to GLC standards, was not appropriate for kinetics of bromination (nonreproducible rate constants were obtained). The acetic acid-*d* used for kinetics of bromination was prepared from calculated amounts of acetic anhydride and deuterium oxide by refluxing the reaction mixture for a few hours followed by distilling off the product. Methyl alcohol and methyl alcohol-*O*-*d* (Merck Sharp & Dohme Canada Ltd.) were refluxed with Br_2 and then distilled twice from bromine and K_2CO_3.[20] Formic acid (>99%) and formic acid-*O*-*d* (≥98% D) (Merck Sharp & Dohme Canada Ltd.) were fractionally distilled from phthalic anhydride. The EtOH–2% H_2O mixture was prepared from absolute ethanol and distilled water.[21] 4-Chlorobenzenesulfenyl chloride was prepared as previously described.[22]

Kinetics. The rates of bromination of alkenes and alkynes were measured as previously reported.[23,7] The rates of 4-chlorobenzenesulfenyl chloride additions to alkenes and alkynes were determined as previously described.[22] All rates were obtained on a Durrum-Gibson or a Cary 16 spectrophotometer. The reported rate coefficients are the mean values of five to seven independent determinations.

Acknowledgment. Continued financial support from the National Research Council of Canada is gratefully acknowledged.

Registry No. 1-Pentene-1, 109-67-1; *cis*-3-hexene, 7642-09-3; styrene, 100-42-5; 1-pentyne, 627-19-0; 3-hexyne, 928-49-4; phenylacetylene, 536-74-3; bromine, 7726-95-6; 4-chlorobenzenesulfenyl chloride, 933-01-7.

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(22) G. H. Schmid, V. M. Csizmadia, V. J. Nowlan, and D. G. Garratt, *Can. J. Chem.*, **50**, 2457 (1972).
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Methyl Substituent Effects upon the Chemistry of 2-Bicyclo[4.1.0]heptyl 3,5-Dinitrobenzoates

Edwin C. Friedrich* and J. Diane Cooper Jassawalla

Department of Chemistry, University of California, Davis, California 95616

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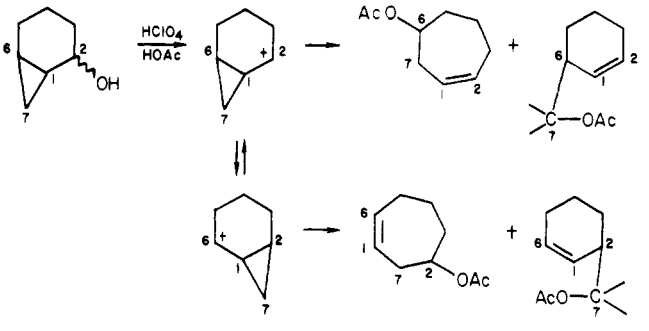
The rates and products of kinetic control in hydrolyses of the unsubstituted and 2-, 6-, and *anti*-7-methyl-substituted 2-bicyclo[4.1.0]heptyl 3,5-dinitrobenzoates in 80% aqueous acetone have been determined. These are compared with similar data for the 1-methyl-substituted 3,5-dinitrobenzoates reported by Wiberg and Chen. Also, they are compared with the results of our previously reported perchloric acid catalyzed alcohol acetolysis studies for the same systems where the products of thermodynamic control and the percentages of cyclopropylcarbinyl–cyclopropylcarbinyl cation rearrangement occurring prior to their formation were investigated. Several important conclusions regarding the detailed reaction pathway for cyclopropylcarbinyl–cyclopropylcarbinyl cation rearrangement in the 2-bicyclo[4.1.0]heptyl system have been derived from these comparisons.

Introduction

We recently[1] reported a study of the effects of individual 1-, 2-, 6-, or *anti*-7-methyl substitution upon the importance of cyclopropylcarbinyl–cyclopropylcarbinyl cation rearrangements[2] in perchloric acid catalyzed acetolyses[3] of 2-bicyclo[4.1.0]heptanols. This was done, with deuterium labels where necessary, through a determination of the relative amounts of the various possible products formed as depicted in Scheme I. In the scheme the numberings of the carbons in the starting material have been retained throughout to illustrate the consequences of the cyclopropylcarbinyl–cyclopropylcarbinyl cation rearrangement upon the natures of the products.

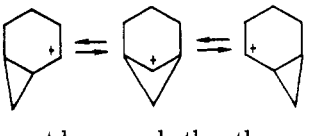
The perchloric acid catalyzed acetolysis procedure provided primarily the homoallylic acetate products of thermodynamic control via repeated reionization of any initially formed bicyclic acetate products of kinetic control. 1-Methyl substitution increased the cyclopropylcarbinyl–cyclopropylcarbinyl cation rearrangement product formed from about 35% to the theoretical maximum of 50%. However, with 2-, 6-, or *anti*-7-methyl substitution the amount of rearrangement product decreased to less

Scheme I



than about 3, 1, and 10%, respectively.

Concerning the 1-methyl substituent effect, this was interpreted as providing possible support for the intervention of a puckered cyclobutyl-type[4] activated complex or intermediate in the cyclopropylcarbinyl–cyclopropylcarbinyl cation rearrangement process.



However, it was not known whether the process is stepwise

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Table I. Rates of Hydrolysis of Some 2-Bicyclo[4.1.0]heptyl 3,5-Dinitrobenzoates in 80% Aqueous Acetone[a]

RODNB	temp, °C, ±0.1 °C	$10^5 k_1$,[b] s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
no CH_3, endo	79.8	15.3 ± 0.9	26.4 ± 2.8	−2 ± 3
	65.3	2.99 ± 0.08		
exo	79.8	20.5 ± 0.8	24.5 ± 1.9	−6 ± 2
	65.3	4.39 ± 0.1		
1-CH_3, endo	79.8	24.6 ± 0.7		
	75.6	17.8 ± 0.2[c]	24.9	−5
	66.2	6.41[c]		
exo	77.6	48.6 ± 0.3[c]	26.0	−2
	65.0	11.8[c]		
2-CH_3[d]	26.8	113 (OPNB)[e]		
	(79.8)	(1.57×10^6)[f]	(26)	
6-CH_3, endo	79.8	190 ± 10	26.4 ± 1.7	+3 ± 2
	65.3	36.5 ± 1.5		
exo	79.8	231 ± 15	23.3 ± 2.1	−5 ± 2
	65.3	53.4 ± 1.3		
7-CH_3,[g] endo	79.8	93.5 ± 4.1	24.9 ± 1.7	−5 ± 2
	65.3	19.6 ± 0.5		
exo	79.8	147 ± 8.7	26.0 ± 2.5	−1 ± 3
	65.3	28.0 ± 1.1		

[a] Concentrations of RODNB in all cases were about 0.01 M (DNB = 3,5-dinitrobenzoate). [b] All runs were done at least in duplicate. The error given is the standard deviation. [c] Data of Wiberg and Chen, *J. Am. Chem. Soc.*, **96**, 3900 (1974). [d] A mixture of isomeric 2-methyl-2-bicyclo[4.1.0]heptyl *p*-nitrobenzoates derived from a 45:55 endo to exo mixture of the corresponding alcohols. [e] A graphically calculated three-point rate constant measured for the *p*-nitrobenzoate mixture. [f] Rate constant estimated from the *p*-nitrobenzoate data by assuming a $\Delta H^{\ddagger}$ of 26 kcal mol^{-1} and a 3,5-dinitrobenzoate to *p*-nitrobenzoate rate ratio of 12. [g] The 7-methyl group is oriented anti to the large ring.

or whether it is all or in part concerted with ionization. The 2-, 6-, and *anti*-7-methyl effects, which decreased the importance of the cyclopropylcarbinyl–cyclopropylcarbinyl cation rearrangements, may do so through increasing charge localization elsewhere relative to that at C_1. This may possibly even be to the point of changing charge-delocalized intermediates to charge-localized species.

One possible approach to obtaining a better understanding of the methyl substituent effect behaviors in the perchloric acid catalyzed acetolyses of the 2-bicyclo[4.1.0]heptanols is to examine the rates and kinetically controlled products of hydrolysis of the corresponding unsubstituted and methyl-substituted 3,5-dinitrobenzoate esters. These results should also be of considerable interest in their own right in connection with the continuing reports[5] dealing with substituent effects on solvolyses of molecules reacting via carbocation intermediates. Our investigations in this area are described below.

Results and Discussion

Synthesis of Starting Materials. Preparations of the unsubstituted, 1-methyl-, and 6-methyl-*endo*- and -*exo*-2-bicyclo[4.1.0]heptanol precursors of the desired 3,5-dinitrobenzoates were carried out according to published procedures or slight modifications of these. The 2-methyl and *anti*-7-methyl alcohols were prepared by us for the first time. Unfortunately, however, we were unable to separate the *endo*- and *exo*-2-methyl-substituted alcohols on other than an analytical scale.

Preparation of the 3,5-dinitrobenzoate derivatives of the unsubstituted and methyl-substituted 2-bicyclo[4.1.0]heptanols was straightforward except with the 2-methyl case. Here, besides having to work with an isomeric mixture of the 2-methyl-2-bicyclo[4.1.0]heptanols, we found that the 3,5-dinitrobenzoates were too reactive for isolation and solvolytic studies. However, the corresponding mixture of *p*-nitrobenzoates fortunately was of sufficient stability for hydrolysis-product studies and a three-point rate run.

Hydrolysis Kinetics. The rates of hydrolysis of the endo and exo unsubstituted, 6-methyl-, and *anti*-7-methyl-2-bicyclo[4.1.0]heptyl 3,5-dinitrobenzoates and of the isomeric mixture of *endo*- and *exo*-2-methyl-2-bicyclo[4.1.0]heptyl *p*-nitrobenzoates were measured in 80% aqueous acetone, and the results are summarized in Table I. Also included in Table I are Wiberg and Chen's data[6] for the 1-methyl-substituted 3,5-dinitrobenzoate system together with the results of one run carried out by us on the 1-methyl endo ester to verify the identity of Wiberg and Chen's materials, solvent system, and reaction conditions with ours.

All of the rate runs exhibited good first-order kinetic behavior. In all of the cases the experimental infinities measured after 10 reaction half-lives were within experimental error of the theoretical infinities except with the isomeric 6-methyl esters where the experimental infinities were about 92–95% of the theoretical values. The one run we carried out on the 1-methyl *endo*-3,5-dinitrobenzoate agreed well with the results of Wiberg and Chen on the same system. Also, for the unsubstituted esters, the rate constants obtained compare well with those measured by Rubenstein and Goering[7] for the corresponding *p*-nitrobenzoates in 80% aqueous acetone.

To ensure that the kinetics being measured were for the desired compounds and not for isomeric 3,5-dinitrobenzoates formed via rapid initial ion-pair return with rearrangement, we isolated the unreacted 3,5-dinitrobenzoate or *p*-nitrobenzoate for each of the systems and analyzed it by NMR after a period of time equivalent to ca. 65% acid production. In the unsubstituted, 1-methyl, and 2-methyl systems the isolated 3,5-dinitrobenzoates or *p*-nitrobenzoates contained less than 5% of the rearranged esters. However, with the 6- and *anti*-7-methyl-substituted 3,5-dinitrobenzoates **1** and **3** both the endo and exo isomers appeared to contain about 20–30% of rearranged allyl-

(5) For example, see: H. C. Brown, C. G. Rao, and M. Ravindranathan, *J. Org. Chem.*, **43**, 4939 (1978).

(6) K. B. Wiberg and W.-f. Chen, *J. Am. Chem. Soc.*, **96**, 3900 (1974).

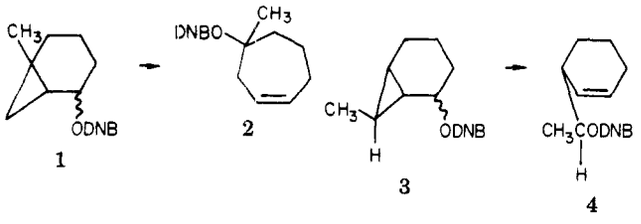
(7) K. E. Rubenstein, Doctoral Dissertation, University of Wisconsin, 1967.

Table II. Products of Hydrolysis of Some 2-Bicyclo[4.1.0]heptyl Nitrobenzoates in 80% Aqueous Acetone in the Presence of $CaCO_3$ after about 5 Reaction Half-Lives[a]

starting ester[b] Y	X	temp, °C	hydrolysis products, %			other
H	ODNB	80	67 ± 3	23 ± 2	10 ± 3	
1-CH_3	ODNB[c]	85	60 ± 1	20 ± 1	18 ± 2	2[d]
2-CH_3	OPNB[e]	27	75 ± 5	25 ± 5		
6-CH_3	ODNB	80			49 ± 3	51 ± 3[f]
7-CH_3	ODNB	80	52 ± 3	15 ± 3		33 ± 3[g]

[a] In all of the cases both the endo and exo starting esters gave, within experimental error, identical product mixtures. [b] "DNB" refers to 3,5-dinitrobenzoate and "PNB" refers to *p*-nitrobenzoate. [c] Data of Wiberg and Chen, *J. Am. Chem. Soc.*, **96**, 3900 (1974), after a 4-h reaction time with an ethyldiisopropylamine buffer. [d] 6-Methyl-*endo*-bicyclo[3.3.0]heptan-6-ol. [e] The starting *p*-nitrobenzoate was prepared from a 45:55 endo to exo mixture of 2-methyl-2-bicyclo[4.1.0]heptanols. [f] 1-Methylbicyclohepta-1,3-diene. [g] The 33% "other" consisted of 31 ± 3% of 3-(1-hydroxyethyl)cyclohexene and 2 ± 1% of a supposed alkadiene product.

carbinyl 3,5-dinitrobenzoates. The NMR absorptions for these in the mixtures were consistent with structures **2** and **4**, respectively.



If both **2** and **4** were completely unreactive under the conditions where the hydrolysis kinetics of their cyclopropylcarbinyl precursors **1** and **3** were run, the 20–30% rearranged ester present in the unreacted ester mixture after about 65% acid production would correspond to an experimental infinity of about 90–95% of the theoretical value for a kinetic run. This is close to the experimental infinity of about 92–95% observed for the 6-methyl system but not to that of nearly 100% exhibited by the *anti*-7-methyl system. The latter observation may result because **4** has a reactivity only slightly lower than that of the *anti*-7-methyl-2-bicyclo[4.1.0]heptyl 3,5-dinitrobenzoates **3** and thus does not survive under the 10 reaction half-lives used for the kinetic infinities. However, this has not been tested experimentally, and, in any case, the amount of ion-pair return is not large enough to have seriously affected the kinetics for the cyclopropylcarbinyl esters.

A comparison of the rate constants at 79.8 °C shown in Table I reveals that, except for the 2-methyl system where insufficient data are available, for all of the systems the exo esters react slightly faster than the corresponding endo esters. This similarity in behavior even when methyl substituents are introduced at various positions on the 2-bicyclo[4.1.0]heptyl cyclopropylcarbinyl system would seem to indicate that, except possibly with the 2-methyl system, the substituents must not be greatly changing the nature of the charge delocalization in the activated complexes for ionization. The 1-methyl, 6-methyl, and *anti*-7-methyl substituents do, however, produce small increases of about two-, ten-, and sixfold, respectively, over the rates for the unsubstituted systems. For the 2-methyl system an approximately 10^5-fold rate increase can be estimated. These results suggest, for either endo or exo leaving groups, that charge delocalization in the 2-bicyclo[4.1.0]heptyl cyclopropylcarbinyl system is taking place simultaneously at the 1, 2, 6, and 7 carbons. This is what would be expected for a bisected bishomoallyl-type activated complex in ionization. However, the relative magnitudes of the rate increases for the 1-, 6-, and 7-methyl substitutions should not be considered as inferring the relative amounts of charge delocalization at these positions. This is because the rate increases may be reflecting not only electronic effects but also small steric and solvation effects.

Hydrolysis Products. The products of hydrolysis of the unsubstituted and 2-, 6-, and *anti*-7-methyl-substituted 2-bicyclo[4.1.0]heptyl 3,5-dinitro- or *p*-nitrobenzoates in 80% aqueous acetone after about 5 half-lives were determined by using a combination of GLC and NMR techniques, and the results obtained are summarized in Table II. Also included in Table II are the hydrolysis products from the 1-methyl-2-bicyclo[4.1.0]heptyl 3,5-dinitrobenzoates reported by Wiberg and Chen.[6] For the systems which we studied, product-stability controls run under the reaction conditions showed no problems with the unsubstituted, 2-methyl, and *anti*-7-methyl systems. On the other hand, with the 6-methyl system a sample of 6-methyl-*endo*-2-bicyclo[4.1.0]heptanol after 6.5 half-lives at 80 °C underwent about 40% rearrangement to yield an approximately 50:50 mixture of 4-methylcyclohepten-4-ol and 1-methylcyclohepta-1,3-diene. However, this again causes no interpretation problems as no bicyclic alcohols were found among the products of the 6-methyl system. The control showed that had significant amounts of bicyclic alcohols been formed, at least some would have survived the reaction conditions to be detected.

On consideration of the hydrolysis product results reported in Table II, several interesting points emerge. First, for all of the systems the nature and yields of the products were independent of the endo or exo ester leaving-group geometries. Also, for all of the systems where 2-bicyclo[4.1.0]heptanol products were obtained, the yield of endo alcohol was about 3 times that of the exo alcohol. This tends to indicate that the endo:exo product ratio depends primarily on steric and not on electronic factors and is in agreement also with the lack of dependence of the endo:exo rate ratio for the 3,5-dinitrobenzoate esters on the methyl substitution pattern.

The close similarities in the distributions of the products from the unsubstituted and 1-methyl-substituted systems are in accord with the observation that the 1-methyl substituent has only a small effect on the rate of hydrolysis in the 2-bicyclo[4.1.0]heptyl system. Thus, the 1-methyl substituent must not be producing either a large steric effect or a large electronic effect upon the 2-bicyclo[4.1.0]heptyl activated complex or reaction intermediate.

On the other hand, the 2-, 6-, and *anti*-7-methyl substituents strongly affect the cyclopropylcarbinyl cation chemistry in the 2-bicyclo[4.1.0]heptyl system. In the 2-methyl case, since no homoallyl products are obtained, the intermediate might be best described as a nondelocalized tertiary cyclopropylcarbinyl cation. By contrast, in the 6-methyl case where no cyclopropylcarbinyl products are obtained, the ionization may be proceeding with concurrent ring opening to give a nondelocalized tertiary homoallyl cation from which the substitution and elimination products are obtained. In the *anti*-7-methyl system, intermediate behavior is observed in which the reaction intermediate must still be a delocalized cyclopropylcarbinyl cation, but with more charge localization being present at the 7-carbon than in the cases of the nonmethyl- and 1-methyl-substituted systems.

Conclusions Related to the Cyclopropylcarbinyl–Cyclopropylcarbinyl Cation Rearrangement Problem. As mentioned in the Introduction, the primary reason for our initial interests in studying the hydrolysis kinetics and products for the methyl-substituted 2-bicyclo[4.1.0]heptyl 3,5-dinitrobenzoates was to gain a better understanding of the methyl-substituent effects observed in our earlier[1] studies of cyclopropylcarbinyl–cyclopropylcarbinyl cation rearrangements in this system by perchloric acid catalyzed alcohol acetolysis. Thus, we had observed that relative to the unsubstituted 2-bicyclo[4.1.0]heptanol, 1-methyl substitution appeared to somewhat increase the importance of the rearrangement. However, 2-, 6-, and *anti*-7-methyl substitution appeared to decrease its importance.

From the results of the present study, it is felt that the decrease in the importance of the cyclopropylcarbinyl–cyclopropylcarbinyl cation rearrangement process relative to solvolysis in the 2-methyl-substituted case stems from ionization in this system proceeding directly to a nondelocalized or only slightly delocalized tertiary cyclopropylcarbinyl cation in which the rearrangement process is unfavorable. This is apparent because of the large rate increase and the exclusive formation of 2-bicyclo[4.1.0]heptyl products of kinetic control in the 2-methyl-substituted ester hydrolysis. Similarly, for the 6-methyl-substituted system, it appears likely that ionization is concerted with cyclopropylcarbinyl–allylcarbinyl ring opening to give a nondelocalized tertiary 4-methylcyclohepten-4-yl cation in which the rearrangement is impossible. This is evidenced by the moderate rate increase and lack of 2-bicyclo[4.1.0]heptyl products of kinetic control in the 6-methyl ester hydrolysis.

The *anti*-7-methyl-2-bicyclo[4.1.0]heptyl system appears from the present results to be of greater interest than the 2- and 6-methyl-substituted systems in connection with obtaining an understanding of the detailed reaction pathway for the cyclopropylcarbinyl–cyclopropylcarbinyl cation rearrangement in the 2-bicyclo[4.1.0]heptyl cation. Thus, the moderate sixfold rate acceleration observed for the *anti*-7-methyl-substituted ester on hydrolysis is similar in magnitude to that for other analogously substituted cyclopropylcarbinyl esters.[3] Also, the fact that both cyclopropylcarbinyl and allylcarbinyl products of kinetic control are found indicates that a delocalized cyclopropylcarbinyl activated complex and cation intermediate must still be involved in the reactions of this system. Therefore, the observation that in the perchloric acid catalyzed alcohol acetolysis the *anti*-7-methyl substitution produced a three- to fourfold decrease in the importance of the cyclopropylcarbinyl–cyclopropylcarbinyl cation rearrangement must mean that in the activated complex for the rearrangement process contributions to charge delocalization involving the 7-position are not important. This is apparently due to the methyl substituent accelerating the rate of acetolysis but having essentially no effect on the rate of the cyclopropylcarbinyl cation rearrangement.

Finally, considering the 1-methyl-2-bicyclo[4.1.0]heptyl 3,5-dinitrobenzoate hydrolysis results of Wiberg and Chen,[6] there are several points especially worthy of comment. First, rate acceleration was produced by the 1-methyl substitution, and both cyclopropylcarbinyl and allylcarbinyl products of kinetic control were obtained on hydrolysis. Thus, it is apparent that here as in the *exo*-7-methyl-substituted system we are dealing with a delocalized cyclopropylcarbinyl activated complex and intermediate. Second, the ratio of cyclopropylcarbinyl to allylcarbinyl products of kinetic control is slightly smaller than for the unsubstituted system. Thus, assuming similar product formation behavior in 80% aqueous acetone and in acetic acid, the greater amount of cyclopropylcarbinyl–cyclopropylcarbinyl cation rearrangement in the 1-methyl system is not simply the result of the overall thermodynamically controlled process leading to allylcarbinyl product requiring a greater number of cyclopropylcarbinyl reionizations than for the unsubstituted system. As a consequence, it would appear that our perchloric acid catalyzed alcohol acetolysis studies[1] do actually provide substantial support for the intervention of a puckered cyclobutyl-type activated complex or intermediate with considerable charge at the 1-carbon for the cyclopropylcarbinyl–cyclopropylcarbinyl cation rearrangement process in the 2-bicyclo[4.1.0]heptyl cation system.

Experimental Section

General Methods. Melting and boiling points are uncorrected. Infrared spectra were obtained by using a Beckman Model IR8 spectrophotometer. NMR spectra were run on a Varian Associates EM360 instrument with chemical shifts measured in ppm (δ) downfield from Me_4Si as an external standard. GLC analyses and separations were carried out by using Varian Series 1400 and Aerograph A90P3 instruments equipped with Pyrex injector inserts. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

***endo*-2-Bicyclo[4.1.0]heptanol.** By use of the LeGoff[8] modification of the Simmons–Smith olefin cyclopropanation procedure, 25 g (0.26 mol) of 2-cyclohexen-1-ol,[9] 52 mL (130 g, 0.75 mol) of methylene bromide, and 90 g (1.4 mol) of 30-mesh granular zinc–copper couple in 250 mL of ether were stirred under reflux for 6 h. After workup by the addition of saturated aqueous ammonium chloride solution, the ethereal layer was washed with saturated sodium carbonate and sodium chloride solutions, dried over anhydrous magnesium sulfate, and distilled through a 60-cm stainless-steel spinning-band column to afford 7.4 g (13%) of the pure alcohol: bp 72–75 °C (11 mm); n^{22}_D 1.4928 [lit.[9] bp 76–77 °C (10 mm); n^{25}_D 1.4886]; NMR (CCl_4) δ 0.4 (m, 2 H, cyclopropyl), 1.0–2.1 (br m, 8 H), 3.4 (s, 1 H, OH), 4.1 (m, 1 H, CHOH).

***endo*-2-Bicyclo[4.1.0]heptyl 3,5-Dinitrobenzoate.** This was prepared by treatment of 2.5 g (0.02 mol) of *endo*-2-bicyclo[4.1.0]heptanol with 5.1 g (0.02 mol) of 3,5-dinitrobenzoyl chloride in about 30 mL of dry pyridine for 2 h at 0 °C. The reaction mixture was poured into a well-stirred mixture of ice and water and the resulting solid filtered and recrystallized from methylcyclohexane to yield 4.5 g (66%) of the desired 3,5-dinitrobenzoate: mp 94–95 °C; NMR (CCl_4) δ 0.3–0.9 (m, 2 H, cyclopropyl), 1.0–2.1 (m, 6 H), 5.5 (m, 1 H, CHODNB), 9.0 (m, 3 H, aromatic).

Anal. Calcd for $C_{14}H_{14}N_2O_6$: C, 54.90; H, 4.58. Found: C, 54.70; H, 4.64.

2-Bicyclo[4.1.0]heptanone. This was prepared in 50% yield by oxidation of *endo*-2-bicyclo[4.1.0]heptanol with chromium

(8) E. LeGoff, *J. Org. Chem.*, **29**, 2048 (1964).
(9) W. G. Dauben and G. H. Berezin, *J. Am. Chem. Soc.*, **85**, 468 (1963).

trioxide in acetone: bp 62–64 °C (7 mm); n^{22}_D 1.4864 [lit.[9] bp 85–85.5 °C (10 mm); n^{25}_D 1.4878]; NMR (neat) δ 1.0 (m, 2 H, cyclopropyl), 1.7 (m, 8 H); IR (neat) 1695 cm^{-1} (C=O str).

***exo*-2-Bicyclo[4.1.0]heptanol.** Reduction of 2-bicyclo[4.1.0]heptanone with lithium aluminum hydride in ether[7] at 0 °C on a small scale gave a 66% crude yield of a 70:30 exo:endo mixture of 2-bicyclo[4.1.0]heptanols. The pure exo isomer was collected by GLC on a 5 ft × 0.25 in., 10% Carbowax 20M–15% KOH on 60–80-mesh firebrick column operated at 115 °C: NMR (CCl_4) δ −0.2 (m, 1 H, cyclopropyl), 1.0–2.1 (br m, 9 H), 2.4 (s, H, OH), 3.8 (m, 1 H, CHOH).

***exo*-2-Bicyclo[4.1.0]heptyl 3,5-Dinitrobenzoate.** This was prepared in 68% yield by reaction of *exo*-2-bicyclo[4.1.0]heptanol with 3,5-dinitrobenzoyl chloride in pyridine and recrystallized from methylcyclohexane: mp 71–72 °C; NMR (CCl_4) δ −0.1 to 0.3 (q, 1 H, cyclopropyl), 0.3–2.2 (m, 8 H), 5.2 (m, 1 H, CHODNB), 8.9 (m, 3 H, aromatic).

Anal. Calcd for $C_{14}H_{14}N_2O_6$: C, 54.90; H, 4.58. Found: C, 54.80; H, 4.63.

2-Methylcyclohex-2-en-1-one. This was prepared in 60% yield from 2-chloro-2-methylcyclohexanone[10] by dehydrochlorination using lithium chloride–lithium carbonate[11] in dry tetrahydrofuran at 120 °C: bp 81–82 °C (31 mm); n^{26}_D 1.4836 [lit.[10] bp 83–85.5 °C (35 mm); n^{25}_D 1.4833]; NMR (CCl_4) δ 1.3–2.1 (br m, 9 H), 6.4 (s, 1 H, vinyl); IR (CCl_4) 1620 cm^{-1} (C=O str).

2-Methylcyclohex-2-en-1-ol. Reduction of 2-methylcyclohex-2-en-1-one with lithium aluminum hydride in ether at 0 °C afforded the alcohol in 71% yield: bp 83 °C (25 mm); n^{22}_D 1.4844 [lit.[9] bp 76–78 °C (18 mm); n^{25}_D 1.4816]; NMR (CCl_4) δ 1.3–2.0 (br m, 9 H), 2.4 (s, 1 H, OH), 3.7 (m, 1 H, CHOH), 5.3 (m, 1 H, vinyl).

1-Methyl-*endo*-2-bicyclo[4.1.0]heptanol. This was prepared in 27% yield by the reaction of 2-methylcyclohex-2-en-1-ol, dibromomethane, and a 30-mesh granular zinc–copper couple in ether at reflux for 4 h: bp 82 °C (18 mm); n^{22}_D 1.4817 [lit.[9] bp 68–70 °C (10 mm); n^{25}_D 1.4784]; NMR (CCl_4) δ 0.0–1.7 (br m, 12 H), 1.8 (s, 1 H, OH), 3.6 (t, 1 H, CHOH).

1-Methyl-*endo*-2-bicyclo[4.1.0]heptyl 3,5-Dinitrobenzoate. The reaction of 1-methyl-*endo*-2-bicyclo[4.1.0]heptanol with 3,5-dinitrobenzoyl chloride in pyridine under the usual conditions followed by workup and recrystallization from methylcyclohexane yielded 39% of the ester: mp 103–104 °C [lit.[6]]; NMR (CCl_4) δ 0.2–2.0 (m, 12 H), 5.1 (t, 1 H, CHODNB), 8.9 (m, 3 H, aromatic).

Isomeric Mixture of 2-Methyl-2-bicyclo[4.1.0]heptanols. To 24 mL of a 1.85 M methyllithium solution in ether (Aldrich) at 0 °C was added 2.5 g (0.023 mol) of 2-bicyclo[4.1.0]heptanone in 10 mL of anhydrous ether. The solution was allowed to warm to room temperature, stirred for 2 h, and poured into ice. After extraction with ether, the ethereal extract was washed with saturated aqueous sodium chloride and dried over magnesium sulfate. Distillation afforded 1.7 g (59%) of a 45:55 endo:exo mixture of 2-methyl-2-bicyclo[4.1.0]heptanols: bp 61 °C (4 mm); NMR (CCl_4) δ 0.1–0.35 (m, 1 H, cyclopropyl), 0.8–2.7 (m, 13 H).

Anal. Calcd for $C_8H_{14}O$: C, 76.19; H, 11.11. Found: C, 76.29; H, 11.20.

Isomeric Mixture of 2-Methyl-2-bicyclo[4.1.0]heptyl *p*-Nitrobenzoates. This was prepared by treatment of 1.0 g (7.9 mmol) of the 45:55 endo:exo mixture of 2-methyl-2-bicyclo[4.1.0]heptanols with 1.5 g (8.8 mmol) of *p*-nitrobenzoyl chloride in pyridine at 0 °C. After standing overnight in the refrigerator at 7 °C, the mixture was filtered to remove pyridinium hydrochloride, and the pyridine was taken off at reduced pressure. Recrystallization of the residual solids from *n*-hexane provided 0.20 g (9%) of the *p*-nitrobenzoate: mp 84–85 °C; NMR (CCl_4) δ 1.0–2.1 (m, 13 H), 8.5 (m, 4 H, aromatic). Due to the instability of the material, an analysis was not attempted.

3-Methylcyclohex-2-en-1-ol. To 18 g (0.17 mol) of 3-methylcyclohex-2-en-1-one[13] in 250 mL of ether at 0 °C was added to 2.0 g (0.053 mol) of lithium aluminum hydride, and the reaction mixture was allowed to stir for 5.5 h. Following the usual workup, distillation yielded 15 g (79%) of the desired alcohol: bp 84–85 °C (21 mm) [lit.[14] bp 83–85 °C (20 mm)]; NMR (CCl_4) δ 1.2–2.3 (br m, 9 H), 4.0 (s, 2 H, CHOH), 5.3 (s, 1 H, vinyl).

6-Methyl-*endo*-2-bicyclo[4.1.0]heptanol. The reaction of 15 g (0.13 mol) of 3-methylcyclohex-2-en-1-ol, 45 g (0.70 mol) of 30-mesh zinc–copper couple,[8] and 67 g (0.38 mol) of dibromomethane in 125 mL of ether at reflux for 4 h gave after workup and distillation 9.9 g (60%) of the bicyclic alcohol: bp 79–81 °C (13 mm); n^{22}_D 1.4795 [lit.[9] bp 74–75 °C (10 mm); n^{25}_D 1.4765]; NMR (CCl_4) δ 0.0–1.8 (br m, 12 H), 2.6 (s, 1 H, OH), 4.0 (m, 1 H, CHOH).

6-Methyl-*endo*-2-bicyclo[4.1.0]heptyl 3,5-Dinitrobenzoate. This was prepared in the usual manner in 59% yield by the reaction of 6-methyl-*endo*-2-bicyclo[4.1.0]heptanol with 3,5-dinitrobenzoyl chloride in pyridine and recrystallized from methylcyclohexane: mp 91–92 °C; NMR (CCl_4) δ 0.2–0.9 (m, 1 H, cyclopropyl), 1.0–2.0 (m, 11 H), 5.4 (m, 1 H, CHODNB), 9.0 (m, 3 H, aromatic).

Anal. Calcd for $C_{15}H_{16}N_2O_6$: C, 56.25; H, 5.00. Found: C, 56.37; H, 5.20.

6-Methyl-2-bicyclo[4.1.0]heptanone. Oxidation of 6-methyl-*endo*-2-bicyclo[4.1.0]heptanol with chromium trioxide in acetone at −10 °C followed by workup and distillation provided a 73% yield of the bicyclic ketone: bp 80–84 °C (13 mm); n^{22}_D 1.4813 [lit.[12] bp 85 °C (10 mm); n^{25}_D 1.4792]; NMR (CCl_4) δ 0.0–2.2 (br m, 12 H); IR 1680 cm^{-1} (C= str).

6-Methyl-*exo*-2-bicyclo[4.1.0]heptanol. Reduction of 6-methyl-2-bicyclo[4.1.0]heptanone with lithium aluminum hydride in ether followed by workup and distillation at 86–87 °C (16 mm) afforded a 79% yield of a 13:87 endo:exo mixture of 6-methyl-2-bicyclo[4.1.0]heptanols. Separation of a pure sample of the exo isomer was accomplished by GLC on a 5 ft × 0.25 in., 10% Carbowax 20M–15% KOH on 60–80 mesh firebrick column run at 105 °C: NMR (CCl_4) δ 0.2–2.2 (br m, 12 H), 2.9 (s, 1 H, OH), 3.8 (m, 1 H, CHOH).

6-Methyl-*exo*-2-bicyclo[4.1.0]heptyl 3,5-Dinitrobenzoate. This was prepared in the usual manner in a 36% yield by the reaction of 6-methyl-*exo*-2-bicyclo[4.1.0]heptanol with 3,5-dinitrobenzoyl chloride in pyridine at 0 °C and recrystallized from methylcyclohexane: mp 62–63 °C; NMR (CCl_4) δ 0.2–2.0 (m, 12 H), 5.2 (t, 1 H, CHODNB), 9.0 (m, 3 H, aromatic).

Anal. Calcd for $C_{15}H_{16}N_2O_6$: C, 56.25; H, 5.00. Found: C, 56.42; H, 5.19.

***anti*-7-Methyl-*endo*-2-bicyclo[4.1.0]heptanol.** A 1.60 M solution of ethylzinc iodide in ether was prepared by refluxing a mixture of zinc–copper couple (prepared by the procedure of Krug and Tang[15] from 130 g (2.0 mol) of zinc dust with 23 g (0.070 mol) of cupric citrate monohydrate[16]) and 80 mL (1.0 mol) of ethyl iodide in about 400 mL of diethyl ether for about 15 h: NMR (ether) δ 0.4 (m, 2 H, CH_2), 1.1 (m, 3 H, CH_3). Then, under a nitrogen atmosphere, 4.9 g (0.050 mol) of cyclohex-2-en-1-ol[9] was added dropwise to 125 mL of the 1.60 M ethylzinc iodide solution. This was followed by 28 g (0.10 mol) of 1,1-diiodoethane,[17] and the resulting mixture was heated under reflux for 3 h. Workup in the usual manner and distillation yielded 4.2 g (67%) of a 70:30 anti:syn mixture of 7-methyl-*endo*-2-bicyclo[4.1.0]heptanols.[18] Separation of a pure sample of the anti isomer was accomplished by GLC on a 5 ft × 0.25 in., 10% Carbowax 20 M–15% KOH on 60–80-mesh firebrick column run at 120 °C: NMR (CCl_4) δ 0.35–2.0 (br m, 12 H), 2.2 (s, 1 H, OH), 4.0 (m, 1 H, CHOH).

Anal. Calcd for $C_8H_{14}O$: C, 76.19; H, 11.11. Found: C, 76.35; H, 11.32.

***anti*-7-Methyl-*endo*-2-bicyclo[4.1.0]heptyl 3,5-Dinitrobenzoate.** This was prepared in 60% yield by the reaction of *anti*-7-methyl-*endo*-2-bicyclo[4.1.0]heptanol with 3,5-dinitro-

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benzoyl chloride in pyridine at 0 °C and recrystallized from methylcyclohexane: mp 84.5–85.5 °C; NMR (CCl_4) δ 0.5–2.0 (m, 12 H), 5.4 (q, 1 H, CHODNB), 9.0 (m, 3 H, aromatic).

Anal. Calcd for $C_{15}H_{16}N_2O_6$: C, 56.25; H, 5.00. Found: C, 56.38; H, 5.11.

***anti*-7-Methyl-*exo*-2-bicyclo[4.1.0]heptanol.** Oxidation of a 70:30 anti:syn mixture of 7-methyl-*endo*-2-bicyclo[4.1.0]heptanols with chromium trioxide in acetone-water at −10° followed by workup and distillation afforded a 78% yield of a 70:30 anti:syn mixture of 7-methyl-2-bicyclo[4.1.0]heptanones: bp 78–82 °C (10 mm); NMR (neat) δ 1.0–1.1 (m, 3 H, CCH_3), 1.1–2.1 (br m, 9 H); IR (neat) 1680 cm^{-1} (C=O str).

Reduction of the isomeric mixture of 7-methyl-2-bicyclo[4.1.0]heptanones with lithium aluminum hydride in ether provided, after workup, an 80% yield of an isomeric mixture consisting of 56% *anti-exo*-, 17% *anti-endo*-, 26% *syn-endo*-, and 17% *syn-exo*-7-methyl-2-bicyclo[4.1.0]heptanols. A pure sample of the desired anti-exo isomer was collected by GLC on a 5 ft × 0.25 in., 10% Carbowax 20M–15% KOH on 60–80-mesh firebrick column run at 115 °C; NMR (CCl_4) δ 0.0–2.1 (br m, 12 H), 2.6 (s, 1 H, OH), 3.8 (t, 1 H, CHOH).

Anal. Calcd for $C_8H_{14}O$: C, 76.19; H, 11.11. Found: C, 75.86; H, 11.12.

***anti*-7-Methyl-*exo*-2-bicyclo[4.1.0]heptyl 3,5-Dinitrobenzoate.** This material was prepared in 50% yield by the reaction of *anti*-7-methyl-*exo*-2-bicyclo[4.1.0]heptanol with 3,5-dinitrobenzoyl chloride in pyridine at 0 °C and recrystallized from methylcyclohexane: mp 76–77 °C; NMR (CCl_4) δ 0.3–2.1 (m, 12 H), 5.3 (m, 1 H, CHODNB), 9.0 (m, 3 H, aromatic).

Anal. Calcd for $C_{15}H_{16}N_2O_6$: C, 56.25; H, 5.00. Found: C, 56.15; H, 5.15.

General Procedures for Hydrolysis Kinetics and Products and for Product and 3,5-Dinitrobenzoate Stability Controls. The procedures followed were all analogous to those described earlier[3] from our laboratory in connection with another investigation. All runs were carried out in duplicate.

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Registry No. *endo*-2-Bicyclo[4.1.0]heptanol, 7432-49-7; 2-cyclohexen-1-ol, 822-67-3; methylene bromide, 74-95-3; *endo*-2-bicyclo[4.1.0]heptyl 3,5-dinitrobenzoate, 52688-97-8; 2-bicyclo[4.1.0]heptanone, 56579-71-6; *exo*-2-bicyclo[4.1.0]heptanol, 31022-87-4; *exo*-2-bicyclo[4.1.0]heptyl 3,5-dinitrobenzoate, 52688-98-9; 2-methylcyclohex-2-en-1-one, 1121-18-2; 2-chloro-2-methylcyclohexanone, 10409-46-8; 2-methylcyclohex-2-en-1-ol, 20461-30-7; 1-methyl-*endo*-2-bicyclo[4.1.0-heptanol, 13388-56-2; 1-methyl-*endo*-2-bicyclo[4.1.0]-heptyl 3,5-dinitrobenzoate, 71785-30-3; *endo*-2-methyl-2-bicyclo[4.1.0]heptanol, 67731-03-7; *exo*-2-methyl-2-bicyclo[4.1.0]heptanol, 67731-02-6; *endo*-2-methyl-2-bicyclo[4.1.0]-heptyl *p*-nitrobenzoate, 71766-61-5; *exo*-2-methyl-2-bicyclo[4.1.0]-heptyl *p*-nitrobenzoate, 71774-57-7; 3-methylcyclohex-2-en-1-one, 1193-18-6; 3-methylcyclohex-2-en-1-ol, 21378-21-2; 6-methyl-*endo*-2-bicyclo[4.1.0]heptanol, 13388-57-3; 6-methyl-*endo*-2-bicyclo[4.1.0]heptanol 3,5-dinitrobenzoate, 71766-62-6; *anti*-7-methyl-*endo*-2-bicyclo[4.1.0]heptanol, 62862-03-7; *syn*-7-methyl-*endo*-2-bicyclo[4.1.0]heptanol, 62862-02-6; *anti*-7-methyl-*endo*-2-bicyclo[4.1.0]heptyl 3,5-dinitrobenzoate, 71785-31-4; *anti*-7-methyl-*exo*-2-bicyclo[4.1.0]heptanol, 67731-05-9; *syn*-7-methyl-*exo*-2-bicyclo[4.1.0]heptanol, 71766-63-7; *anti*-7-methyl-2-bicyclo[4.1.0]heptanone, 71766-64-8; *syn*-7-methyl-2-bicyclo[4.1.0]heptanone, 71806-60-5; *anti*-7-methyl-*exo*-2-bicyclo[4.1.0]heptyl 3,5-dinitrobenzoate, 71785-27-8; 4-methylcyclohepten-4-ol, 71766-65-9; 1-methylcyclohepta-1,3-diene, 14947-22-9; 6-methyl-2-bicyclo[4.1.0]heptanone, 14845-41-1; 6-methyl-*exo*-2-bicyclo[4.1.0]heptanol, 67731-04-8; 6-methyl-*exo*-2-bicyclo[4.1.0]heptanol 3,5-dinitrobenzoate, 71766-66-0.

Lewis Acid Induced Cyclizations of Ethylenetricarboxylates

Barry B. Snider* and David M. Roush

Department of Chemistry, Princeton University, Princeton, New Jersey 08540

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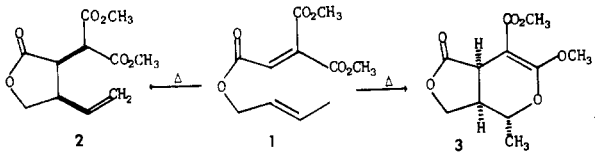
Treatment of allylic dimethyl ethylenetricarboxylates (**1**, **5**) with ferric chloride gives high yields of β-chloroalkyl γ-lactones (**4**, **6**) with stereospecific trans addition of carbon and chlorine to the double bond. With the cyclohexenyl triester **13**, only one of eight possible diastereomers is formed. Trimethyl ethylenetricarboxylate (**24**) adds to alkenes in the presence of ferric chloride in a cis fashion to give γ-lactones **26**, **28**, **30**, and **32**, arising from zwitterion formation followed by rapid attack of the carbonyl oxygen on the cation.

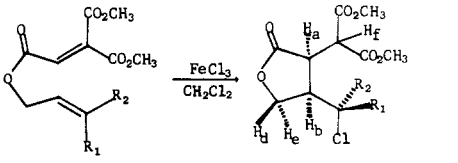
We are interested in developing intramolecular ene reactions[1] of unsaturated esters of allylic alcohols as a route to β-alkenyl-α-methylene lactones such as alantolactone.[2] We recently reported that acyclic allylic dimethyl ethylenetricarboxylates such as **1** react at 130 °C to give mixtures



2 **1** **3**

of the expected ene adduct **2** and a Diels–Alder adduct **3** which may be of value in iridoid synthesis.[3] Unfortunately, with the cyclohexenyl analogue **13** no reaction occurs prior to slow decomposition at 200 °C. Since the ene adducts of cycloalkenyl esters are needed to produce the desired fused α-methylene lactones we decided to investigate the effect of Lewis acids on this reaction.

Treatment of *trans*-2-butenyl triester **1** with ferric chloride in methylene chloride for 30 min at 25 °C gives an 85% yield of the chlorolactone **4**. The *cis*-2-butenyl



1, R_1 = H, R_2 = CH_3
5, R_1 = CH_3, R_2 = H
7, R_1, R_2 = CH_3
9, R_1 = H, R_2 = Ph

4, R_1 = H_c, R_2 = CH_3
6, R_1 = CH_3, R_2 = H_c
8, R_1, R_2 = CH_3
10, R_1 = H_c, R_2 = Ph
11, R_1 = Ph, R_2 = H_c

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