to measure the decay rates for **8** and **10**. The values for the steady-state radical concentration and second-order decay constants are given in Table II.

Table II. Decay of Ketyl Radicals in Isopropyl Alcohol Solution

Compound	$[R_0] \times 10^6$ M	$K_t[R_0] \times 10^{-2}$ sec^{-1}	$K_t \times 10^{-8}$ M^{-1} sec^{-1}
Pyruvic acid (**6**)	6.0	11.4	1.9
Ethyl pyruvate (**7**)	4.7	14.0	3.0
p-Methoxyphenyl-glyoxylic acid (**9**)	3.1	9.9	3.2
	1.9	8.0	4.2
Ethyl phenyl-glyoxalate (**11**)	3.2	1.5	4.7
	3.1	1.1	3.5

Product studies have shown that the radicals derived from pyruvic acid, ethyl pyruvate, and ethyl phenylglyoxalate terminate almost entirely by coupling (step 4).[17-20] Although the photochemistry of **9** has not been studied, it should be similar to that of **8** which yields a radical coupling product.[16]

The observed second-order decay rates are of the same order of magnitude as those previously observed for coupling of other ketyl radicals. Representative values are given in Table III.

It can be seen that the rates of coupling for ketyl radicals which have been studied fall in the range 5×10^7 M^{-1} sec^{-1} to 5×10^8 M^{-1} sec^{-1} although the radicals are derived from monoketones, α-diketones, α-keto acids, or α-keto esters.

Table III. Representative Rates of Radical Coupling in Isopropyl Alcohol

Compound	Rate $\times 10^{-8}$ M^{-1} sec^{-1}	Ref
3,4-Dimethylbenzophenone	4.8	3
Benzophenone	1.1	3
p-Bromobenzophenone	0.50	3
Biacetyl	3.9	1
Benzil	3.3	1
Anisil	4.2	1

Acknowledgments. We wish to thank Dr. Edwin J. Hamilton, Jr., and Dr. Chin-Hua Wu for their advice and encouragement. This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, Contract No. AF 49(638)-1479.

Solvolysis of Bicyclo[4.2.0]octyl and Bicyclo[3.2.0]heptyl 1-(3,5-Dinitrobenzoates)[1]

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Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06520. *Received November 8, 1968*

Abstract: The synthesis of *trans*-fused bridgehead substituted derivatives is described, along with data regarding the carbon–carbon bond cleavage in the lithium aluminum hydride reduction of cyclobutene oxides. The rates and products of solvolysis are determined for both *cis*- and *trans*-fused derivatives. The two isomers and the corresponding spiro cyclopropylcarbinyl derivatives give the same product mixtures which contain both cyclobutanols and cyclopropylcarbinols. The details of the reactions and the possibility of hydrogen migration with the *trans*-fused compounds are discussed.

It now seems fairly clear from our work[3] and that of others[4] that the conformation of the cyclobutane ring and of its substituents is of major importance in determining the reactivity of cyclobutyl derivatives. In most cases, one has little control over the conformation of the ring. However, a 1,2 bridge has the potential for considerable conformational control.

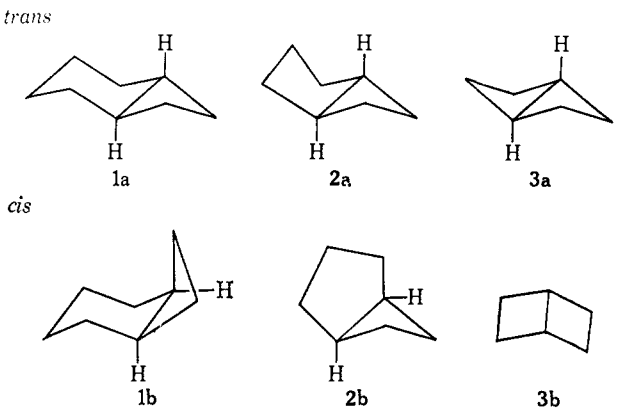
(1) This investigation was supported by Public Health Service Grant GM12800 from the National Institute of General Medical Science.

(2) Taken in part from the Ph.D. Thesis of J. E. H., 1968; NIH Predoctoral Fellow, 1965–1968.

(3) K. B. Wiberg and R. A. Fenoglio, *Tetrahedron Lett.*, 1273 (1963); K. B. Wiberg and B. A. Hess, Jr., *J. Am. Chem. Soc.*, 89, 3015 (1967).

(4) I. Lillien and R. A. Doughty, *Tetrahedron Lett.*, 3953 (1967).

Let us consider *cis* and *trans* fusion of four-, five-, and six-membered rings onto a cyclobutane ring. A cyclo-



butane ring has a dihedral angle between the two three-carbon planes of about 35°,[5] and similar angles have been found with substituted cyclobutanes,[6] including *cis*- and *trans*-1,3-disubstituted.[7] The ring puckering results from an attempt to minimize torsional strain. The equilibrium geometry gives a torsional angle of about 24°, and relieves about 35% of the torsional strain.[7]

The torsional angles for a cyclohexane ring are 56°,[8] considerably larger than that for cyclobutane. Thus, with either *cis* or *trans* fusion, the cyclohexane ring should attempt to increase the cyclobutane torsional angles, leading to smaller bond angles and a smaller cross-ring distance. The effect should be similar for both *cis* and *trans* fusion, leading to little difference in energy between **1a** and **1b**.

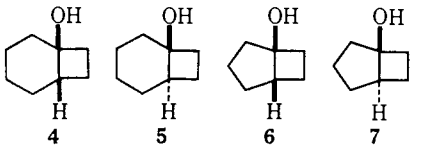
A cyclopentane ring has considerably smaller torsional angles than does cyclohexane. *cis* fusion presents no difficulty, but may lead to a somewhat flattened cyclobutane ring. On the other hand, *trans* fusion is possible only if the torsional angles of both rings are increased, resulting in increased bond angle strain. Thus, one might anticipate that *cis*-bicyclo[3.2.0]heptane (**2b**) would have a normal strain energy, and the *trans* isomer, **2a**, would have a significantly larger strain energy. Similar conclusions may be drawn about **3a** and **b**. *cis* fusion of a four-membered ring should lead to a relatively planar structure whereas *trans* fusion would require 60° torsional angles and a 70.5° internal C–C–C bond angle.

With these ideas in mind, we have begun an investigation of derivatives of **1**–**3** which are substituted in the cyclobutane ring. A number of *cis*-fused derivatives are known. However, few *trans*-fused compounds have been made. Meinwald, *et al.*,[9] have described the synthesis of **2a** having a substituent in the cyclopentane ring, and Corey, *et al.*,[10] have obtained a derivative of **3a** *via* the photochemical condensation of cyclohexenone with an ethylenic compound. In this paper we consider bridgehead substituted derivatives of **1** and **2** and in the following paper we consider compounds substituted at a cyclobutane methylene group.

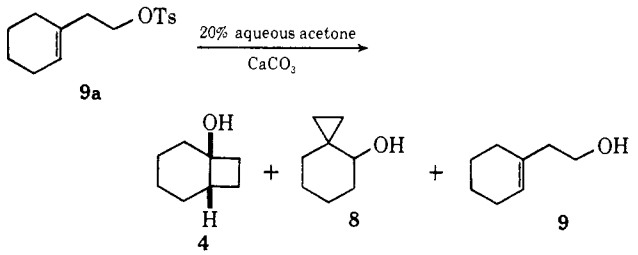
(5) P. N. Skanke, Thesis, Oslo, 1960.
(6) W. G. Rothschild and B. P. Dailey, *J. Chem. Phys.*, **36**, 2931 (1962); H. Kim and W. D. Gwinn, *ibid.*, **44**, 865 (1966); W. G. Rothschild, *ibid.*, **45**, 1214 (1966).
(7) K. B. Wiberg and G. M. Lampman, *J. Am. Chem. Soc.*, **88**, 4429 (1966); J. B. Lambert and J. D. Roberts, *ibid.*, **87**, 3884 (1965). Some *trans*-1,3-disubstituted cyclobutanes have been found to be planar in the solid state (T. N. Margulis and M. Fischer, *ibid.*, **89**, 223 (1967)), but here intermolecular hydrogen bonding is probably an important factor (*cf.* E. Adman and T. N. Margulis, *ibid.*, **90**, 4517 (1968)).
(8) R. A. Wohl, *Chimia*, **18**, 219 (1964).
(9) J. Meinwald, J. J. Tufariello, and J. J. Hurst, *J. Org. Chem.*, **29**, 2914 (1964).
(10) E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *J. Am. Chem. Soc.*, **86**, 5570 (1964).

Syntheses

The compounds of interest in the present context are



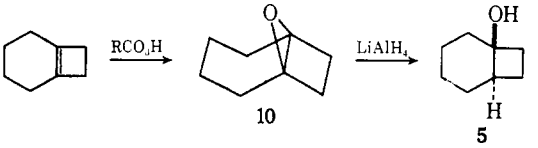
4–**7**. The preparation of **4** has been described by Hanack and Schneider.[11] They reported 65% **8** and



33% **4**. However, we found 5% **8** and 85% **4**. The difference resulted from the fact that they stirred the reaction mixture whereas we allowed it to stand unstirred. The equilibration of **4** and **8** may be effected by dilute acid, and **4** predominates. Presumably, in the absence of stirring, calcium carbonate is not sufficiently effective as a buffer to prevent equilibration.

Attempts were made to convert **4** to the tosylate. However, the reaction did not proceed at a significant rate, probably due to the steric effects in the tertiary alcohol. An attempt was made to prepare the methanesulfonate using the more reactive methanesulfonyl chloride–triethylamine mixture. However, the major product was 2-(Δ^1-cyclohexenyl)ethyl mesylate. The 3,5-dinitrobenzoate was prepared in the usual fashion and had mp 108–108.5°.

trans-Bicyclo[4.2.0]octan-1-ol, **5**, was prepared by the lithium aluminum hydride reduction of 9-oxatricyclo-[4.2.1.$0^{1,6}$]nonane (**10**). $\Delta^{1,6}$-Bicyclo[4.2.0]octene was



prepared by the method of Kirmse and Pook,[12] and was readily converted to **10** with *m*-chloroperbenzoic acid. The reduction of **10** with lithium aluminum hydride in refluxing ether proceeded very slowly, 8 days being required for complete reduction. The major product was **5** (89%) and small amounts of spiro[2.5]octan-4-ol and cyclooctanol were also found. The reaction mixture was separated into its components by preparative vpc.

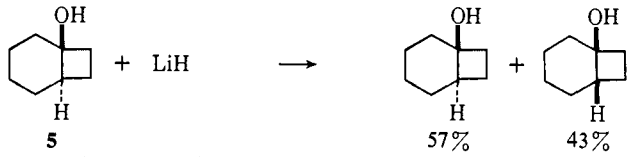
The reduction of **10** with lithium in ethylamine gave only the *cis*-isomer **4** as the product. The structure of

(11) M. Hanack and H.-J. Schneider, *Angew. Chem. Intern. Ed. Engl.*, **4**, 976 (1965); **6**, 666 (1967); *Ann.*, **686**, 8 (1965).
(12) W. Kirmse and K.-H. Pook, *Angew. Chem. Intern. Ed. Engl.*, **5**, 594 (1966).

5 is inferred from the facts that it is different from the *cis* isomer, that its nmr spectrum indicates it to be a tertiary alcohol (no bands below τ 7.5), and that lithium aluminum hydride reduction of epoxides proceeds with inversion of configuration.[13] On the other hand, lithium in ethylamine is not stereospecific[14] and probably would give the more stable isomer. Further evidence concerning the structural assignment will be given below.

When the reduction of **10** was carried out in refluxing tetrahydrofuran, a quite different product distribution was found. Here, the major product was cyclooctanol (53%), and only 33% **5** was obtained. The remainder of the product mixture contained mainly spiro[2.5]-octan-4-ol, but may also have contained some *cis*-bicyclo[4.2.0]octan-1-ol since the latter two could not be separated on the vpc column which was used.

The formation of cyclooctanol resembles the cyclobutene epoxide cleavage reactions discussed by Paquette, *et al.*[15] In order to gain further insight into the nature of the cleavage reaction, a number of experiments were performed to determine the stability of **1a** to various reaction conditions. The following reactions were carried out in refluxing 1,2-dimethoxyethane for 3 days. The isomerization observed when the



5 57% 43%

0.8 mmole 10 mmoles

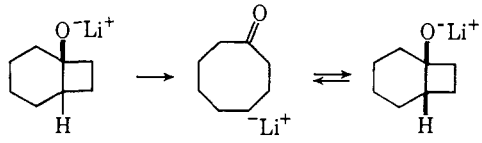
5 + LiH + $LiAlH_4$ → 100% 0%

0.4 mmole 4 mmoles 2 mmoles

5 + LiH + $Al(O\text{-}t\text{-}Bu)_3$ → 97% 3%

0.4 mmole 8 mmoles 4 mmoles

lithium salt was heated is probably due to the reaction



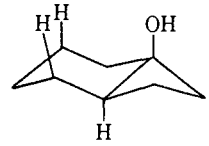
The results obtained clearly indicate that the aluminum alkoxide does not undergo this type of isomerization. In accord with the conclusions of Paquette, the carbanion formed in the cleavage of the cyclobutane ring may be captured by aluminum hydride to give a species which on further reduction and hydrolysis will give cyclooctanol. The aluminum hydride may well participate in the cleavage of the cyclobutane ring, particularly in the cases studied by Paquette where the reduction is much more rapid than in the present case.

The reaction of **5** with 3,5-dinitrobenzoyl chloride in pyridine did not proceed at room temperature (unlike the *cis* isomer); but the reaction did proceed on a steam bath giving the derivative with mp 140.2–140.8°. The unusually low reactivity of **5** probably results from the hydroxyl group being axial, and steric effects due to axial hydrogens on the cyclohexane ring.

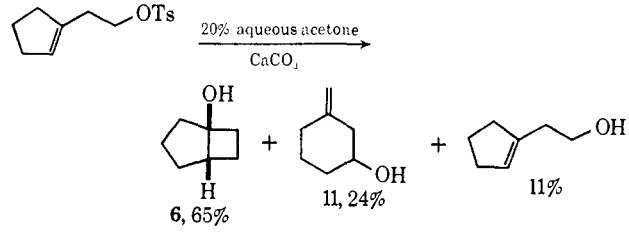
(13) A. Rosowsky in "Heterocyclic Compounds with Three- and Four-membered Rings; Part One," E. Weissburger, Ed., Interscience Publishers, New York, N. Y., 1964, pp 199–221.

(14) A. S. Hallsworth and H. B. Henbest, *J. Chem. Soc.*, 4604 (1957).

(15) L. A. Paquette, A. A. Youssef, and M. L. Wise, *J. Am. Chem. Soc.*, **89**, 5246 (1967).

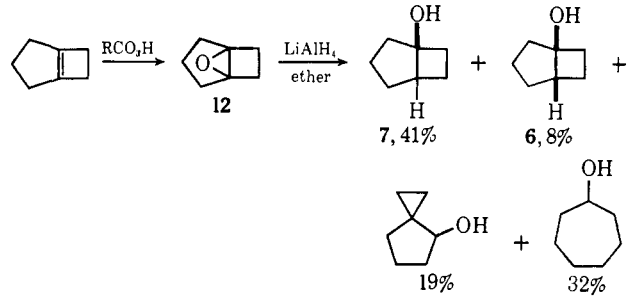


cis-Bicyclo[3.2.0]heptan-1-ol (**6**) was prepared by the same method as used for **4**.[16] The ratio of **6** to 3-



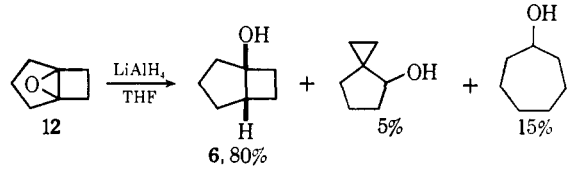
methylenecyclohexanol (**11**) is very similar to that found by Closson and Kwiatkowski[16] when they treated spiro-[2.4]heptan-4-ol with *p*-nitrobenzoic acid. The 3,5-dinitrobenzoate of **6** was prepared in the usual fashion and had mp 141–141.5°.

trans-Bicyclo[3.2.0]heptan-1-ol (**7**) was prepared in the same fashion as used for **5**. The reduction of **12**



proceeded extremely slowly in refluxing ether and required about 4 weeks to go to completion. A mixture of four products was obtained. The bicyclic alcohols could be separated from cycloheptanol by preparative vpc. The mixture of bicyclic alcohols was converted to 3,5-dinitrobenzoates, and the derivative was fractionally crystallized from hexane to give pure *trans*-bicyclo-[3.2.0]heptyl 1-(3,5-dinitrobenzoate), mp 89–90°.

Reduction of **12** with lithium aluminum hydride in refluxing tetrahydrofuran proceeded more rapidly (7 days) but gave a less favorable product distribution. Here, the *trans*-isomer **7** was not found and the *cis*-isomer **6** became the major product. The formation of



6 as the major product in tetrahydrofuran probably involves the cleavage mechanism indicated above. The larger proportion of *cis* product as compared to the reduction of **10** probably results from the increased strain energy of **12**. In this case, the cleavage reaction does not require aluminum hydride, for reaction with the latter would lead to cycloheptanol as the product rather than **6**.

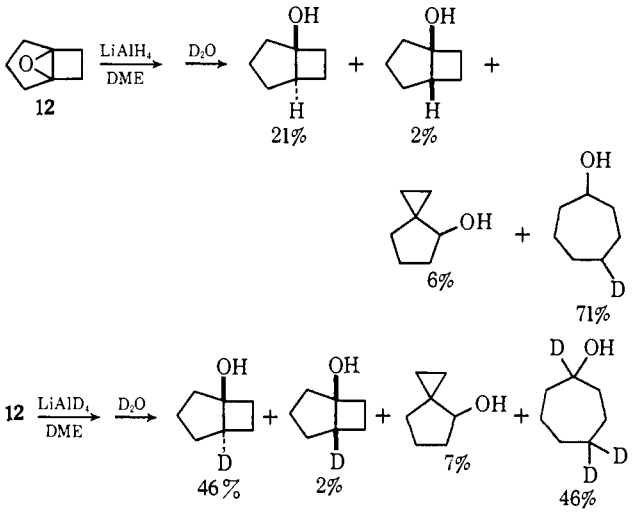
(16) W. D. Closson and G. T. Kwiatkowski, *Tetrahedron*, **21**, 2779 (1965).

Table I. Rates of Solvolysis of 3,5-Dinitrobenzoates in 80% Aqueous Acetone

3,5-Dinitrobenzoate	T, °C	k, sec^{-1}	Internal return, %	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, eu
cis-Bicyclo[4.2.0]octyl-1 (**4**)	140.0	8.35×10^{-4}	0	30.2	0
	120.0	1.22×10^{-4}			
	100.0	1.44×10^{-5} [a]			
trans-Bicyclo[4.2.0]octyl-1 (**5**)	100.0	2.40×10^{-4}	29	26.9	−3
	80.0	2.90×10^{-4}			
Spiro[2.5]octyl-4	120.0	6.23×10^{-4}	15	24.5	−11
	100.0	1.10×10^{-4}			
1-Methylcyclobutyl	160.0	5.78×10^{-5}	0	29.7	−10
	140.0	1.02×10^{-5}			
	100.0	1.95×10^{-7} [a]			
t-Butyl	140.0	6.92×10^{-4}	0	28.3	−5
	100.0	1.55×10^{-5}			

[a] Extrapolated rate constant.

The reduction also was carried out using lithium aluminum deuteride and using deuterium oxide for hydrolysis. Here dimethoxyethane was used as the solvent for it was found to give more cycloheptanol than either ether or tetrahydrofuran. The results are shown below. The formation of cycloheptanol-d_1 in the first



case and -d_3 in the second clearly indicates that a compound with a carbon–aluminum bond is the precursor of cycloheptanol. The conditions for the two reactions were not the same, and so the difference in product ratio is probably due to the difference in conditions rather than to an isotope effect. The solvent effects are not at all clear, and Paquette's[15] explanation for them cannot apply in the present case.

The structure of the epoxide **12** is interesting in itself. It appears to be one of a little studied group of compounds for which all bonds to the bridgehead carbons lie in one hemisphere (*i.e.*, on the side of a plane). These compounds, which include tricyclo[2.2.1.0^{1,4}]heptane and the corresponding smaller ring compounds, pose interesting problems in hybridization and promise to have unusually high reactivity. The properties and reactivity of **12** and of its all-carbon analog will be considered in a subsequent paper.

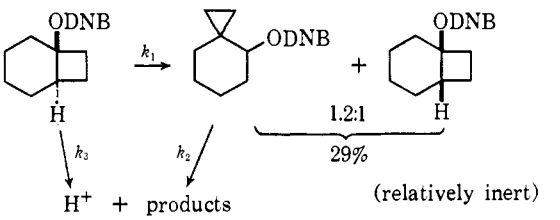
Results and Discussion

The rates of solvolysis of the 3,5-dinitrobenzoates of **4**, **5**, and spiro[2.5]octan-4-ol were determined in 80% aqueous acetone under oxygen-free conditions. The rate constants are summarized in Table I, and the relative rates of reaction are given in Table II.

Table II. Relative Rates of Solvolysis at 100°

3,5-Dinitrobenzoate	Relative rate	
cis-Bicyclo[4.2.0]octyl-1	1.00	74
trans-Bicyclo[4.2.0]octyl-1	16.7	1.23×10^{3}
Spiro[2.5]octyl-4	7.5	560
1-Methylcyclobutyl	1.35×10^{-2}	1.00
t-Butyl	1.18	80

The solvolysis of *cis*-bicyclo[4.2.0]octyl 1-(3,5-dinitrobenzoate) in 80% aqueous acetone proceeded with simple first-order kinetics. *trans*-Bicyclo[4.2.0]octyl 1-(3,5-dinitrobenzoate), however, gave two internal return products, *cis*-bicyclo[4.2.0]octyl 1-(3,5-dinitrobenzoate) and spiro[2.5]octyl 4-(3,5-dinitrobenzoate). The rates of reaction of both products were determined, and the former was found to be essentially unreactive under the reaction conditions. The process was then treated as a set of consecutive first-order reactions. Using the ex-

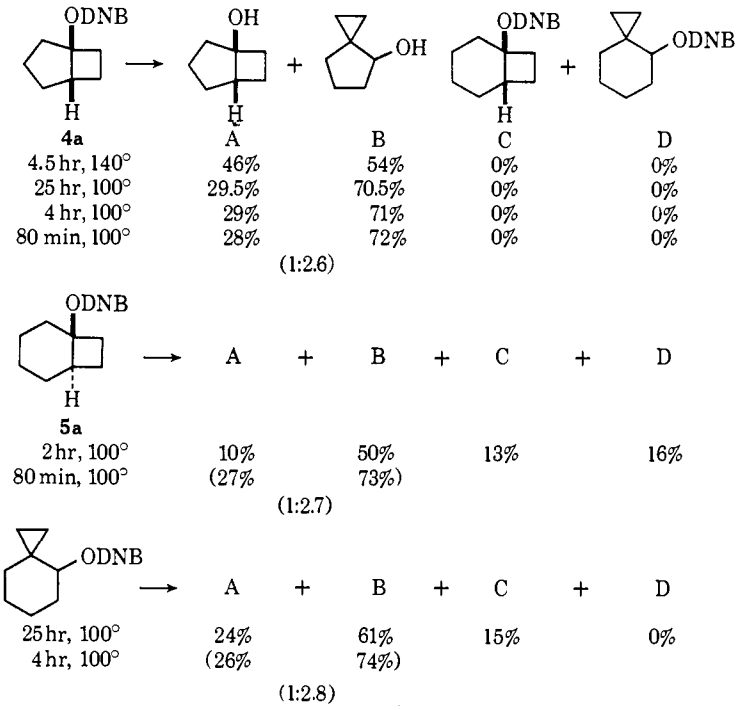


perimental value of k_2, k_1 and k_3 were obtained by fitting the experimental data for each solvolytic run. The rate constant given in Table I is the sum of k_1 and k_3, or the apparent total rate of ionization.

Spiro[2.5]octyl 4-(3,5-dinitrobenzoate) underwent solvolysis with 15% internal return to *cis*-bicyclo[4.2.0]-octyl 1-(3,5-dinitrobenzoate). The rate constants were determined as described above, and again the rate constants are the sum of k_1 and k_3.

The product studies were carried out in 80% acetone buffered with 2,6-lutidine. After work-up, the products were analyzed using vpc and nmr spectroscopy. It was found that the products underwent further slow reaction even in the presence of the buffer and therefore the product ratios were determined down to relatively small conversions. The results are shown below.

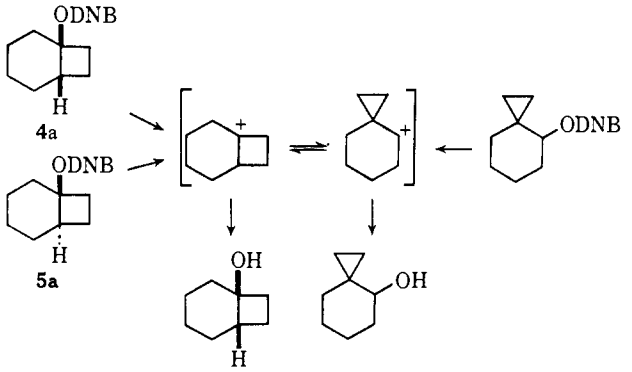
The *trans* isomer is 17 times as reactive as the *cis* isomer (Table II). If this difference is in any way a reflection of the difference in ground-state energies, we may conclude that the difference in energy may not be more than 2–3 kcal/mole. The rates of solvolysis of the



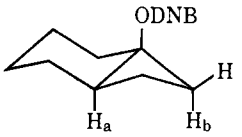
	A	B	C	D
4a				
4.5 hr, 140°	46%	54%	0%	0%
25 hr, 100°	29.5%	70.5%	0%	0%
4 hr, 100°	29%	71%	0%	0%
80 min, 100°	28%	72%	0%	0%
	(1:2.6)			
5a				
2 hr, 100°	10%	50%	13%	16%
80 min, 100°	(27%	73%)		
	(1:2.7)			
25 hr, 100°	24%	61%	15%	0%
4 hr, 100°	(26%	74%)		
	(1:2.8)			

cis isomer and spiro[2.5]octyl 4-dinitrobenzoate are in a ratio of 1:8. Since the equilibrium ratio of the two alcohols is 14:1, the rate difference is largely a reflection of the difference in ground-state energies.

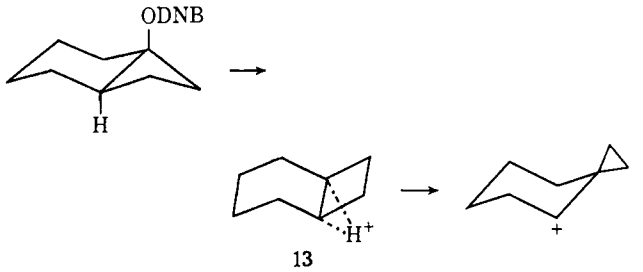
The product distribution, when determined under conditions which would minimize equilibrium of the alcohols, gave within experimental error the same ratio of alcohol products. If the products are assumed to be formed from the corresponding cations, the reactions may be described as shown. Several questions remain.



First, what is the structure of the bicyclo[4.2.0]octyl-1 cation? Is it planar or is it puckered? Second, is it possible that both products are derived from the same cation, which would probably be the spiro[2.5]octyl-4 cation? Third, if two cations are involved, which is first formed in the ionization of **5a**? If we consider its structure



it can be seen that two modes of reaction are possible. The first is simple ionization, leading to flattening at the bridgehead, giving the same ion as formed from **4a**. The second involves participation of H_a in the ionization process,[17] leading to relief of some of the strain associated with *trans*-ring fusion, and ultimately giving the spiro[2.5]octyl-4 cation. This type of hydrogen migration has been found in the reactions of other cyclobutane derivatives.[4,17] It should be possible to distinguish



among some of these possibilities by studying suitably labeled compounds, and such studies are in progress.

The rate of solvolysis of *cis*-bicyclo[4.2.0]octyl 1-(3,5-dinitrobenzoate) (**4a**) is essentially the same as that of *t*-butyl dinitrobenzoate, and it is considerably more reactive than 1-methylcyclobutyl dinitrobenzoate. The lower reactivity of the latter as compared to *t*-butyl dinitrobenzoate is expected since the four-membered ring should hinder the formation of a trigonal center.[18] The higher reactivity of **4a** is probably not due to driving force for ionization since products corresponding to **4a** are obtained in the solvolysis. One explanation may be that the cation derived from **4a** is not planar. Thus, it is possible that this cyclobutyl cation possesses special stability due to a favorable conformation for cross-ring interaction.[19]

If 1-methylcyclobutyl 3,5-dinitrobenzoate were in a puckered conformation, one of the two 1 substituents must be axial. As a result, a planar conformation may have the lower energy. The lower reactivity of the

(17) The migration of H_b does not occur, for products derived from the resulting ion are not formed (*cf.* K. B. Wiberg and J. G. Pfeiffer, *J. Am. Chem. Soc.*, **92**, 553 (1970)).
(18) H. C. Brown and M. Borkowski, *ibid.*, 74, 1849 (1952).
(19) K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968).

Table III. Rates of Solvolysis of 3,5-Dinitrobenzoate in 80% Aqueous Acetone

3,5-Dinitrobenzoate	T, °C	k, sec^{-1}	Internal return, %	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, eu
cis-Bicyclo[3.2.0]heptyl-1	140.0	8.34×10^{-5}	0	32.2	0
	120.0	1.08×10^{-5}			
	50.0	1.16×10^{-9} [a]			
trans-Bicyclo[3.2.0]heptyl-1	50.0	4.79×10^{-4}	43	23.7	−1
	30.0	3.95×10^{-5}			
Spiro[2.4]heptyl-4	100.0	5.00×10^{-4}	16	24.2	−9
	80.0	7.46×10^{-5}			
	50.0	2.78×10^{-6} [a]			
1-Methylcyclobutyl	160.0	5.77×10^{-5}	0	29.7	−10
	140.0	1.02×10^{-5}			
	50.0	3.37×10^{-10} [a]			
t-Butyl	140.0	6.92×10^{-4}	0	28.3	−5
	100.0	1.55×10^{-5}			
	50.0	3.64×10^{-8} [a]			

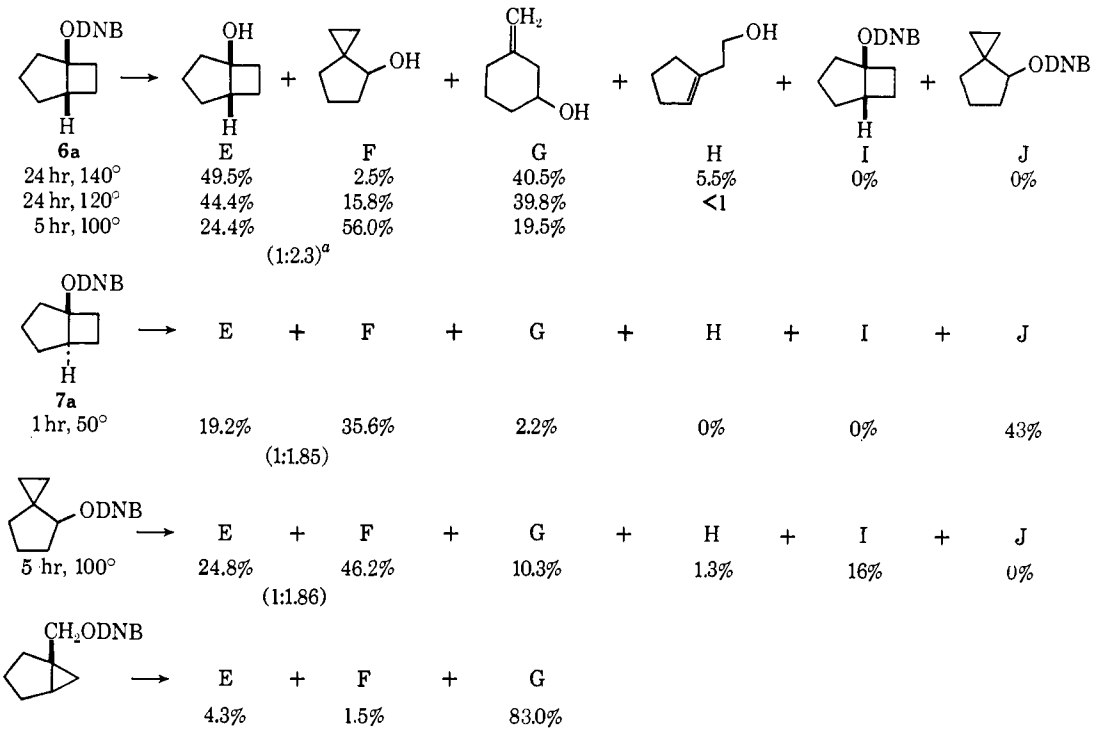
[a] Extrapolated rate constant.

Table IV. Relative Rates of Solvolysis at 50°

3,5-Dinitrobenzoate	Relative rate	
cis-Bicyclo[3.2.0]heptyl-1	1.00	3.6
trans-Bicyclo[3.2.0]heptyl-1	4.1×10^5	1.5×10^6
Spiro[2.4]heptyl-4	2.4×10^3	8.6×10^3
1-Methylcyclobutyl	0.28	1.00
t-Butyl	30	107

methylcyclobutyl derivative may result from the strain energy involved in puckering the ring sufficiently to permit a cross-ring interaction. The *cis*-bicyclo[4.2.0]-octyl-1 derivative should have a particularly favorable conformation for such an interaction since the cyclobutane ring is probably more puckered than normal.

striking change from the bicyclo[4.2.0]octane derivatives is the large difference in reactivity caused by going from *cis* to *trans* fusion. With the bicyclooctane derivatives, the ratio was 1:17, whereas with the bicycloheptane derivatives, it is $1:1.4 \times 10^5$. This appears to result from two factors. First, there is a decrease in reactivity of the *cis*-fused isomer in going to the bicycloheptanes. This is presumably a result of the increased strain in the cation resulting from the smaller ring fused to the cyclobutane ring. Second, there is an increase in reactivity by a factor of 1.2×10^3 in going to the *trans*-fused bicycloheptane which probably results from the increase in strain on going from a *trans*-fused six-membered ring to a five-membered ring. The extra strain may then be at least 5 kcal/mole.



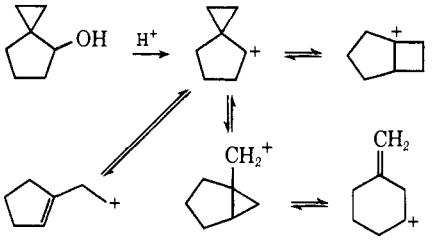
[a] This value is subject to a considerably higher uncertainty than the other values since the time corresponds to only 1/30 of a half-life and the amount of product was then quite small.

We may now turn to the bicyclo[3.2.0]heptane derivatives. The rate constants are summarized in Table III and the relative rates are found in Table IV. The most

The products of the reaction were determined in the usual fashion and were as shown.[16] The ratios of the alcohol products of the solvolysis of **6a**, **7a**, and spiro-

[2.4]heptyl 4-dinitrobenzoate are similar, suggesting that a scheme such as described for the previous group of compounds may apply here also.

The formation of 3-methylenecyclohexanol and cyclopentenylethanol probably involves further reaction of the initially formed products since the proportions decrease with decreasing reaction time. Closson and Kwiatkowski[16] found that the solvolysis of bicyclo[3.1.0]hexane-1-methyl *p*-nitrobenzoate in 60% acetone gave 83% 3-methylenecyclohexanol. They also found that treatment of spiro[2.4]heptan-4-ol with *p*-nitrobenzoic acid in 60% acetone at 100° for 2 hr produced a mixture of 63.5% *cis*-bicyclo[3.2.0]heptan-1-ol and 36.5% 3-methylenecyclohexanol which was stable and did not change with time.



Experimental Section[20]

cis-**Bicyclo[4.2.0]octan-1-ol.** Into each of five 500-ml round-bottomed long-necked flasks was placed 12 g of finely powdered calcium carbonate. Then 22 g of 2-(Δ^1-cyclohexenyl)ethyl tosylate[11] and 450 ml of a solution of 80% water and 20% acetone (by volume) was added to each flask. The flasks were sealed off and placed in a constant-temperature bath at 75°. They were shaken once every 2 days. After 14 days the flasks were removed from the thermostat, cooled to ice temperature, and opened. The combined reaction mixture was extracted with six 300-ml portions of ether. The combined ether extract was washed with 200 ml of water and 200 ml of saturated sodium chloride solution, and then dried over anhydrous potassium carbonate. The ether was removed by distillation and the residue distilled to give a semisolid distillate, bp 90–100° (10 mm). This mixture was separated into its components by preparative scale vpc on a 20 ft × $^3/_8$ in. column packed with 20% DEGS on 70/80 mesh Anachrom U. The products were identified by comparison of their spectral and physical properties with values given in the literature.[11] In order of elution, the products were spiro[2.5]octan-4-ol (5%), *cis*-bicyclo[4.2.0]octan-1-ol (85%), mp 52.5° (lit.[11] mp 51.5–52.5°), and 2-(Δ^1-cyclohexenyl)-ethanol (10%). The yield of pure *cis*-bicyclo[4.2.0]octan-1-ol was 22 g (39%).

cis-**Bicyclo[4.2.0]octyl 1-(3,5-Dinitrobenzoate).** A solution of 1.26 g (0.01 mole) of *cis*-bicyclo[4.2.0]octan-1-ol in 25 ml of dry pyridine was prepared and cooled to 0°. Then 2.30 g (0.01 mole) of 3,5-dinitrobenzoyl chloride was added and the solution allowed to stand in a refrigerator for 2 days. The reaction mixture was poured into ether, washed with ice-cold 10% hydrochloric acid until the washings were acidic, and then washed with 10% sodium carbonate solution and saturated salt solution and dried over anhydrous magnesium sulfate. The ether was removed using a rotary evaporator to give a crystalline solid which was recrystallized from hexane, mp 108–108.5°. The yield was 2.2 g (70%).

Spiro[2.5]octyl 4-(3,5-Dinitrobenzoate). The reaction of 1.10 g of spiro[2.5]octan-4-ol with 2.18 g of 3,5-dinitrobenzoyl chloride was effected as described above. The product was recrystallized twice from hexane and had mp 111–112°.

9-Oxatricyclo[4.2.1.0^{1,6}]nonane. A solution of 7.25 g (0.067 mole) of $\Delta^{1,6}$-bicyclo[4.2.0]octene[12] in 50 ml of methylene chloride was prepared in a 250-ml flask equipped with a magnetic stirrer and a pressure-equalizing addition funnel and cooled in an ice bath. A solution of 11.5 g (0.067 mole) of *m*-chloroperbenzoic acid in 150 ml of methylene chloride was then added dropwise over a period of 20 min and the solution was stirred for an additional 2 hr. The reaction mixture was washed with two 200-ml portions of saturated sodium bicarbonate solution. The sodium bicarbonate wash solution was extracted with 50 ml of methylene chloride. The methylene chloride solutions were combined and washed with 150 ml of saturated salt solution and dried over anhydrous potassium carbonate. The solvent was distilled through a 35-cm column fitted with a reflux head. The product from three separate reaction batches was combined and distilled through a 20-cm Vigreux column and the fraction with bp 70–80° (50–55 mm) was collected to give 17 g (98%) of the product which was about 90% pure according to its nmr spectrum. An analytical sample was purified by vpc on a 9 ft × $^3/_8$ in. 20% DEGS on Anachrom U column at 150° and had a retention time of 3 min.

Anal. Calcd for $C_8H_{12}O$: C, 77.4; H, 9.7. Found: C, 77.4, 77.3; H, 9.9, 9.8.

trans-**Bicyclo[4.2.0]octan-1-ol.** To a 500-ml three-necked flask equipped with a mechanical stirrer, reflux condenser with a drying tube, and an addition funnel, was added 10 g (0.26 mole) of powdered lithium aluminum hydride and 30 ml of dry ether. A solution of 12.4 g (0.10 mole) of 9-oxatricyclo[4.2.1.0^{1,6}]nonane in 25 ml of dry ether was added and the mixture heated to reflux with stirring for 8 days. The reaction was worked up by adding successively 10 ml of water, 10 g of 15% sodium hydroxide solution, and 30 ml of water. The granular precipitate was filtered and washed with ether. The ether solution was dried over anhydrous potassium carbonate and the ether removed by distillation. The residue was purified by preparative vpc using a 12 ft × 0.75 in. 20% DEGS on 50/60 mesh Anachrom U column at 160°. The products were *trans*-bicyclo[4.2.0]octan-1-ol (89.3%), spiro[2.5]octan-4-ol (9%), and cyclooctanol (1.7%). The retention times were 8, 10, and 15 min.

Spiro[2.5]octan-4-ol and cyclooctanol were identified by comparison of their nmr spectrum with those of authentic samples. *trans*-Bicyclo[4.2.0]octan-1-ol was identified by its nmr spectrum and by comparison of its melting point, 28.6–28.8°, with that of *cis*-bicyclo[4.2.0]octan-1-ol, mp 52.5°. The yield of the pure alcohol was 6.0 g (48%). Further evidence for the structural assignment may be found in the base-catalyzed rearrangement of the *trans*-alcohol to the *cis*-alcohol (see below).

The 3,5-dinitrobenzoate was prepared from 1.0 g of the alcohol and 1.90 g of 3,5-dinitrobenzoyl chloride as described above except that heating on a steam bath for 15 min was required. The crude product was recrystallized from hexane to give 1.2 g (47%) of *trans*-bicyclo[4.2.0]octyl 1-(3,5-dinitrobenzoate), mp 140.2–140.8°.

Anal. Calcd for $C_{15}H_{16}N_2O_6$: C, 56.2; H, 5.0; N, 8.4. Found: C, 56.6, 56.6; H, 5.1, 5.2; N, 8.8, 8.8.

Reduction of 9-Oxatricyclo[4.2.1.0^{1,6}]nonane with Lithium Aluminum Hydride in Tetrahydrofuran. To a 100-ml three-necked round-bottomed flask equipped with a mechanical stirrer, reflux condenser with a drying tube, and an addition funnel, was added 2.0 g (0.053 mole) of powdered lithium aluminum hydride and 30 ml of dry tetrahydrofuran. A solution of 2.0 g of 9-oxatricyclo[4.2.1.0^{1,6}]nonane in 15 ml of dry tetrahydrofuran was added and the solution warmed to 35–40° for 10 hr and then to reflux for 50 hr. The mixture was cooled and 2 g of water, 2 g of 15% sodium hydroxide solution, and 6 g of water were added. The granular precipitate was filtered and the tetrahydrofuran solution was dried over anhydrous potassium carbonate. The solvent was removed by distillation and the remaining material was separated into its components by vpc on a 9 ft × $^3/_8$ in. 20% DEGS column at 160°. The products were *trans*-bicyclo[4.2.0]octan-1-ol (83%), spiro[2.5]-octan-4-ol (14.8%), and cyclooctanol (53.2%). The retention times were 2, 2.5, and 4.2 min.

Reduction of 9-Oxatricyclo[4.2.1.0^{1,6}]nonane with Lithium in Ethylamine. Into a 25-ml three-necked round-bottomed flask equipped with a mechanical stirrer and two reflux condensers, one of which was fitted with a gas inlet tube and the other with a drying tube, was condensed about 15 ml of ethylamine. The flask was cooled in an ice bath and ice water was run through the condensers. Lithium metal (0.25 g, 0.036 g·atom) was added, the solution stirred at 0° for 30 min, and 0.40 g (32 mmoles) of 9-octatricyclo[4.2.1.0^{1,6}]-nonane in about 3 ml of ethylamine was added. The color of the reaction mixture changed from deep blue to white in about 15 min. The ethylamine was evaporated by allowing the reaction flask to warm to room temperature; 15 ml of water was added and the products were extracted with two 10-ml portions of ether. The ether solution was dried over anhydrous potassium carbonate and the ether distilled off. Vpc analysis on a 9 ft × $^3/_8$ in. 20% DEGS column at 150° showed only one product which was collected and identified as *cis*-bicyclo[4.2.0]octan-1-ol, mp 52.5°.

Treatment of *trans*-Bicyclo[4.2.0]octan-1-ol with Lithium Hydride in 1,2-Dimethoxyethane. A solution of 100 mg of *trans*-bicyclo-

(20) The nmr spectra of key compounds may be found in the Ph.D. Thesis of J. E. H.

[4.2.0]octan-1-ol in 10 ml of dry 1,2-dimethoxyethane was treated with 80 mg of lithium hydride. The mixture was heated to reflux with stirring for 3 days. The mixture was cooled, 1 ml of water was added to decompose the lithium hydride, and 20 ml of ether was added. The ether solution was washed with two 10-ml portions of water and dried over anhydrous potassium carbonate. After distilling off the ether, analysis of the residue by vpc on 30 ft × 3/8 in. 20% DEGS column at 155° showed two components: *trans*-bicyclo[4.2.0]octan-1-ol (56.5%) and *cis*-bicyclo[4.2.0]octan-1-ol (43.5%).

Treatment of *trans*-Bicyclo[4.2.0]octan-1-ol with Lithium Hydride and Aluminum *t*-Butoxide. A solution of 50 mg of *trans*-bicyclo-[4.2.0]octan-1-ol in 10 ml of dry 1,2-dimethoxyethane was prepared in a 25-ml flask and 65 mg of lithium hydride and 1.0 g of aluminum *t*-butoxide were added. The mixture was heated to reflux with stirring for 3 days. The reaction mixture was cooled, 2 ml of water and 50 ml of ether were added, and the solid material was filtered off and washed with ether. The ether solution was washed with two 25-ml portions of water and 15 ml of saturated salt solution, and dried over anhydrous potassium carbonate. The ether was distilled and the residue was analyzed by vpc on a 30 ft × 3/8 in. 20% DEGS column at 155°. The product consisted of a mixture of approximately 98% *trans*-bicyclo[4.2.0]octan-1-ol and 2% *cis*-bicyclo-[4.2.0]octan-1-ol.

Treatment of *trans*-Bicyclo[4.2.0]octan-1-ol with Lithium Hydride and Lithium Aluminum Hydride in 1,2-Dimethoxyethane. A. With More Than 1 Equiv of Lithium Aluminum Hydride. A solution of 50 mg of *trans*-bicyclo[4.2.0]octan-1-ol in 10 ml of dry 1,2-dimethoxyethane was treated with 32 mg of lithium hydride and 80 mg of lithium aluminum hydride and the mixture was heated to reflux with stirring for 3 days. The reaction mixture was cooled, diluted with 10 ml of ether, and 3 ml of water was cautiously added. The solid precipitate was filtered, washed with ether, and the ether solution washed with two 25-ml portions of water and 15 ml of saturated salt solution, and dried over anhydrous potassium carbonate. The ether was distilled and the residue analyzed by vpc on 30 × 3/8 in. 20% DEGS column. The only product was *trans*-bicyclo-[4.2.0]octan-1-ol.

B. With Less Than 1 Equiv of Lithium Aluminum Hydride. A solution of 50 mg of *trans*-bicyclo[4.2.0]octan-1-ol in 5 ml of dry 1,2-dimethoxyethane was treated with 16 mg of lithium hydride and 2 mg of lithium aluminum hydride, and the mixture was heated to reflux with stirring for 3 days. The reaction mixture was worked up as described in part A. The products were identified as *trans*-bicyclo[4.2.0]octan-ol (63.2%), spiro[2.5]octan-4-ol (trace), *cis*-bicyclo[4.2.0]octan-1-ol (30.8%), an unknown compound (6%), and a trace of cyclooctanone. No cyclooctanol could be detected.

Acid-Catalyzed Isomerization of *cis*-Bicyclo[4.2.0]octan-1-ol. A solution of 100 mg of *cis*-bicyclo[4.2.0]octan-1-ol, 20 mg of 3,5-dinitrobenzoic acid, and 5 ml of 80% aqueous acetone was prepared and divided into two equal portions, each of which was sealed into a glass ampoule and placed in a thermostat at 120°. One tube was removed from the thermostat after 48 hr and the other after 11 days. Each solution was poured into 20 ml of ether, washed with 20 ml of saturated sodium bicarbonate solution and 20 ml of saturated salt solution, and dried over anhydrous potassium carbonate. The ether was distilled and the product analyzed by vpc on a 30 ft × 3/8 in. 20% DEGS column at 155°. The products were identified by comparison of retention times with those of authentic samples by coinjection. After 48 hr the product consisted mainly of spiro[2.5]-octan-4-ol (11%), *cis*-bicyclo[4.2.0]octan-1-ol (80%), and 2-(Δ^1-cyclohexenyl)ethanol (9%). After 11 days the product mixture consisted of spiro[2.5]octan-4-ol (3.5%), *cis*-bicyclo[4.2.0]octan-1-ol (50.5%), and 2-(Δ^1-cyclohexenyl)ethanol (46%). The final ratio of spiro alcohol to bicyclic alcohol was 1:14.

Acid-Catalyzed Isomerization of Spiro[2.5]octan-4-ol. The isomerization of 100 mg of spiro[2.5]octan-4-ol in 80% aqueous acetone was carried out as described above. After 48 hr the product mixture consisted of spiro[2.5]octan-4-ol (39%), *cis*-bicyclo[4.2.0]-octan-1-ol (58%), and 2-(Δ^1-cyclohexenyl)ethanol (3%). After 9 days the product mixture consisted of spiro[2.5]octan-4-ol (6.3%), *cis*-bicyclo[4.2.0]octan-1-ol (86.5%), and 2-(Δ^1-cyclohexenyl)ethanol (7.2%). The final ratio of spiro alcohol to bicyclic alcohol was 1:14 in good agreement with the value found above.

Solvolysis of *cis*-Bicyclo[4.2.0]octyl 1-(3,5-Dinitrobenzoate) in 80% Aqueous Acetone. A solution of 1.0 g (3.12 mmoles) of *cis*-bicyclo[4.2.0]octyl 1-(3,5-dinitrobenzoate), 0.67 g (6.24 mmoles) of 2,6-lutidine, and 130 ml of 80% aqueous acetone was prepared, sealed in a tube, and placed in a thermostat at 140°. After 4.5 hr, the tube was removed from the thermostat, cooled, and opened. Most of the acetone was removed by distillation and the remaining aqueous solution was saturated with sodium chloride and extracted with three 50-ml portions of ether. The combined ether extract was washed with ice-cold 10% hydrochloric acid, saturated sodium bicarbonate solution, and saturated salt solution, and dried over anhydrous potassium carbonate. The ether was distilled off and the residue separated into its components by vpc using a 30 ft × 3/8 in. 20% DEGS column at 150°. The products were spiro[2.5]-octan-4-ol (54%), retention time 37 min, and *cis*-bicyclo[4.2.0]-octan-1-ol (46%), retention time 39 min.

Solvolysis of *trans*-Bicyclo[4.2.0]octyl 1-(3,5-Dinitrobenzoate) in 80% Aqueous Acetone. A solution of 1.05 g (3.26 mmoles) of *trans*-bicyclo[4.2.0]octyl 1-(3,5-dinitrobenzoate), 1.2 g (11 mmoles) of 2,6-lutidine, and 125 ml of 80% aqueous acetone was sealed in a tube and placed in a thermostat at 100°. After 2 hr the tube was removed from the thermostat, cooled, and opened and the contents were poured into 200 ml of water and allowed to stand overnight in order to crystallize the remaining 3,5-dinitrobenzoate ester. The solid ester was filtered off and the filtrate saturated with sodium chloride and extracted with three 50-ml portions of ether. The combined ether extract was washed with ice-cold 10% hydrochloric acid, saturated sodium bicarbonate solution, and saturated salt solution, and dried over anhydrous potassium carbonate. The ether was removed by distillation and the product composition determined by vpc as described above. The products were spiro[2.5]octan-4-ol (70.5%) and *cis*-bicyclo[4.2.0]octan-1-ol (29.5%).

The recovered 3,5-dinitrobenzoate ester (200 mg) was thoroughly dried under high vacuum to be certain that it was not contaminated with alcoholic products of the solvolysis. It was then reduced with 500 mg of lithium aluminum hydride in 25 ml of dry ether. After work-up and removal of the solvent the residue was analyzed by vpc under the conditions described above and found to consist of *trans*-bicyclo[4.2.0]octan-1-ol (43%), spiro[2.5]octan-4-ol (32.6%), and *cis*-bicyclo[4.2.0]octan-1-ol (24.4%). The ratio of spiro[2.5]-octan-4-ol to *cis*-bicyclo[4.2.0]octan-1-ol was 54.4:45.4.

Solvolysis of Spiro[2.5]octyl 4-(3,5-Dinitrobenzoate) in 80% Aqueous Acetone. A solution of 1.0 g (3.12 mmoles) of spiro[2.5]-octyl 4-(3,5-dinitrobenzoate), 0.67 g of 2,6-lutidine, and 130 ml of 80% aqueous acetone was sealed in a flask and placed in a thermostat at 100°. After 25 hr it was removed from the thermostat, cooled, opened, and most of the acetone distilled off. The aqueous solution was saturated with sodium chloride and extracted with four 50-ml portions of ether. The combined ether extract was washed with ice-cold 10% hydrochloric acid, saturated sodium bicarbonate solution, and saturated sodium chloride solution, and dried over anhydrous potassium carbonate. The ether was distilled off and the residue analyzed by vpc on a 30 ft × 3/8 in. 20% DEGS column at 150°. The products were spiro[2.5]octan-4-ol (72%) and *cis*-bicyclo[4.2.0]octan-1-ol (28%).

In a separate experiment, the solvolysis was stopped after two half-lives (5 hr) and the remaining ester recovered, thoroughly dried, and reduced with lithium aluminum hydride and the alcoholic products identified by vpc. The products were mainly spiro[2.5]-octan-4-ol with a small amount of *cis*-bicyclo[4.2.0]octan-1-ol.

***cis*-Bicyclo[3.2.0]heptan-1-ol.** To each of five 500-ml long-necked round-bottomed flasks was added 15 g of powdered calcium carbonate, 17 g of 2-(Δ^1-cyclopentyl)ethyl tosylate,[16] and 425 ml of 20% aqueous acetone (by volume). The flasks were sealed off and placed in a thermostat at 80°. After 10 days the reaction flasks were removed from the thermostat, cooled to 0°, opened, and the combined contents saturated with sodium chloride and extracted with six 150-ml portions of ether. The combined ether extract was washed twice with saturated salt solution, dried over anhydrous potassium carbonate, and the ether distilled off. The crude product was purified first by bulb-to-bulb distillation giving 22 g of crude product and then separated into its components by vpc on a 20 ft × 3/8 in. 20% DEGS column at 150°. The mixture consisted of *cis*-bicyclo[3.2.0]heptan-1-ol (65%), 3-methylenecyclohexanol (23.6%), and 2-(Δ^1-cyclopentyl)ethanol (11.4%). The retention times were 16.5, 19.7, and 26 min. The products were identified by comparison of their nmr spectra with those of authentic samples or literature descriptions. The *cis*-bicyclo[3.2.0]heptan-1-ol was also identified by its melting point, 51–52° (lit.[16] mp 47–48°). The yield of the pure alcohol was 6.2 g (12.7%) based on starting 2-(Δ^1-cyclopentenyl)ethanol.

The alcohol was converted to its 3,5-dinitrobenzoate which was recrystallized twice from a hexane–benzene mixture to give 70% recovery of *cis*-bicyclo[3.2.0]heptyl 1-(3,5-dinitrobenzoate), mp 141–141.5°.

8-Oxatricyclo[3.2.1.0^{1,5}]octane. A solution of 5.7 g (0.061 mole) of $\Delta^{1,5}$-bicyclo[3.2.0]heptene[12] in 50 ml of methylene chloride was added to a 200-ml round-bottomed flask equipped with a magnetic stirrer and an addition funnel and the flask was cooled in an ice bath. A solution of *m*-chloroperbenzoic acid (11.2 g, 0.65 mole) in 100 ml of methylene chloride was then added at a rate slow enough to keep the temperature solution below the boiling point of methylene chloride. Precipitation of *m*-chlorobenzoic acid began after about two-thirds of the peracid solution had been added. After the addition was completed, the solution was allowed to stand for 10 min and then worked up by washing with two 200-ml portions of saturated sodium bicarbonate solution. The combined sodium bicarbonate wash solution was extracted with 50 ml of methylene chloride and the methylene chloride solutions were combined and washed with saturated salt solutions. After drying over anhydrous potassium carbonate, the methylene chloride was distilled off through a 35-cm vacuum-jacketed packed column. The crude product from three epoxidations was combined and distilled through a 20-cm Vigreux column to give 13 g (65%) of 8-oxatricyclo[3.2.1.0^{1,5}]octane, bp 57–60° (44 mm). An analytical sample was purified by vpc on a 9 ft × 3/8 in. 20% DEGS column at 140°, retention time 4 min.

Anal. Calcd for $C_7H_{10}O$: C, 76.3; H, 9.2. Found: C, 76.3, 76.3; H, 9.1, 9.2.

***trans*-Bicyclo[3.2.0]heptan-1-ol.** A slurry of 6.0 g (0.154 mole) of powdered lithium aluminum hydride in 100 ml of dried ether was prepared in a 250-ml three-necked round-bottomed flask, equipped with a mechanical stirrer, reflux condenser with drying tube, and an addition funnel, and 6.0 g (0.55 mole) of 8-oxatricyclo[3.2.1.0^{1,5}]-octane in 50 ml of dry ether was added. The mixture was heated to reflux with stirring for 20 days at which time another 5 g of lithium aluminum hydride was added, and stirring at the reflux temperature continued for a further 7 days. Work-up was accomplished by adding 11 ml of water, 11 g of 15% sodium hydroxide solution, and finally 33 ml of water. The precipitate was filtered, washed with ether, and the ether solution dried over anhydrous potassium carbonate. The ether was distilled off and the residue was analyzed by vpc on 3 ft × 3/8 in. 20% DEGS column at 150°. A mixture of four products was found. Three of these products could not be effectively separated from one another by vpc on any column which was available. The fourth product which was collected and identified by comparison of its nmr spectrum with an authentic sample was cycloheptanol. The nmr spectrum of the mixture of the other three products revealed the presence of spiro-[2.4]heptan-4-ol as a minor product identified by comparison with the nmr spectrum of the authentic sample. Comparison of the vpc retention time with that of an authentic sample of *cis*-bicyclo-[3.2.0]heptan-1-ol showed that this compound was a minor component of the mixture. The major component was *trans*-bicyclo-[3.2.0]heptan-1-ol. The products of the reduction were spiro[2.4]-heptan-4-ol (19%), *trans*-bicyclo[3.2.0]heptan-1-ol (41%), *cis*-bicyclo[3.2.0]heptan-1-ol (8%), and cycloheptanol (32%).

The mixture of the three bicyclic alcohols obtained above (1.5 g, 0.0134 mole) was dissolved in 30 ml of dry pyridine, 3.7 g (0.016 mole) of 3,5-dinitrobenzoyl chloride was added, and the solution was warmed on a steam bath for 10 min. The mixture was allowed to stand overnight at room temperature. The solution was diluted with 100 ml of ether, ice was added, and the solution was washed with ice-cold 10% hydrochloric acid until the washings were acidic. The ether solution was washed with saturated sodium bicarbonate solution and saturated salt solution, and dried over anhydrous magnesium sulfate. The ether was removed with the aid of a rotary evaporator leaving a viscous oil which solidified on standing. This material was dissolved in 80 ml of hexane with enough benzene added to effect solution. The crystalline material which precipitated upon cooling was filtered and recrystallized from hexane. Two distinct types of crystals were noticeable. The first formed crystals were cubic in shape while the crystals which were formed later were fine needles. The crystalline material was filtered, taken up in boiling hexane, cooled, and seeded with the crystals of the cubic type. After 3 hr at 0° the crystals which formed (all cubic) were filtered off and dried under vacuum. The material was identified by its nmr spectrum as *trans*-bicyclo[3.2.0]heptyl 1-(3,5-dinitrobenzoate), mp 89–90°. The nmr spectrum had bands at τ −0.47–0.07 (3 H, complex multiplet characteristic of a 3,5-dinitrobenzoate), 7.43–8.35 (11 H, at least two superimposed multiplets with major peaks at 7.69 and 8.06).

Anal. Calcd for $C_{14}H_{14}O_6N_2$: C, 54.9; H, 4.6; N, 9.2. Found: C, 54.9, 55.0; H, 4.7, 4.7; N, 9.0, 9.2.

Spiro[2.4]heptyl 4-(3,5-Dinitrobenzoate). The alcohol was converted to its 3,5-dinitrobenzoate as described above. Recrystallization from hexane gave 75% spiro[2.4]heptyl 4-(3,5-dinitrobenzoate), mp 85.5–86.5°.

Solvolysis of *cis*-Bicyclo[3.2.0]heptyl 1-(3,5-Dinitrobenzoate) in 80% Aqueous Acetone. A solution of 1.0 g (3.28 mmoles) of *cis*-bicyclo[3.2.0]heptyl 1-(3,5-dinitrobenzoate), 0.70 g (6.55 mmoles) of 2,6-lutidine, and 130 ml of 80% aqueous acetone was sealed in a flask and placed in a 140° thermostat. After 24 hr the tube was removed, cooled, opened, and most of the acetone removed by distillation. The aqueous residue was saturated with sodium chloride and extracted with three 25-ml portions of ether. The combined ether extract was washed with ice-cold 10% hydrochloric acid, saturated sodium bicarbonate solution, and saturated salt solution, and dried over anhydrous potassium carbonate. The products were separated by vpc on a 30 ft × 3/8 in. 20% DEGS column at 160°. The products were spiro[2.4]heptan-4-ol (2.5%), *cis*-bicyclo[3.2.0]heptan-1-ol (49.5%), 3-methylenecyclohexanol (40.5%), an unknown product (2%), and 2-(Δ^1-cyclopentenyl)ethanol (5.5%).

Solvolysis of *trans*-Bicyclo[3.2.0]heptyl 1-(3,5-Dinitrobenzoate) in 80% Aqueous Acetone. *trans*-Bicyclo[3.2.0]heptyl 1-(3,5-dinitrobenzoate) (100 mg), 107 mg of 2,6-lutidine, and 25 ml of 80% aqueous acetone was sealed in a tube and placed in a 50° thermostat. After 1 hr the tube was removed and opened, and 50 ml of water added to precipitate the 3,5-dinitrobenzoate ester. This solution was allowed to stand overnight at room temperature to ensure complete precipitation and then filtered. The filtrate was saturated with sodium chloride and extracted with three 30-ml portions of ether. The combined ether extract was washed with 50 ml of saturated salt solution and dried over anhydrous potassium carbonate. The ether was distilled off through a 35-cm vacuum-jacketed packed column and the residue was analyzed by vpc on a 30 ft × 3/8 in. 20% DEGS column at 150°. The products were spiro[2.4]heptan-4-ol (62.5%), *cis*-bicyclo[3.2.0]heptan-4-ol (33.6%), and 3-methylenecyclohexanol (3.9%).

The precipitated 3,5-dinitrobenzoate ester was thoroughly washed with water and dried under vacuum. It was identified as spiro-[2.4]heptyl 4-(3,5-dinitrobenzoate) by comparison of its nmr spectrum with that of an authentic sample.

Solvolysis of Spiro[2.4]heptyl 4-(3,5-Dinitrobenzoate) in 80% Aqueous Acetone. To a 200-ml long-necked round-bottomed flask was added 1.00 g (3.28 mmoles) of spiro[2.4]heptyl 4-(3,5-dinitrobenzoate), 0.70 g (6.55 mmoles) of 2,6-lutidine, and 100 ml of 80% aqueous acetone. The flask was sealed and placed in a 100° thermostat for 5 hr, removed, cooled, and opened and most of the acetone distilled off. The aqueous residue was placed in a refrigerator overnight and the solid precipitate which formed was filtered off. The filtrate was saturated with sodium chloride and extracted with four 40-ml portions of ether. The combined ether extract was washed with ice-cold 10% hydrochloric acid, saturated sodium bicarbonate solution, and saturated salt solution, and dried over anhydrous potassium carbonate. The ether was distilled off and the residue analyzed by vpc. The products were spiro[2.4]heptan-4-ol (55%), *cis*-bicyclo[3.2.0]heptan-1-ol (29.8%), 3-methylenecyclohexanol (12.4%), an unknown product (1.3%), and 2-(Δ^1-cyclopentenyl)ethanol (1.6%).

The recovered 3,5-dinitrobenzoate ester was recrystallized from a hexane–benzene mixture, mp 139–140°. Its nmr spectrum was identical with that of an authentic sample of *cis*-bicyclo[3.2.0]-heptyl 1-(3,5-dinitrobenzoate), mp 141–141.5°.

The Reduction of 8-Oxatricyclo[3.2.1.0^{1,5}]octane with Lithium Aluminum Hydride in Tetrahydrofuran. To a slurry of 2.0 g (0.053 mole) of lithium aluminum hydride in 50 ml of dry tetrahydrofuran was added 2.0 g (0.018 mole) of 8-oxatricyclo[3.2.1.0^{1,5}]octane in 25 ml of dry tetrahydrofuran. The mixture was heated to reflux with stirring for 7 days, then 2.0 g of water, 2.0 g of 15% sodium hydroxide solution, and 6.0 g of water were added. The granular precipitate was removed by filtration and the tetrahydrofuran solution was dried over anhydrous potassium carbonate. The solvent was distilled and the residue analyzed by vpc on a 30 ft × 3/8 in. 20% DEGS column at 150°. The products were spiro[2.4]heptan-4-ol (5%), *cis*-bicyclo[3.2.0]heptan-1-ol (80%), mp 51–52°, and cycloheptanol (15%). There was no detectable quantity of *trans*-bicyclo[3.2.0]heptan-1-ol.

Reduction of 8-Oxatricyclo[3.2.1.0^{1,5}]octane with Lithium Aluminum Hydride and 1,2-Dimethoxyethane. To a slurry of 2.5 g (0.066 mole) of lithium aluminum hydride and 50 ml of dry 1,2-dimethoxyethane was added a solution of 2.5 g (0.023 mole) of 8-oxytricyclo[3.2.1.0^{1,5}]octane in 20 ml of dry 1,2-dimethoxyethane. The mixture was heated to reflux with stirring for 4 days. The

mixture was cooled, 12 g of deuterium oxide added dropwise, the solid precipitate removed by filtration, and 100 ml of ether added to the filtrate. The ethereal solution was washed with two 100-ml portions of water and 100 ml of saturated salt solution, and dried over anhydrous potassium carbonate. The solvent was removed by distillation and the residue separated into two fractions by preparative scale vpc using a 9 ft × 3/8 in. 20% DEGS column at 150°. The nmr spectrum of the two fractions indicated that the first (29% of the mixture) was actually a mixture of compounds, while the second (71%) was pure cycloheptanol. The first vpc fraction showed a parent peak with *m/e* 112 in its mass spectrum which corresponds to a molecular formula of $C_7H_{12}O$. The mass spectrum of the second fraction (cycloheptanol) showed a parent peak with *m/e* 115 which corresponds to a molecular formula of $C_7H_{13}DO$. Analysis on a 30 ft × 3/8 in. 20% DEGS column at 150° indicated the presence of the following: spiro[2.4]heptan-4-ol (6.1%), *trans*-bicyclo[3.2.0]heptan-1-ol (20.8%), *cis*-bicyclo[3.2.0]heptan-1-ol (1.8%), and cycloheptanol (71.3%).

Reduction of 8-Oxatricyclo[3.2.1.0^{1,5}]octane with Lithium Aluminum Deuteride in 1,2-Dimethoxyethane. The reaction was carried out as described above using 1.13 g (27.2 mmoles) of lithium aluminum deuteride and 3.0 g (27.2 mmoles) of 8-oxatricyclo[3.2.1.0^{1,5}]octane. Deuterium oxide was used to decompose the excess lithium aluminum deuteride. Vpc analysis on a 30 ft × 3/8 in. 20% DEGS column showed the products to be spiro[2.4]heptan-4-ol (6.7%), *trans*-bicyclo[3.2.0]heptan-1-ol (45.5%), *cis*-bicyclo[3.2.0]heptan-1-ol (2.1%), and cycloheptanol (45.6%). The material was separated into a mixture of bicyclic components and cycloheptanol by preparative vpc. The mass spectrum of the first fraction containing the bicyclic compounds showed a parent peak *m/e* 113 which corresponds to a molecular formula of $C_7H_{11}DO$. The second component (cycloheptanol) had a parent peak with *m/e* 117, which corresponds to a molecular formula of $C_7H_{11}D_3O$.

Kinetic Method. Acetone was purified by distillation from potassium permanganate and degassed by boiling for several minutes. Distilled water was degassed in the same manner. The solvents and solutions were handled in an oxygen-free drybox in order to minimize oxidation of the solvent which occurs at higher temperatures. In all cases, the solvent was 80% (by volume) acetone.

In each case, 50 ml of a 0.01100 *M* solution of the 3,5-dinitrobenzoate was prepared, and 3.2-ml portions were sealed into ampoules. A set of ampoules was immersed in an oil bath at the appropriate temperature. After allowing 5–10 min for temperature equilibration, the zero point was taken. The ampoules were removed from the bath and plunged into ice–water to stop the solvolyses. After warming to room temperature, a 3.00-ml portion of the solution was removed and titrated with 0.0100 *M* sodium hydroxide solution to a brom thymol blue end point. Infinity titers were determined after 10 half-lives.

When the internal return products (if any) were unreactive, the rate constants were determined from

$$\ln (V - V_\infty) = -kt + b$$

and the slope was evaluated by the method of least squares. The rate constants thus obtained correspond to the sum of the rates of solvolysis and internal return. When the internal return product was reactive, its rate constant was determined, and the values of k_1 and k_3 (solvolysis and internal return) were obtained by minimizing the deviation between observed and calculated titers using a computer.

Solvolysis of *cis*- and *trans*-Fused Bicyclo[4.2.0]octyl 7-Tosylates[1]

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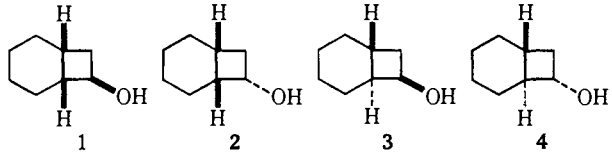
Abstract: The synthesis of *trans*-fused bicyclo[4.2.0]octyl-7 derivatives is described. The solvolytic reactions of both *cis*- and *trans*-fused tosylates have been studied. It is concluded that a disrotatory cyclobutane ring opening is involved in those cases in which rate acceleration is found, and that the process proceeds so that maximum orbital overlap is maintained. The application of this type of process to the present data and to other data is considered. Evidence also is presented indicating that the symmetrical and unsymmetrical cyclopropylcarbinyl cations have only a small difference in energy.

In a continuation of our work on *trans*-fused bicyclic cyclobutane derivatives, we have examined the reactions of derivatives of compounds **1–4**. A *cis* ring fusion, as in **1** and **2**, leads to a flexible molecule since one bond from the attached ring must occupy an axial position and the other an equatorial position. Thus, a substituent in the 7 position may occupy an equatorial position in either **1** or **2**. On the other hand, a *trans* ring fusion leads to a rigid system in which a 7 substituent is forced to occupy either an axial or an equatorial position.



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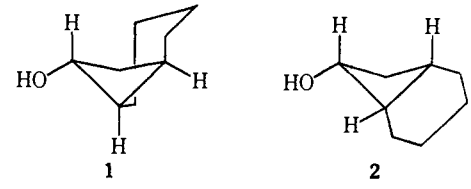

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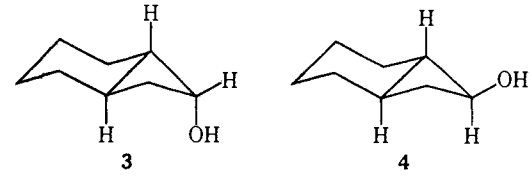

3 4

It was hoped that the variety of structural features found with **1–4** would permit a more detailed examination of the question of the nature of the species formed

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(2) Taken in part from the Ph.D. Thesis of J. G. P., 1968; NIH predoctoral fellow, 1965–1968.