Ceric Ammonium Nitrate Oxidation of Cyclic Ketones

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Ceric ammonium nitrate oxidation of cyclohexanone, cyclopentanone, and norbornanone gives nitrato-carboxylic acids, oxidation of adamantanone and adamantan-2-ol gives the lactone **14**.

Par oxydation avec le nitrate cérique d'ammonium, la cyclohexanone, la cyclopentanone, et la norbornanone donnent des acides nitrato-carboxyliques correspondants. L'oxydation de l'adamantanone ou de l'adamantanol-2 conduit à la lactone **14** correspondante.

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Ceric ion in various coordinated forms is a strong oxidizing agent. Numerous reports of utilizing Ce(IV) to oxidize organic compounds have appeared in the literature (1). In particular, Ce(IV) oxidation of alcohols has received much attention in recent years, as an outgrowth of the colorimetric detection and quantitative determination of these substrates. It is known that Ce(IV) ion forms 1:1 complexes with alcohols which rapidly collapse to the products.

The studies by Trahanovsky and coworkers, *inter alia*, on ceric ammonium nitrate (CAN) oxidation of a number of organic compounds have uncovered some useful applications. Thus, benzylic and cyclopropylcarbinyl alcohols are oxidized to the corresponding aldehydes (2) in good yields, α-glycols are cleaved (3) in analogy to the lead tetraacetate reaction and cycloheptatriene has been oxidized to benzaldehyde, benzene, and carbon monoxide (4). CAN also oxidizes benzylic methylene groups to the carbonyl derivatives (5) and it has also been used in regeneration of the parent ketones from their oximes and semicarbazones (6). More recently, oxidative cleavages of bicyclo-[2.2.1]-2-heptanols and bicyclo[2.2.2]-2-octanol (7), of alkylphenylcarbinols (8), of 1,2-diarylethanols and 1-aryl-2,3-diphenylpropan-2-ols (9) have also been reported.

Under more drastic conditions, carbonyl compounds such as aliphatic aldehydes and ketones are attacked by Ce(IV) ions to yield formic acid and carbon dioxide as ultimate products (1). Consequently, almost all the pertinent investigations have been limited to reaction kinetics and mechanistic aspects, without probing into the synthetic utility of these oxidations.

In connection with a certain synthetic program, we have been interested in the oxidation of cyclic ketones with ceric salts, specifically with CAN. At present, we wish to report the results of such oxidation performed on a few representative cyclic ketones.

Results and Discussion

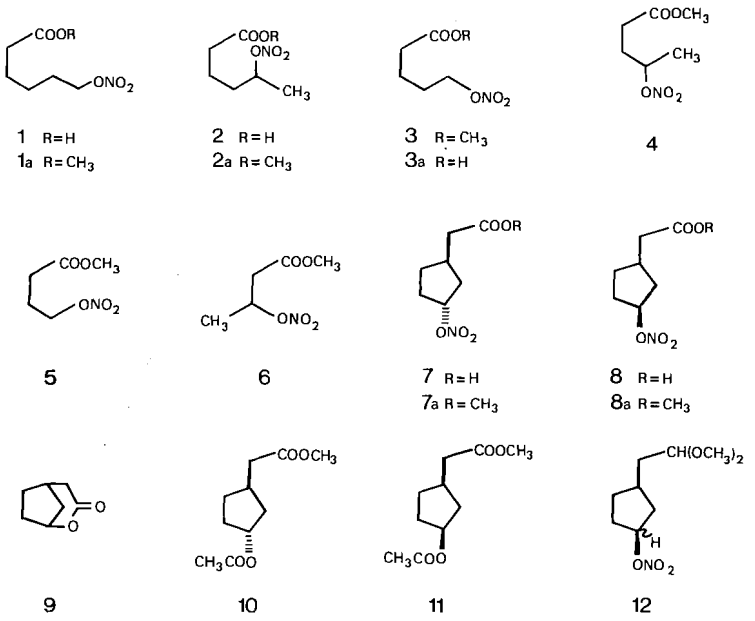
Our standard conditions of oxidation involve the treatment of ketone with 4 mol equiv of CAN at 60° in aqueous acetonitrile, until discoloration of the orange solution is complete. The major fractions isolated from oxidation of cyclohexanone, cyclopentanone, and norbornanone are acidic in nature. The combined yields of these products are of *ca.* 50%.

Cyclohexanone gave a mixture of 6- and 5-nitratohexanoic acids in a ratio of 3:2. The structures of these compounds were deduced from the i.r., n.m.r., and mass spectra, and have been verified by comparison of their methyl esters **1***a* and **2***a* with authentic specimens prepared by unambiguous routes.

Cyclopentanone yielded a more complex mixture of acidic products. The v.p.c. analysis of the derived methyl esters indicated the presence of four major components in the ratio of 24:16:34:26 identified as **3**, **4**, **5**, and **6** respectively, on basis of spectral data. Authentication of **3** has been made by its preparation from methyl 5-hydroxypentanoate.

Next we focused our attention to the oxidation of 2-norbornanone. Two nitrato-carboxylic acids **7** and **8** were obtained. The v.p.c. analysis of the derived methyl esters (**7***a* and **8***a*) indicated that the *trans*-epimer was present in larger

[1]A. P. Sloan Fellow, 1970–1972.



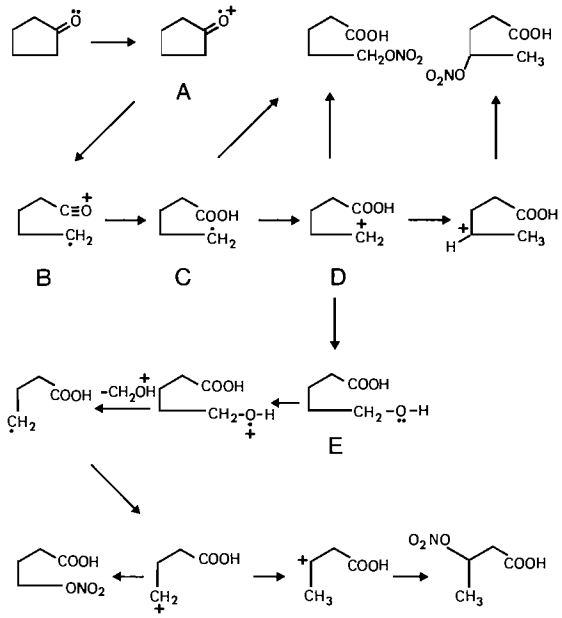
quantity (ratio of 3:2). Hydrolysis of the crude acidic products (**7** and **8**) furnished a mixture of hydroxyacids which was subsequently esterified and oxidized by Collins reagent (10) to methyl 3-oxocyclopentane acetate, identical with a sample prepared from 2-oxabicyclo[3.2.1]octan-3-one (**9**). Characterization and stereochemical assignments of the oxidation products were carried out as the following. Saponification of **7***a* and **8***a* and treatment with *p*-toluenesulfonic acid in benzene gave a mixture of lactone **9** and *trans*-3-hydroxycyclopentane acetic acid, which were readily separated. The *trans*-acid has been converted to the acetoxyester **10**; the lactone **9** was similarly transformed into the epimeric *cis*-acetoxyester **11**.

It was reported that the *exo*- or *endo*-norbornanol probably gives only *cis*-3-nitratocyclopentane acetaldehyde besides two cyclopentene acetaldehydes (7). We have, therefore, repeated the oxidation and converted the higher boiling aldehyde fraction into the dimethyl acetal **12**, thence to the methyl ester by ozonolysis (11). This ester sample has been shown by v.p.c. to contain two components corresponding to **7***a* and **8***a*, the *trans*-epimer being slightly predominant.

The rates of CAN oxidation of all three ketones mentioned above are similar; the reaction is generally complete within 1–1.5 h at 60°. However, camphor was found to be stable under the same conditions for at least 20 h, during which time CAN was slowly consumed (solvent oxidation). This observation led us to believe that the oxidation requires a close approach of the ketone and CAN, perhaps a complex formation is involved. Since Ce(IV) is coordinated by 8 to 12 atoms and thus the cerium species is fairly bulky, complex formation with camphor must be difficult. The success of isoborneol in undergoing CAN oxidation (7) is somewhat understandable, if one takes into consideration the great stability difference between a Ce(IV) alkoxide and a weakly coordinated (C=O → Ce(IV)) complex in judging the relative reactivities.

We envision that nitratocarboxylic acids arise from electron-transfer from the carbonyl oxygen to Ce(IV) within the CAN–ketone complex to generate a cation-radical **A** (Scheme 1). This cation-radical would then suffer a C—C bond fission (**A** → **B**) and react with water in the medium (**B** → **C**); the free radical can be further oxidized by electron transfer (**C** → **D**) or by ligand-transfer (12) to yield the final products. Generation of nitrato derivatives *via* this mechanism has previously been discussed by Trahanovsky *et al.* (7).

In order to account for the formation of acids having a secondary nitrato group, a



SCHEME 1

competitive oxidation of **C** by an electron-transfer process is proposed. The incipient carbonium ion **D** could undergo 1,2-hybride shift prior to its capture by the nitrate anion.

Degradation of one-carbon fragment observed during CAN oxidation of cyclopentanone poses an interesting problem. 5-Nitratopentanoic acid (*3a*) was recovered unchanged when exposed to CAN, hence it is not a precursor of the other three nitratocarboxylic acids. A similar result was obtained with δ-valerolactone. However, oxidation of the sodium salt of 5-hydroxypentanoic acid with CAN gave γ-butyrolactone in 50% yield. Consequently, loss of a one-carbon fragment might be explained by partial capture of the carbonium ion **D** to give **E** which can then be further oxidized and fragmented as outlined in Scheme 1.

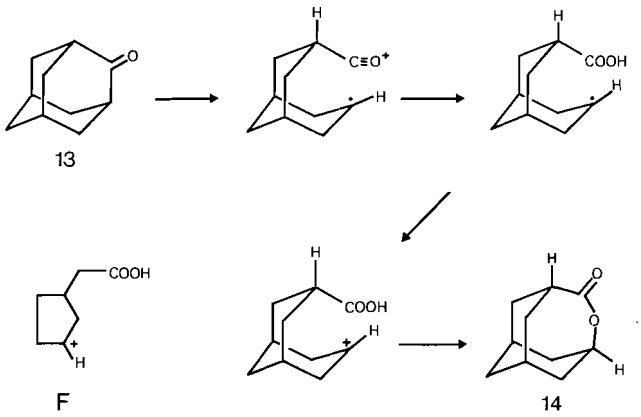
We have also studied the CAN oxidation of adamantanone (**13**)[2] which is structurally unique with respect to its rigid and nonenolizable nature. Thus adamantanone was allowed to react with 4 equiv of CAN in aqueous acetonitrile at 60°; discoloration (orange to faintly yellow) was observed at the end of 3 h. The rate of the reaction is slower than those of the ordinary ketones such as cyclopentanone and cyclohexanone; yet the reaction was quite clean, for only a single spot was detected by t.l.c. The product was isolated in 73% yield after sublimation, and was shown to be identical with the lactone **14** (13) obtained from *m*-chloroperbenzoic acid oxidation of adamantanone.

It is instructive to consider the above finding in light of a similar reaction of norbornanone. Whereas the result of adamantanone oxidation may be interpreted as illustrated in Scheme 2, in the case of norbornanone, lactonization of a possible intermediate such as **F** would be discouraged by the introduction of strain in reforming a bridged ring system. Furthermore, the entropy factor must play an important role in suppressing lactone formation. Consequently, monocyclic nitrato-carboxylic acids resulted.

Structurally constrained ketones are expected to behave in analogy to adamantanone; thus the present work may indicate a welcoming alternative to the classical Baeyer–Villiger oxidation, particularly where peracid-sensitive groupings such as olefinic linkages are present in the molecule.

CAN oxidation of adamantan-2-ol also afforded the lactone **14** in 50% yield. Adaman-

[2]In our laboratories, this reaction has been named "CANADA" reaction.



SCHEME 2

tanone was shown to be the intermediate (v.p.c.). In sharp contrast to the oxidation of bicyclic alcohols (7) which led to exclusively ring cleavage products at a fast rate, the conversion of adamantan-2-ol into the ketone, even in the presence of excess oxidizing agent, was not complete before a considerable amount of the lactone had been accumulated. In other words, the reaction cannot be stopped cleanly at the ketone stage for further oxidation takes place at a competitive rate.

From the foregoing results, one might conclude that CAN oxidations of bridged bicyclic alcohols are rather special cases (7). In general, CAN oxidations of secondary alcohols give rise to ketones which are susceptible to oxidative cleavage. Hintz and Johnson (14) reported the oxidations of cyclopentanol and cyclohexanol to the corresponding ketones with ceric sulfate.

Experimental

The i.r. spectra were taken on a Perkin–Elmer 257 Spectrophotometer; n.m.r. spectra (τ-value) were recorded on a Varian A-60 spectrometer in solvent indicated and with TMS as standard. The m.s. were run in a Hitachi–Perkin Elmer RMU-6 Spectrometer. The v.p.c. analyses were done on a Hewlett–Packard 5750 Research Chromatograph. Organic solutions were dried over anhydrous magnesium sulfate and Florisil was used in all the column chromatography. Microanalyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

CAN Oxidation of Cyclohexanone

A solution of cyclohexanone (4.0 g, 40 mmol) in acetonitrile (100 ml) was treated with ceric ammonium nitrate (87.7 g, 160 mmol) in water (300 ml). The resulting solution was heated at 60° with stirring for 1 h. It was saturated with sodium chloride and extracted with chloroform. The acidic products (2.33 g) were isolated from the chloroform solution by extraction with aqueous sodium bicarbonate followed by reacidification and extraction with ether. From the chloroform layer, cyclohexanone (1.54 g) was recovered. The crude acidic mixture (2.33 g) was esterified with ethereal diazomethane and separated by preparative v.p.c. (6 ft, 10% Carbowax 20 M column, 165°).

Compound **1***a*, retention time 19.0 min; i.r.: ν_{max} ($CHCl_3$) 1735, 1635, and 1280 cm^{-1}; n.m.r.: τ ($CDCl_3$) 5.45 (2H, triplet, $J = 6.0$ Hz, CH_2ONO_2), 6.28 (3H, singlet, $COOCH_3$), 7.62 (2H, triplet, $J = 6.0$ Hz, CH_2COO), and 7.95–8.70 (6H, multiplet, CH_2); m.s.: *m/e* 160 ($M^+ - OCH_3$) and 129 ($M^+ - ONO_2$).

Anal. Calcd. for $C_7H_{13}NO_5$: C, 43.98; H, 6.80. Found: 44.25; H, 7.05.

Compound **2***a*, retention time 11.6 min; i.r.: ν_{max} ($CHCl_3$) 1735, 1630, and 1280 cm^{-1}; n.m.r.: τ ($CDCl_3$) 4.90 (1H, multiplet, —CH-ONO_2), 6.31 (3H, singlet, $COOCH_3$), 7.62 (2H, multiplet, CH_2COO), 8.27 (4H, multiplet, CH_2), and 8.63 (3H, doublet, $J = 6.0$ Hz, CH_3); m.s.: *m/e* 160 ($M^+ - OCH_3$) and 129 ($M^+ - ONO_2$).

Anal. Calcd. for $C_7H_{13}NO_5$: C, 43.98; H, 6.80. Found: C, 44.25; H, 6.98.

Methyl 6-Nitratohexanoate (1a)

To the nitrating agent (15) prepared from 70% nitric acid (40 ml, 0.96 mol) and acetic anhydride (304 ml, 3.2 mol) at −5° was added methyl 6-hydroxyhexanoate (3.5 g, 24 mmol) during 20 min. The excess reagent was carefully destroyed with water and the resulting mixture was extracted with chloroform. The organic phase was separated, washed with water until neutral to litmus, dried, and evaporated. Short-path distillation gave **1***a* (3.88 g, 84.3%).

Methyl 5-Nitratohexanoate (2a)

The nitrating agent (15) was prepared from 70% nitric acid (20 ml, 0.48 mol) and acetic anhydride (152 ml, 1.6 *M*) at −5°. Treatment of methyl 5-hydroxyhexanoate (1.70 g, 12 mmol) with the nitrating agent for 20 min, and work-up as described in the preceding paragraph furnished the crude ester **2***a*. Column chromatography yielded the pure ester (1.68 g, 76%).

CAN Oxidation of Cyclopentanone

Cyclopentanone (8.4 g, 0.1 mol) in acetonitrile (200 ml) was oxidized with CAN (219.3 g, 0.4 mol) in water (600 ml)

at 60° for 4 h. Chloroform extraction of the reaction mixture saturated with sodium chloride, yielded a mixture of acidic and neutral products. The acidic material (4.8 g) was isolated by extraction with aqueous sodium bicarbonate followed by acidification and extraction with ether. Esterification of the acids with ethereal diazomethane followed by column chromatography gave a mixture of methyl esters (4.8 g). The v.p.c. analysis (6 ft, 10% Carbowax 20 M column, 130°) showed the presence of four major compounds which were isolated by preparative v.p.c.

Ester **3**, 24%, retention time 52.5 min; i.r.: ν_{max} ($CHCl_3$), 1735, 1635, and 1280 cm^{-1}; n.m.r.: τ (CCl_4) 5.55 (2H, diffuse triplet, $J = 6.0$ Hz, CH_2ONO_2), 6.38 (3H, singlet, $COOCH_3$), 7.68 (2H, diffuse triplet, $J = 6.0$ Hz, CH_2COO), and 8.1–8.5 (4H, multiplet, CH_2); m.s.: *m/e* 146 ($M^+ - OCH_3$) and 115 ($M^+ - ONO_2$).

Anal. Calcd. for $C_6H_{11}NO_5$: C, 40.67; H, 6.21. Found: C, 40.80; H, 6.25.

Ester **4**, 16% (>92% pure) retention time 26.7 min; i.r.: ν_{max} ($CHCl_3$) 1735, 1635, and 1280 cm^{-1}; n.m.r.: τ (CCl_4) 4.93 (1H, sextet, $J = 6.0$ Hz, $CHONO_2$), 6.37 (3H, singlet, $COOCH_3$), 7.3–8.4 (4H, multiplet, CH_2), and 8.62 (3H, doublet, $J = 6.0$ Hz, CH_3); m.s.: *m/e* 146 ($M^+ - OCH_3$) and 115 ($M^+ - ONO_2$).

Ester **5**, 34% (97% pure), retention time 30.0 min; i.r.: ν_{max} ($CHCl_3$) 1735, 1635, and 1280 cm^{-1}; n.m.r.: τ (CCl_4) 5.50 (2H, triplet, $J = 6.0$ Hz, CH_2ONO_2), 6.34 (3H, singlet, $COOCH_3$), and 7.4–8.2 (4H, multiplet, CH_2); m.s.: *m/e* 132 ($M^+ - OCH_3$) and 101 ($M^+ - ONO_2$).

Ester **6**, 26%, retention time 15.0 min; i.r.: ν_{max} ($CHCl_3$) 1740, 1640, and 1280 cm^{-1}; n.m.r.: τ (CCl_4) 4.59 (1H, sextet, $J = 6.5$ Hz, $CHONO_2$), 6.33 (3H, singlet, $COOCH_3$), 7.40 (2H, octet, $J_{AB} = 16$, $J_{AX} = J_{BX} = 6.5$ Hz, CH_2COO), and 8.57 (3H, doublet, $J = 6.5$ Hz, CH_3); m.s.: *m/e* 132 ($M^+ - OCH_3$) and 101 ($M^+ - ONO_2$).

*Methyl 5-Nitratopentanoate (**3**)*

The nitrating agent (15) prepared from 70% nitric acid (13.3 ml, 0.32 mol) and acetic anhydride (101 ml, 1.06 mol) at −5° was mixed thoroughly with methyl 5-hydroxypentanoate (1.05 g, 8 mmol) for 20 min. After addition of water, the reaction mixture was extracted with chloroform to give the crude nitrato ester. Column chromatography yielded methyl 5-nitratopentanoate (**3**, 1.20 g, 85%).

CAN Oxidation of Sodium 5-Hydroxypentanoate

δ-Valerolactone (1.009 g, 0.01 mol) was heated to reflux with an aqueous solution (20 ml) of sodium hydroxide (400 mg, 0.01 mol) during 48 h. Ceric ammonium nitrate (21.93 g, 0.04 mol) was dissolved in water (10 ml), acetonitrile (60 ml) then added, and the mixture was heated at 60° for 18 h. Sodium chloride was then added and the mixture was extracted with ether. The organic phase was washed with an aqueous solution of sodium bicarbonate, dried, and evaporated to dryness yielding a neutral substance (486 mg) which was identified as γ-butyrolactone by comparison (i.r., n.m.r., and v.p.c.) with an authentic sample.

Acidification of the aqueous phase and extraction with ether gave a small quantity (10 mg) of acidic material which was not further investigated.

Methyl 3-Nitratocyclopentane Acetate (7a and 8a)

(a) CAN Oxidation of Norbornan-2-one

A solution of norbornanone (1.1 g, 10 mmol) in acetonitrile (20 ml) was warmed at 60° with CAN (22.0 g, 40 mmol) in water (60 ml), for 1.5 h. It was cooled, saturated with sodium chloride, extracted with chloroform. An acidic mixture was obtained from the chloroform extract. Esterification of this mixture with diazomethane gave the crude methyl esters 7*a* and 8*a* (935 mg). The v.p.c. analysis (6 ft, 10% Carbowax 20 M column, 165°) showed the presence of two compounds (retention time: 28.0 and 29.4 min) in a ~3:2 ratio; i.r.: ν_{max} ($CHCl_3$) 1735, 1635, and 1280 cm^{-1}; n.m.r.: τ ($CDCl_3$) 4.50 (1H, multiplet, $CHONO_2$), 6.27 (3H, singlet, $COOCH_3$), 7.56 (2H, multiplet, CH_2COO), and 7.70–8.90 (7H, multiplet); m.s.: *m/e* 172 ($M^+ - OCH_3$) and 141 ($M^+ - ONO_2$).

*(b) Ozonolysis of 3-Nitratocyclopentane Acetaldehyde Dimethyl Acetal (**12**)*

A mixture of 3-nitratocyclopentane acetaldehyde (7) (2.08 g, 12 mmol), trimethyl orthoformate (1.27 g, 12 mmol), *p*-toluenesulfonic acid (40 mg) in anhydrous methanol (5 ml) was kept under reflux for 4 h. It was cooled, diluted with ether (300 ml) and washed with water. Evaporation of the dried ethereal solution gave an oil which was further purified by column chromatography to give the dimethyl acetal **12** (2.02 g, 77%); i.r.: ν_{max} ($CHCl_3$) 1630 and 1280 cm^{-1}; n.m.r.: τ ($CDCl_3$) 4.55 (1H, multiplet, $CHONO_2$), 5.56 (1H, triplet, $J = 5.5$ Hz, $CH(OMe)_2$), 6.65 (6H, singlet, OCH_3), and 7.2–8.9 (9H, multiplet); m.s.: *m/e* 188 ($M^+ - OCH_3$).

The dimethyl acetal **12** (1.0 g, 4.5 mmol) in ethyl acetate (100 ml) was ozonyzed at 0° for 2h. The solvent was stripped off and the residue was dissolved in ether, washed with aqueous sodium carbonate and water. The dried ethereal solution was evaporated *in vacuo* and the product was chromatographed to give the methyl esters 7*a* and 8*a* (850 mg, 91%). The v.p.c. analysis indicated a mixture of two compounds in a ~3:2 ratio.

*2-Oxabicyclo[3.4.1]octan-3-one (**9**) and Methyl trans-3-Acetoxycyclopentane Acetate (**10**)*

A mixture of esters 7*a* and 8*a* (5.0 g) and aqueous sodium hydroxide (200 ml, 0.75 *N*) was refluxed for 15 h. It was cooled, acidified, and extracted with ether. On evaporation of the dried organic phase a yellow oil (2.7 g) was obtained. This oil was dissolved in benzene (175 ml) containing a trace of *p*-toluenesulfonic acid, and heated for 3 h under a Dean–Stark trap to convert the *cis*-hydroxy acid into the lactone **9**. The benzene solution was extracted with sodium bicarbonate which upon reacidification and ether extraction yielded *trans*-3-hydroxycyclopentane acetic acid (1.4 g). The neutral compound obtained by concentration of the benzene layer was shown to be 2-oxabicyclo[3.3.1]octan-3-one (**9**) (0.8 g).

An ethereal solution of *trans*-3-hydroxycyclopentane acetic acid (1.4 g) described in the preceding paragraph, was treated with an excess diazomethane to afford the methyl ester (1.41 g); i.r.: ν_{max} ($CHCl_3$) 3710, 3470, and 1730 cm^{-1}; n.m.r.: τ ($CDCl_3$) 5.73 (1H, multiplet, CHOH), 5.93 (1H, singlet, OH), and 6.34 (3H, singlet, $COOCH_3$). Acetylation of the crude product with acetic anhydride (10 ml) and pyridine (10 ml) at room temperature for 24 h yielded methyl *trans*-3-acetoxycyclopentane acetate (6 ft, 10% SE-30 column, 150°, retention time 9.5 min); i.r.: ν_{max} ($CHCl_3$) 1735 cm^{-1}; n.m.r.: τ ($CDCl_3$) 4.75 (1H, multiplet, CHOAc), 6.28 (3H, singlet, $COOCH_3$), and 7.97 (3H, singlet, $OCOCH_3$); m.s.: *m/e* 169 ($M^+ - OCH_3$), 157 ($M^+ - CH_3CO$), and 140 ($M^+ - CH_3COOH$).

Anal. Calcd. for $C_{10}H_{16}O_4$: C, 60.00; H, 8.00. Found: C, 60.25; H, 8.08.

Methyl cis-3-Acetoxycyclopentane Acetate (11)

2-Oxabicyclo [3.2.1]octan-3-one (**9**) (2.44 g, 19 mmol) dissolved in anhydrous methanol (50 ml) was stirred with sodium methoxide (1.04 g, 19 mmol) at room temperature for 2 h. The solvent was removed *in vacuo* and the residue was distributed between chloroform and water. Acidification of the alkaline solution followed by extraction with ether yielded the starting lactone **9** (1.06 g). Concentration of the chloroform solution gave methyl *cis*-3-hydroxycyclopentane acetate (1.82 g); i.r.: ν_{max} ($CHCl_3$) 3610, 3460, and 1735 cm^{-1}; n.m.r.; τ (CCl_4) 5.73 (1H, quintet, $J = 5.0$ Hz, CHOAc), 5.93 (1H, singlet, OH), and 6.34 (3H, singlet, $COOCH_3$). Acetylation of the hydroxy ester (0.80 g) with acetic anhydride and pyridine furnished methyl *cis*-3-acetoxycyclopentane acetate (**11**) (0.85 g, 84%). The analytical sample was collected from v.p.c. (6 ft, 10% SE-30 column, 150°, retention time 8.72 min); i.r.: ν_{max} ($CHCl_3$) 1735 cm^{-1}; n.m.r.: τ ($CDCl_3$) 4.86 (1H, multiplet, CHOAc), 6.35 (3H, singlet, $COOCH_3$), and 8.04 (3H, singlet, $OOCH_3$); m.s.: *m/e* 157 ($M^+ - CH_3CO$) and 140 ($M^+ - CH_3CO_2H$).

Anal. Calcd. for $C_{10}H_{16}O_4$: C, 60.00; H, 8.00. Found: C, 59.78; H, 8.09.

Methyl 3-Oxocyclopentane Acetate

(a) From Methyl cis-3-Hydroxycyclopentane Acetate

To an ice cooled Collins reagent (10) (9.75 g, 38 mmol) in dry methylene chloride (200 ml) was added a solution of methyl *cis*-3-hydroxycyclopentane acetate (1.0 g, 6.3 mmol) in methylene chloride (20 ml). After stirring at room temperature for 20 min, water was added. The organic phase was treated with activated charcoal and dried. Removal of solvent and short-path distillation (bath temperature 105°/0.1 mm) of the residue afforded methyl 3-oxocyclopentane acetate (862 mg, 86%); i.r.: ν_{max} ($CHCl_3$) 1745 and 1740 cm^{-1}; n.m.r.: τ (CCl_4) 6.30 (3H, singlet, $COOCH_3$), and 7.20–8.70 (9H, multiplet); m.s.: *m/e* 156 (M^+).

Anal. Calcd. for $C_8H_{12}O_3$: C, 61.54; H, 7.69. Found: C, 61.34; H, 7.83.

(b) From cis- and trans-3-Hydroxycyclopentane Acetic Acid

A mixture of the 3-hydroxycyclopentane acetic acid (*cis*-, *trans*-epimers) (1.12 g, 7.8 mmol), potassium carbonate (1.33 g, 9.6 mmol) and iodomethane (6 ml) in acetone (40 ml) was kept under reflux (16). An additional quantity (6 ml) of iodomethane was added after 1.5 h and the total heating time was 5 h. Acetone was removed, the residue was taken up with chloroform and washed with water. The dried chloroform solution was evaporated to give the epimeric methyl 3-hydroxycyclopentane acetates (926 mg, 75%). Oxidation of a portion of the crude product (690 mg, 4.3 mmol) with Collins reagent (6.66 g, 25.8 mmol) in methylene chloride (150 ml) at room temperature gave a ketoester (552 mg, 86%) identical with methyl 3-oxocyclopentane acetate described above.

CAN Oxidation of Adamantanone

To a solution of adamantanone (1.0 g, 6.6 mmol) in acetonitrile (15 ml) was added ceric ammonium nitrate (15.0 g, 27.3 mmol) in water (30 ml). The resulting solution was stirred magnetically at 60° for 3 h during which time the orange color faded to faintly yellow. It was cooled, poured into brine, and extracted with chloroform. The extracts were dried and evaporated to give a soft solid mass (t.l.c. homogeneous). Sublimation of this material at 130–150° (bath temperature) under water aspirator pressure furnished lactone **14** (815 mg, 73.4% yield, m.p. 285–287°; lit. (13) m.p. 288–290°); i.r.: ν_{max} ($CHCl_3$) 1718 cm^{-1}; n.m.r.: τ ($CDCl_3$) 5.43 (1H, quintet, $J = 3.0$ Hz), 6.88 (1H, quintet, $J = 3.5$ Hz), and 7.8–8.3 (12 H, multiplet).

CAN Oxidation of Adamantan-2-ol

Adamantanol (475 mg, 3.2 mmol) in acetonitrile (10 mg) was treated with CAN (14.25 g, 26 mmol) in water (30 ml) during 3 h at 60°. After cooling to room temperature, the reaction mixture was extracted with chloroform. Evaporation of the dried extracts yielded a yellowish waxy solid which was sublimed to give lactone **14** (250 mg, 50% yield).

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