center at C-2 as no change was observed in the nmr spectrum of either compound at elevated temperatures. In dimethyl sulfoxide-d_6 a chemical transformation occurred at elevated temperatures. This reaction is currently under investigation.

Experimental Section

Melting points were taken on a Thomas-Hoover melting point apparatus in open capillaries and are uncorrected. Infrared spectra were taken on a Perkin-Elmer Model 137B Infracord with sodium chloride optics using polystyrene as a calibration. Nuclear magnetic resonance spectra were taken on a Varian A-60 spectrometer in carbon tetrachloride or deuteriochloroform (unless indicated otherwise) with tetramethylsilane as an internal reference. Gas chromatography was done on an Aerograph Model 661 flame ionization instrument using $^1/_8$-in. stainless steel columns. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Umbellulone 1 (1-Isopropyl-4-methylbicyclo[3.1.0]hex-3-en-2-one).—Umbellulone was extracted from oil of mountain laurel (Fritszche) by the method of Wienhaus and Todenhöfer[8] and had bp 90–92° (10 mm) [lit.[9] 80° (5 mm)]; infrared 5.89 (C=O), 9.74 μ (cyclopropane); nmr δ 5.18 (1 H, C=CH, broad singlet), 2.09 (3 H, $\mathbf{CH_3}C$=, doublet), 2.00 [1 H, $-C\mathbf{H}(CH_3)_2$, septet], complex absorption 0.8–1.4 (9 H).

Umbellulol 2 and 3 (1-Isopropyl-4-methylbicyclo[3.1.0]hex-3-en-2-ol).—A suspension of lithium aluminum hydride (2.50 g, 0.066 mol) in 250 ml of anhydrous ether was stirred at room temperature for 40 min. To this ether solution, cooled in an ice bath, a solution of umbellulone (20 g, 0.133 mol) in 30 ml of anhydrous ether was added over a 35-min period. The ice bath was removed and the solution stirred for 24 hr. Saturated ammonium chloride was added until the solid dissolved, the ether layer decanted, and the aqueous layer extracted with ether. The combined ether extracts were washed three times with water, and dried (anhydrous sodium sulfate); the ether was removed on a rotatory evaporator. The crude product (19.8 g) was separated by column chromatography (Alumina, Fisher A-540 plus 3% by weight of water) with pentane–ether–methanol mixtures. The ratio of umbellulone, liquid unsaturated alcohol, and solid unsaturated alcohol was 4:56:31 eluted with pentane–ether (7:3), pentane–ether (1:1) and ether–methanol (8:2), respectively.

The liquid unsaturated alcohol (fraction A, **2**) exhibited the following spectra: infrared 2.99 (hydroxyl group), 6.09 (double bond), 9.69 and 9.94 μ (cyclopropane); nmr broad singlet at δ 5.0 (1 H, >C=CH–), broad singlet at 4.25 (1 H, –CHOH–), septet centered at 2.44 [1 H, $CH(CH_3)_2$], singlet at 1.74 (3 H, CH_3C=), multiplet centered at 0.85 (2 H, cyclopropyl), multiplet centered at 1.46 (1 H, cyclopropyl) and two doublets centered at 1.05 and 0.66 [6 H, J = 7 cps, $(CH_3)_2CH$]. The OH absorption was a function of the concentration of the solution, bp 80–82° (8 mm).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.76; H, 10.73.

The solid unsaturated alcohol (fraction B, **3**) was recrystallized from 95% alcohol giving material of mp 52.0–52.5° and exhibited the following spectra: infrared 3.05 (hydroxyl group), 6.07 (double bond), 9.65, 9.75 and 9.92 μ (cyclopropane ring?); nmr singlet at δ 4.79 (2 H, >C=CH– and CHOH), singlet at 1.70 (3 H, CH_3C=), multiplet at 1.35 (1 H, cyclopropane?), multiplet at 0.55 (2 H, cyclopropane) and a pair of doublets around 0.95 [7 H, J = 7 cps, $(\mathbf{CH_3})_2CH$]. The position of the OH absorption shifted with concentration. Both alcohols were reoxidized to the starting material (umbellulone) with chromium trioxide–pyridine in good yields.

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.85; H, 10.58.

Reduction of Umbellulone with Sodium Borohydride.—A solution of sodium borohydride (0.494 g, 0.013 mol) and sodium hydroxide (0.19 g, 0.0025 mol) in 50 ml of water was dropped slowly into a stirred solution of umbellulone (2.0 g, 0.013 mol) in methanol (50 ml). The reaction mixture was stirred at room temperature for 24 hr. A saturated solution of ammonium chloride was added until all the solids dissolved. The product was extracted with ether, dried over sodium sulfate and the ether removed on a rotatory evaporator. The crude product (1.89 g) was analyzed by gas chromatography (15% Carbowax 1000 on Chromosorb W, 5 ft × $^1/_8$ in., 100°, nitrogen flow rate 40 ml/min). Using known mixtures, the ratio of saturated alcohol, unsaturated alcohol, umbellulone, and dihydroumbellulone was 68.6:14:7.9:5.7. Their retention times increased in the order dihydroumbellulone, saturated alcohol, unsaturated alcohol, umbellulone.

Reduction of Umbellulone with Lithium Borohydride.—Following the same method as with lithium aluminum hydride, umbellulone (2.54 g, 0.0169 mol) was reduced by lithium borohydride (0.15 g, 0.0069 mol) in ether. The crude product (2.32 g) was analyzed by gas chromatography and indicated unsaturated alcohol (62.8%), saturated alcohol (33.3%), saturated ketone (2.9%), and umbellulone (1%).

Reduction of Umbellulone with Lithium Aluminum Tri-*t*-butoxyhydride.—The lithium aluminum hydride procedure was followed. Umbellulone (5.0 g, 0.033 mol) was reduced with lithium tri-*t*-butoxyhydride (8.5 g, 0.033 mol) in ether giving 4.7 g of crude material. Analysis by gas chromatography indicated dihydroumbellulone (79.6%), umbellulone (16.6%), and saturated plus unsaturated alcohols (3.8%).

Reduction of Piperitone.[10]—The same methods were used as with umbellulone. Analysis was by gas chromatography (15% Carbowax 1000 on Chromosorb W, 5 ft × $^1/_8$ in., 108°).

Reduction of Pulegone.[10]—The same methods were used as with umbellulone. Analysis was by gas chromatography (15% Carbowax 1000 on Chromosorb W, 5 ft × $^1/_8$ in., 108°).

Registry No.—**1**, 546-78-1; **2**, 18750-22-6; **3**, 18750-23-7.

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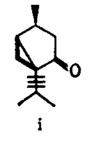
[7] Professor R. H. Eastman has pointed out that the same nonequivalence of methyl groups has been observed in the hydride reduction of dihydroumbellulone (i); J. N. Lowe, *Dissertation*, Stanford University, 1963. The assignment of configuration of the reduction products was made on the basis of steric arguments but the difference in chemical shift of the isopropyl groups is just the opposite of ours (*i.e.*, the major reduction product has nearly equivalent methyl groups while the minor one exhibits a large difference). While the assignment of configuration in dihydroumbellulone (i) rests on firm grounds, the difference in chemical shifts in the reduction products may be related to the difference in planarity of the five-membered ring in the umbellulols and dihydroumbellulols.



i

[8] H. Wienhaus and K. T. Todenhöfer, *Schimmel's Berichte*, 285 (1929).

[9] J. W. Wheeler, Jr., and R. H. Eastman, *J. Amer. Chem. Soc.*, **81**, 236 (1959).

[10] J. T. Baker Chemical Co.

The Synthesis of an A-Furano Steroid

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Kalamazoo, Michigan

Received August 26, 1968

Numerous modifications of the steroid nucleus have been prepared in the search for an endocrine agent with a novel spectrum of biological activity. The substitution of a heteroatom such as nitrogen or oxygen for carbon seems an especially intriguing modification, for transport and metabolism may be altered without doing violence to the shape of the molecule. Thus a host of aza steroids are now known.[1]

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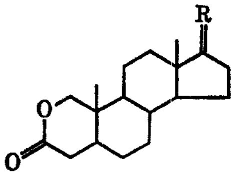
[1] See, for example, S. Rakhit and M. Gut, *J. Org. Chem.*, **30**, 639 (1965); N. J. Dorrenbos and R. E. Havranek, *ibid.*, **30**, 2474 (1965).

The oxa steroids, particularly those possessing oxygen in the A ring, are perhaps of greater interest since at least two classes (**1** and **2**) have been reported to exhibit endocrine properties.[2,3]



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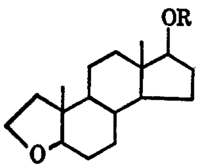

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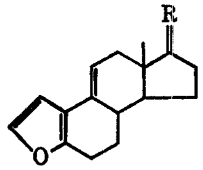
In order to investigate the aromatic A ring equivalent of **2**, we undertook the synthesis of **3**. The recent work of Julia[4,5] suggested that a convenient entree to this system would be the rearrangement of an epoxy ketone to a furan used by those authors to prepare compounds such as **4**. Since we planned to add



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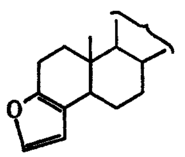

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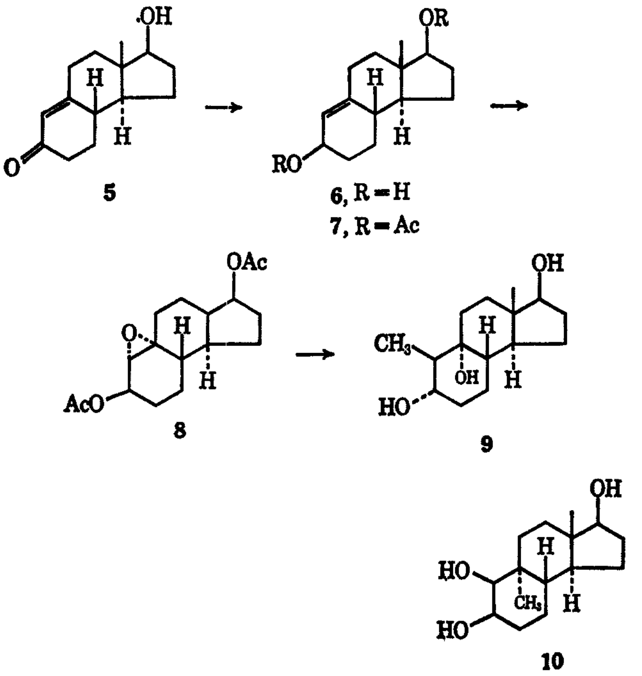
the A ring as the final step, the familiar tricyclic ketone **5**[6] was a convenient starting point for the current work (Scheme I).

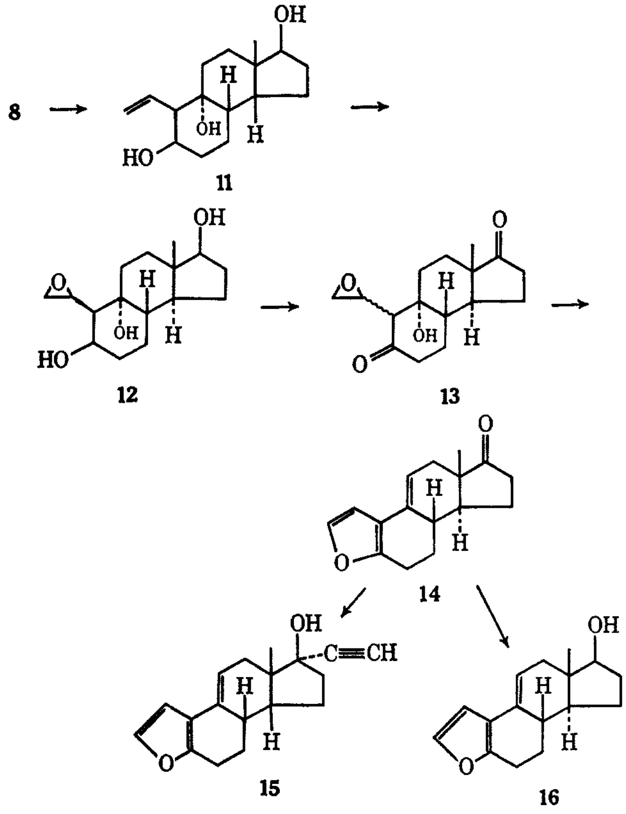
SCHEME I



Reduction of the ketone with lithium aluminum tritertiarybutoxyhydride led to a single diol (**6**) which was assigned to the stereochemistry shown by analogy to the steroids (Scheme I). Acetylation proceeded uneventfully to give **7**. Though epoxidation of acetate **7** would, on the basis of Henbests' work, be expected to give α-oxide **8**,[7] it was decided to determine independently the stereochemistry of that oxide. The product of **7** with *m*-chloroperbenzoic acid was allowed to react with a large excess of methyl magnesium bromide. The fact that the nmr of the resulting triol exhibits a methyl doublet (δ 0.80, J = 7.5 cps) allows us to assign structure **9** to this compound and **8** to the oxide; diaxial opening[8] of the β-oxide corresponding to **8** would have yielded **10**, which would have shown the newly introduced methyl group as a singlet.

Reaction of the epoxide **8** with vinylmagnesium bromide gave a workable yield of **11** (Scheme II);

SCHEME II



this compound was epoxidized in turn with trifluoroperacetic acid to afford the oxide as an amorphous gum (single spot on tlc). Brief treatment with Jones reagent gave the desired diketone **13**. The structure of this compound is supported by the finding that it shows a single deuterium oxide exchangeable proton in the nmr spectrum. This last product was then rearranged to furan **14** by means of boron trifluoride etherate. The crystalline tetracyclic product exhibited three vinyl protons in the nmr spectrum, two of which (δ 7.2 and 6.48) are known to be characteristic of a furan.[9] The ultraviolet absorptions shown by **14** at 208 mμ (ε 13,100) and 237 (12,250) confirm the presence of the conjugated furan ring.

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(2) R. Pappo and C. Jung, *Tetrahedron Lett.*, No. 9, 365 (1962).

(3) S. D. Levine, *J. Med. Chem.*, **8**, 537 (1965).

(4) S. Julia and P. Simon, *Bull. Soc. Chim. Fr.*, 331 (1964).

(5) S. Julia and C. Moutounier, *ibid.*, 979 (1964).

(6) L. S. Chinn and H. L. Dryden, Jr., *J. Org. Chem.*, **26**, 3904 (1961).

(7) W. B. Henbest and B. J. Lovell, *J. Chem. Soc.*, 1958 (1957).

(8) A. Furst and P. A. Plattner, Abstract of Papers, 12th International Congress of Pure and Applied Chemistry, New York, N. Y., 1951, p. 409.

(9) N. S. Bhacca, L. F. Johnston, and J. N. Schoolery, NMR Spectra Catalog, Varian Associates, Palo Alto, Calif., 1962, p 50.

The "17" ketone was then converted into 17β alcohol **16** and 17-ethynyl carbinol **15** by means of lithium tri-*t*-butoxyaluminum hydride and the acetylene–ethylenediamine complex, respectively.

Experimental Section[10,11]

2,3,3a,4,5,7,8,9,9aβ,9bα-Decahydro-3aβ-methyl-1H-cyclopenta[*a*]-naphthalene-3β,7β-diol (6).—Powdered lithium tri-*t*-butoxyaluminum hydride (18 g, 0.07 mol) was added to a well-stirred solution of 9.0 g (0.041 mol) of the tricyclic ketone **5** in 180 ml of THF. At the end of 5 hr the mixture was poured into saturated aqueous ammonium chloride and water. The inorganic gel was removed by filtration through Celite. The organic layer was separated, washed with water and brine and taken to dryness under vacuum. The residual solid was recrystallized from ethyl acetate–cyclohexane to afford 8.31 g (91%) of **6**: mp 133–139°; ν_{max} (mull) 3300, 1655 cm^{-1}. The analytical sample from an earlier run melted at 134–138°.

Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.64; H, 10.22.

2,3,3a,4,5,7,8,9,9aβ,9bα-Decahydro-3aβ-methyl-1H-cyclopenta-[*a*]naphthalene-3β,7β-diol Diacetate (7).—A suspension of 8.31 g (0.41 mol) of the diol in 20 ml of pyridine and 40 ml of acetic anhydride was stirred until the material was all in solution (45 min) and then allowed to stand at room temperature for 3.75 hr. The solution was poured into ice–water and the solid which separated collected on a filter. This was recrystallized from petroleum ether (bp 30–60°) (cooling in freezer) to give 9.42 g (82%) of **7**, mp 60–66°. A sample from a previous run was recrystallized to a melting point of 67.5–69° and showed ν_{max} (mull) 1730, 1655 cm^{-1}.

Anal. Calcd for $C_{18}H_{26}O_4$: C, 70.56; H, 8.55. Found: C, 70.62; H, 8.65.

2,3,3a,4,5,7,8,9,9aβ,9bα-Decahydro-3aβ-methyl-1H-cyclopenta[*a*]naphthalene-3β,7β-diol 5aα,6α-Oxide Diacetate (8).—To an ice-cooled solution of 5.0 g (0.016 mol) of the diacetate in 100 ml of ether there was added 3.20 g (0.019 mol) of *m*-chloroperbenzoic acid in 50 ml of ether. The solution was allowed to stand at room temperature for 72 hr and then washed in turn with aqueous sodium bicarbonate, water and brine. The solid which remained when the solution wss taken to dryness was recrystallized twice from Skellysolve B. There was obtained 3.73 g (71%) of **8**, mp 140–141°. The analytical sample from another run melted at 139-141° and showed ν_{max} (mull) 1735, 1725, 1250 cm^{-1}.

Anal. Calcd for $C_{18}H_{26}O_5$: C, 67.05; H, 8.13. Found: C, 66.77; H, 8.21.

2,3,3a,4,5,6,7,8,9,9aβ,9bα-Dodecahydro-3aβ,6β-dimethyl-1H-cyclopenta[*a*]naphthalene-3β,5aα,7β-triol (9).—To a solution of 0.65 g (2 mmol) of the oxide in 10 ml of THF there was added 10 ml of 2 *M* methylmagnesium bromide in benzene–THF. Following 3 hr heating under reflux the solution was cooled in ice and treated with 10 ml each of saturated aqueous ammonium chloride and water. Ether was added and the organic layer washed with water and brine. The solid which remained when the solution was taken to dryness was rercystallized from acetone–cyclohexane. There was obtained 0.22 g (43%) of **9**: mp 181.5–184°; the nmr spectrum shows a new methyl group as a doublet (J = 7.5 cps) at δ 0.80.

Anal. Calcd for $C_{15}H_{26}O_3$: C, 70.83; H, 10.30. Found: C, 70.46; H, 10.64.

2,3,3a,4,5,5a,6,7,8,9,9aβ,9bα-Dodecahydro-3aβ-methyl-6β-vinyl-1H-cyclopenta[*a*]naphthalene-3β,5aα,7β-triol (11).—A solution of 12.2 ml (0.18 mol) of redistilled vinyl bromide in 100 ml of THF was added to 4.55 g (0.19 mol) of magnesium over 1.5 hr with mechanical stirring. The mixture was warmed at reflux for 30 min and allowed to cool to room temperature. To this Grignard reagent there was then added a solution of 5.69 g (0.018 mol) of oxide **8** in 50 ml of THF. The solution was heated on the steam bath with good mechanical stirring for an additional 3 hr. The mixture was then worked up as directly above. The crude gummy product was chromatographed over Florisil (elution with 10% acetone) and the crystalline fractions combined (1 drop of water had to be added to each fraction to induce crystallization). This was crystallized from acetone–cyclohexane (and 1 drop of water) to yield 4.74 g (97%) of **11**, mp 104–107°. The analytical sample from a smaller run melted at 100° and showed ν_{max} (mull) 3460, 3360, 1685, 1635 cm^{-1}.

Anal. Calcd for $C_{16}H_{26}O_3 \cdot 0.5H_2O$: C, 69.78; H, 9.88. Found: C, 70.15; H, 10.00.

2,3,3a,4,5,5a,6,7,8,9,9aβ,9bα-Dodecahydro-3aβ-methyl-6β-oxyranyl-1H-cyclopenta[*a*]naphthalene-3β,5aα,7β-triol (12).—Trifluoroperacetic acid was prepared from 12.6 ml of the anhydride and 2.06 ml of 90% hydrogen peroxide in 25 ml of methylene chloride. The volume of the solution was brought to exactly 50 ml with methylene chloride. A 3-ml portion of this solution was added dropwise to a mixture of 0.69 g (2.5 mmol) of **11** and 1.2 g of sodium carbonate in 10 ml each of methylene chloride and chloroform. Following 1 hr of heating at reflux the mixture was allowed to cool. The solid was collected on a filter and the filtrate taken to dryness. There was obtained 0.28 g of solid. The material collected on the filter was taken up in water and methylene chloride. The organic layer was separated and taken to dryness to give an additional 0.29 g of product. The organic materials were combined and chromatographed on Florisil (elution with 30% acetone). There was obtained 0.40 g (56%) of an amorphous solid which gives a single spot on tlc.

1,2,3a,4,5,5a,8,9,9aβ,9bα-Decahydro-5aα-hydroxy-3aβ-methyl-6ξ-oxiranyl-3H-cyclopenta[*a*]naphthalene-3,7(6H)-dione (13).—To an ice-cooled solution of 0.40 g (1.4 mmol) of amorphous triol **12** in 25 ml of acetone there was added dropwise 0.75 ml of Jones reagent. After 10 min, the bulk of the solvent was removed on the rotary evaporator. The residual gum was dissolved in water and methylene chloride–chloroform. The organic layer was washed with water and brine and taken to dryness. The residual solid was recrystallized twice from ethyl acetate–cyclohexane to give 208 mg (52%) of **13**: mp 172–174°; ν_{max} 3400, 1760, 1725 cm^{-1}. The nmr spectrum shows only one proton exchangeable with D_2O.

Anal. Calcd for $C_{16}H_{22}O_4$: C, 69.04; H, 7.97. Found: C, 68.05; H, 8.28.

***dl*-3-Oxa-A-norestra-1,5(10),9(11)-trien-17-one (14).**—A suspension of 208 mg (0.75 mmol) of oxide **13** and 0.25 ml of boron trifluoride etherate in 6 ml each of dry ether and THF was stirred at room temperature (solution occurred in 10 min). At the end of 2 hr the solution was diluted with ether, washed with aqueous sodium bicarbonate, water and brine and taken to dryness. The residual solid was chromatographed on Florisil (elution with 10% acetone) to give 107 mg (45%) of **14**: mp 123–127° (a single recrystallization from Skellysolve B raised the melting point to 130–132°); λ_{max} 208 (ε 13,100), 237 (12,250); ν_{max} 1730, 1645, 1615, 1510 cm^{-1} (mull); nmr, furan CH at δ 7.2 and 6.48, 11 vinyl CH at δ 5.7.

Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 78.82; H, 7.50.

3-Oxa-A,19-dinor-17α-pregn-1,5(10),9(11)-trien-20-yn-17-ol (15).—Lithium acetylide–ethylenediamine complex (0.40 g, 4.6 mmol) was added to a solution of 0.40 g (1.7 mmol) of ketone **14** in 10 ml of freshly distilled dimethyl sulfoxide. Following 20 hr standing at room temperature, ether and saturated aqueous ammonium chloride were added. The organic layer was separated, washed with water and brine and taken to dryness. The residual foam was chromatographed over 50 ml of Florisil (elution with 2% acetone). The crystalline fractions were combined and recrystallized from aqueous methanol. There was obtained 182 mg (50%) of **15**: mp 144–147°; ν_{max} (mull) 3500, 3260, 2090 cm^{-1}.

Anal. Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.54; H, 7.73.

3-Oxa-A-norestra-1,5(10),9(11)-trien-17β-ol (16).—To a solution of 0.40 g (1.7 mmol) of ketone **14** in 25 ml of THF, there was added 0.45 g (1.8 mmol) of lithium tri-*t*-butoxyaluminum hydride. At the end of 3 hr an additional 0.10 g (0.4 mmol) of the hydride was added. At the end of a total reaction time of 5 hr, the solution was treated with saturated aqueous ammonium chloride and ether. The precipitated solid was removed by filtration and washed well with ether. The organic layer from the combined filtrates was separated, washed with water and brine and taken to dryness. A single recrystallization of the solid residue from acetone–Skellysolve B gave 0.34 g (84%) of **16**: mp 184–185.5°; ν_{max} (mull) 3320, 3240 cm^{-1}.

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[10] All melting points are uncorrected and are reported as obtained on a Thomas–Hoover melting point apparatus; nmr spectra were obtained in deuteriochloroform on a Varian A-60A instrument.

[11] The authors are indebted to the Department of Physical and Analytical Chemistry of The Upjohn Co. for elemental analysis and spectral determinations.

Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.55; H, 8.60.

Registry No.—**6**, 18634-49-6; **7**, 18634-50-9; **8**, 18634-51-0; **9**, 18634-52-1; **11**, 18634-53-2; **13**, 18634-54-3; **14**, 18634-55-4; **15**, 18634-56-5; **16**, 18634-57-6.

Reaction of Lead Tetraacetate with Isophorone[1]

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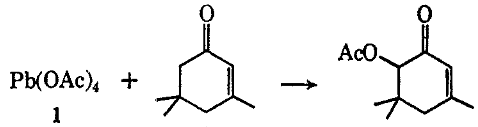
Received September 1, 1968

The reaction of lead tetraacetate (**1**) with isophorone (**2**) was studied and an improved procedure for the preparation of 6-acetoxyisophorone (**3**) is reported. As indicated,[2] when acetic acid was used as a solvent, acetate **3** could be isolated in only 38% yield. Using benzene as a solvent in the presence of CaH_2 or BF_3,[3] only slightly better yields were observed. Benzene and $CaCO_3$ [4] gave yields of 74% but the best yields were obtained using benzene alone where the product was isolated by crystallization in 78% yield. The yields could be increased by distillation of the mother liquors.[2] As with saturated ketones,[5] the reaction was faster in acetic acid, or in the presence of acids[3] or bases.



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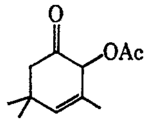

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It is of interest that acetate **3** was the only product observed. Gas chromatograms of the crude reaction mixtures and mother liquors remaining after crystallization of the product showed only starting material, acetate **3**, and with the crude reaction mixtures, usually 1% or less other materials. These minor components could be other products, or oxidation products of the trace impurities (<1%) in the starting material. In the case of the uncatalyzed reaction in benzene, approximately 99% of the organic starting material was accounted for either as acetate **3** or unreacted starting material. Other products might have been expected since rearrangements are known to occur,[6,7] and, since isophorone is known to enolize approximately equally in both directions[8,9] and the enol form is apparently the species that is attacked,[10] products such as **4** might also have been expected. However, **4** could have rearranged to **3** under the conditions of the reaction since a similar rearrangement is known.[11] The structural assignment of **3** was confirmed by its ir and nmr spectra.

Experimental Section

Melting points were taken on a Thomas-Hoover apparatus and are uncorrected. Infrared spectra were taken on a Perkin-Elmer 337 spectrometer; nmr spectra were recorded on a Varian HA-60 spectrometer using $DCCl_3$ as a solvent and tetramethylsilane as an internal standard. Gas chromatograms were obtained with a Perkin-Elmer 154L instrument using a thermal conductivity detector and a column of 0.25 in. × 5 ft 5% neophentylglycol sebacate on nonacid washed Chromosorb W with the He flow rate at 60 ml/min. Peak areas were determined by the height times width at half-height method and the peak areas due to **3** were multiplied by 1.2 to correct for detector response differences. Microanalyses were performed by M-H-W Laboratories of Garden City, Mich. The lead tetraacetate was dried over KOH under reduced pressure. Tests for completion were made with KI–starch indicator paper.

Reaction of Isophorone with $Pb(OAc)_4$ in Benzene.—A mixture of 150 ml of benzene, 10.0 g (0.0725 mol) of **2**, and 35.0 g (0.0787 mol) of $Pb(OAc)_4$ was refluxed with stirring for 90 hr. The mixture was cooled, washed once with water, saturated NaCl, saturated $NaHCO_3$, and saturated NaCl; the organic layer was dried ($MgSO_4$) and filtered; and solvent was removed at 45° under reduced pressure giving 14.0 g of light yellow solid. Vpc analysis at 200° of the crude product dissolved in ether showed 3% starting material, 1% minor component, and 96% acetate **3**. The ether solution was concentrated by evaporation to give 8.99 g of **3**, mp 76–78°, (lit.[2] mp 77–77.5°). A second crop of 2.08 g brought the total to 11.07 g (78%). A vpc analysis at 198° showed the 2.69 g of material in the mother liquor to be 69% **3**, 28% **2**, and approximately 1% each of three minor components. Vpc analysis at 240° of the crude reaction mixture and the mother liquors remaining after crystallization of **3** showed no additional products to be present.

The product **3** exhibited the following properties: bp 136–137° (9 mm) [lit.[2] 141–145° (12 mm)]; ir (KBr) 1740 (ester C=O), 1675 (C=O), 1635 (C=C), 1238 cm^{-1} (C—O—C); nmr δ 5.92 (m, 1, with line spacings of 1.1 Hz, olefinic proton), 5.22 (s, 1, CHOAc), 2.20 (s, 3), 1.97 (s, 3), 1.1 (s, 3), 0.98 (s, 3).

Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.21; H, 8.53.

Registry No.—**1**, 546-67-8; **2**, 78-59-1; **3**, 19019-49-9.

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Ring Expansion of Tetramethyl-1,3-cyclobutanedione with Difluoramine[1]

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Recent advances in the chemistry of difluoramine have demonstrated its utility in the synthesis of a

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