Synthesis of exaltone and *dl*-muscone based on 1,5,9-cyclododecatriene

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Bicyclo [9:4:1] hexadecan-16-one is prepared from cyclododecanone *via* four steps: ethoxycarbonylation, condensation with 1,4-dibromobutane, saponification, and decarboxylation. Photolysis of the bicyclic ketone yields a ketene which is trapped with methanol to afford methyl cyclopentadecanecarboxylate or alternatively oxidized to exaltone directly. The ester is also converted into exaltone *via* five steps. *dl*-Muscone is prepared by applying the same scheme to cyclotridecanone with 14-methylbicyclo-[10:3:1] hexadecan-16-one as the key intermediate.

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Owing to Wilke's discovery of butadienecyclotrimerization, 1,5,9-cyclododecatriene and cyclododecanone (1) have become readily accessible. Ohloff, Eschenmoser and others (1, 2) have recently published elegant syntheses of exaltone (cyclopentadecanone) (12) and *dl*-muscone (3methylcyclopentadecanone) (25) starting from these 12-membered cyclic compounds. We wish to describe a different route which involves the key intermediates, 4 and 18, both containing a 15-membered ring bridged by a carbonyl group. Photolysis of 4 and 18 has been shown to afford cyclopentadecanecarboxylates 7 and 20, which are converted to 12 and 25 in 44 and 19° overall yields based on 4 and 18, respectively.¹ A similar photolysis of bicyclo [5.2.1]decan-10one was previously recorded by Gutsche et al. (4).

Ethoxycarbonylation of 1 (5) gave 2 which was treated with sodium hydride and 1,4-dibromobutane in toluene to afford the cyclized ketoester 3. Heating of 3 with sulfuric acid in glacial acetic acid furnished the desired bicycloketone 4 as a sharp melting solid in 72% overall yield based on 2. Attempted condensation of 1 with 1,4-dibromobutane yielded an approximately 1:1 mixture of 4 and a spiro isomer 5.²

The ketone 4 proved homogeneous upon attempted thin-layer chromatographic (t.l.c.) and gas-liquid chromatographic (g.l.c.) separation and, therefore, is assumed to be the thermodynamically more stable isomer of the possible cis and trans isomers. The stereochemistry has not been determined yet. Any carbonyl derivatives of 4 could not be obtained and this was ascribed to the steric hindrance around the carbonyl group, as inspection of Dreiding models indicated that the preferred conformation should be the one with the carbonyl group almost buried in the nonamethylene group for either the *cis* or *trans* isomer. The observed inertness of 4 towards ring cleavage by oxidizing agents can be explained in the same way.

The n,π^* -excitation of the hindered ketone 4 was found to cause the ring-cleavage in the desired way. Irradiation of a 3% methanolic solution of 4 was carried out by means of a 200 W high pressure mercury arc with a Pyrex filter for 20–30 h. The volatile product (80% recovery by weight) consisted of a C₁₅-hydrocarbon fraction (32%) and methyl cyclopentadecanecarboxylate (7) (68%) by g.l.c. analysis. The hydrocarbon fraction was not investigated in detail.

Irradiation of 4 was examined in several solvents, and the use of halogenated ones such as methylene bromide or carbon tetrachloride was found to decrease the amount of hydrocarbon byproducts remarkably. Thus, irradiation of a 2% solution of 4 in a mixture of methanol and carbon tetrachloride (1:6 by volume) gave 7 as the only distillable product in 73% yield.

In support of Gutsche's mechanism (4) on this kind of photolytic ring cleavage, irradiation of **4** in cyclohexane gave a solution, whose infrared spectrum (i.r.) showed absorption at 2140 cm⁻¹ characteristic of the ketene $6.^3$

Oxidation of this ketene with oxygen should

¹The exaltone synthesis has appeared in a preliminary form (3).

²Opitz and Mildenberger obtained bicyclic ketones homologous to 4 from the reactions of dihalides with enamines of 5, 6, and 7 membered cyclic ketones (6). We thank one of the referees for this suggestion.

³Chapman and Lassila (7) claim the first identification of a ketene intermediate in the type I cleavage of ketone photolysis. See, however, refs. 3 and 4.

CANADIAN JOURNAL OF CHEMISTRY. VOL. 47, 1969



furnish exaltone (12) directly. Irradiation of a 3% solution of 4 in cyclohexane while bubbling oxygen through the solution afforded 12 in 20-30% yields, but hydrocarbon by-products and polymeric substances were produced together with 12 and separation gave rise to some difficulties. In contrast, the isolated ester 7 gave better yields of 12 by successive treatments mentioned below.

Hydrolysis of 7 followed by decarboxylation according to Barton's procedure (8) gave a mixture of iodocyclopentadecane (9) and its acetolysis product 10. The acetolysis was completed by the action of mercuric acetate in acetic acid, and the resulting acetate 10 was hydrolyzed to cyclopentadecanol (11). Oxidation of 11 by Brown's method (9) gave exaltone (12) in 61 % overall yield based on 7.

Theoretically *dl*-muscone (25) should be obtained by using methyl-substituted 4 as an intermediate. In order to minimize the possibility of obtaining methylcyclopentadecanone having the methyl group at unsuitable positions, it seemed more appropriate to go through 18. First we prepared the bicycloketone 16 to examine its photochemistry as a model experiment.

Cyclotridecanone (13) has been prepared from 1,5,9-cyclododecatriene by several methods (10). Attempted condensation of the ethoxycarbonylated ketone 14 with 1,3-dibromopropane in the presence of 2 mole equivalents of sodium

1108

NOZAKI ET AL.: SYNTHESIS OF EXALTONE AND dl-MUSCONE



hydride failed to afford the desired cyclization product due to side reactions. Condensation in the presence of one mole equivalent of sodium hydride gave the 3-bromopropyl-substituted ketoester 15, which was not isolated. Treatment of the crude 15 with sulfuric acid was found to effect the cyclization as well as the elimination of the ethoxycarbonyl group simultaneously. The bicycloketone 16 was isolated as a sharp melting solid in a 31% overall yield based on 14 and proved to be homogeneous upon t.l.c. and g.l.c. analyses. This bicycloketone is also assumed to be the thermodynamically more stable isomer. In contrast to 4, the isomer 16 gave an oxime. Irradiation of 16 in methanolic solution furnished methyl cyclopentadecanecarboxylate (7) in a 55% yield.

Attempted synthesis of 18 by means of the reaction of 14 with 1,3-dibromo-2-methylpropane failed, as this halide proved to be inert under the usual conditions for the condensation, possibly due to the steric hindrance of the methyl group (11). Direct condensation of cyclotridecanone (13) with 3-chloro-2-chloromethylpropene proceeded smoothly to afford the cyclized product 17 in a 57% yield. Catalytic hydrogenation of 17 gave quantitatively the desired ketone 18. Both ketones 17 and 18 gave one peak upon g.l.c., but two spots (ca. 1:1) on t.l.c. analysis. The stereochemistry is open to research in the future.

Photolysis of 18 in methanol gave methyl 3-methylcyclopentadecanecarboxylate (20) in a 33% yield. This was transformed into *dl*-muscone in a 58% overall yield based on 20 by means of a similar sequence of reactions as used in the exaltone synthesis. The stereochemistry of compounds 20–24 has not been determined.

Experimental

All temperatures are uncorrected. Nuclear magnetic resonance (n.m.r.) spectra were obtained on JOEL

C-60-H spectrometer in CCl₄ solutions with tetramethylsilane as reference. Chemical shifts are given in p.p.m. from this reference together with the multiplicity of signals indicated in an abbreviated form: s for singlet, d for doublet, t for triplet, and m for multiplet, respectively. Gas-liquid chromatography analyses were performed on a 2 m column of SE 30 on Chromsorb W (10%) with helium as a carrier gas at 160–180°. Thin-layer chromatography analyses were conducted on Silica-gel G with *n*-hexane and ethyl acetate (10:1) as a developing solvent.

Bicyclo[9.4.1] hexadecan-16-one (4)

To a suspension of sodium hydride (7.2 g, 0.3 mole) in anhydrous xylene mixture (30 ml) was slowly added a solution of 2-carbethoxycyclododecanone (2) (5) (38.1 g, 0.15 mole) in xylenes (80 ml) with stirring at room temperature under nitrogen atmosphere. After evolution of hydrogen was complete, 1,4-dibromobutane (32.4 g, 0.15 mole) was added in one portion. On heating the mixture at 80–90° another mole equivalent of hydrogen evolved. Heating and stirring were continued until hydrogen evolution had subsided (15 h). After cooling, the mixture was treated with water and extracted with ether. The organic layer was washed with water, dried (Na₂SO₄), and concentrated in vacuo to give crude 3 (48.3 g) as a yellow viscous oil. Alkaline hydrolysis of this oily ketoester and subsequent recrystallization from benzene-hexane gave bicyclo[9·4·1]hexadecan-16-one-1carboxylic acid as colorless crystals, m.p. 141-142° (decomp.). Infrared (Nujol): 3600-2400, 1720-1690 cm⁻¹ (C=0, COOH)

Anal. Calcd. for C₁₇H₂₈O₃: C, 72.8; H, 10.1. Found: C, 72.3; H, 10.2.

The crude 3 (48.3 g) was dissolved in a mixture of acetic acid (300 ml), water (120 ml), and concentrated sulfuric acid (80 ml), and the solution was heated at reflux for 10 h. After cooling and treatment with water, the mixture was extracted with *n*-hexane. The extracts were combined, washed with water, dried (Na₂SO₄), and concentrated *in vacuo*. Vacuum distillation of the resulting semisolid gave 4 (25.4 g: 72% based on 2) as a colorless solid, b.p. 110–115°/0.1 mm, m.p. 80–84°. Recrystallization from methanol afforded an analytical sample melting at 86–87°. Infrared (Nujol): 1700 cm⁻¹ (C=O). Nuclear magnetic resonance: δ 3.2–2.6 m (2H), 2.3–0.9 m (a peak at 1.25) (26H).

Anal. Calcd. for C₁₆H₂₈O: C, 81.3; H, 11.9. Found: C, 81.4; H, 12.2.

In another procedure, a mixture of sodium hydride (4.8 g: 0.2 mole), cyclododecanone (1) (18.2 g: 0.1 mole), 1,4-dibromobutane (21.6 g: 0.1 mole), and anhydrous xylenes (50 ml) was stirred at $80-90^{\circ}$ under nitrogen

1109

atmosphere for 40 h, when hydrogen evolution was complete. After cooling and treatment with water, the mixture was extracted with *n*-hexane. The extracts were combined, washed with water, dried (Na₂SO₄), and concentrated. Distillation of the resulting oil gave a colorless oil (10.3 g), b.p. 110–120°/0.15 mm, which solidified on standing, m.p. 40–70°. Fractional recrystallization from methanol gave two crystalline materials, 4 (3.1 g: 13%) melting at 86–87° and a spiroketone 5 (4.5 g: 19%) melting data. Infrared (Nujol): 1710 cm⁻¹ (C=O). Nuclear magnetic resonance: δ 2.5 diffused *t* (2H), 2.3–1.0 m (a peak at 1.25) (26 H).

Anal. Calcd. for C₁₆H₂₈O: C, 81.3; H, 11.9. Found: C, 81.1; H, 12.1.

Photolysis of Bicyclo[9.4.1]hexadecan-16-one (4)

A solution of 4 (8.3 g: 0.035 mole) in methanol (280 ml) was well degassed and subjected to irradiation with an immersion type 200 W high pressure mercury arc sealed in a cooling water mantle made of Pyrex glass. The photo-reaction was monitored by means of i.r., and the irradiation was interrupted when the 1700 cm⁻¹ band characteristics to the starting bicyclic ketone had disappeared (20-30 h). Evaporation of the solvent followed by vacuum distillation gave a colorless oil (6.6 g), b.p. 70-130°/0.1 mm. Gas-liquid chromatography analysis indicated that this oil consisted of a 32:68 mixture of C_{15} -hydrocarbons and methyl cyclopentadecanecarboxylate (7). The mixture was subjected to alkaline hydrolysis. and free carboxylic acid 8 was separated (4.2 g: 47%yield based on 4), m.p. 65-66° (from ethanol) (reported (12) m.p. 52-54°). Infrared (Nujol): 3300-2400, 1710-1690 cm⁻¹ (COOH). The *p*-phenylphenacyl ester of 8 was obtained by the usual method, m.p. 101.5-102° (from ethanol)

Anal. Calcd. for $C_{30}H_{40}O_3$: C, 80.3; H, 9.0. Found: C, 80.3; H, 9.1.

The hydrocarbon mixture, b.p. $70-80^{\circ}/0.3$ mm, consisted of at least three components (g.l.c.) and absorbed about 0.3 mole equivalent of hydrogen on catalytic hydrogenation.

Anal. Calcd. for C₁₅H₂₈: C, 86.5; H, 13.5. Found: C, 86.9; H, 13.4.

In another procedure, a solution of the bicyclic ketone 4 (4.7 g: 0.02 mole) in methanol (30 ml) and carbon tetrachloride (180 ml) was similarly photolyzed. Evaporation of the solvent followed by vacuum distillation gave methyl cyclopentadecanecarboxylate (7) as a colorless oil (3.9 g: 73 %), b.p. 117–120°/0.1 mm, which proved to be homogeneous on g.l.c. and t.l.c. Infrared (neat): 1750, 1195, 1160 cm⁻¹ (COOCH₃). Nuclear magnetic resonance: δ 3.60 s (3H), 2.5–2.1 m (1H), 1.35 s (28H).

Anal. Calcd. for C₁₇H₃₂O₂: C, 76.1; H, 12.0. Found: C, 76.5; H, 11.9.

Direct conversion of 4 to 12 was attained as follows: into a solution of 4 (2 g) in cyclohexane (70 ml) placed in a Pyrex tube, oxygen gas was bubbled through a narrow inlet tube at a rate of 60–70 ml/min at room temperature under external irradiation with a 200 W high pressure mercury arc for 30 h. Distillation of the mixture gave a colorless oil (1.0–1.3 g), b.p. 100–130°/0.3 mm, which was a mixture of several components (g.l.c.). Purification by preparative g.l.c. yielded cyclopentadecanone (12) as a colorless solid, m.p. and mixed m.p. $61-62^{\circ}$ (reported (13) m.p. 63°), semicarbazone, m.p. and mixed m.p. 187-188° (from ethanol) (reported (13) m.p. 188°). Infrared of **12** was completely superimposable with that of authentic exaltone. The yields ranged from 20 to 30% (determined from the peak area of g.l.c.).

The intermediacy of a ketene in this photolysis was shown as follows. A solution of 4 (1 g) in cyclohexane (70 ml) was irradiated for 20 h with a high pressure mercury arc through a Pyrex filter. The i.r. of the cyclohexane solution showed an absorption band at 2140 cm⁻¹. Attempted isolation of the ketene failed.

Cyclopentadecyl Acetate (10)

A mixture of cyclopentadecanecarboxylic acid (8) (5.1 g: 0.02 mole) and mercuric acetate (25.4 g: 0.08 mole) in benzene (200 ml) was heated at reflux with stirring in a nitrogen atmosphere while being irradiated by a 500 W tungsten lamp for 30 min. To this mixture under the same condition was added dropwise a saturated solution of iodine in benzene until the color-discharge was no longer observed (1.5 h). After cooling, the inorganic substances were removed by filtration. The filtrate was washed with aqueous sodium thiosulfate solution and then with water, dried (Na₂SO₄), and concentrated in vacuo. The residual oil (5.5 g) gave two spots on t.l.c. and strong i.r. bands at 1750 and 1250 cm⁻¹ This crude oil was dissolved in acetic acid (100 ml), and the solution was heated on a steam bath with mercuric acetate (10 g) for 3 h. After treatment with water, the mixture was extracted with benzene. The extracts were combined, washed with water, dried (Na₂SO₄), and concentrated to about 10 ml. The concentrated solution was passed through a short alumina column and distilled in vacuo to give 10 (4.0 g: 74%) as a colorless oil, b.p. 105-108°/0.06 mm. Infrared (neat): 1750, 1250 cm⁻ (OAc). Nuclear magnetic resonance: δ 5.0-4.5 m (1H), 1.89 s (3H), 1.35 s (28H).

Anal. Calcd. for $C_{17}H_{32}O_2$: C, 76.1; H, 12.0. Found: C, 76.1; H, 12.1.

Cyclopentadecanol (11)

Alkaline hydrolysis of the acetate **10** (2.5 g) in the usual manner afforded cyclopentadecanol (**11**) (2.0 g: 95%) as a colorless solid, m.p. $74-76^{\circ}$ (from *n*-hexane) (reported (14) m.p. 81°). The i.r. of **11** was superimposable on that of an authentic sample prepared from exaltone by lithium aluminium hydride reduction. The phenylurethane of **11** was prepared in the usual way and recrystallized from methanol, m.p. and mixed m.p. 102–103° (reported (14) m.p. 104°).

Cyclopentadecanone (12)

To a solution of 11 (1.1 g: 5 mmoles) in ether (20 ml) was added a mixture of sodium dichromate dihydrate (1.0 g: 3.4 mmoles), water (10 ml), and concentrated sulfuric acid (0.8 ml) in the course of 0.5 h under stirring at room temperature. Stirring was continued for an additional 3 h. The ethereal layer was washed with water, dried (Na₂SO₄), and concentrated *in vacuo*. Distillation gave 12 as a colorless solid (1.0 g: 91%), b.p. 101–103°/ 0.2 mm, m.p. 57–60°. Recrystallization from methanol gave an analytically pure sample, m.p. and mixed m.p. 61–62°, semicarbazone, m.p. and mixed m.p. 187–188°.

Comparison of i.r. of 12 with that of the authentic exaltone also confirmed the identity.

2-Carbethoxycyclotridecanone (14)

To a mixture of sodium hydride (4.8 g: 0.2 mole) and diethyl carbonate (150 ml) was added a solution of cyclotridecanone (13) (19.6 g: 0.1 mole) in diethyl carbonate (30 ml) in the course of 2 h with stirring under nitrogen atmosphere. Stirring was continued at room temperature until hydrogen evolution had ceased (15 h). After treatment with water and acidification with dilute hydrochloric acid, the mixture was extracted with ether. The organic layer was washed with water, dried (Na_2SO_4), and concentrated. Distillation of the residue gave 14 (25.1 g: 94%) as a colorless solid, b.p. 130-135°/0.15 mm, m.p. 63-66°. Recrystallization from methanol afforded colorless needles melting at 66-67°. Infrared (Nujol): 1750, 1195 (COOR), 1708 cm⁻¹ (C=O).

Anal. Calcd. for C₁₆H₂₈O₃: C, 71.6; H, 10.5. Found: C, 71.5; H, 10.6.

Bicyclo[10.3.1] hexadecan-16-one (16)

Condensation of 14 with 1,3-dibromopropane attempted similarly as mentioned for the preparation of 4 gave an intractable oily mixture instead of the desired cyclization product. The following procedure was found to give the best results. A mixture of 14 (20.8 g: 0.0776 mole), sodium hydride (1.87 g: 0.078 mole), and xylenes (35 ml) was stirred until hydrogen evolution was complete, and then 1,3-dibromopropane (47 g: 0.23 mole) was added in one portion. The whole mixture was stirred at 80-90° for 30 h. Treatment with water and extraction with ether followed by concentration of the extracts gave a yellow oil, which was dissolved in a mixture of acetic acid (160 ml), water (80 ml), and concentrated sulfuric acid (80 ml). This solution was heated to reflux for 5 h. After cooling, the mixture was diluted with water and extracted with *n*-hexane. The organic layer was washed, dried (Na₂SO₄), and distilled to give 16 (5.7 g: 31%) as a colorless solid, b.p. 122-126°/0.2 mm, m.p. 49-53°. Thinlayer chromatography and g.l.c. indicated the homogeneity of 16. Recrystallization from methanol gave an analytically pure sample melting at 54–55°. Infrared (Nujol): 1710 cm⁻¹ (C=O). Nuclear magnetic resonance: all protons appeared at δ 3.0–1.0 with poor resolution (a peak at 1.28).

Anal. Calcd. for C₁₆H₂₈O: C, 81.3; H, 11.9. Found: C. 81.1: H. 12.2.

The oxime of 16 was obtained in the usual manner, m.p. 143-144° (from ethanol). Infrared (Nujol): 3300 cm⁻¹ (OH).

Anal. Calcd. for C16H29NO: C, 76.4; H, 11.6; N, 5.6. Found: C, 75.7; H, 11.5; N, 5.5.

The unsatisfactory analysis of carbon might possibly be ascribed to the presence of some impurity, but further purification was impossible due to the lack of material.

Photolysis of Bicyclo[10.3.1]hexadecan-16-one (16)

A solution of 16 (2.4 g) in methanol (200 ml) was photolyzed as described for the photolysis of 4 while monitoring by g.l.c. The crude reaction mixture was immediately hydrolyzed with ethanolic potassium hydroxide, and the acidic fraction was secured in the usual manner. Reesterification of the latter with diazomethane followed by vacuum distillation gave methyl

cyclopentadecanecarboxylate (7) (1.5 g: 55%), which was identical with the specimen obtained from 4 upon comparison of i.r., retention time on g.l.c., and m.p. of *p*-phenylphenacyl ester of the free acid (8).

1111

14-Methylenebicyclo[$10 \cdot 3 \cdot 1$]hexadecan-16-one (17)

A mixture of cyclotridecanone (13) (19.6 g: 0.1 mole), sodium hydride (4.8 g: 0.2 mole), 3-chloro-2-chloromethylpropene (15) (12.5 g: 0.1 mole), and toluene (30 ml) was stirred at 90-100° after nitrogen flushing, until hydrogen evolution was complete (60 h). The reaction mixture was treated with water and extracted with nhexane. The extracts were combined, washed with water, dried (Na₂SO₄), and concentrated. On vacuum distillation of the residue, cyclotridecanone (13) (3.9 g) boiling at 80–100°/0.3 mm was recovered, and 17 (11.3 g: 57 %based on consumed 13) was obtained as a colorless solid, b.p. 115-120°/0.3 mm, m.p. 57-62° which showed a single peak on g.l.c. Recrystallization from ethanol gave a sample melting at 63-66.5°, but further recrystallizations failed to give a sharper melting point. Thin-layer chromatography of recrystallized 17 gave two equal spots. Infrared (Nujol): 3090, 1650, 895 (=CH₂), 1710 cm⁻¹ (C=O). Nuclear magnetic resonance: δ 4.79 s (2H), 2.8–1.9 m (6H), 1.6-0.8 m (a peak at 1.25) (20 H).

Anal. Calcd. for C17H28O: C, 82.2; H, 11.4. Found: C, 81.9; H, 11.7.

14-Methylbicyclo[$10\cdot 3\cdot 1$]hexadecan-16-one (18)

A solution of the unsaturated ketone 17 (11 g) in ethanol (100 ml) was stirred under an atmospheric pressure of hydrogen in the presence of palladium-oncarbon (10%) (0.5 g). It took 23 h for completion of hydrogen absorption. The catalyst was removed by filtration, and the filtrate was distilled in vacuo to give **18** (10.8 g: 98%) as a colorless solid, b.p. $135-137^{\circ}/0.4$ mm, m.p. 49-53°. Recrystallization was not attempted. Infrared (Nujol): 1710 cm⁻¹ (C=O). Nuclear magnetic resonance: all protons appeared at δ 3.0–0.8 with poor resolution (peaks at 1.30, 0.98, 0.88).

Anal. Calcd. for C₁₇H₃₀O: C, 81.5; H, 12.1. Found: C, 81.5; H, 12.3.

Methyl 3-Methylcyclopentadecanecarboxylate (20)

A solution of 18 (9.5 g) in methanol (500 ml) was photolyzed as mentioned above. The crude product was hydrolyzed with ethanolic potassium hydroxide and the acidic substance was separated and reesterified with diazomethane to methyl ester, which was distilled in vacuo to give 20 (3.5 g: 33 %), b.p. 104°/0.04 mm. Gas-liquid chromatography and thin-layer chromatography gave a single peak and spot, respectively. Infrared (neat): 1740, 1195, 1160 cm⁻¹ (COOCH₃). Nuclear magnetic resonance: δ 3.60 s (3 H), 2.6–2.1 m (1 H), 1.7–1.1 m (a peak at 1.35) (27 H), 0.88 diffused d (3 H).

Anal. Calcd. for C₁₈H₃₄O₂: C, 76.5; H, 12.1. Found: С, 76.8; Н, 11.8.

The use of halogenated solvents in this photolysis did not improve the yield of 20.

The methyl ester 20 was hydrolyzed again with ethanolic potassium hydroxide to give free acid 21 (96% yield) as a colorless viscous liquid.

3-Methylcyclopentadecyl Acetate (23)

The acid 21 (2.68 g: 0.01 mole) was converted into a

mixture of iodide 22 and acetate 23 with mercuric acetate (12.7 g: 0.04 mole) in benzene (100 ml) and a saturated benzene solution of iodine by the method mentioned above for 8. The mixture was acetolyzed to pure 23 with mercuric acetate (10 g) in acetic acid (100 ml) as before. Vacuum distillation gave 23 (2.3 g: 82%) as a colorless oil, b.p. 107-110°/0.08 mm. Infrared (neat): 1740, 1240 cm⁻¹ (OAc). Nuclear magnetic resonance: δ 5.0–4.5 m (1 H), 1.90 s (3 H), 1.8-1.1 m (a peak at 1.34) (27 H), 0.88 diffused d (3 H).

Anal. Calcd. for C₁₈H₃₄O₂: C, 76.5; H, 12.1. Found: C, 76.8; H, 12.0.

3-Methylcyclopentadecanol (24)

Alkaline hydrolysis of the acetate 23 (2.0 g) in the usual manner gave crude alcohol 24 (1.6 g: 94%) as an oil, which was subjected immediately to the next oxidation reaction without further purification. Infrared (neat): 3350 cm⁻¹ (OH).

3-Methylcyclopentadecanone (25)

To the crude alcohol 24 (0.6 g: 2.5 mmoles) dissolved in ether (10 ml) was added under stirring a mixture of sodium dichromate dihydrate (0.5 g: 1.7 mmoles), concentrated sulfuric acid (0.4 ml), and water (5 ml) in one portion. After stirring the whole mixture for 2 h, working-up followed by distillation gave 25 (0.47 g: 78%), b.p. 106-107°/0.2 mm. Infrared (neat): 1710 cm⁻¹ (C==O). Nuclear magnetic resonance: δ 2.6-2.2 m (4 H), 2.1-1.1 m (a peak at 1.30) (23 H), 0.90 diffused d (3 H). Anal. Calcd. for C₁₆H₃₀O: C, 80.6; H, 12.7. Found:

C, 80.4; H, 12.8. The semicarbazone of 25 melted at 130-131° (from

methanol) (reported (16) m.p. 131-132°).

Anal. Calcd. for C₁₇H₃₃N₃O: C, 69.1; H, 11.3; N, 14.2. Found: C, 68.9; H, 11.3; N, 13.7.

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1112