radiated for 120 min with eight 3100-Å Rayonet lamps. Addition of 1.0 mL of standard naphthalene solution to the reaction mixture permitted quantitative GC analysis, which indicated the following composition: 7.9% **3**-*c*, 85% **3**-*t*, 3.6% **4**-*t*, and 3.4% **6**.

Irradiation of *trans*-Cinnamyl Methyl Ether (4-*t*) Sensitized by 1,4-Dimethoxybenzene in Acetonitrile. A 10.0-mL acetonitrile solution of **4**-*t* (0.0837 g, 5.66×10^{-4} mol) and DMB (0.171 g, 1.24×10^{-3} mol) was deaerated with Ar for 10 min, capped, and irradiated for 120 min with eight 3100-Å Rayonet lamps. After addition of 1.0 mL of a standard naphthalene solution, the reaction mixture was quantitatively analyzed by GC to contain 81.5% **4**-*t* and 18.5% **4**-*c* only.

Irradiation of *trans*-Cinnamyl Methyl Ether (4-*t*) Sensitized by 1,4-Dimethoxybenzene in Methanol. A 10.0-mL methanol solution of **4**-*t* (0.0910 g, 6.15×10^{-4} mol) and DMB (0.167 g, 1.21×10^{-3} mol) was deaerated with Ar for 10 min, capped, and irradiated for 120 min with eight 3100-Å Rayonet lamps. At the end of this time, 1.0 mL of a standard naphthalene solution was added and the reaction mixture was quantitatively analyzed by GC to contain 5.8% **6**, 13.6% **4**-*c*, and 80.6% **4**-*t*.

Registry No. **1**-*c*, 77134-01-1; **1**-*t*, 21040-45-9; **2**-*t*, 50555-04-9; **3**-*t*, 4407-36-7; **4**-*t*, 22688-03-5; **5**, 7217-71-2; acetone, 67-64-1; 1,4-dimethoxybenzene, 150-78-7; 9,10-dimethoxy-2-ethylanthracene, 26708-04-3; 2-methoxynaphthalene, 93-04-9; *N*,*N*-dimethylaniline, 121-69-7; naphthalene, 91-20-3; *p*-xylene, 106-42-3; toluene, 108-88-3; 9,10-dimethoxyanthracene, 2395-97-3; benzene, 71-43-2; piperylene, 504-60-9.

2-Methyl Substituent Effects in the Antihomoaromatic Cycloprop[2,3]inden-1-yl Cation

Edwin C. Friedrich* and George De Lucca

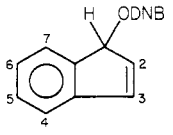
Department of Chemistry, University of California, Davis, California 95616

Received April 6, 1983

The rates and products of hydrolysis of the *endo*- and *exo*-2-methylcycloprop[2,3]inden-1-yl 3,5-dinitrobenzoates in 80% aqueous acetone have been determined. These are compared with similar data for the corresponding unsubstituted esters and for the 1-methyl-substituted and unsubstituted *endo*- and *exo*-2-bicyclo[3.1.0]hexyl 3,5-dinitrobenzoate model systems. This was done in connection with reports that toward acid-catalyzed epimerization in 50% aqueous dioxane at 80 °C 2-methyl substitution caused a 250-fold rate deceleration in the *endo*-cycloprop[2,3]inden-1-ol system. For the endo 3,5-dinitrobenzoates the 2-methyl substituent did produce a rate decrease; however, this was only by a factor of about 1.2 at 80 °C. In the 2-bicyclo[3.1.0]hexyl model system, the corresponding 1-methyl substitution caused approximately a 2-fold rate increase.

Introduction

Several papers have appeared from our laboratory during the past 5 years concerning the effects of methyl substitution on the rates of formation and products of reaction of the antiaromatic inden-1-yl and antihomoaromatic cycloprop[2,3]inden-1-yl cations. For example, Friedrich and Tam[1] found that methyl substitution at the 5- and 3-positions of inden-1-yl 3,5-dinitrobenzoate (**1**)



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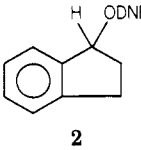

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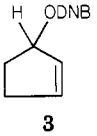

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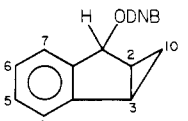
resulted in rate accelerations at 21 °C of about 70 and 1100, respectively, for solvolyses in trifluoroethanol. These were similar in magnitude to those found for methyl substitution in the corresponding nonantiaromatic model systems **2** and **3**. Thus, it was concluded that the nature and magnitude of charge delocalization into the benzene-ring and double-bond carbons of the inden-1-yl cation are virtually unaffected by antiaromatic effects.

In contrast to the results obtained with the inden-1-yl system, Friedrich et al.[2] found with cycloprop[2,3]inden-1-yl 3,5-dinitrobenzoate (**4**) that methyl substituent effects do not parallel those seen with the model system **5**. For



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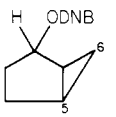

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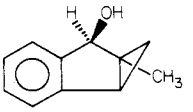
example, in 80% aqueous acetone at 80 °C, 3- and *anti*-10-methyl substitution caused rate accelerations of about 1.2 and 17, respectively, in the cycloprop[2,3]inden-]-yl system. On the other hand, for the corresponding 5- and *anti*-6-methyl-substituted 2-bicyclo[3.1.0]hexyl 3,5-dinitrobenzoate model systems, rate accelerations of 22[3] and 8.3,[4] respectively, were observed under the same reaction conditions.

In connection with the latter results, it was of considerable interest to note a report in 1981 by Răzuş and coworkers[5] of their investigations of the magnitudes of methyl substituent effects in perchloric acid catalyzed isomerizations of the 2- or 3-methyl-substituted *endo*-cycloprop[2,3]inden-1-ols (**6** and **7**) in 50% aqueous diox-



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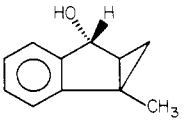

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(1) Friedrich, E. C.; Tam, T. M. *J. Org. Chem.* **1982**, *47*, 315.
(2) Friedrich, E. C.; Taggart, D. B.; Saleh, M. A. *J. Org. Chem.* **1977**, *42*, 1437.
(3) Friedrich, E. C.; Saleh, M. A. *J. Am. Chem. Soc.* **1973**, *95*, 2617.
(4) Friedrich, E. C.; Biresaw, G.; Saleh, M. A. *J. Org. Chem.* **1983**, *48*, 1435.
(5) Răzuş, A. C.; Wertheimer, V.; Glatz, A. M.; Arvay, Z. S.; Badea, F. *Rev. Roum. Chim.* **1981**, *26*, 457.

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Table I. Rates of Hydrolysis of Some Cycloprop[2,3]inden-1-yl 3,5-Dinitrobenzoates in 80% Aqueous Acetone

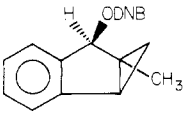
compound	temp, °C	$10^5 k_1$, s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
unsubstituted-*endo*[a]	100.0	22.0 ± 0.4		
	80.0	2.77 ± 0.09	26.4 ± 0.7	−5.0 ± 2.1
unsubstituted-*exo*[a]	100.0	25.7 ± 0.7		
	80.0	3.29 ± 0.04	26.2 ± 0.5	−5.2 ± 1.4
2-Me-*endo*	100.0	18.1 ± 0.5		
	80.0	2.29 ± 0.07	26.4 ± 0.7	−5.1 ± 1.6
2-Me-*exo*	100.0	29.1 ± 0.6		
	80.0	3.63 ± 0.1	26.4 ± 0.1	−4.4 ± 0.4

[a] Data from ref 2.

ane. They found that the rates of epimerization of 3-methyl-substituted and unsubstituted cycloprop[2,3]-inden-1-ols are very close in magnitude. This is in agreement with the 3,5-dinitrobenzoate hydrolysis results of Friedrich et al.[2] However, they reported that the 2-methyl substitution appears to cause a rate deceleration of about 250 for 0.3 M perchloric acid catalyzed epimerization of *endo*-cycloprop[2,3]inden-1-ol in 1:1 dioxane–water at 79.5 °C to *exo*-cycloprop[2,3]indene-1-ol.

Although, as mentioned earlier, studies in our laboratory of 3- and 10-methyl-substituted cycloprop[2,3]inden-1-yl 3,5-dinitrobenzoates revealed substituent-effect behaviors that did not parallel those seen in nonantihomoaromatic model systems, it was difficult to understand how a 2-methyl substituent could produce a large rate deceleration. Instead, it would have been anticipated that the 2-methyl substituent would behave similarly to the 3-methyl substituent and produce a small rate acceleration.

Because of the apparent controversy and interest that are present, we undertook a detailed investigation of 2-methyl substitution in the cycloprop[2,3]inden-1-yl system. For this study we wanted to examine the solvolytic behaviors of the *endo*- and *exo*-2-methylcycloprop[2,3]-inden-1-yl 3,5-dinitrobenzoates (**8** and **9**) and to compare these with the corresponding results observed for the unsubstituted systems and for suitable model system.



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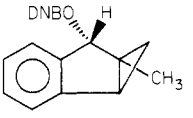

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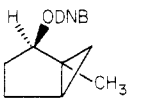
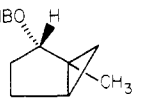
Results and Discussion

Synthesis of Starting Materials. 2-Methylinden-1-one was prepared following the procedure of Floyd and Allen[6] starting with a Reformatsky condensation of benzaldehyde and ethyl 2-bromopropionate. Reduction of the ketone with lithium aluminum hydride in ether at −78 °C gave 2-methylinden-1-ol, which was cyclopropanated by using a modification[7] of the Simmons–Smith procedure to give *endo*-2-methylcycloprop[2,3]inden-1-ol (**6**), which was converted into **8**. Hydrolysis of a portion of this 3,5-dinitrobenzoate in 80% aqueous acetone at 100 °C gave an 80:20 mixture of *exo*- and *endo*-2-methylcycloprop-[2,3]inden-1-ols. Conversion of this isomeric alcohol mixture into the corresponding 3,5-dinitrobenzoates followed by several recrystallizations from chloroform–pentane gave *exo*-2-methylcycloprop[2,3]inden-1-yl 3,5-dinitrobenzoate (**9**), which was greater than 95% isomerically pure.

For use as model systems to gauge the effects of a 2-methyl substituent on the cycloprop[2,3]inden-1-yl cation, the *endo*- and *exo*-1-methyl-2-bicyclo[3.1.0]hexyl 3,5-dinitrobenzoates (**10** and **11**) were needed. The endo-alcohol



10



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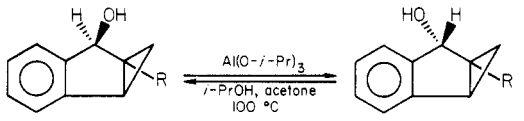
precursor of **10** was prepared by $LiAlH_4$ in ether reduction of 2-methyl-2-cyclopenten-1-one[8] followed by Simmons–Smith cyclopropanation[7] of the resulting allylic alcohol. The exo-alcohol precursor of **11** was obtained by aluminum isopropoxide in isopropyl alcohol equilibration of the endo alcohol to a 70:30 exo–endo mixture. The pure exo alcohol was isolated from the mixture by preparative-scale GLC. Preparation of the 3,5-dinitrobenzoates **10** and **11** were accomplished in the usual manner by using 3,5-dinitrobenzoyl chloride in pyridine.

Kinetic and Product Studies. The rates of hydrolysis of the *endo*- and *exo*-2-methylcycloprop[2,3]inden-1-yl 3,5-dinitrobenzoates (**8** and **9**) were measured at 80.0 and 100.0 °C in 80% aqueous acetone, and the results are summarized in Table I. Both esters exhibited good first-order kinetic behaviors and gave experimental infinities that were close to theoretical. Controls indicated that after heating at 100 °C for periods of time sufficient for 50% acid production, the initially pure dinitrobenzoates **8** and **9** underwent less than 10% isomerization due to ion-pair return.

In comparison of the kinetic results for the unsubstituted and 2-methyl-substituted cycloprop[2,3]inden-1-yl esters (Table I), it is seen that a small rate retardation effect caused by the methyl substituent is observed for the endo isomer. However, the magnitude of the effect is considerably smaller than that which may be inferred from the data reported by Rżuş and co-workers[5] from their study of acid-catalyzed rearrangement of the corresponding alcohols.[9]

It is of interest to note with the 2-methyl-substituted system that the endo–exo rate ratio of 0.63 at 80 °C is slightly smaller than that of 0.84 found for the unsubstituted system. This results from a combination of slight rate retardation of the endo isomer and slight rate acceleration of the exo isomer by the 2-methyl substituent as compared to the unsubstituted system and can be explained by considering aluminum isopropoxide in isopropyl alcohol equilibration data for the two systems. It is seen

(6) Floyd, M. B.; Allen, G. R. Jr. *J. Org. Chem.* **1970**, *35*, 2647.
(7) Rawson, R. J.; Harrison, I. T. *J. Org. Chem.* **1970**, *35*, 2057.
(8) (a) Traverso, G.; Pollini, G. P.; De Giuli, G.; Barco, A.; Invernizzi-Gamba, A.; *Gazz. Chim. Ital.* **1971**, *101*, 225. (b) Funk, R. L.; Vollhardt, P. C. *Synthesis* **1980**, 118.
(9) It is felt that this discrepancy may be a consequence of incorrect assignments of structures by Răzuş and co-workers.[5] Their results could be explained if the initial 8% of material they assigned as having the 2-methyl-*exo*-cycloprop[2,3]-inden-1-ol structure were actually an impurity and if the 2-methyl-*exo*- and *endo*-cycloprop[2,3]inden-1-ols were not separable under their analytical conditions. Both possibilities seem likely in light of available data.

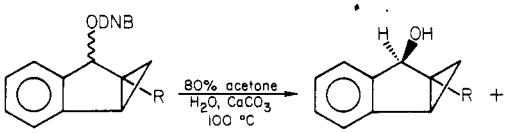


endo exo

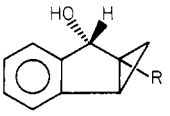
endo-exo
R = H 25:75
R = CH_3 45:55

that the 2-methyl substituent exerts a small steric effect that destabilizes the exo alcohol relative to the endo. The same steric effect should also be present in the *exo*-2-methylcycloprop[2,3]inden-1-yl 3,5-dinitrobenzoate, resulting in the larger k_{CH_3}/k_H value for the exo isomer and also in the smaller k_{endo}/k_{exo} rate ratio when compared to the unsubstituted system.

The hydrolysis products of the *endo*- and *exo*-2-methylcycloprop[2,3]inden-1-yl 3,5-dinitrobenzoates (**8** and **9**) were determined at 100 °C after 5 half-lives for acid production in 80% aqueous acetone buffered with calcium carbonate and are shown in eq 1 together with the results obtained earlier[2] for the corresponding unsubstituted derivatives. Within experimental error, both endo and exo



endo or exo R = H 20 ± 2%
R = CH_3 14 ± 2%



(1)

80 ± 2%
86 ± 2%

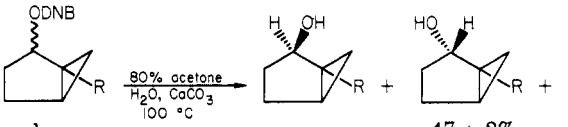
derivatives gave identical product mixtures. Controls run on the *endo*-2-methylcycloprop[2,3]inden-1-ol product under the conditions of the product study revealed that less than 5% isomerization or rearrangement to other materials had occurred.

In comparison of the products of hydrolysis of the isomeric 2-methylcycloprop[2,3]inden-1-yl 3,5-dinitrobenzoates with those for the unsubstituted parent compound, it is seen that both give only *endo*- and *exo*-cycloprop[2,3]inden-1-ols with the exo alcohol predominating. It is of interest to note that the exo–endo product ratio for the 2-methyl-substituted system is slightly higher than that for the unsubstituted system despite the fact that one would have anticipated the 2-methyl substituent to exhibit a steric effect decreasing solvent attack from the exo side. This points to the presence of a stereoelectronic effect for the cycloprop[2,3]inden-1-yl system that favors exo solvent attack.

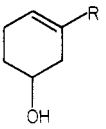
To be able to better understand how the 2-methyl substituent is affecting the cycloprop[2,3]inden-1-yl system, it was of importance to also study the hydrolyses of the *endo*- and *exo*-1-methyl-2-bicyclo[3.1.0]hexyl 3,5-dinitrobenzoates (**10** and **11**). The 2-bicyclo[3.1.0]hexyl system has a similar cyclopropylcarbonyl structure to that of the cycloprop[2,3]inden-1-yl system but in which antihomoaromatic effects are absent.

The rates of hydrolysis of **10** and **11** were measured at 80.0 and 100.0 °C in 80% aqueous acetone, and the results are given in Table II together with data for the corresponding unsubstituted esters for comparison. Controls on both the exo and endo esters showed that after heating at 100 °C for periods of time required for 50% acid production, less than 5% isomerization or other rearrangement had occurred.

The hydrolysis products of **10** and **11** were determined at 100 °C after 5 half-lives for acid production in 80% aqueous acetone. These are shown in eq together with similar data for the corresponding unsubstituted systems.[3]



endo or exo R = H 31 ± 2% 47 ± 2%
R = CH_3 22 ± 2% 25 ± 2%



(2)

22 ± 2%
53 ± 2%

Within experimental error, both the endo and exo derivatives gave identical product mixtures. Comparison with the data for the parent system reveals that the major effect of the 1-methyl substituent has been to increase the percentage of the ring-opened 3-cyclohexen-1-ol product at the expense of the bicyclo[3.1.0]hexyl products. This could be due to an electronic effect of the 1-methyl group that stabilizes the activated complex leading to the homoallylic alcohol product. The structure of the 3-methyl-3-cyclohexen-1-ol was confirmed by comparison with an authentic sample synthesized by literature procedures.[10] Controls run on the initially pure *endo*-1-methyl-2-bicyclo[3.1.0]-hexanol under similar conditions as for the product study indicated that only about 10% isomerization or rearrangement to other materials had occurred.

Returning to the kinetic data in Table II, it is seen that, in comparison to the parent 2-bicyclo[3.1.0]hexyl 3,5-dinitrobenzoate system, the 1-methyl substituent produces an acceleration in the rate of hydrolysis by a factor of about 2. This is similar in magnitude to the corresponding methyl substituent effects of about 5 observed by other workers[11] at the cyclopropyl methine carbon in the open-chain cyclopropylcarbinyl system. Thus, in the absence of antihomoaromatic effects, one might expect a methyl substituent in the corresponding 2-position of the cycloprop[2,3]inden-1-yl system to also accelerate the rate of hydrolysis by a factor of 2 and not to cause a slight decrease in reactivity as observed for the endo system.

It is interesting to note that the endo–exo rate ratio at 80 °C of 0.84 for the 1-methyl-substituted 2-bicyclo-[3.1.0]hexyl 3,5-dinitrobenzoates is somewhat lower than that of 1.2[3] for the unsubstituted system. This is related to the higher k_{CH_3}/k_H rate ratio of 2.4 at 80 °C for the exo isomer as compared to that of 1.6 for the endo isomer. A possible explanation stems from the observation that on aluminum isopropoxide in isopropyl alcohol equilibration the percentage of exo alcohol present at equilibrium for the 1-methyl-substituted 2-bicyclo[3.1.0]hexanol is 30%, while for the unsubstituted alcohols the percentage of exo alcohol has been reported[3] to be 65%. These results indicated that the 1-methyl substituent is exhibiting a destabilizing steric effect upon the exo alcohol. This destabilizing effect should also be reflected in the *exo*-1-

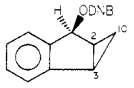
(10) (a) Birch, A. J. *J. Chem. Soc.* **1946**, 593. (b) Mitsui, S.; Ito, M.; Namba, A.; Senda, Y. *J. Catal.* **1975**, *36*, 119.
(11) (a) Schleyer, P. v. R.; Van Dine, G. W. *J. Am. Chem. Soc.* **1966**, *88*, 2321. (b) Roberts, D. D. *J. Org. Chem.* **1969**, *34*, 285.

Table II. Rates of Hydrolysis of Some 2-Bicyclo[3.1.0]hexyl 3,5-Dinitrobenzoates in 80% Aqueous Acetone

compound	temp, °C	$10^5 k_1$, s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
unsubstituted-*endo*[a]	100.0	1.24 ± 0.07	24.2 ± 0.3	−16.5 ± 0.8
	80.0	0.184 ± 0.011		
unsubstituted-*exo*[a]	100.0	1.15 ± 0.07	26.1 ± 0.4	−11.7 ± 1.0
	80.0	0.152 ± 0.019		
1-Me-*endo*	100.0	2.53 ± 0.11		
	80.0	0.301 ± 0.015	27.2 ± 0.5	−8.1 ± 1.5
1-Me-*exo*	100.0	2.72 ± 0.09		
	80.0	0.360 ± 0.010	25.7 ± 0.3	−11.0 ± 0.9

[a] Data for ref 3.

Table III. Methyl Substituent Effects in *endo*-Cycloprop[2,3]inden-1-yl 3,5-Dinitrobenzoate and Related Systems in 80% Aqueous Acetone at 80 °C

system	position of methyl substituent	k_{CH_3}/k_H
	2	0.83
	3	1.3[a]
	10	17[a]
	1	1.6
	5	22[b]
	6	8.3[c]

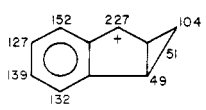
[a] Reference 2. [b] Reference 3. [c] Reference 4.

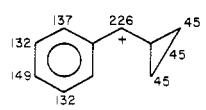
methyl-2-bicyclo[3.1.0]hexyl 3,5-dinitrobenzoate, resulting in it being more reactive than would be expected if the 1-methyl substituent is only exhibiting electronic effects, as with the *endo*-1-methyl isomer. The same steric factor is reflected in the exo–endo hydrolysis product ratio of 1.1 for the 1-methyl system, which is smaller than that of 1.3[3] for the unsubstituted system.

Table III summarizes the magnitudes of the various methyl substituent effects observed with the antihomoaromatic cycloprop[2,3]inden-1-yl 3,5-dinitrobenzoates and in several related nonantihomoaromatic model systems in 80% aqueous acetone at 80 °C. Only the data for the endo isomers are given, as with the exo isomers there is evidence for not only electronic but also steric effects with the 2-methyl-substituted derivatives.

It is of importance to note that the 2- and 3-methyl substituent effects in the cycloprop[2,3]inden-1-yl system are smaller than for the corresponding values in the model systems. However, the 10-methyl substituent effect is larger. The smaller substituent effects in the 2- and 3-positions have been explained as resulting from less delocalization of charge at these positions as a result of an antihomoaromatic interaction.

Similar conclusions as those given above regarding the electron delocalization in the cycloprop[2,3]inden-1-yl cation may be reached by considering ^{13}C NMR chemical shift data published by Olah and co-workers.[12] These





reveal considerable charge delocalization at the C-10 cyclopropyl carbon. However, they provide no electronic explanation as to why in our work the 2-methyl substituent produces a slight rate deceleration. Thus, the best explanation for the 2-methyl substituent effect must simply be one involving steric hindrance to solvation.

Experiment Section

General Procedures. Melting points and boiling points are uncorrected. NMR spectra were run on Varian Associates EM 360 and EM 390 instruments, and chemical shifts are reported in ppm downfield from tetramethylsilane internal or external standard. All analytical and preparative-scale GLC separations were accomplished by using an Aerograph A90P3 instrument equipped with a Pyrex injector insert and columns packed with 20% 3-nitro-3-methylpimelonitrile on 60/80 mesh non-acid-washed Chromosorb W. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

***endo*-2-Methylcycloprop[2,3]inden-1-yl 3,5-Dinitrobenzoate.** A sample of *endo*-2-methylcycloprop[2,3]inden-1-ol was prepared by a procedure similar to that reported by Wertheimer and co-workers[13] as a light yellow oil: NMR (CCl_4) δ 0.5 (m, 1 H, cyclopropyl), 0.7 (dd, 1 H, J = 4.5 and 7.5 Hz, cyclopropyl), 1.4 (s, 3 H, CH_3), 2.2 (dd, 1 H, J = 3.0 and 7.5 Hz, cyclopropyl), 3.2 (brs, 1 H, OH), 5.1 (brs, 1 H, CHOH), 7.0 (brs, 4 H, aromatic). To 3.0 g (18 mmol) of this material in 50 mL of dry pyridine was added 4.4 g (19 mmol) of recrystallized 3,5-dinitrobenzoyl chloride. After reacting for 2 h at 0 °C, the mixture was worked up following the usual procedure. The crude ester was recrystallized from 50 mL of 1:1 pentane–chloroform to give 3.1 g (49% yield) of a yellow powdery solid: mp 147–149 °C; NMR ($CDCl_3$) δ 1.1 (m, 2 H, cyclopropyl), 1.6 (s, 3 H, CH_3), 2.3 (m, 1 H, cyclopropyl), 6.7 (s, 1 H, CHO), 7.2 (brs, 4 H, aromatic), 9.2 (s, 3 H, aromatic).

Anal. Calcd for $C_{18}H_{14}N_2O_6$: C, 61.02; H, 3.98. Found: C, 60.67; H, 4.07.

***exo*-2-Methylcycloprop[2,3]inden-1-yl 3,5-Dinitrobenzoate.** A mixture of *endo*-2-methylcycloprop[2,3]inden-1-ol (4.8 g, 30 mmol), aluminum isopropoxide (6.4 g, 31 mmol), isopropyl alcohol (60 mL), and acetone (0.25 mL) was sealed in a Pyrex aampule and heated for 3 days at 100 °C. Workup gave 4.7 g of a 45:55 endo–exo mixture of 2-methylcycloprop[2,3]inden-1-ols. Various attempts to separate the mixture by using GLC techniques were unsuccessful. However, the exo isomer could be distinguished in the mixture by its characteristic ^1H NMR ($CDCl_3$) absorption at δ 0.2 (t, 1 H, cyclopropyl), 1.0 (q, 1 H, cyclopropyl), and 4.7 (brs, 1 H, CHOH).

Reaction of 4.5 g (28 mmol) of the isomeric mixture of alcohols with 8.4 g (36 mmol) of 3,5-dinitrobenzoyl chloride in 70 mL of pyridine was allowed to proceed at 0 °C for 2 h. The crude ester product obtained after workup was dissolved in 20 mL of 80% aqueous acetone, sealed in a large Pyrex ampule together with 3.6 g (36 mmol) of calcium carbonate, and heated at 100 °C for 6 h. Workup gave 3.7 g of an 80:30 exo–endo mixture of 2-methylcycloprop[2,3]inden-1-ols. Reaction of this mixture with 6.6 g (29 mmol) of 3,5-dinitrobenzoyl chloride in 50 mL of pyridine gave a crude ester product, which after two recrystallizations from 50 mL of 2:3 chloroform–pentane gave 1.5 g of pure *exo*-2-methylcycloprop[2,3]inden-1-yl 35-dinitrobenzoate. None of the endo isomer could be detected by NMR. Exo isomer: mp 153–158 °C; NMR ($CDCl_3$) δ 0.5 (m, 1 H, cyclopropyl), 1.2 (m, 1 H, cyclopropyl), 1.4 (s, 3 H, CH_3), 2.5 (m, 1 H, cyclopropyl), 6.3 (brs,

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1 H, CHO), 7.0–7.5 (m, 4 H, aromatic), 9.2 (s, 3 H, aromatic).

Anal. Calcd for $C_{18}H_{14}N_2O_6$: C, 61.02; H, 3.98. Found: C, 60.87; H, 4.06.

***endo*-1-Methylbicyclo[3.1.0]hexan-2-yl 3,5-Dinitrobenzoate.** The cyclopropanation of 8.6 g (88 mmol) of 2-methyl-2-cyclopenten-1-ol[8] with 17 g (260 mmol) of zinc dust, 2.6 g (26 mmol) of cuprous chloride, and 47 g (180 mmol) of methylene iodide in 30 mL of ether for 8 h in the usual manner[7] gave after workup and distillation 6.0 g (61% yield) of *endo*-1-methylbicyclo[3.1.0]hexan-2-ol: bp 50–52 °C (4.5 mm); n^{23}_D 1.4690°; NMR (CCl_4) δ 0.2 (m, 1 H, cyclopropyl), 0.7 (m, H, cyclopropyl), 1.0 (m, 1 H, cyclopropyl), 1.2 (s, 3 H, CH_3), 1.4–1.9 (m, 4 H), 3.2 (brs, 1 H, OH), 4.1 (m, 1 H, CHOH).

Following the usual procedure, 2.0 g (18 mmol) of *endo*-1-methylbicyclo[3.1.0]hexan-2-ol and 5.5 g (23 mmol) of 3,5-dinitrobenzoyl chloride in 50 mL of pyridine gave, after recrystallization from 100 mL of methylcyclohexane, 3.6 g (66% yield) of the ester as small needlelike, white crystals: mp 107–110 °C; NMR ($CDCl_3$) δ 0.5 (m, 1 H, cyclopropyl), 0.9 (m, 1 H, cyclopropyl), 1.2 (s, 3 H, CH_3), 1.0–2.3 (m, 5 H), 5.6 (t, 1 H, J = 7 Hz, CHO), 9.2 (s, 3 H, aromatic).

Anal. Calcd for $C_{14}H_{14}N_2O_6$: C, 55.03; H, 4.61. Found: C, 54.90; H, 4.63.

***exo*-1-Methylbicyclo[3.1.0]hexan-2-yl 3,5-Dinitrobenzoate.** Equilibration of 3.6 g (28 mmol) of *endo*-1-methylbicyclo[3.1.0]hexan-2-ol using 5.5 g (27 mmol) of aluminum isopropoxide, 65 mL of isopropyl alcohol, and 0.25 mL of acetone for 3 days at 100–105 °C in a Pyrex ampule gave after workup and distillation 2.9 g (81% yield) of a 70:30 mixture of *endo*- and *exo*-1-methylbicyclo[3.1.0]hexan-2-ols. The exo alcohol was isolated by preparative GLC: NMR (CCl_4) δ 0.2 (d, 2 H, J = 6 Hz, cyclopropyl), 1.2 (s, 3 H, CH_3), 0.9–2.2 (m, 6 H), 3.9 (m, 1 H, CHO).

Following the usual procedure, the reaction of 0.48 g (4.3 mmol) of *exo*-1-methylbicyclo[3.1.0]hexan-2-ol and 1.3 g (5.6 mmol) of 3,5-dinitrobenzoyl chloride in 30 mL of pyridine for 2 h at 0 °C gave, after recrystallization from 40 mL of methylcyclohexane, 0.90 g (69% yield) of the *exo*-3,5-dinitrobenzoate: mp 120–120.5 °C; NMR (CCl_4) δ 0.5 (d, 2 H, J = 5.5 Hz, cyclopropyl), 1.2 (s, 3 H, CH_3), 1.3–2.1 (m, 5 H), 5.4 (m, 1 H, CHO), 9.2 (s, 3 H, aromatic).

Anal. Calcd for $C_{14}H_{14}N_2O_6$: C, 55.03; H, 4.61. Found: C, 54.80; H, 4.64.

Kinetic Studies. The 80 vol % aqueous acetone solvent, sodium methoxide in methanol titrant, kinetic procedures, and controls were similar to those described previously.[2,3]

Hydrolysis Products. Hydrolysis product determinations and controls were similar to those described previously.[2,3] The *endo*- and *exo*-2-methylcycloprop[2,3]inden-1-yl 3,5-dinitrobenzoates gave only the corresponding endo and exo alcohols as products. These were readily determined by using ^{1}H NMR techniques as described earlier. The hydrolysis products of the *endo*- and *exo*-1-methyl-2-bicyclo[3.1.0]hexyl 3,5-dinitrobenzoates were determined by GLC on a 20% 3-nitro-3-methylpimelonitrile column to be a mixture of the *endo*- and *exo*-1-methyl-2-bicyclo[3.1.0]hexanols together with a major amount of 3-methyl-3-cyclohexen-1-ol. The structure of the latter material was demonstrated by comparing its GLC retention time and ^{1}H NMR spectrum with those of an authentic sample prepared according to literature procedures:[10] NMR (CCl_4) δ 1.3–2.4 (m, 6H), 1.6 (s, 3 H, CH_3), 3.4 (s, 1 H, OH), 3.7 (m, 1 H, CHOH), 5.3 (m, 1 H, CH=C).

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Synthesis of Cyclic Azomethine Imines from Aza β-Lactams. Conversion of 3-Oxo-1,2-diazetidinium Tosylates into 1-Substituted 3-Oxo-1,2-diazetidinium Inner Salts[1,2]

Edward C. Taylor,* Robert J. Clemens, and Huw M. L. Davies

Department of Chemistry, Princeton University, Princeton, New Jersey 08544

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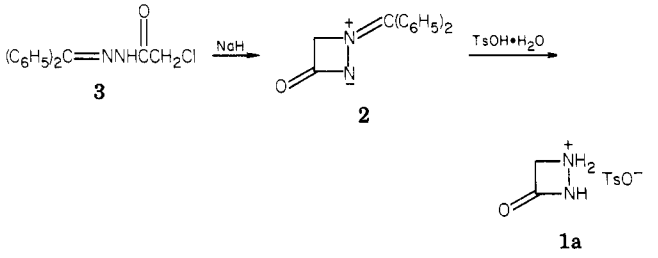
Dehydrohalogenation of (α-haloacyl)hydrazones of benzophenone gives 1-(diphenylmethylene)-3-oxo-1,2-diazetidinium inner salts (**2**, **5**, **6**), which are hydrolyzed with 1 molar equiv of *p*-toluenesulfonic acid monohydrate in CH_2Cl_2 to give 3-oxo-1,2-diazetidinium tosylates (**1**). Several procedures have been found for the transformation of these aza β-lactams to previously inaccessible 3-oxo-1,2-diazetidinium inner salts (**4**) by reaction with aromatic aldehydes, aralkyl ketones, and dialkyl ketones. 2,7-Disubstituted 1,3,6,8-tetraazatricyclo[6.2.0.0^{3,6}]decane-4,9-diones (**11**), which are dimers of ylides corresponding to **4**, are obtained by condensation of **1** with aliphatic aldehydes.

We have recently described a simple synthesis of the novel aza β-lactam 3-oxo-1,2-diazetidinium tosylate (**1a**) by stoichiometric acid-catalyzed hydrolysis of 1-(diphenylmethylene)-3-oxo-1,2-diazetidinium inner salt (**2**). This latter compound, as well as a number of related 1-(diarylmethylene) derivatives, resulted from an unexpectedly facile intramolecular dehydrohalogenation of (α-chloroacyl)hydrazones of the respective diaryl ketones (e.g., **3**).[3] Since preliminary experiments have shown that



3 2 1a

ylides such as **2**, as well as the parent 3-oxo-1,2-diazetidinium tosylate (**1a**), are versatile, reactive precursors of

(1) We are deeply indebted to Eli Lilly & Co. for their generous financial support of this work.

(2) Preliminary communication: Taylor, E. C.; Davies, H. M. L.; Clemens, R. J.; Yanagisawa, H.; Haley, N. F. *J. Am. Chem. Soc.* **1981**, *103*, 7660–7661.

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