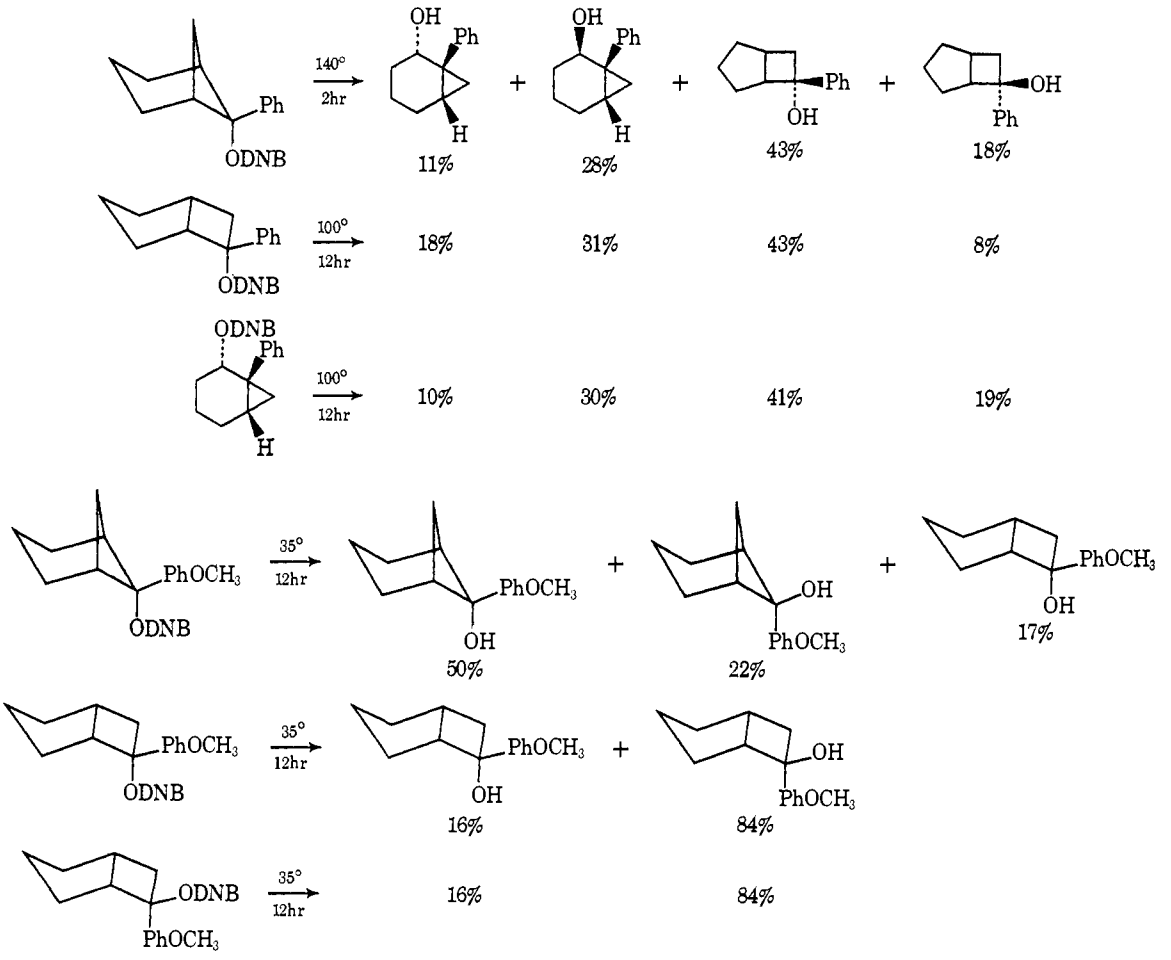


Table VI. Relative Rate Comparisons for Aryl Substitution

Compd	k_{Ph}/k_{CH_3}[a]	$k/k_{cyclobutyl}$[a]	k_{endo}/k_{exo}
6-Phenyl-*endo*-bicyclo-[3.1.1]heptyl-6	3.16	1.58	
6-Phenyl-*endo*-bicyclo-[3.2.0]heptyl-6	82.4	0.76	
1-Phenylcyclobutyl	1950	(1.00)	
1-Phenylcyclohexyl	145	6.2	
	k_{CH_3OPh}/k_{Ph}[b]	*b*	
6-Anisyl-*endo*-bicyclo-[3.1.1]heptyl-6	600	0.2	
6-Anisyl-*endo*-bicyclo-[3.2.0]heptyl-6	3000	0.39	0.05
6-Anisyl-*exo*-bicyclo-[3.2.0]heptyl-6		5.0	
1-Anisylcyclobutyl	6000	(1.00)	
1-Anisylcyclohexyl	8000	5.6	

[a] Comparison at 100°. [b] Comparison at 25°.

isomer of the 6-methylbicyclo[3.2.0]heptan-6-ol, replacement of the α-methyl by α-phenyl leads to the formation of both the exo and endo isomers of 6-phenylbicyclo[3.2.0]heptan-6-ol. The observation with the α-methyl reactant suggested that the 1-methylbicyclo[4.1.0]heptyl-1 cation was more stable than the 6-methylbicyclo[3.2.0]heptyl-6 cation. Conversely, the formation of the two bicyclo[3.2.0]heptanol products with the α-phenyl substituent suggests that the relative energies of the two types of cations are reversed. This is in accord with the greater stabilization of a cation by an α-phenyl substituent as compared to an α-methyl substituent.

The relatively high k_{Ph}/k_{CH_3} ratio found with the cyclobutyl derivative appears to be related to the change in stabilization at the cationic series as the α substituent is changed. Thus, when the substituent is H, the $k_{cyclobutyl}/k_{cyclohexyl}$ ratio is 5, and it decreases to 0.01 when the charge is localized by a methyl substituent. A phenyl substituent raises the value to 0.16, and it is unchanged on going to *p*-anisyl. The low ratio for an α-methyl group probably is close to the true value for localized cation in four- and six-membered rings. Both phenyl and anisyl lead to strong stabilization of the cationic center by π delocalization. The force constants at this center may thereby be decreased leading to a smaller difference in angle strain between the two cations.

A *p*-anisyl group does succeed in repressing the rearrangement of the bicyclo[3.1.1]heptyl cation, and for the first time, unrearranged alcohols were formed as products. Correspondingly, the bicyclo[3.1.1]heptyl-6 and bicyclo[3.2.0]heptyl-6 derivatives no longer lead to the same product mixtures.

The close similarity in α-substituent effects between cyclobutyl, *endo*-bicyclo[3.1.1]heptyl-6, and bicyclo-[3.2.0]heptyl-6 dinitrobenzoates strongly suggests that all three ionize in a similar fashion. The rate acceleration found with all three may be derived either from a stabilization of the cyclobutyl cation when the leaving group is equatorial[10] or from the driving force for rearrangement to a more stable ion. In view of the observation that the more reactive cyclobutyl derivatives always lead to rearranged products,[11] it appears that the latter possibility is the more likely one. All of the available experimental evidence suggests that a cyclobutyl cation is normally less stable than the cyclopropylcarbinyl cation which could be formed *via* its rearrangement. The cyclobutyl cation can be stabilized only when good charge delocalizing substituents are introduced at the α position.

(10) K. B. Wiberg, *Tetrahedron*, 24, 1083 (1968).

(11) *Cf.* K. B. Wiberg, B. A. Hess, Jr., and A. J. Ashe III, "Carbonium Ions," Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Interscience, New York, N. Y., 1972.

Experimental Section

6-Phenyl-*endo*-bicyclo[3.1.1]heptan-6-ol. Phenyllithium was prepared from 4.7 g (0.03 mol) of bromobenzene and 0.42 g of lithium in 60 ml of ether. A solution of 2.5 g (0.023 mol) of bicyclo[3.1.1]-heptan-6-one[4] in 5 ml of ether was added, and the mixture was treated with 15 ml of saturated ammonium chloride solution. The organic layer was washed with saturated sodium bicarbonate solution, dried over magnesium sulfate, and distilled giving 2.5 g (59%) of the alcohol, bp 139–142° (0.4–0.5 mm). It was converted to the 3,5-dinitrobenzoate, which after recrystallization from hexane had mp 145–147°.

Anal. Calcd for $C_{20}H_{18}O_6N_2$: C, 62.8; H, 4.7; N, 7.3. Found: C, 62.6, 62.7; H, 4.8, 4.8; N, 7.3, 7.2.

6-Phenyl-*endo*-bicyclo[3.2.0]heptan-6-ol. To the phenyl Grignard reagent prepared from 4.7 g of bromobenzene, 0.8 g of magnesium, and 50 ml of ether was added 3.3 g (0.03 mol) of bicyclo[3.2.0]-heptan-6-one[5] in 20 ml of ether. The reaction mixture was worked up as described above giving 3.5 g (62%) of the alcohol, bp 126–129° (0.25 mm). It was converted to the 3,5-dinitrobenzoate, which after recrystallization from hexane had mp 114–115°.

Anal. Calcd for $C_{20}H_{18}O_6N_2$: C, 62.8; H, 4.7; N, 7.3. Found: C, 62.6, 62.6; H, 4.8, 4.9; N, 7.4, 7.5.

1-Phenyl-*cis*-bicyclo[4.1.0]heptan-2-ol. To a stirred mixture of 100 ml of ether, 13.2 g of zinc–copper couple, and 0.1 g of iodine was added 58 g of methylene iodide. After the initial reaction, the mixture was stirred at reflux for 30 min. A solution of 16 g (0.092 mol) of 2-phenyl-Δ^2-cyclohexen-1-ol[12] in 40 ml of ether was added over 20 min, and stirring at reflux was continued overnight. Saturated ammonium chloride solution (60 ml) was added, and the ether solution was washed with a saturated salt solution. Distillation gave 12 g (70%) of the alcohol, bp 115° at 2.2 mm. It was converted to the 3,5-dinitrobenzoate which after recrystallization from hexane had mp 91–92°.

Anal. Calcd for $C_{20}H_{18}O_6N_2$: C, 62.8; H, 4.7; N, 7.3. Found: C, 62.6, 62.6; H, 4.8, 4.8; N, 7.3, 7.3.

6-Anisyl-*endo*-bicyclo[3.1.1]heptan-6-ol. The anisyl Grignard reagent was prepared from 1.7 g (1 mmol) of *p*-bromoanisole and 0.25 g of magnesium in 50 ml of ether. The addition of 1 g (0.9 mmol) of bicyclo[3.1.1]heptan-6-one in 20 ml of ether was followed by the usual work-up. Removal of the solvent gave 1.02 g (52%) of the crude alcohol. It was converted to the 3,5-dinitrobenzoate which after recrystallization from hexane had mp 94–95°.

Anal. Calcd for $C_{21}H_{20}O_7N_2$: C, 61.2; H, 4.9; N, 6.8. Found: C, 61.1, 61.2; H, 5.1, 5.1; N, 6.9, 7.0.

6-Anisyl-*endo*-bicyclo[3.2.0]heptan-6-ol. This alcohol was prepared as above using bicyclo[3.2.0]heptan-6-one, giving 60% of the crude alcohol. It was converted to the 3,5-dinitrobenzoate which after recrystallization from hexane had mp 91.5–92.5°.

Anal. Calcd for $C_{21}H_{20}O_7N_2$: C, 61.2; H, 4.9; N, 6.8. Found: C, 61.1, 61.0; H, 5.0, 4.9; N, 6.8, 6.9.

Product Studies. 6-Methyl-*endo*-bicyclo[3.1.1]heptyl-6 3,5-Dinitrobenzoate in 80% Aqueous Acetone. A solution of 0.71 g (2.2 mmol) of the dinitrobenzoate and 0.57 g (4.4 mmol) of ethyldiisopropylamine in 80 ml of 80% acetone was sealed in a thick-walled tube and heated at 100° for 12 hr. Most of the acetone was removed by distillation, and the remaining solution was saturated with sodium chloride and extracted with three 50-ml portions of ether. The ether solution was washed with ice-cold 10% hydrochloric acid solution, saturated sodium bicarbonate solution, and saturated salt solution. After drying over potassium carbonate, the ether was removed and the residue was bulb-to-bulb distillated under vacuum at 150°. The solid which remained was the internal return product and was identified as 3-methyl-Δ^3-cyclohepten-1 3,5-dinitrobenzoate. The distillate was analyzed by vpc using a 20 ft × 3/8 in. 20% DEGS column at 150°. The components were collected and identified by comparison of their nmr spectra with those of authentic compounds. The products were: 6-methyl-

(12) W. Treibs and M. Weissenfels, *Chem. Ber.*, 93, 1374 (1960).

endo-bicyclo[3.2.0]heptan-6-ol (1%, 27 min), 1-methyl-*cis*-bicyclo-[4.1.0]heptan-2-ol (53%, 42 min), 1-methyl-*trans*-bicyclo[4.1.0]-heptan-2-ol (19%, 46 min), 3-methyl-Δ^3-cycloheptenol (27%, 62 min).

6-Methyl-*exo*-bicyclo[3.1.1]heptyl-6 3,5-Dinitrobenzoate. A solution of 0.64 g of the dinitrobenzoate and 0.52 g of ethyldiisopropylamine in 50 ml of 80% acetone was sealed in 3.2-ml portions in 15 ampoules. After heating at 160° for 36 hr, the tubes were opened and worked up as described above. The same products were obtained as described above, but in addition, 64% of olefin was formed. When the reaction was carried out for only 12 hr, the olefin decreased to 12% and the other products were formed in 4, 37, 12, and 35%, respectively, of the volatile product.

The product studies for the other 3,5-dinitrobenzoates were carried out as described above giving the results which are tabulated in Table II.

6-Phenyl-*endo*-bicyclo[3.1.1]heptyl-6 3,5-Dinitrobenzoate. A solution of 1.34 g of the dinitrobenzoate and 0.9 g of ethyldiisopropylamine in 120 ml of 80% acetone was sealed in a tube and heated to 140° for 4 hr. Another similar sample was heated for 2 hr. The reaction mixture was worked up as described above, and the products were analyzed by vpc using a 10 ft × $^3/_8$ in. didecyl phthalate column at 150°. After 4 hr, the products were: 6-phenyl-*endo*-bicyclo[3.2.0]heptan-6-ol (19%, 11 min), 1-phenyl-*cis*-bicyclo[4.1.0]heptan-2-ol (15%, 25 min), 1-phenyl-*trans*-bicyclo[4.1.0]heptan-2-ol (38%, 28 min), and 3-phenyl-Δ^3-cycloheptenol (28%, 42 min). After 2 hr, the products were formed in 43, 11, 28, and 18%, respectively.

6-Phenyl-*endo*-bicyclo[3.2.0]heptyl-6 3,5-Dinitrobenzoate. The study was carried out as described above. After 12 hr at 100°, the above products were formed in 20, 30, 39, and 11%, respectively, whereas after 2 hr at 100° they were 43, 18, 31, and 8%.

1-Phenyl-*cis*-bicyclo[4.1.0]heptyl-2 3,5-Dinitrobenzoate. The study was carried out as described above. After 12 hr at 100° the above products were formed in 24, 18, 41, and 17%, respectively, whereas after 2 hr at 100° they were 41, 10, 30, and 19%.

6-Anisyl-*endo*-bicyclo[3.1.1]heptyl-6 3,5-Dinitrobenzoate. A solution of 1.1 g of the dinitrobenzoate and 0.6 g of ethyldiisopropylamine in 50 ml of 80% acetone was heated to 35° for 12 hr. The reaction mixture was worked up as described above and the ether was removed by distillation. The products could not be analyzed by vpc because of their relative instability. They could, however, be analyzed by nmr (100 MHz) by comparison with spectra of authentic samples. The products were found to be 6-anisyl-*endo*-bicyclo[3.1.1]heptan-6-ol (50%), 6-anisyl-*exo*-bicyclo[3.2.0]-heptan-6-ol (17%), 11% of an unknown compound, and 22% of a compound which appears to be 6-anisyl-*exo*-bicyclo[3.1.1]heptan-6-ol. The spectrum of this latter compound was similar to that of the endo isomer, and the relationship between the spectra of the two anisyl compounds was close to that between the two corresponding 6-methyl compounds.

6-Anisyl-*endo*-bicyclo[3.2.0]heptyl-6 3,5-Dinitrobenzoate. A solution of 2.2 g of the dinitrobenzoate and 1.2 g of ethyldiisopropylamine in 100 ml of 80% acetone was heated to 35° for 12 hr. After work-up as described above and removal of the solvent ether, the residue was analyzed by nmr. There were two components. 6-Anisyl-*endo*-bicyclo[3.2.0]heptan-6-ol formed 16% of the product, and the other compound (84%) appeared to be 6-anisyl-*exo*-bicyclo[3.2.0]heptan-6-ol. The spectrum of the latter was similar to that of the endo isomer, and the relationship between the spectra of the two anisyl compounds was close to that between the two corresponding 6-methyl compounds.

6-Anisyl-*exo*-bicyclo[3.2.0]heptyl-6 3,5-Dinitrobenzoate. The reaction mixture from a product run as described above (1.8 g of a mixture of 84% exo and 16% endo) was converted to the 3,5-dinitrobenzoate. This material was used for a product study and gave a mixture of 16% 6-anisyl-*endo*-bicyclo[3.2.0]heptan-6-ol and 84% 6-anisyl-*exo*-bicyclo[3.2.0]heptan-6-ol.

Kinetic Studies. Solutions of the 3,5-dinitrobenzoates were prepared in 80% (by volume) aqueous acetone. Aliquots (3.2 ml) were sealed in ampoules and were heated in a thermostatic bath. The first ampoule was withdrawn after 5–10 min and taken as the zero point. Periodically, ampoules were withdrawn, cooled in ice–water, and opened. A 3.0-ml sample was withdrawn and was titrated with standard sodium hydroxide solution using Bromthymol Blue. Infinity titres were determined after 10 half-lives. Rate constants were calculated by the method of least squares. Four runs were made for each compound, and duplicate runs usually agreed within 2%. Temperatures were either determined using a Hewlett-Packard quartz thermometer or a mercury thermometer which had been compared with the quartz thermometer.

Relative Rates. The relative rates of reaction given in Table III could not all be determined directly because of the very large range of reactivity. The rate of solvolysis of *endo*-bicyclo[2.1.1]-hexyl-5 3,5-dinitrobenzoate has been determined in 80% acetone,[3] and the ratio of the rates of solvolysis of *endo*-bicyclo[2.1.1]hexyl-5 and endo-bicyclo[3.1.1]heptyl-6 dinitrobenzoates was assumed to be the same as that observed for the tosylates.[3]

The rates of solvolysis of cyclobutyl and cyclohexyl 3,5-dinitrobenzoates were determined at 150° in 60% acetone.[13] The rates in 80% acetone were assumed to be less by a factor of 3.[14] The rates at 100° were estimated assuming $\Delta H^{\ddagger} \approx 30$ kcal/mol. The ratios of the rates of solvolysis of *exo*- and *endo*-bicyclo[3.1.1]-hexyl-6 and *exo*- and *endo*-bicyclo[3.2.0]hexyl-6 3,5-dinitrobenzoates were assumed to be equal to the ratios observed in the acetolysis of the tosylates.[3] The exo derivatives had such low reactivity that it was not practical to measure the rates of solvolysis of their dinitrobenzoates.

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(13) We thank Dr. Takayuki Nakahira for determining the rates of solvolysis.

(14) The factor of 3 is based on the difference in Y values for the two solvent mixtures (*cf.* A. Streitwieser, *Chem. Rev.*, **56**, 620 (1956).