Anal. Calcd for $C_{20}H_{26}O_8$: C, 60.90; H, 6.64. Found: C, 60.98; H, 6.68.

Registry No.—**2**, 510-35-0; **3**, 36492-45-2; **4**, 29598-38-7; **5**, 34167-05-0; **6**, 29598-40-1; **6a**, 29598-41-2; **7**, 36539-92-1; **9**, 36492-47-4; **10**, 36492-48-5; **11**, 36492-50-9; **11a**, 36492-49-6; **13a**, 36492-51-0; **13b**, 36563-78-7; **14**, 36492-52-1; **15**, 36492-53-2; **16**, 36492-54-3; **16a**, 36492-55-4; **17**, 36492-56-5; **17a**, 36492-57-6; **18**, 36492-58-7; **18a**, 36492-59-8; **19**, 36492-60-1; **19a**, 36492-61-2; **20**, 36492-62-3; **20-6β-d_1**, 36492-63-4; **20a**, 36492-64-5; **21**, 36492-65-6; **21-6β-12,12-d_3**, 36492-66-7; **22**, 36492-67-8; **23**, 36492-68-9; **24**, 36492-69-0; **24** C-6 epimer, 36492-70-3; **25**, 36492-71-4; **26**, 36492-72-5; **28**, 36492-73-6; **29a**, 36492-74-7; **31**, 36492-75-8; **31a**, 36492-76-9; **32**, 36492-77-0; **32a**, 36492-78-1; **33**, 36492-79-2; **34**, 36492-80-5; **34a**, 36594-88-4.

Acknowledgment.—We gratefully acknowledge financial assistance from the National Institutes of Health under Grant No. R01-GM13441 from the Division of General Medical Sciences and under Biomedical Sciences Support Grant RR-07054 from the General Research Support Branch, Division of Research Resources, Bureau of Health Professions Education and Manpower Training. We also wish to thank Professor Wesley Cocker (Trinity College, Dublin, Ireland) and Dr. F. R. Smith (MacFarlan Smith Ltd., Edinburgh, Scotland) for generous supplies of β-santonin.

Notes

Synthesis of Diterpenoid Acids. XII.[1] Preparation of a Lactone Related to *cis*-Dehydrodeisopropylabietic Acid

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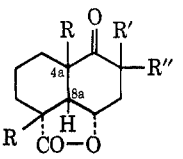
Received July 21, 1972

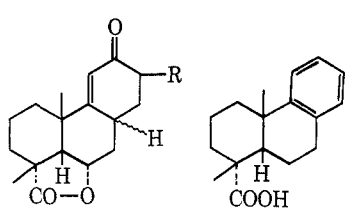
We have described the preparation of the bicyclic cis keto lactone **1a** as an intermediate in the synthesis of diterpenoid acids.[2] In the present work we have added an aromatic ring C in the hope that it would then be possible to epimerize the bridgehead hydrogen,[1,3] and thus obtain diterpenoid acids related to abietic acid.

The Robinson–Mannich annelation failed with **1a**. However, the hydroxymethylene compound **1b** reacted with trimethyl-3-oxobutylammonium iodide in the presence of base to give the diketo aldehydo lactone **1c**, which, after prolonged treatment with sodium ethoxide, underwent an aldol cyclization to form **2a**. Apparently the formation of the third ring is hindered by the presence of the lactone, since the cyclization went more smoothly in the presence of aqueous base; in the work-up of this reaction the lactone was reclosed by heating the crude product in benzene with *p*-toluenesulfonic acid.[4]

We also prepared **2a** from **1a** by an approach similar to that used by Dutta in his synthesis of *cis*-dehydrodeisopropylabietic acid (**3**).[3] Compound **1a** was converted in poor yield to the Mannich base **1d**, whose

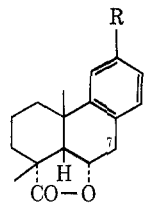


1a, R = CH_3; R′ = R″ = H
b, R = CH_3; R′R″ = C(OH)H
c, R = CH_3; R′ = CHO; R″ = $CH_2CH_2C(=O)CH_3$
d, R = CH_3, R′ = $CH_2N(CH_3)_2$; R″ = H
e, R = CH_3; R′ = $CH_2N^+(CH_3)_3I^-$; R″ = H
f, R = CH_3; R′R″ = CH_2
g, R = H; R′R″ = $CHSC_4H_9$

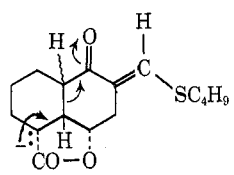


2a, R = H
b, R = $COOC_2H_5$

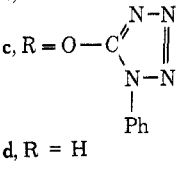
3



4a, R = OCH_2Ph
b, R = OH



5



c, R = O—C(=N—N(Ph)—N=)
d, R = H

methiodide **1e** condensed with acetoacetic ester to give crude **2b**. By carrying out the Mannich reaction of **1a** in refluxing isoamyl alcohol we obtained the methylene derivative **1f**, which condensed with acetoacetic ester to give **2b** and **2a** in poor yields. The structures of compounds **1b–f**, **2a**, and **2b** are based on spectral and analytical data.

The preparation of **2a** *via* the formyl derivative **1b** is more satisfactory than the one *via* the methylene derivative **1f** and was the one normally used. However, the product from both routes melted over a range of 5°. The nmr spectra showed that the main product

(1) Part XI: A. Kröniger and D. M. S. Wheeler, *Tetrahedron*, **28**, 255 (1972).
(2) A. C. Ghosh, K. Mori, A. C. Rieke, S. K. Roy, and D. M. S. Wheeler, *J. Org. Chem.*, **32**, 722 (1967).
(3) C. T. Mathew, G. C. Banerjee, and P. C. Dutta, *J. Org. Chem.*, **30**, 2754 (1965).
(4) S. K. Roy and D. M. S. Wheeler, *J. Chem. Soc.*, 2155 (1963).

(signal for vinyl proton at 6.05 ppm) was contaminated by a closely related second product (vinyl signal at 6.15 ppm). We attribute the mixture to the existence of **2a** in two forms epimeric at C_8.

We attempted to prepare *cis*-dehydrodeisopropylabietic acid[3] by aromatizing ring C, removing the phenol, and cleaving the lactone. Treatment of **2a** with cupric bromide in benzyl alcohol[5] gave the benzyl ether **4a**, which was hydrogenolyzed to the phenol **4b**. The phenolic group was removed by hydrogenolysis of the phenyltetrazolyl ether (**4c**)[7] to give **4d**. Our **4d** had a similar melting point and an identical infrared spectrum to **4d** of known stereochemistry previously prepared by Mahapatra and Dodson[8-10] using an entirely different route. This confirms that the stereochemistries we assigned earlier[2] and those in the present paper are correct.[11]

In trying to remove the lactone group by oxidation at C_7 followed by hydrogenolysis (*cf.* ref 13) we were not able to oxidize **4d** with chromic acid even under strong conditions. Other attempts to remove the lactone also failed. We also were unsuccessful in applying to **2a** the route used by Dutta and coworkers in their synthesis of **3**.[3]

The presence of sp^2 carbons at the C_5 and C_6 positions of **1b**, **4c**, and **4d** restricts rotation about the C_5–C_6 bond.[14] Studies with models suggest that the most stable conformation of these compounds is not that of **1a**[15] but rather one in which the C_8–O bond is axial to ring B; ring B is in a twist-boat conformation, while ring A is a chair. In such a conformation the dihedral angle of C_8–H with each of the C_7–H's is 60° (J_{calcd} = 2.5 Hz[16]) and the angle C_8H–$C_{8a}H$ is about 10° (J_{calcd} = 9.5 Hz[16]). These calculated coupling constants are consistent with the observed values. The conformation we have deduced for **4c** and **4d** differs from that normally adopted by compounds related to isodehydroabietic acid.[17]

Since it is well established that resin acids with ring C aromatic are readily oxidized by chromic acid,[9,18] the resistance of **4d** to oxidation was unexpected. Examination of the conformation of **4d** indicates a 1,4 interaction between the C_4 α H and the C_7 α H, which would, presumably, be relieved by oxidation of C_7 to a ketone. The initial stage of the oxidation of a benzylic position by chromic acid involves the removal of a hydride ion or hydrogen atom by the oxidant.[19] It seems likely that of the two hydrogens at C_7, removal of the α hydrogen (axial to ring B) would enable the developing radical or positive charge to fulfill better the stereoelectronic conditions for conjugation with the ring than would the removal of the 7β hydrogen. However, in the conformation adopted by **4d** the 7α H is on the concave side of the molecule and so not easily accessible to attack by the reagent.[20] In view of our failure to cleave the lactone **4d** to the corresponding acid and the length of the synthesis to **4d**, we have abandoned this approach to synthesizing diterpenoid acids in favor of another route.[1]

Experimental Section[21]

***cis*-Decahydro-6-formyl-8α-hydroxy-1β,4a-dimethyl-5-oxonaphthalene-1α-carboxylic Acid Lactone (1b).**—Sodium hydride (0.45 g, 51.7% suspension in oil) was added to a cooled solution (0°) of the keto lactone **1a** (0.45 g) in ethyl formate (5 ml) in a nitrogen atmosphere. A drop of dry methanol was added and the mixture was stirred at 0° for 1.5 hr. Ether (5 ml) was added, the stirring was continued for 3.5 hr, and the mixture was treated with water (10 ml) and then extracted with ether. The combined ethereal solutions were extracted with aqueous sodium hydroxide (2 *N*). The combined aqueous extracts were acidified and extracted with ethyl acetate. The ethyl acetate solution was washed with saturated aqueous sodium chloride, dried (Na_2SO_4), and evaporated to yield a brown oil which crystallized on treatment with ether to give **1b**: mp 119–122° (0.51 g); ν_{max} 1760, 1640, and 1580 cm^{-1}; nmr δ 0.70–2.60 (13 H, m, with s at 1.22 and 1.33 and d, J = 6.5 Hz at 2.37), 2.80 (2 H, d, J = 3.5 Hz, $=CCH_2CO-$), 4.85–5.20 (1 H, d of t, J = 3.5 and 6.5 Hz, OCH), and 7.55 (1 H, broad s, C=CH). This product was used in the following reaction without further purification.

***cis*-Decahydro-6-formyl-6-(3′-butanone)-8α-hydroxy-1β,4a-dimethyl-5-oxonaphthalene-1α-carboxylic Acid Lactone (1c).**—A solution of trimethyl-3-oxobutylammonium iodide (15 g) in methanol (20 ml) was added dropwise (20 min) in a nitrogen atmosphere to a cooled mixture (0°) of sodium methoxide (from 0.30 g of sodium) in methanol (10 ml) and the formyl compound **1b** (3.2 g obtained from 2.5 g of **1a**) in methanol (25 ml). The mixture was stirred for 25 hr at room temperature, and the solvent was removed under reduced pressure. The residue was treated with saturated aqueous sodium chloride (20 ml, pH *ca.* 8), and the mixture was acidified and then extracted with ethyl acetate. The ethyl acetate solution was washed with saturated aqueous sodium chloride, dried (Na_2SO_4), and concentrated. The residue in benzene was chromatographed on Florisil and the product eluted in ether was obtained as an oil (3.6 g) which crystallized from ether to give material with mp 149–156° (2.4 g). Further crystallization from chloroform–ether gave **1c**: mp 152–153°; ν_{max} 1780, 1720, and 1705 cm^{-1} (sh); nmr ($CHCl_3$) δ 0.80–4.00 (22 H, m with s at 1.30, 1.40, and 2.13) and 4.80–5.10 (1 H, m, HCO–).

Anal. Calcd for $C_{18}H_{24}O_5$: C, 67.48; H, 7.55; O, 24.97. Found: C, 67.17; H, 7.37; O, 25.52.

***cis*-Decahydro-6-methylene-8α-hydroxy-1β,4a-dimethyl-5-oxonaphthalene-1α-carboxylic Acid Lactone (1f).**—A mixture of the keto lactone **1a** (0.88 g), dimethylamine hydrochloride (0.50 g), paraformaldehyde (0.52 g) in isoamyl alcohol (25 ml), and concentrated hydrochloric acid (4 drops) was refluxed in a nitrogen atmosphere for 5 hr, and then diluted with water and extracted with ethyl acetate. The combined ethyl acetate extracts were dried (Na_2SO_4) and the solvent was removed to give a neutral product (2.74 g, contains isoamyl alcohol) which was chromatographed on Florisil. The material (1.12 g) eluted in ethyl

(5) Our use of benzyl alcohol in place of methyl alcohol[6] was to facilitate the cleavage of the phenolic ether at the next stage.

(6) A. W. Fort, *J. Org. Chem.*, **26**, 765 (1961).

(7) W. J. Musliner and J. W. Gates, *J. Amer. Chem. Soc.*, **88**, 4271 (1966).

(8) R. M. Dodson, personal communication.

(9) S. N. Mahapatra and R. M. Dodson, *Chem. Ind. (London)*, 253 (1963).

(10) We are grateful to Dr. R. M. Dodson for informing us of his synthesis of **4d** and for supplying us with a copy of its infrared spectrum.

(11) In earlier work,[2] we assigned the stereochemistry of the product **1a** on the basis that, in the methylation of **1g**, the lactone ring controlled the stereochemistry at C_1 and that the stereochemistry at C_{8a} was not affected by the reaction. It was possible that the latter assumption was incorrect (see **5**).[12]

(12) We thank Drs. N. A. LeBel and M. J. T. Robinson for pointing out this possibility to one of us (D. M. S. W.).

(13) A. E. Lickei, A. C. Rieke, and D. M. S. Wheeler, *J. Org. Chem.*, **32**, 1647 (1967).

(14) In this paragraph we use decalin numbering for compounds **4b** and **4c** as well as for **1b**.

(15) G. A. Gallup, M. L. Maheshwari, S. K. Roy, and D. M. S. Wheeler, *Tetrahedron*, **24**, 5769 (1968).

(16) N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, San Francisco, Calif., 1964, p 50.

(17) E. Wenkert, A. Afonso, P. Beak, R. W. J. Carney, P. W. Jeffs, and J. D. McChesney, *J. Org. Chem.*, **30**, 713 (1965).

(18) E. Wenkert and B. G. Jackson, *J. Amer. Chem. Soc.*, **80**, 211 (1958).

(19) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Menlo Park, Calif., 1972, pp 285–288.

(20) R. B. Woodward, F. A. Bader, H. Bickel, A. J. Frey, and R. W. Kierstead, *Tetrahedron*, **2**, 1 (1958).

(21) Unless otherwise stated infrared spectra were determined for chloroform solutions on Perkin-Elmer 137 and 237 infrared spectrometers, and nmr spectra on $CDCl_3$ solutions on Varian A-60 and A-60D spectrometers.

acetate crystallized from ether–light petroleum to give the methylene compound, **1f**, mp 134–135° (0.40 g) and 123–130° (0.15 g). The former material was recrystallized further from ethanol for analysis: ν_{max} 1775, 1694, and 1620 cm^{-1}; nmr δ 0.80–2.70 (13 H, m, with s at 1.22 and 1.30), 3.00–3.30 (2 H, m, $-CH_2CO-$), 4.75–5.20 (1 H, m, OCH), 5.30–5.50 (1 H, m, =CH), and 6.18–6.38 (1 H, m, =CH).

Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.56; H, 7.90.

The aqueous portion from the reaction was treated with potassium carbonate at 0°, the solution was saturated with sodium chloride, and the basic product was isolated by extraction with ethyl acetate. Evaporation of the dried (Na_2SO_4) ethyl acetate solution gave the Mannich base **1d** (0.04 g), mp 94–99°, ν_{max} 1775, 1705, and 1620 cm^{-1} (weak). This compound with methyl iodide gave a yellow methiodide **1e**, mp 125° dec.

The preparation of **1f** was also carried out by refluxing **1a**, paraformaldehyde, and dimethylamine hydrochloride in dimethoxyethane for 68 hr.

***cis*-10α-Hydroxy-1β,4a-dimethyl-6-oxo-1,2,3,4,4a,6,7,8,8a,9,-10,10a-dodecahydrophenanthrene-1α-carboxylic Acid Lactone (2a).** **A.**—A mixture of the diketo aldehydo lactone **1c** (2.7 g, mp 152–155°, from 2.5 g of the keto aldehyde **1b**), potassium hydroxide (8.0 g), methanol (100 ml), and water (50 ml) was stirred under nitrogen for 70 hr. The solvent was evaporated, the residue was treated with water (100 ml), and the mixture was acidified to pH 2 with concentrated hydrochloric acid. The product was extracted with ethyl acetate and the ethyl acetate solution was washed with water and dried (Na_2SO_4). Removal of the solvent gave the crude product as a brown residue. A solution of the residue in benzene with *p*-toluenesulfonic acid was refluxed for 16 hr with a water separator; it was then washed with dilute aqueous sodium carbonate and water and dried (Na_2SO_4). Evaporation of the solvent gave a dark brown oil (2.2 g) whose infrared spectrum did not show a band corresponding to a saturated ketone but did show strong absorption corresponding to an unsaturated ketone. Chromatography of this oil on Florisil and elution with ethyl acetate gave a brown oil (1.8 g) which solidified on trituration with ether. Two crystallizations from ether gave the unsaturated ketone **2a**: mp 158–163° (1.1 g); nmr δ 1.00–2.90 (20 H, m with overlapping singlets at 1.30 and 1.40), 4.80–5.20 (1 H, m, –OCH), and 6.05 (d, J = 2 Hz, =CH) and 6.15 (d, J = 3 Hz, =CH) (the two peaks together integrate to 1 H). After several recrystallizations from methanol–hexane (with a trace of ether) the ketone **2a** was obtained as needles: mp 168.5–173° (with slight decomposition); ν_{max} 1770, 1665, and 1605 cm^{-1}; spectrum identical with that of material, mp 169–175° from B.

B.—In a typical procedure, a solution of the methylene compound, **1f** (0.80 g), in ethanol (25 ml) was added at 0° under N_2 to a stirred mixture of ethyl acetoacetate (0.56 g), and sodium ethoxide (from 0.2 g of sodium) in ethanol (5 ml) which had been stirred for 1 hr at 0°. The mixture was stirred for 8 hr and refluxed for 9 hr. Water was added to the mixture, which was concentrated under vacuum on a water bath, more water was added, and the product was extracted in ethyl acetate. The ethyl acetate was dried and evaporated to yield crude product (0.51 g), ν_{max} 1773, 1713 (very weak), 1665, and 1608 cm^{-1}, which tlc showed contained two major fractions. The aqueous mixture was acidified and then extracted with ethyl acetate to yield further product [0.48 g, ν_{max} 1762, 1710, 1660, and 1603 cm^{-1} (weak)] which was a complex mixture (tlc).

The material obtained in the first ethyl acetate extraction of several reactions was chromatographed repeatedly on Florisil. The product **2b** corresponding to the faster running tlc spot was eluted in benzene: mp 171–174° (yield about 5%) raised after crystallization from ether–light petroleum to mp 174–175°; ν_{max} 1767, 1663, and 1625 cm^{-1}; λ_{max} 247 nm (ϵ 11,000) and 315 (3000); nmr δ 0.90–3.35 (21 H, m, with sharp peaks at 1.05, 1.24, 1.33, 1.38, 1.44, and 1.56), 4.00–4.70 (2 H, m, OCH_2-CH_3), 4.90–5.35 (1 H, m, –OCH), 7.07 (1 H, s, =CH), and 7.83 (1 H, s, –OH). Structure **2b** is assigned to this compound.

Anal. Calcd for $C_{20}H_{26}O_5$: C, 69.34; H, 7.57. Found: C, 69.31; H, 7.41.

Later fractions from the column eluted in benzene–ether (3:1) gave material which after crystallization from ether had mp 163–169° (yield less than 5%) raised by crystallization from ethanol–ether to mp 169–175°; ν_{max} 1772, 1663, and 1603 cm^{-1} (identical with material **2a**, mp 168.5–173°, prepared in A above); nmr ($CHCl_3$) δ 0.8–3.0 (m, with strong s at 1.29 and weak s at 1.42), 4.90–5.20 (m, –OCH), and 6.05 (d, with trace of d at 6.18, C=CH). (The nmr spectrum was very similar to the nmr spectrum of the major component of the product with mp 158–163° in A above.)

Anal. Calcd for $C_{17}H_{22}O_3$: C, 74.47; H, 8.08. Found: C, 74.35; H, 8.21.

***cis*-12-Benzyloxy-6α-hydroxydehydrodeisopropylabietic Acid Lactone (4a).**—A solution of the unsaturated ketone **2a** (1.1 g) in benzyl alcohol (25 ml) was heated with cupric bromide (1.6 g) at 70° for 2.5 hr in a N_2 atmosphere. Ether was added to the cooled mixture, which was filtered. The ether was removed under reduced pressure and the benzyl alcohol was removed by steam distillation. The residue was dissolved in chloroform and the chloroform solution was washed, dried (Na_2SO_4), and concentrated. A solution of the brown residue in benzene was chromatographed on Florisil, and the material eluted in benzene–ether (1:1) crystallized from ether to give **4a**: mp 176° (780 mg), raised after further crystallizations from ether–chloroform and ether to 179.5–180.5°; ν_{max} 1760 cm^{-1}; nmr δ 0.8–2.5 (13 H, m with s at 1.17 and 1.32 and d, J = 7 Hz, at 2.28), 3.0–3.2 (2 H, $-CH_2$ aromatic, d, J = 4 Hz), 4.75–5.20 (3 H, m, $PhCH_2O$ + OCH), 6.6–7.2 (3 H, m, $C_{arom}H$), and 7.38 (5 H, s, $C_{arom}H$).

Anal. Calcd for $C_{24}H_{26}O_3$: C, 79.53; H, 7.23; O, 13.24. Found: C, 79.22; H, 7.25; O, 13.10.

***cis*-12-(5′-1′-phenyl-1-*H*-tetrazolyloxy)-6α-hydroxydehydrodeisopropylabietic Acid Lactone (4c).**—A solution of the benzyl ether **4a** (0.75 g) in methanol (200 ml) and concentrated sulfuric acid (2 drops) was hydrogenated in the presence of palladium on charcoal (10%, 0.2 g). After an uptake of 45 ml of H_2 (in 15 min) the solution was filtered, and the filtrate was concentrated to a small volume and extracted with chloroform. The chloroform solution was washed with water, dried (Na_2SO_4), and evaporated to yield the phenol **4b**: mp 214–216° (0.55 g); ν_{max}^{KBr} 1740 cm^{-1}; nmr peaks (deuterioacetone, material was poorly soluble) δ 0.70–3.00 (16 H, m, with s at 0.80 and 0.92), 4.6–4.9 (1 H, m, –OCH), and 6.1–6.8 (3 H, m, $C_{arom}H$).

A mixture of the phenol **4b** (0.53 g), 5-chloro-1-phenyl-1*H*-tetrazole (0.36 g), anhydrous potassium carbonate (1.0 g), and dimethylformamide (40 ml) was heated at 80° for 8 hr in a N_2 atmosphere, and then diluted with ethyl acetate (200 ml). The ethyl acetate solution was washed with ice–water several times, the aqueous phase was back extracted with ethyl acetate, and the back extracts were washed with water. The combined ethyl acetate solutions were dried (Na_2SO_4) and evaporated to yield an oil. Any remaining traces of dimethylformamide were removed *in vacuo* and the residue was crystallized on treatment with ether and light petroleum, yielding the ether **4c** as a pale yellow solid, mp 139–141° (750 mg). The product after three crystallizations from methanol was colorless: mp 142–143°; ν_{max} 1765 cm^{-1}; nmr δ 1.00–2.50 (13 H, m, with s at 1.25 and 1.32 and d, J = 7 Hz, at 2.38), 3.20 (2 H, d, J = 4 Hz, $C_{arom}CH_2$–), 5.00–5.35 (1 H, d of t, J = 4 and 7 Hz, –OCH), and 7.20–8.00 (8 H, m, $C_{arom}H$).

Anal. Calcd for $C_{24}H_{24}O_3N_4$: C, 69.21; H, 5.81; N, 13.45. Found: C, 69.15; H, 5.75; N, 13.62.

***cis*-6α-Hydroxydehydrodeisopropylabietic Acid Lactone (4d).**—A solution of the tetrazolyl ether **4c** (0.70 g) in ethanol (200 ml) was shaken in a hydrogen atmosphere at 45 psi at 28° for 21 hr in the presence of palladium on charcoal (10%, 0.50 g). The solution was filtered and the filtrate was concentrated. A solution of the residue (0.69 g) in benzene was chromatographed on Florisil, and the product **4d** (0.30 g) was eluted in benzene and some early fractions of benzene–ether (98:2). Crystallization from ether–light petroleum gave **4d**: mp 151–152° (0.23 g); ν_{max} 1760 cm^{-1}; nmr δ 1.00–2.50 (13 H, m, with s at 1.18 and 1.32, and d, J = 7 Hz, at 2.33), 3.17 (2 H, d, J = 4 Hz, $C_{arom}CH_2$–), 4.90–5.25 (1 H, d of t, J = 4 and 7 Hz, –OCH), and 7.10–7.40 (4 H, m, C_{arom} H). Dodson's compound had mp 154–155° and the infrared spectra (Nujol) of his compound and ours were identical.

Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.68; H, 7.81. Found: C, 79.35; H, 7.90.

The lactone **4d** was recovered unchanged (a) on treatment with chromium trioxide in 90% acetic acid at room temperature for 16 hr; (b) on heating with chromium trioxide in glacial acetic acid for 5 hr on a steam bath; and (c) on refluxing with selenium dioxide in 95% acetic acid for 70 hr.

Registry No.—**1b**, 36794-36-2; **1c**, 36807-65-5; **1d**, 36807-66-6; **1e**, 36807-67-7; **1f**, 36807-68-8; **2a**,

36803-46-0; **2b**, 36803-47-1; **4a**, 36807-69-9; **4b**, 36807-70-2; **4c**, 36807-71-3; **4d**, 36807-72-4.

Acknowledgments.—This work was supported by grants from the National Cancer Institute (CAO 5796) the Research Council of the University of Nebraska, and the American Cancer Society.

Photochemical Syntheses of Spiro[4.5]decane-1,6-dione

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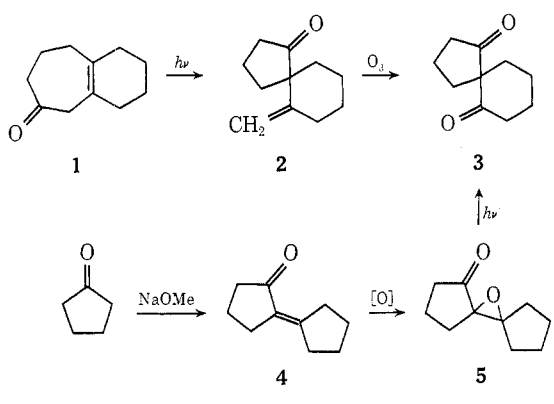
Received May 24, 1972

Recently the photoisomerization of the β,γ-unsaturated ketone bicyclo[5.4.0]undec-1(7)-en-3-one (**1**) to the β,γ-unsaturated spiro ketone 6-methylenespiro-[4.5]decan-1-one (**2**) was reported.[1] We now wish to describe the ozonolysis of **2** to the spiro 1,3 diketone **3** and the facile photochemical synthesis of **3**.



1 2 3 4 5

The structure of the spiro ketone **2** was proved by physical methods and by catalytic reduction of the exocyclic methylene group to two isomeric methyl ketones, one of which is known.[2] To confirm that the exocyclic methylene group was attached to the six-membered ring, **2** was ozonized to yield the spiro 1,3 diketone **3**. The infrared spectrum of **2** showed $\bar{\nu}_{max}$ at 1735 cm^{-1} due to the carbonyl stretching frequency of a cyclopentanone, whereas **3** had $\bar{\nu}_{max}$ at 1732 and 1698 cm^{-1} due to cyclopentanone and cyclohexanone rings, respectively.

Since it is well known in the steroid series that photolysis of α,β-epoxy ketones yields 1,3 diketones,[3] photolysis of the epoxy ketone **5** should yield the desired spiro 1,3 diketone **3**. The precursor required for this photorearrangement was the ketone **5**. This epoxy ketone **5** can be readily obtained by an aldol condensation of cyclopentanone followed by epoxidation. Epoxidation of the aldol product **4** with perbenzoic acid or with 30% hydrogen peroxide and base gave the epoxide **5** in low yield; however, *m*-chloroperbenzoic acid gave **5** in 47% yield.

Direct irradiation of **5** in benzene, hexane, ether, and methanol with a medium-pressure mercury arc (Hanovia type L), using a Pyrex filter, afforded the spiro 1,3 diketone **3** in 25% yield. A second unidentified product **6** was also observed in trace amounts such that the ratio of formation of **3**:**6** was 7:1.

Photolysis of **5** in the presence of a series of photosensitizers such that the sensitizer absorbed >90% of the light gave the following results: benzaldehyde (E_T = 72 kcal)[4] and benzophenone (69 kcal)[4] led to a substantial decrease in the rate of formation of **3**, whereas acetone (77 kcal)[5] and acetophenone (74 kcal)[4] led to an increase in the rate of reaction. These results indicate that a triplet state with an energy level above 72 kcal and below 74 kcal leads to the spiro 1,3-diketone **3**. Furthermore, sensitized photolysis of **5** also leads to the formation of **3** and **6** in the ratio of 7:1. Since the product distribution in such sensitized runs provides a "fingerprint" characteristic of the triplet, it would be exceedingly fortuitous for another species to give the same "fingerprint," and we therefore conclude that the triplet is the reacting species in the direct runs as well.[6]

Photolysis of **5** in the presence of the quenchers piperylene, naphthalene, and biphenyl indicated a slight increase in the rate of photoisomerization in the case of naphthalene. These results indicate that the triplet state has an extremely short lifetime and does not undergo diffusion-controlled quenching. The increase in the rate of reaction in the case of naphthalene is probably due to sensitization of the singlet state of **5**.[7]

The photorearrangement described here offers a rapid method for the synthesis of the spiro[4.5]decanes found as the skeletons of a number of interesting sesquiterpenes.[8,9] Furthermore, this method should be general and provide an alternative synthetic route to spiro molecules.

Experimental Section[10]

Ozonolysis of 6-Methylenespiro[4.5]decan-1-one (2).—A solution of 30 mg (0.183 mmol) of 6-methylenespiro[4.5]decan-1-one,[1] one drop of water, and 10 ml of ethyl acetate was stirred at 0° for 10 min while ozone was passed through the solution. Then 1.0 ml of water and 0.2 g of zinc dust were added, and the mixture was stirred at room temperature overnight. The ethyl acetate solution was filtered, washed with water until neutral, dried

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(10) Melting points were determined with a Thomas-Hoover melting point apparatus and are uncorrected. Ir spectra were recorded with a Perkin-Elmer Infracord Model 137 spectrometer fitted with sodium chloride prisms. Ultraviolet spectra were determined in methanol with a Cary 14 recording spectrometer. Nmr spectra were obtained with Varian A-60-A and XL100 spectrometers. The mass spectra were on an AE1 MS-9 mass spectrometer at an ionizing energy of 70 eV. Microanalysis were performed by Micro-Analysis Inc., Wilmington, Del.