3β-Acetoxy-2α,3α-oxidocholestane (IX, 850 mg) was heated with morpholine as above except under a nitrogen atmosphere. Evaporation of the solvent and careful crystallization from acetone yielded 550 mg of Xb. One further recrystallization from Skellysolve F (bp 40–50°) gave ketone Xb: mp 148–150°; ν_{max} 1710, 1280 cm^{-1}.

Anal. Calcd for $C_{31}H_{53}NO_2$: C, 78.92; H, 11.32. Found: C, 79.14; H, 11.06.

Crystallization of Xb from 95% ethanol or bubbling air through a solution of Xb led to products containing variable amounts of Xb and XII as indicated by infrared absorption at 1710 and 1675 cm^{-1}.

2α-(2′,6′-Dimethylmorpholino)cholestan-3-one (Xc) was prepared as described for Xb using 2,6-dimethylmorpholine. The product was crystallized from acetone (850 mg), mp 147–150°. Its infrared spectrum showed peaks at 1720 and 1675 cm^{-1} indicative of a mixture of saturated and unsaturated amino ketone.

Anal. Calcd for $C_{33}H_{57}NO_2$ (saturated ketone): C, 79.30; H, 11.50. Found: C, 79.54; H, 11.58.

2-Morpholino-1-cholesten-3-one (XII).—Amino ketone Xb (180 mg) in 3 ml of morpholine was heated on a steam bath for 60 min. During this time oxygen was passed through the solution. Work-up as above and crystallization of the product from methanol yielded 100 mg of pure, unsaturated amino ketone XII: mp 171–172°; λ_{max} 297 mμ (ε 2820); ν_{max} 1675 (conjugated C=O), 1612 (conjugated C=C); nmr τ 4.5 (broadened singlet).

Anal. Calcd for $C_{31}H_{51}NO_2$: C, 79.26; H, 10.94. Found: C, 79.26; H, 11.03.

2α-Morpholinocholestan-3β-ol (XI).—To a solution of 350 mg of crude amino ketone Xb in 30 ml of methanol at 30° was added sodium borohydride in large excess (*ca.* 700 mg). After 3.5 hr the solution was poured into ice–water and extracted with ether. Evaporation and crystallization from acetone gave 290 mg of XI, mp 179–180°.

Anal. Calcd for $C_{31}H_{55}NO_2$: C, 78.59; H, 11.70. Found: C, 78.75; H, 11.67.

Androstan-17-one Hydrazone.—A solution of 2.1 g of androstan-17-one, mp 118–118.5°, in 20 ml of ethanol, 10 ml of triethylamine, and 15 ml of hydrazine hydrate was refluxed for 90 min, after which time it was poured into ice–water. The precipitate was collected by filtration, washed with water, and dried (2.2 g). Crystallization of the product from methanol–water furnished white crystals: mp 154–156°; ν_{max} 3350 (NH), 1670 (C=N), 930 cm^{-1}.

Anal. Calcd for $C_{19}H_{32}N_2$: C, 79.16; H, 11.11. Found: C, 79.26; H, 11.26.

17-Bromo-16-androstene.—A solution of N-bromosuccinimide (3 g) in 30 ml of dry pyridine was added, dropwise, to a cold solution of the androstan-17-one hydrazone (2.10 g) in dry pyridine (40 ml) with agitation. Nitrogen gas was evolved during the reaction. After the addition, the mixture was stirred for an additional 15 min. The solution was poured into ice–water and extracted with chloroform. After washing with 10% of hydrochloric acid, water and drying over magnesium sulfate, the solvent was evaporated and the residue was crystallized from acetone (1.4 g). Two more crystallizations brought the melting point to 122–124°; ν_{max} 1600 cm^{-1} (C=C).

Anal. Calcd for $C_{19}H_{29}Br$: C, 67.65; H, 8.60. Found: C, 67.56; H, 8.71.

17β-Bromo-16α,17α-oxidoandrostane (Ia).—Bromo epoxide Ia (1.0 g) was obtained from 1.4 g of 17-bromo-16-androstene as described for I. It melted at 164–165° after one recrystallization from methanol–acetone: ν_{max} 850–750 cm^{-1} (four peaks characteristic for the bromooxidoandrostane).

Anal. Calcd for $C_{19}H_{29}BrO$: C, 64.58; H, 8.21. Found: C, 64.75; H, 8.32.

16β-Morpholinoandrostan-17-one (IIf).—Bromo epoxide Ia (0.6 g) was heated under reflux for 4 hr with an excess of morpholine and worked up as before to yield 330 mg of IIf after recrystallization from methanol: mp 174–176°; ν_{max} 1740 cm^{-1}.

Anal. Calcd for $C_{23}H_{37}NO_2$: C, 76.83; H, 10.37. Found: C, 76.91; H, 10.40.

Registry No.—17-Bromo-16-androsten-3β-ol acetate, 7481-29-0; I, 7541-70-0; IIa, 7458-96-0; IIb, 7458-97-1; IIc, 7458-98-2; IId, 7541-71-1; IIe, 7491-66-9; 3β-hydroxy-16β-morpholinoandrost-17-one, 3000-34-8; IIIa, 5986-91-4; IIIb, 5986-90-3; VIa, 7547-75-3; VIa hydrochloride, 7548-18-7; VIa picrate, 7548-19-8; VIb, 7541-73-3; VIc, 5986-98-1; VII, 7541-74-4; IX, 7459-00-9; Xa, 7459-01-0; Xb, 7459-02-1; Xc, 7541-75-5; XII, 7459-03-2; XI, 7459-04-3; androst-17-one hydrazone, 7459-05-4; 17-bromo-16-androstene, 7459-06-5; Ia, 7481-31-4; IIf, 7459-07-6.

Acknowledgment.—We are grateful to the Public Health Service (Grant CA-04474 by the National Cancer Institute) and to the J. G. and F. C. Searle Fund for support of this work.

Preparation and Solvolysis of *trans*-3-Vinylcyclopentyl Bromide

JOHN P. SCHAEFER AND JERRY HIGGINS

Department of Chemistry, University of Arizona, Tucson, Arizona

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Norcamphor was oxidized under Baeyer–Villiger conditions to its lactone (**3**) which on reaction with dimethylamine gave N,N-dimethyl-*cis*-3-hydroxycyclopentylacetamide (**4**). Reduction of **4** to the corresponding amine (**5**) followed by oxidation with hydrogen peroxide and pyrolysis produced *cis*-3-vinylcyclopentanol (**6**) which was converted to *trans*-3-vinylcyclopentyl bromide (**1**) by reaction with triphenylphosphine dibromide. Solvolysis of **1** and of the tosylate of **6** under a variety of conditions gave only derivatives of **6** and its epimer and the solvolysis of **1** was found to be unassisted. Stereoelectronic factors responsible for these observations are evaluated and discussed.

Bartlett[1-5] and his associates have recently published the results of a comprehensive study of the solvolyses of 1-(Δ^3-cyclopentenyl)-2-ethyl arenesulfonates and some related compounds and have used their data to support arguments for the intervention of a "non-classical" norbornyl cation during the solvolytic process. This contention is based upon the observation of enhanced rates of solvolysis and the formation of bicyclic products for compounds in which interaction between the unsaturated center and the incipient carbonium ion is stereoelectronically favorable. A factor which complicates this interpretation of their data is that in the reactions of 1-(Δ^3-cyclopentenyl)-2-ethyl tosylate, considerable driving force for both participation and cyclization must arise from the conversion of a primary to a secondary cation. In fact, as Bartlett[2] pointed out, in the solvolysis of 1-(Δ^3-cyclo-

(1) P. D. Bartlett and S. Bank, *J. Am. Chem. Soc.*, **83**, 2591 (1961).
(2) P. D. Bartlett, S. Bank, R. J. Crawford, and G. H. Schmid, *ibid.*, **87**, 1288 (1965).
(3) P. D. Bartlett and G. D. Sargent, *ibid.*, **87**, 1297 (1965).
(4) P. D. Bartlett, W. D. Closson, and T. J. Cogdell, *ibid.*, **87**, 1308 (1965).
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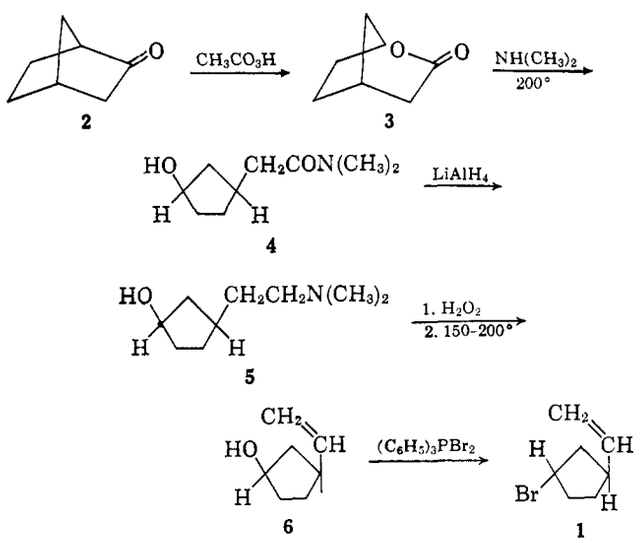
pentenyl)-2-propyl *p*-nitrobenzenesulfonate both the kinetic driving force and extent of participation are reduced relative to the primary system. This complication necessarily weakens any arguments which ascribe the interesting behavior of this system to the unusual properties of the norbornyl cation.

A system which would avoid this difficulty (but which has some inherent drawbacks of its own) is represented by *trans*-3-vinylcyclopentyl bromide (**1**). The preparation of this compound is outlined below in Scheme I.

SCHEME I



Utilizing the procedure of Meinwald and Frauenglass,[6] norcamphor (**2**) was oxidized to the lactone (**3**); reaction of **3** with dimethylamine in an autoclave heated to 200° for 2 days gave N,N-dimethyl-*cis*-3-hydroxycyclopentylacetamide (**4**) in 88% yield. Reduction of the amide by lithium aluminum hydride proceeded smoothly and the tertiary amine (**5**) was obtained in 90% yield. Oxidation of **5** to the corresponding N-oxide with hydrogen peroxide was exothermic and gave a viscous oil which readily crystallized on standing. Pyrolysis of the N-oxide at 160–200° produced *cis*-3-vinylcyclopentanol in an over-all yield of 68% from **5**. The stereochemistry of compounds **4**, **5**, and **6** follows from the method of synthesis and the assigned structures were documented by ample spectral and analytical data.

To invert the configuration at C-1, **6** was treated with triphenylphosphine dibromide in dimethylformamide, and **1**, a colorless oil, was isolated in 73% yield after purification. The stereochemical assignment to **1** is based upon earlier work in similar systems which demonstrated that the mechanistic course of the reaction of triphenylphosphine dibromide with alcohols proceeds with inversion of configuration. Horner, Oediger, and Hoffmann[7] showed that the reaction of menthol with this reagent gave only neomenthyl bromide. Similarly, we[8] have found that the conversion of optically active *endo*-norbornanol to *exo*-norbornyl bromide is accompanied by no loss in optical purity.

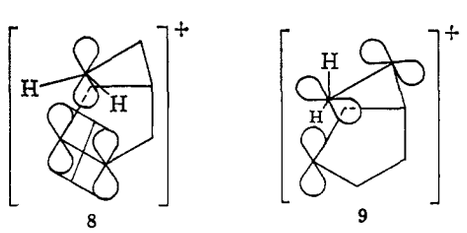
Product studies of the solvolysis reactions of **1** were carried out under a variety of conditions. When **1** was dissolved in 97–100% formic acid containing equimolar amounts of sodium formate and silver perchlorate a precipitate of silver bromide was rapidly formed. The product was saponified and the alcohol was isolated by vapor phase chromatography and identified as 3-vinylcyclopentanol (stereochemistry not ascertained) by its retention time and infrared spectrum. Within the limits of detectability (<1%) no norbornanol or other products were present.

Repetition of this experiment in water containing silver nitrate also produced 3-vinylcyclopentanol and no norbornanol. A 3,5-dinitrobenzoate of the product melted at 74.8–75.4° whereas an authentic sample of the 3,5-dinitrobenzoate of **6** melts at 81.0–81.7°; an equimolar mixture of these two samples melted at 76.1–78.8°. These results indicate that the product of solvolysis is a mixture of isomers which is probably rich in the expected *cis* alcohol.

Reaction of **6** with *p*-toluenesulfonyl chloride in pyridine gave a crystalline tosylate of the *cis* alcohol. Solvolysis of the tosylate in glacial acetic acid containing potassium acetate gave an oil which, within experimental error (<1%), contained no norbornyl acetate as ascertained by vapor phase chromatography. After purification, the product was found to be 3-vinylcyclopentyl acetate on the basis of its infrared and nmr spectra and elemental analysis. No attempt was made to determine the stereochemistry of the solvolysis product. The above experiments all indicate that *the 3-vinylcyclopentyl cation does not cyclize to the norbornyl cation.*

Despite the absence of cyclized products from the solvolysis reaction, the possibility of participation by the double bond during the ionization step still existed. Accordingly, rate studies in 50% aqueous ethanol were initiated with cyclopentyl bromide (**7**) serving as a model compound. Rate constants for **7** and **1** were $1.4 \pm 0.2 \times 10^{-3}$ sec^{-1} and $6.2 \pm 0.2 \times 10^{-4}$ sec^{-1}, respectively, at 69.64° which corresponds to a decrease in solvolysis rate by a factor of about 2 upon introduction of the double bond. This effect is consistent with that expected purely on the basis of the rate decreasing inductive effect of a nonparticipating double bond in the proximity of the reaction center.[4] The results of the above kinetic and product studies were not unexpected and although they provide no further insight to the nature or stability of the norbornyl cation, they do serve to point out some steric and electronic factors of importance in the π route to cyclization during solvolysis.

The first factor which must be considered is whether the carbon atoms which are hypothetically involved in the cyclization process are capable of sufficiently close approach so that interaction between p and π orbitals can occur. If we compare Dreiding models of the 1-(Δ^3-cyclopentyl)-2-ethyl cation (**8**) of Bartlett[1,2] and the 3-vinylcyclopentyl cation (**9**) generated



8 9

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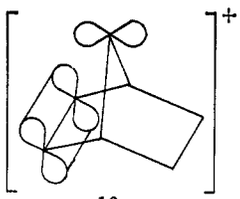
in this study, it becomes apparent that the geometry of these ions is such that the distance of approach between interacting centers is approximately 0.4 A less in **8** than in **9** if no compression strain is introduced. A more serious difficulty with **9**, however, is that a vinylic hydrogen will offer considerable steric interference to orbital interaction. Both of these objections could probably be overcome at a small additional expenditure of energy by introducing a degree of torsional strain into the cation.

A second factor which must be considered when contrasting the behaviors of **8** and **9** is the different types of orbital overlap in the two systems. Favorable overlap in **8** is evident from the enhanced rate of solvolysis, its precursor and the formation of cyclized products. This type of p–π interaction is also encountered in the formation of stable metal ion–olefin complexes and is evidently energetically favorable.[9]

A system which is similar to **9** from an electronic viewpoint is the 7-bicyclo[2.2.1]heptenyl cation (**10**).



10

In this carbonium ion, overlap is sufficiently important to cause an enormous solvolysis rate increase[10] relative to the saturated analog of the tosylate leading to **10**. The prognosis for overlap is less favorable for **9**, however, since, at best, interaction between only a portion of the π bond and the p orbital can occur.

A third barrier to successful cyclization becomes apparent from a consideration of the conversion of **9** to the norbornyl cation if it is assumed that orbital overlap in **9** is possible and significant. As a σ bond between the interacting orbitals is formed, rotation of the terminal methylene group would have to occur, destroying the π bond; the cation which would be forming would of necessity be a *classical* norbornyl cation and therefore provide little driving force for cyclization. In view of the complexities involved, however, it is not possible for us to draw any firm conclusions regarding which of the abovementioned factors are ultimately responsible for the failure to observe a conversion of **1** to the norbornyl system. This decision must be deferred until studies with other model compounds give us a better understanding of the relative importance of the various stereoelectronic factors involved in the π route to ring closures.

Experimental Section

Oxidation of Norcamphor.—The Baeyer–Villiger oxidation of norcamphor was accomplished by a procedure similar to that described by Meinwald and Frauenglass.[6] From 20 g of ketone there was obtained 17.5 g (77%) of lactone, bp 73–75° (0.05 mm).

N,N-Dimethyl-*cis*-hydroxycyclopentylacetamide.—To 122 g (0.9 mole) of the lactone was added an excess of dimethylamine and 1.0 g of dimethylamine hydrochloride and the mixture was heated in an autoclave at 200° for 2 days. Distillation of the product gave 145 g (0.85 mole) (88%) of amide, bp 111–113° (0.05 mm), n^{26}D 1.4950. The infrared spectrum showed maxima at 3400 (OH) and 1650 cm^{-1} (C=O), and the nmr spectrum was consistent with the formulated structure. *Anal.* Calcd for $C_9H_{17}NO_2$: C, 63.13; H, 10.01; N, 8.18. Found: C, 62.91; H, 9.48; N, 8.67.

Reduction of the Amide.—To 145 g (0.85 mole) of the above amide dissolved in 500 ml of diethyl ether was added 34 g of lithium aluminum hydride in 1 l. of diethyl ether and the solution was stirred overnight at room temperature. The solution was worked up by adding 60 ml of water followed by 50 ml of 50% sodium hyroxide solution, filtering to remove solids, and distilling the dried ether solution. The product (120 g, 90%) was collected at 74–76° (0.5 mm), n^{20}D 1.4652. The infrared spectrum indicated the presence of hydroxyl (3375 cm^{-1}) and the absence of a carbonyl, and the nmr spectrum was consistent with the formulated structure **5**. *Anal.* Calcd for $C_9H_{19}NO$: C, 68.74; H, 12.18; N, 8.91. Found: C, 68.95; H, 12.28; N, 9.28.

***cis*-3-Vinylcyclopentanol.**—To 20 g of amine (**5**) in 50 ml of methanol was added dropwise, 80 ml of 30% hydrogen peroxide. The solution was stirred overnight and the excess hydrogen peroxide was decomposed with activated platinum. The solution was concentrated under vacuum to give a heavy oil which readily crystallized.

The crystalline N-oxide was pyrolized at 160–200° to give 9.3 g (68%) of product, bp 87–89° (26 mm), n^{28}D 1.4665. The infrared spectrum showed absorption at 3345 (OH), 1650, and 910 cm^{-1} (vinyl), and the nmr spectrum was consistent with the formulated structure **6**. *Anal.* Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 74.47; H, 11.03.

***cis*-3-Vinylcyclopentyl 3,5-Dinitrobenzoate.**—One gram of *cis*-3-vinylcyclopentanol was dissolved in 3 ml of anhydrous pyridine and an equimolar quantity of 3,5-dinitrobenzoyl chloride was added. The solution ws heated to reflux and then stirred at room temperature for 30 min. A sufficient amount of ice was added to precipitate the product which was filtered, washed with 10% sodium carbonate, and recrystallized twice from 95% ethanol to give 0.51 g of product melting at 81.0–81.7°. *Anal.* Calcd for $C_{14}H_{14}N_2O_6$: C, 54.94; H, 4.61; N, 9.15. Found: C, 54.69; H, 4.67; N, 9.37.

***trans*-1-Bromo-3-vinylcyclopentane.**—To 14.1 g (0.054 mole) of triphenylphosphine in 50 ml of dry dimethylformamide was added dropwise with cooling 8.7 g (0.054 mole) of bromide. To this solution was added 6.0 g (0.053 mole) of *cis*-3-vinylcyclopentanol. The solution was heated at 80–130° and dimethylformamide plus product was collected at 26 mm. The solution was diluted with 500 ml of water, neutralized, extracted with ether, and distilled twice to give 6.8 g (73%) product, bp 66.0–67.5° (26 mm), n^{26}D 1.4958. *Anal.* Calcd for $C_7H_{11}Br$, C, 48.02; H, 6.29. Found: C, 48.11; H, 6.57.

***cis*-3-Vinylcyclopentyl Tosylate.**—To 1 g of *cis*-3-vinylcyclopentanol in 5 ml of pyridine was added 1.7 g *p*-toluenesulfonyl chloride. The solution was warmed for 5 min and then allowed to stand for 10 hr. The solution was diluted with 25 ml of cold water and a viscous oil separated. The product was extracted with ethyl ether, dried over magnesium sulfate, and concentrated to give 0.95 g of *cis*-3-vinylcyclopentyl tosylate which crystallized from hexane. The product melted at 40.8–41.4° and decomposed at elevated temperatures. The nmr spectrum showed three hydrogens at δ 2.4, one vinyl hydrogen at 4.7, two vinyl hydrogens at 4.85, one hydrogen at 5.0, four aromatic hydrogens between 7 and 8, and seven additional hydrogens in the range 1.0–2.55. *Anal.* Calcd for $C_{14}H_{18}O_3S$: C, 63.14; H, 6.81. Found: C, 63.46; H, 6.94.

Acetolysis of *cis*-3-Vinylcyclopentyl Tosylate.—To 10 ml of glacial acetic acid containing 0.2 g of potassium acetate was added 0.55 g of tosylate and the reaction was heated at 100° for 8 hr. The reaction solution was then added to 75 ml of ice water, extracted with ethyl ether, dried, and concentrated to give a light brown oil. The 3-vinylcyclopentyl acetate (stereochemistry not determined) was isolated and purified only for analytical purposes by gas chromatography (Aerograph, Wilkens Instrument and Research Inc.) using a 5 ft × 0.25 in. Carbowax column. No detectable norbornyl acetate was present. Infrared spectra showed no hydroxyl absorption in range 3400, strong absorption at 1745 and 1240, and sharp bands at 1644 and 916 cm^{-1}, and nmr showed three hydrogens at δ 1.9, four hydrogens in the range 4.7–6.0, and seven additional hydrogens between

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1.0 and 3.0. *Anal.* Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.42; H, 9.38.

Solvolysis of *trans*-1-Bromo-3-vinylcyclopentane.—To 1.3 g of silver perchlorate in 15 ml of formic acid (97–100%) buffered with an equimolar quantity of sodium formate was added 0.8 g of *trans*-1-bromo-3-vinylcyclopentane and the reaction was stirred for 10 min. A 10% *M* excess of 20% sodium hydroxide solution was added and the solution was stirred 2 hr. The product was extracted with ethyl ether, dried, and concentrated to give 0.29 g of brown oil. The product was isolated and purified by analytical vpc using a 5 ft × 0.25 in. Carbowax column to give 3-vinylcyclopentanol (stereochemistry not determined) as the major product. The product was identified by comparison of its vpc retention time and of its infrared spectrum with an authentic sample.

Solvolysis of *trans*-1-Bromo-3-vinylcyclopentane in 50% Aqueous Ethanol.—The solvolysis was carried out at 69.64 ± 0.01° (temperature calibrated with National Bureau of Standards thermometer and deviation averaged over a period of 3 days) utilizing the conductimetric technique to give absolute rate constants for cyclopentyl bromide as $1.4 \pm 0.2 \times 10^{-3}$ sec^{-1} and for *trans*-1-bromo-3-vinylcyclopentane as $6.2 \pm 0.2 \times 10^{-4}$ sec^{-1}.

Solvolysis of *trans*-1-Bromo-3-vinylcyclopentane in Aqueous Silver Nitrate.—Four grams of *trans*-1-bromo-3-vinylcyclopentane was added dropwise to 6 g of silver nitrate in 100 ml of water and the solution was stirred for 30–45 min and then the silver bromide was filtered. The reaction mixture was extracted twice with 50-ml portions of ethyl ether, dried, and concentrated to give 1.4 g of crude product. The reaction product was isolated and purified by analytical vpc and identified by comparison of its vpc retention time and its infrared spectrum with those of an authentic sample, and the 3,5-dinitrobenzoate was prepared as above. The 3,5-dinitrobenzoate melted at 74.8–75.4° (low melting probably owing to *cis–trans* isomers) and the mixture melting point with the *cis*-3-vinylcyclopentyl benzoate was 76.1–78.8°. *Anal.* Calcd for $C_{14}H_{14}N_2O_8$: C, 54.94; H, 4.61; N, 9.15. Found: C, 55.07; H, 4.49; N, 8.83.

Registry No.—**3**, 5724-61-8; **4**, 7442-41-3; **1**, 7442-42-4; **6**, 7442-43-5; **5**, 7442-44-6; *cis*-3-vinylcyclopentyl 3,5-dinitrobenzoate, 7430-87-7; *cis*-3-vinylcyclopentyl tosylate, 7442-45-7; 3-vinylcyclopentyl acetate, 7442-46-8; *trans*-3-vinylcyclopentyl 3,5-dinitrobenzoate, 7430-88-8; 3-vinylcyclopentanol, 7442-71-9; **7**, 137-43-9.

The Mechanism of Oxidation of Cyclic Alcohols by Cerium(IV)[1]

HAROLD L. HINTZ[2,3] AND DONALD C. JOHNSON

The Institute of Paper Chemistry, Appleton, Wisconsin

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Cerium(IV) oxidations of a series of cyclic alcohols and glycols were studied in 1.0 *M* perchloric acid and in mixed sulfuric and perchloric acids. The results are related to the oxidation phase of the cerium(IV) initiation of graft polymerization onto cellulose. Definite evidence was obtained for formation of cerium(IV) complexes with *cis*- and *trans*-1,2-cyclohexanediols, *trans*-2-methoxycyclohexanol, and cyclohexanol in 1.0 *M* perchloric acid. The magnitudes of the equilibrium constants for complex formation indicated that the 1,2-cyclohexanediols form chelate complexes. In mixtures of sulfuric and perchloric acids there were no large differences in the over-all oxidation rates of *cis*- and *trans*-1,2-cyclohexanediol or of *cis*- and *trans*-1,2-cyclopentanediol. The effect of ring size was considerable, however, with the cyclopentanediols reacting much more rapidly (200–1000-fold) than cyclohexanediols. A study of the effect of sulfate ion concentration indicated that $CeSO_4^{2+}$ is the most reactive of the cerium(IV)–sulfate complexes present in the sulfuric–perchloric acid systems. The relative reactivities of the cellulose model compounds, *trans*-1,2-cyclohexanediol, cyclohexanemethanol, and tetrahydropyran-2-methanol, suggested that cerium(IV) oxidation of cellulose will occur mainly, but not exclusively, at the C_2–C_3 glycol.

The oxidations of alcohols and glycols by cerium(IV) are generally believed to proceed by disproportionation of coordination complexes. Evidence for complex formation has been obtained by kinetic and spectrophotometric methods in cerium(IV) oxidations of many compounds in perchloric and nitric acid media.[4–9] Complex formation has been detected in cerium(IV) oxidations in sulfuric acid media only in a few instances.[10–12] Reactions in sulfuric acid often follow second-order kinetics,[8,13–16] and a direct oxidation mechanism, without complex formation, has been suggested for oxidations in this acid.[14] However, it is also possible that oxidation proceeds through an intermediate complex, but with a small equilibrium constant for complex formation.

The complex formed in the cerium(IV) oxidation of a 1,2-glycol may be either a chelate complex or an acyclic complex in which only one hydroxyl is coordinated with the cerium(IV). Littler and Waters[17] concluded from studies of the relative rates of oxidation of certain glycols and their monomethyl ethers that cerium(IV) oxidations of 1,2 glycols proceed by an acyclic mechanism. On the other hand, Duke and Forist[4] assumed that both hydroxyls of 2,3-butanediol coordinate with cerium(IV), and the spectrophotometric measurements of Offner[18] clearly suggest the possibility of chelate complex formation with cerium(IV). The nature of the complexes formed in the oxidation of 1,2 glycols by

(1) (a) This paper is a portion of a thesis submitted by H. L. H. in partial fulfillment of the requirements of The Institute of Paper Chemistry for the degree of Doctor of Philosophy from Lawrence University, Appleton, Wis., Jan 1966. (b) Presented in part at the Winter Meeting of the American Chemical Society, Phoenix, Ariz., Jan 1966.

(2) National Science Foundation Cooperative Graduate Fellow, 1962–1965.

(3) West Virginia Pulp and Paper Co., Charleston, S. C.

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