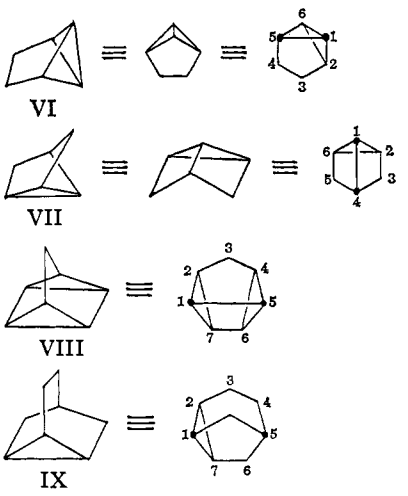
Chart V



Structure	IUPAC name	Name to be replaced
VI	tricyclo[3.1.0.0^{2,6}]hexane	tricyclo[2.1.1.0^{5,6}]-hexane[35-39]
VII	tricyclo[2.2.0.0^{2,6}]hexane[40]	tricyclo[2.1.1.0^{2,5}]-hexane[41]
VIII	tetracyclo[3.2.0.0^{2,7}.0^{4,6}]-heptane	quadricyclo[2.2.1.0^{2,6}.0^{3,5}]-heptane[42,43]
IX	tricyclo[3.2.1.0^{2,7}]octane[44]	tricyclo[2.2.2.0^{2,6}]octane[45]

It is to be hoped that the IUPAC and "Ring Index" suggestions, which are both unambiguous and easy to follow, will be used more uniformly in the future.

(36) J. Meinwald, C. Swithenbank, and A. Lewis, *J. Am. Chem. Soc.*, **85**, 1880 (1963).
(37) A. Small, *ibid.*, **86**, 2091 (1964).
(38) S. Masamune and N. T. Castelluci, *Proc. Chem. Soc.*, 298 (1964).
(39) H. G. Viehe, R. Merényi, J. F. M. Oth, J. R. Senders, and P. Valange, *Angew. Chem. Intern. Ed. Engl.*, **3**, 755 (1964).
(40) D. M. Lemal and K. S. Shim, *J. Am. Chem. Soc.*, **86**, 1550 (1964).
(41) J. Meinwald, 18th National Organic Chemistry Symposium, Columbus, Ohio, June 16–20, 1963, Abstracts, p 37; J. K. Crandall, doctoral dissertation submitted to Cornell University, 1963.
(42) S. J. Cristol and R. L. Snell, *J. Am. Chem. Soc.*, **80**, 1950 (1958).
(43) G. S. Hammond, P. Wyatt, C. D. DeBoer, and N. J. Turro, *ibid.*, **86**, 2532 (1964).
(44) W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963).
(45) C. A. Grob and J. Hostynek, *Helv. Chim. Acta*, **46**, 1676 (1963).

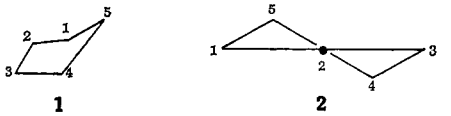
Fused Small-Ring Compounds. II. Solvolysis Reactions of Some *cis*- and *trans*-Bicyclo[3.2.0]heptane Derivatives[1,2]

Jerrold Meinwald, Paul Anderson,[3] and Joseph J. Tufariello[4]

Contribution from the Department of Chemistry, Cornell University, Ithaca, New York. *Received October 1, 1965*

Abstract: The *p*-toluenesulfonate esters of the *exo* and *endo* isomers of *cis*-bicyclo[3.2.0]heptan-3-ol, *cis*-bicyclo[3.2.0]hept-6-en-3-ol, and of *trans*-bicyclo[3.2.0]heptan-3-ol have been prepared and subjected to acetolysis at 75°. All five esters gave chiefly unrearranged products; the *cis* esters yielded acetates with predominant inversion at C_3. The bicyclic esters were generally less reactive than cyclopentyl *p*-toluenesulfonate by relatively small factors. *trans*-Bicyclo[3.2.0]heptan-3-ol *p*-toluenesulfonate proved to be the least reactive compound in this series, solvolyzing at a rate less than 2×10^{-2} times that of cyclopentyl *p*-toluenesulfonate. These results show what range of solvolysis reaction rate effects may be expected for rather extreme changes in cyclopentane conformations.

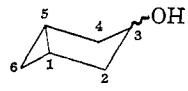
The contributions of conformational reasoning to the analysis of the chemistry of six-membered rings have been impressive.[5] Although a valuable start has also been made in the analogous analysis of five-membered rings, the impact of this reasoning has been relatively small to date, in part because of the great conformational mobility of simple cyclopentyl systems.[6] Two important conformations for the cyclopentane ring have come to be known as the *envelope* form (**1**) and the *half-chair* form (**2**).[7] In the first of these, four carbon atoms are coplanar (1, 2, 3, and 4 in formula **1**), with the fifth somewhat out of plane. In the second, only three carbon atoms are coplanar (1, 2, and 3 in formula **2**), and the remaining two are above and below this plane. Whereas it is difficult to specify the conformations of simply substituted cyclopentanes, because of the mobility characteristic of the five-membered ring, the fusion of a cyclopentane to a less flexible ring should serve to fix the geometry of the over-all system more firmly, thus providing an opportunity to examine the properties associated with specific cyclopentyl conformations.



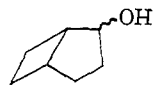
The chemistry of a number of compounds of this general type (*i.e.*, a cyclopentane fused to a smaller ring) has already been studied. Outstanding examples are provided by the work of Winstein and his coworkers, who have investigated the reactions of the *exo*

(1) The partial support of this work by a research grant (GM 10090) provided by the National Institutes of Health is acknowledged with pleasure.
(2) For the initial publication in this series, see J. Meinwald, J. J. Tufariello, and J. J. Hursi, *J. Org. Chem.*, **29**, 2914 (1964).
(3) National Institutes of Health Postdoctoral Fellow, 1963–1964.
(4) National Institutes of Health Postdoctoral Fellow, 1962–1963.
(5) For an excellent recent summary, see E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.
(6) See ref 5, pp 248–252.
(7) F. V. Brutcher, T. Roberts, S. J. Barr, and N. Pearson, *J. Am. Chem. Soc.*, **81**, 4915 (1959).

and *endo* arenesulfonates of the *cis*-bicyclo[3.1.0]hexan-3-ols (**3**)[8] and *cis*-bicyclo[3.2.0]heptan-2-ols (**4**).[9] These compounds are of special interest in connection with the possibility of anchimerically assisted ionizations.



3

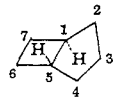


4

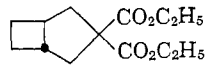
Thus, the *endo* sulfonate ester of **3** suffers solvolysis with complete retention of configuration, and shows redistribution of an appropriately placed deuterium label in accord with expectations based on delocalization of the electrons in the C_1–C_5 bond during ionization.

An *exo*/*endo* reactivity ratio of about 100 in the case of the acetolysis of the *p*-bromobenzenesulfonate ester of **4** again suggests neighboring group participation for the *exo*-oriented cyclobutylcarbinyl system of **4**. From acetolysis of this *exo* ester the only unrearranged acetate has the *exo* configuration, and extensive rearrangement to 7-norbornyl products is observed, once more in accord with carbon participation in the ionization. It was our purpose in the present study to examine molecules in which chiefly *steric* factors could be expected to control reactivity, and in which electronic effects such as those which seem to be important in the reactions of compounds derived from **3** and **4** might be minimal.

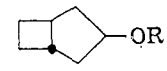
From a consideration of Dreiding molecular models, the *trans*-bicyclo[3.2.0]hexane nucleus (**5**) would appear to be an interesting one, since *trans* joining of the four- and five-membered rings seems to require a severe distortion of both rings, and should hold the cyclopentane ring in an extreme "half-chair" conformation. Thus, if an attempt is made to construct a Dreiding model of **5**,



5



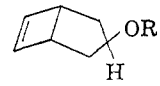
6



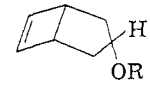
7

a; R = H
b; R = $SO_2C_7H_7$

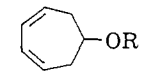
leaving the closing of the C_2–C_3 bond to last, the distance between C_2 and C_3 is found to be about twice that of a normal carbon–carbon single bond, even in the best possible conformation for cyclization. That the models are misleading is apparent from the recent successful synthesis of a representative of this ring system (**6**) in better than 60% yield *via* a classical technique in which it is exactly such a bond which is made last.[2,10] Our recent synthesis of *trans*-bicyclo[3.2.0]heptan-3-ol (**7a**) *via* **6** was carried out to permit a solvolytic study of the corresponding *p*-toluenesulfonate ester (**7b**). In **7b**, no unusual electronic effects are to be expected, and we hoped to see what, if any, effect the enforced extreme half-chair conformation would have on the reactivity of the tosyloxy substituent. To provide a frame of reference, it seemed desirable to obtain comparison data for the closely related *cis*-bicyclo[3.2.0]heptan-3-ol derivatives, which also suffer restriction of the cyclopentane ring (now in the envelope form) as a result of fusion to a cyclobutane ring, but which are conformationally more mobile than their *trans* isomers. The *exo* and *endo* isomers of bicyclo[3.2.0]hept-6-en-3-ol (**8a** and **9a**) have been characterized,[11] and the *endo* isomer (**9a**) is readily obtained pure by chromatography of the mixture produced by photocyclization of cyclohepta-3,5-dien-1-ol (**10a**).



8a, R = H
8b, R = Tos

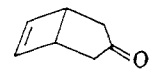


9a, R = H
9b, R = Tos

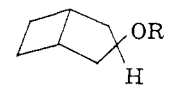


10a, R = H
10b, R = Ac

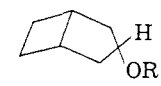
Since the *exo*/*endo* ratio in this cyclization is only 1:4, the *exo* isomer was prepared by oxidizing the mixture of stereoisomers to the ketone **11**, which then gave chiefly the desired epimer upon reduction with sodium and ethanol. (The hypothesis that the preferential formation of **9a** from **10a** might be due to internal hydrogen bonding in the starting material proved to be unfounded, since irradiation of the corresponding acetate (**10b**) again gave a 4:1 *endo*/*exo* product preference.)



11

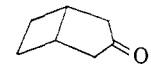


12a, R = H
12b, R = Tos



13a, R = H
13b, R = Tos

Catalytic hydrogenation of **8a** and **9a** gave the desired saturated alcohols **12a** and **13a** in pure form. Alternatively, these alcohols could be obtained by hydrogenation of a mixture of the unsaturated epimers, followed by column chromatography. The structures of these *cis*-bicyclo[3.2.0]heptan-3-ols were confirmed by chromic acid oxidation of both epimers to give *cis*-biyclo-[3.2.0]heptan-3-one (**14**), identical with an authentic sample.[12]



14

All four of the *cis*-fused alcohols (**8a**, **9a**, **12a**, and **13a**) were converted readily into crystalline *p*-toluenesulfonate esters (**8b**, **9b**, **12b**, **13b**) by treatment with *p*-toluenesulfonyl chloride in pyridine. The single *p*-toluenesulfonate ester in the *trans* series (**7b**) proved to be an oil. However, all five of the esters were characterized by infrared and nmr spectra, as well as by elemental analysis.

These five esters all were subjected to acetolysis at 75° in 100% acetic acid buffered with sodium acetate.[13] The products appeared to be chiefly acetates, and were examined gas chromatographically both as acetates and as the corresponding alcohols, following a preliminary reductive cleavage with lithium aluminum hydride.

(8) S. Winstein and J. Sonnenberg, *J. Am. Chem. Soc.*, **83**, 3235 (1961); **83**, 3244 (1961); *cf.* E. J. Corey and R. L. Dawson, *ibid.*, **85**, 1782 (1963).

(9) S. Winstein, F. Gadient, E. T. Stafford, and P. E. Klinedinst, Jr., *ibid.*, **80**, 5895 (1958). Although these workers refer to their compounds as "*cis*" and "*trans*," these prefixes were employed to designate simply the stereochemistry of the 2-substituent (in place of using *endo* and *exo*). In reality, all of their compounds are *cis* fused.

(10) N. L. Allinger, M. Nakazaki, and V. Zalkow, *ibid.*, **81**, 4074 (1959).

(11) O. L. Chapman, D. J. Pasto, G. W. Borden, and A. A. Griswold, *ibid.*, **84**, 1220 (1962).

(12) We are indebted to Dr. R. Srinivasan for providing an authentic sample of **14**.

(13) S. Winstein, E. Grunwald, and L. Ingraham, *J. Am. Chem. Soc.*, 70, 821 (1948).

For **8b**, in which the possibility of π-electron involvement either *during* or *after* the ionization step needed to be taken into account, no evidence for such participation could be obtained from the products isolated. Thus, this *exo* ester gave chiefly a mixture of unrearranged *endo* and *exo* acetates with the *endo* (inverted) acetate predominating. Double-bond participation should have resulted either in the formation of some tricyclic product, or in a preference for retention rather than inversion of configuration at C_3.

The pattern set by **8b** was followed by **9b**, **12b**, and **13b**, all of which retained their carbon skeletons unrearranged, but showed predominant inversion of configuration at C_3. In the case of **7b**, where *exo* and *endo* forms do not exist, simply unrearranged acetate was isolated. These results, summarized in Table I, in which neither structural nor configurational anomalies appear, are in harmony with the assumption that the behavior of these cyclopentane derivatives would not be complicated by electronic factors.

Table I. Rates and Products from Acetolyses at 75°

p-Toluenesulfonate	Rate const, sec^{-1}	Rate rel to cyclopentyl system	Acetate composition % *endo*	% *exo*
Cyclopentyl	5.41×10^{-4}	1.00	...	...
exo-Bicyclo[3.1.0]-hex-3-yl	5.1×10^{-5}	0.094	100	...
endo-Bicyclo[3.1.0]-hex-3-yl	6.9×10^{-4}	1.28	98	...
7b	9.76×10^{-6}	0.018	...	...
8b	1.26×10^{-5}	0.023	83	17
9b	2.60×10^{-5}	0.048	9	91
12b	9.50×10^{-5}	0.18	94	6
13b	1.50×10^{-4}	0.28	7	93
trans-Bicyclo[3.3.0]-oct-3-yl	4.81×10^{-5}	0.089	...	...

The kinetic data presented in Table I give additional support for this view. A number of comparisons are of interest. Thus, for the unsaturated compounds, the relative reactivity of the *exo* and *endo* esters (k_1(**8b**)/k_1(**9b**)) is only about 0.5, clearly showing the lack of anchimeric assistance for the *exo* case. It is also noteworthy that the double bond brings about a roughly sixfold *deceleration* in solvolysis rate (comparing with the *cis*, saturated compounds **12b** and **13b**) probably attributable to the inductive effect of the unsaturation. Again, in the *cis*, saturated series, the *exo* isomer is less reactive than its *endo* epimer (k_1(**12b**)/k_1(**13b**) = 0.67). This slightly greater reactivity for the *endo* isomers may be a reflection of a small relief of nonbonded interactions upon ionization, or of greater ease of solvation at the back of the reactive center (C_3) in these *endo* stereoisomers.

The reactivity of the *trans* ester (**7b**) compared to that of the parent cyclopentyl derivative is lower by a factor of *ca.* 55. Since there is no reason to anticipate electronic effects of any importance, it is tempting to rationalize this fairly marked retardation on the basis of a steric effect. One possibility might be that the C–C–C angle at C_3 of **7b** is smaller than the corresponding angle in the parent cyclopentane, discouraging the development of the trigonal carbon at C_3 necessary in the transition state for the solvolysis.[14] Examination of the relevant carbonyl stretching frequencies in the infrared spectra of the corresponding ketones,[14,15] however, fails to reveal a significant difference. Another factor which would act in the right direction can be derived from the unique conformation of **7b**. It has already been pointed out that this compound should exist with its five-membered ring in an extreme half-chair form. In this conformation, the nonbonded repulsion between the departing tosyloxy group and its neighboring hydrogen atoms at C_2 and C_4 (or the "torsional strain") should be significantly less than the torsional strain in the more nearly planar cyclopentane itself. This contrast would serve to enhance the reactivity of the parent system relative to **7b**,[14] and might account for the observed results.

In summary, it has been observed that the fusion of a four-membered ring to a cyclopentane nucleus, in either a *cis* or *trans* arrangement, lowers the reactivity of a substituent at C_3 for carbonium ion reactions. In the case of the *trans*-fused ring system, the solvolysis rate is depressed by a factor of about 55. This lowering in rate may be attributed to the removal of a considerable amount of Pitzer strain in this fused system compared to that in simple cyclopentyl derivatives, thus lowering the driving force for ionization. It is possible, however, that other factors which have not yet been considered also play a role in bringing about the observed rate lowering.[16] It is interesting to note that the restriction of the cyclopentyl nucleus to *either* the envelope conformation (in the *cis* compounds studied) *or* to the half-chair conformation (in the *trans* system) causes the resulting compounds to show a lower solvolytic reactivity than that of the unencumbered cyclopentyl system.

Experimental Section

Infrared spectra were taken of pure liquids on a Perkin-Elmer Model 137B spectrophotometer, unless otherwise noted. Nmr spectra were taken in carbon tetrachloride on a Varian Model A-60 instrument. Melting points were determined in open capillaries and are uncorrected. Glpc analyses were carried out on an Aerograph Model 600 Hy-fl unit; preparative separations were carried out on a modified Beckman Model GC-2 vapor fractometer.

cis,endo-**Bicyclo[3.2.0]heptan-3-ol (13a).** The following modification of the procedure of Chapman[11] was used to prepare a mixture of *exo*- and *endo*-bicyclo[3.2.0]hept-6-en-3-ol, **8a** and **9a**, respectively. A solution of 4.4 g of 3,5-cycloheptadienol (**10a**) in 1 l. of ether was irradiated under nitrogen for 13 hr with a Vycor-filtered 200-w Hanovia immersion lamp. Removal of the solvent under reduced pressure and distillation of the residue at 11 mm and a bath temperature of 90–108° gave 4.1 g of a mixture of **8a** and **9a**. Vapor phase chromatographic analysis of this mixture on 20% Carbowax 20M at 185° indicated a composition of 78% **9a** (retention time 7.0 min) and 22% **8a** (retention time 10.3 min). This epimeric mixture was chromatographed on a column of 120 g of activity 2.5 (Brockmann) neutral Woelm alumina. The pure *endo* epimer **9a** was eluted with pentane, while 1:3 ether–pentane eluted the *exo* epimer **8a**. Catalytic hydrogenation of 2.2 g of **9a** in 20 ml of ethyl acetate containing prereduced Adams catalyst resulted in the uptake of 1 equiv of hydrogen. Removal of the solvent under reduced pressure and distillation of the residue at 102° and 12 mm gave 1.9 g of **13a**: mp 43.5–45°; infrared spectrum

(14) P. von R. Schleyer, *J. Am. Chem. Soc.*, **86**, 1854, 1856 (1964); C. S. Foote, *ibid.*, **86**, 1853 (1964).

(15) J. O. Halford, *J. Chem. Phys.*, **24**, 830 (1956).

(16) For example, the rate variations observed in the series of compounds under consideration might be partially attributed to rate-retarding inductive effects of the fused small-membered rings. This point is being investigated further.

(neat) 2.7, 3.05, 8.85, 9.92, and 10.5 μ; nmr spectrum τ 5.55 (multiplet), 5.8 (singlet), 7.25 (multiplet), and 2.0 (multiplet).

Anal. Calcd for $C_7H_{12}O$: C, 74.98; H, 10.78. Found: C, 75.16; H, 10.86.

***cis,exo*-Bicyclo[3.2.0]heptan-3-ol (12a).** Jones oxidation[17] of 8.4 g of the mixture of **8a** and **9a** obtained above gave 6.3 g of bicyclo[3.2.0]hex-6-en-3-one (**11**). To a solution of 6.3 g of **11** in 65 ml of absolute ethanol was added portionwise with stirring 5.6 g of sodium over 1.5 hr. The reaction mixture was stirred under reflux for an additional 3.0 hr, cooled in an ice bath, and diluted with saturated aqueous ammonium chloride solution. The aqueous solution was extracted with ether (three 150-ml portions). The combined ether extracts were dried over anhydrous magnesium sulfate, separated from the drying agent by filtration, and concentrated under reduced pressure. Distillation of the concentrate at 11 mm gave 4.1 g (65%) of a mixture of **8a** and **9a**, bp 74–81°. Vapor phase chromatographic analysis of this mixture on 20% Carbowax at 185° indicated a composition of 77% **8a** (retention time 10.3 min) and 23% **9a** (retention time 7.0 min). Chromatographic separation of this mixture was effected on a column of 120 g of activity 2.5 neutral Woelm alumina. Elution with pentane gave 0.7 g of pure **9a**. Elution with 1:3 ether–pentane gave 2.5 g of pure **8a**. Catalytic hydrogenation of 2.2 g of **8a** in 20 ml of ethyl acetate containing prereduced Adams catalyst resulted in the uptake of 1 equiv of hydrogen. Removal of the solvent under reduced pressure and distillation of the residue at 8 mm with a pot temperature of 102–112° gave 2.0 g of **12a**: bp 80–81° (8 mm); infrared spectrum (neat) 2.7, 2.95, and 8.69 μ; nmr spectrum τ 5.25 (multiplet), 5.81 (singlet), 7.15 (multiplet), and 1.92 (multiplet).

Anal. Calcd for $C_7H_{12}O$: C, 74.98; H, 10.78. Found: C, 75.24; H, 10.95.

Jones Oxidation of 12a and 13a to 14. A stirred solution of 250 mg of *cis,endo*-bicyclo[3.2.0]heptan-3-ol (**13a**) in 25 ml of acetone was titrated with Jones reagent[17] until an orange coloration persisted in the solution. After 5 min of additional stirring, the excess oxidant was destroyed with a few drops of isopropyl alcohol. The solution was diluted with water and extracted several times with ether. The ether extract was washed thoroughly with dilute sodium bicarbonate solution and water. After drying over anhydrous magnesium sulfate, the ether extract was separated from the drying agent by filtration, and the filtrate was concentrated under reduced pressure. Distillation of the residue at 14 mm and a bath temperature of 85–95° gave 184 mg (74%) of *cis*-bicyclo[3.2.0]heptan-3-one (**14**): infrared spectrum (neat) 3.38, 5.73, 7.13, 7.88, 7.97, 8.60, and 9.68 μ. Vapor phase chromatographic analysis on a column of 20% Carbowax 20M at 185° indicated the presence of one component with a retention time of 6.5 min. The infrared spectrum and the vapor phase chromatograph were identical with those of an authentic sample of **14** obtained from Dr. R. Srinivasan.

Jones reagent oxidation of a stirred solution of 180 mg of *cis,exo*-bicyclo[3.2.0]heptan-3-ol (**12a**) in 25 ml of acetone as described above gave 128 mg (71%) of **14**. The infrared spectrum and vapor phase chromatograph of this sample were identical with those of the sample prepared above.

***cis,endo*-Bicyclo[3.2.0]heptan-3-ol *p*-Toluenesulfonate (13b).** To a solution of 1.2 g of **13a** in 4 ml of dry pyridine was added 2.20 g of *p*-toluenesulfonyl chloride at 0°. After 30 hr at 0°, the reaction mixture was poured into ice-diluted hydrochloric acid and was extracted several times with ether. The ethereal solution was washed thoroughly with water and dilute aqueous sodium bicarbonate solution, followed by drying over anhydrous magnesium sulfate. Removal of the drying agent by filtration, and removal of the solvent under reduced pressure, gave 2.8 g of crystalline material. Four recrystallizations from hot hexane gave 2.0 g (69%) of **13b**: mp 54.5–55.5°; infrared spectrum (Nujol) 6.31, 10.62, and 13.85 μ; nmr spectrum (CCl_4) τ 2.39 (quartet), 4.84 (multiplet), 7.20 (broad singlet), 7.05 (singlet), and 8.00 (multiplet).

Anal. Calcd for $C_{14}H_{18}SO_3$: C, 63.14; H, 6.84; S, 12.01. Found: C, 63.05; H, 6.83; S, 12.01.

***cis,exo*-Bicyclo[3.2.0]heptan-3-ol *p*-Toluenesulfonate (12b).** To 1.60 g of **12a** in 5 ml of dry pyridine was added 3.00 g of *p*-toluenesulfonyl chloride at 0°. The reaction mixture was allowed to stand for 24 hr at 0°, and then worked up as described above to give 3.5 g of crystalline material. Five recrystallizations from hot hexane gave 2.4 g (63%) of **12b**: mp 44–45°; infrared spectrum (Nujol) 6.32, 10.30, and 11.89 μ; nmr spectrum (CCl_4) τ 2.40 (quartet), 4.83 (multiplet), 7.25 (broad), 7.55 (singlet), and 8.15 (multiplet).

Anal. Calcd for $C_{14}H_{18}SO_3$: C, 63.14; H, 6.84; S, 12.01. Found: C, 63.34; H, 6.89; S, 11.85.

***cis,endo*-Bicyclo[3.2.0]hept-6-en-3-ol *p*-Toluenesulfonate (9b).** To 2.0 g of **9a** in 5 ml of dry pyridine was added 3.6 g of *p*-toluenesulfonyl chloride at 0°. After the reaction mixture had been allowed to stand for 20 hr at 0°, it was worked up in the usual manner. Four recrystallizations of the crude reaction product from hot hexane gave 2.6 g (54%) of **9b**: mp 63–64°; infrared spectrum (Nujol) 6.25, 9.25, 10.58, 11.85, 13.25, and 14.34 μ; nmr spectrum (CCl_4) τ 2.45 (quartet), 3.97 (singlet), 4.9 (triplet), 6.75 (doublet), 7.58 (singlet), and 1.85 (multiplet).

Anal. Calcd for $C_{14}H_{16}SO_3$: C, 63.63; H, 6.10; S, 12.11. Found: C, 63.55; H, 6.21; S, 11.96.

***cis,exo*-Bicyclo[3.2.0]hept-6-en-3-ol *p*-Toluenesulfonate (8b).** To 1.4 g of **8a** in 4 ml of dry pyridine was added 2.6 g of *p*-toluenesulfonyl chloride at 0°. The reaction mixture was allowed to stand at 0° for 15 hr. Work-up in the usual manner and five recrystallizations of the crude reaction product from hot hexane gave 1.8 g (54%) of **8b**: mp 48–50°; infrared spectrum (Nujol) 6.25, 10.12, 11.75, 12.23, and 13.40 μ; nmr spectrum (CCl_4) τ 2.45 (quartet), 4.10 (singlet), 5.19 (quintet), 6.75 (doublet), 7.50 (singlet), and 1.8 (multiplet).

Anal. Calcd for $C_{14}H_{16}SO_3$: C, 63.63; H, 6.10; S, 12.11. Found: C, 63.53; H, 6.13; S, 12.19.

***trans*-Bicyclo[3.2.0]heptan-3-ol *p*-Toluenesulfonate (7b).** The *trans* alcohol **7a** (896 mg, 8 mmoles) was placed in 3 ml of pyridine. The solution was cooled to 0° in an ice bath. *p*-Toluenesulfonyl chloride (1.68 g, 8.8 mmoles) was added in small portions over a 10-min period. The mixture was stirred at 0° for 3 hr, then placed in the refrigerator overnight. Water was added to decompose excess *p*-toluenesulfonyl chloride. Dilute hydrochloric acid then was added to neutralize the pyridine. The solution was extracted with ether. The ether solution was washed with dilute hydrochloric acid, water, aqueous sodium carbonate, water, and then dried over magnesium sulfate. The ether was removed to leave **7b** as an oil (1.75 g, 82%) which was kept in a rotary evaporator at reduced pressure for 2 hr to remove traces of solvent.

Anal. Calcd for $C_{14}H_{18}SO_3$: C, 63.14; H, 6.84; S, 12.01. Found: C, 62.98; H, 6.89; S, 12.30.

Lithium Aluminum Hydride Reduction of *cis*-Bicyclo[3.2.0]heptan-3-one (14). A solution of 200 mg of **14**[11,12] in 10 ml of ether was added dropwise with stirring to a suspension of 300 mg of lithium aluminum hydride in 50 ml of ether. The reaction mixture was stirred for 30 min and then hydrolyzed by dropwise addition of water. The inorganic salts were separated by filtration and washed thoroughly with ether. The ether filtrate was concentrated under reduced pressure. Distillation of the concentrate at 102° and 12 mm gave 174 mg of a mixture of **12a** and **13a**. Vapor phase chromatographic analysis of this mixture on 10% Carbowax 20M on Firebrick at 155° indicated a composition of 23% **12a** (retention time 10.7 min) and 77% **13a** (retention time 9.5 min). An infrared spectrum of this mixture was identical with that of a mixture of authentic **12a** and **13a** having this composition.

Sodium–Alcohol Reduction of 14. To a solution of 200 mg of **14** in 8 ml of absolute ethanol 250 mg of sodium was added portionwise with stirring. The reaction mixture was heated under reflux for 1 hr, cooled, and poured into cold saturated ammonium chloride solution. The aqueous solution was extracted several times with ether. The combined ether extracts were dried over anhydrous sodium sulfate, separated from the drying agent by filtration, and concentrated under reduced pressure. Vapor phase chromatographic analysis of the concentrate on 10% Carbowax at 155° indicated a composition of 58% **12a** and 42% **13a**.

Kinetic Measurements. The solvolysis reactions were run at 74.98 ± 0.02° in anhydrous acetic acid solution[13] which was 0.0501 *N* in both sodium acetate and tosylate. Two-milliliter samples in individual sealed ampoules were removed at appropriate intervals and cooled in an ice bath. After warming to room temperature a 1-ml aliquot was removed and titrated with 0.0207 *N* perchloric acid in acetic acid, using brom phenol blue as indicator.[13] All rate measurements were followed for 3 half-lives. At least two runs were made on each tosylate for which a rate constant is reported.

Solvolyses of 13b, 12b, 9b, 8b, and 7b. Acetolyses of **13b, 12b, 9b, 8b,** and **7b** under the conditions described above showed excellent first-order kinetics in at least two runs each, giving rate constants of $1.50 \times 10^{-4} \pm 0.02$ sec^{-1}, $0.95 \times 10^{-4} \pm 0.05$ sec^{-1}, $2.60 \times 10^{-3} \pm 0.06$ sec^{-1}, $1.26 \times 10^{-5} \pm 0.04$ sec^{-1}, and $9.76 \times 10^{-6} \pm 0.05$ sec^{-1}, respectively.

(17) K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

Product Analysis for Acetolysis of 13b. The solvolysis of 660 mg of **13b** under the conditions described above was stopped after 8 half-lives. The solvolysis mixture was cooled and poured into a mixture of ice and saturated sodium carbonate solution. The resultant acetates were extracted with ether and dried over anhydrous magnesium sulfate. The drying agent was removed by filtration, and the filtrate was concentrated under reduced pressure. The ethereal concentrate was added to a stirred slurry of lithium aluminum hydride (0.75 g) in dry ether (50 ml). After stirring for 1 hr, the reaction mixture was hydrolyzed by dropwise addition of water. Removal of the inorganic salts by filtration followed by evaporation of the solvent under reduced pressure and distillation of the residue at 12 mm with a pot temperature of 90–115° gave 152 mg (54%) of a mixture of **12a** and **13a**. Vapor phase chromatography on a column of 10% Carbowax 20M on Firebrick at 160° indicated the presence of three components. The relative amounts of these components were 93% of **12a** (retention time 8.8 min) and 7% of **13a** (retention time 7.5 min). An infrared spectrum of this mixture was identical with a spectrum of the mixed authentic alcohols, **12a** and **13a**; the third component (retention time 8.3 min) was estimated to comprise not more than 5–10% of the mixture.

Product Analysis for Acetolysis of 12b. The solvolysis of 660 mg of **12b** was stopped after 8 half-lives. Work-up and isolation of the solvolysis products was the same as that described above for the solvolysis of **13b**. Vapor phase chromatography of the product mixture on a column of 10% Carbowax 20M at 160° revealed that the relative composition was 94% of **13a**, and 6% of **12a**. An infrared spectrum of this mixture was identical with a spectrum of this composition of authentic **12a** and **13a**. A minor component was not identified.

Product Analysis for Acetolysis of 9b. The solvolysis of 660 mg of **9b** was allowed to proceed for 8 half-lives. Work-up and isolation of the solvolysis products was the same as that described above for the solvolysis of **13b**. Vapor phase chromatographic analysis of the product mixture on a column of 20% Carbowax 20M at 185° indicated the presence of 9% of **9a** (retention time 7.0 min) and 91% of **8a** (retention time 10.3 min). An infrared spectrum of this mixture was identical with a spectrum of the mixed authentic alcohols, **8a** and **9a**.

Product Analysis for Acetolysis of 8b. The solvolysis of 660 mg of **8b** was allowed to proceed for 8 half-lives. Work-up and isolation of the solvolysis products was the same as that described above for the solvolysis of **13b**. Vapor phase chromatographic analysis of the product mixture on a column of 10% Carbowax 20M at 160° indicated the relative composition of the mixture to be 84% of **9a** (retention time 4.5 min) and 16% of **8a** (retention time 7.85 min). An infrared spectrum of this mixture was identical with a spectrum of the mixed authentic alcohols, **8a** and **9a**. A minor component with a 5.5-min retention time was not identified.

Structure and Synthesis of the Major Components in the Hairpencil Secretion of a Male Butterfly, *Lycorea ceres ceres* (Cramer)[1]

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Abstract: Males of the tropical butterfly, *Lycorea ceres ceres* (Cramer), possess elaborate retractable organs, the hairpencils, which appear to play an important role in courtship. As a first step toward identifying a new pheromone from this source, hairpencils were removed from live males and extracted with organic solvents. The extract was found to consist of three major components, proved to be 2,3-dihydro-7-methyl-1H-pyrrolizin-1-one (**5**), cetyl acetate (**9**), and *cis*-vaccenyl acetate (**16**) on the basis of chemical and physical evidence. These structures were confirmed by independent syntheses.

In a stimulating study of the courtship behavior of the Queen butterfly [*Danaus gilippus berenice* (Cramer)], Brower, *et al.*,[2] call attention to many significant contributions to the development of biology which have resulted from investigating the sexual behavior of the Lepidoptera. One field that has received particular impetus in this way is that of chemical communication, an area of "molecular biology" which is, nevertheless, still in its infancy.[3] The present paper describes chemical studies which may ultimately prove relevant to this growing area of research.

It has long been known that male butterflies throughout the tropical subfamily Danainae generally possess a pair of elaborate organs, called hairpencils, which can be extruded from the end of the abdomen.[4] In the Queen butterfly, the male has been observed to brush the hairpencils across the anterior end of the female in flight. This treatment appears to induce the female to settle on available herbage. After continued "hairpencilling," copulation occurs. The hairpencils and their associated glandular cells therefore seem to play an important role in courtship, and are thought to be concerned with the production and/or dissemination of a "sexual scent."[2] The exact biological role of such scents, which remarkably enough are often agreeable to man, remains to be defined. It has been speculated that they may form part of "a chemical language that prevents interspecific hybridization in nature."[2] In spite of the obvious interest such a function would have, no study of the chemical nature of these hairpencil secretions has been reported. We now present the results of a chemical study of the hairpencil secretion obtained from the Trinidad butterfly *Lycorea ceres ceres* (Cramer),

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(2) L. P. Brower, J. V. Z. Brower, and F. P. Cranston, *Zoologica*, **50**, 1 (1965).

(3) For an excellent recent review of this subject, see E. O. Wilson and W. H. Bossert, *Recent Progr. Hormone Res.*, **14**, 673 (1963).

(4) F. Müller speculated on the function of these organs as long ago as 1877 (see ref 2).