tive amine), boiling points, uv absorption maximums, and refractive indices are shown in Table I.

TABLE I

Diene	% yield	Bp, °C (mm)	Uv (pentane), nm (ε)	$n^{25}D$
5[a]	60.0	109–111°	232 (15,500)	1.4896
6	40.0	140–143°	233 (25,500)	1.4986
7	86.5	87–89° (57)	228 (19,700)	1.5079
			234 (21,000)	
8	57.0	92–96° (150)	234 (22,500)	1.4852

[a] W. J. Bailey and J. C. Goossens, *J. Amer. Chem. Soc.*, **78**, 2804 (1955). I. N. Nazarov and N. V. Kuznetsov, *Dokl. Akad. Nauk SSSR*, **111**, 358 (1956); *Chem. Abstr.*, **51**, 9504*d* (1957).

Experimental Section

Boiling points are uncorrected. Refractive indices were obtained on a Bausch and Lomb Abbe refractometer. Uv, ir, and nmr spectra were determined on Cary 14, Beckman IR-5, and Varian A-60 instruments, respectively. Satisfactory elemental analyses were obtained on all new compounds.

Cyclohexene-1-carboxylic acid,[5] cycloheptene-1-carboxylic acid,[5] and cyclooctene-1-carboxylic acid[6] were prepared by previously published methods. The following method is the general method used to prepare all of the dienes.

1-Cyano-3,5-dimethylcyclohexene.—A mixture of 3,5-dimethylcyclohexanone (114.0 g, 0.91 mol) and hydrogen cyanide[7] (54.0 g, 2.0 mol) in 200 ml of 95% ethanol with 2 drops of 50% aqueous potassium hydroxide was allowed to stand for 18 hr in a tightly closed flask. The solution was then made acidic with saturated aqueous oxalic acid solution. After the ethanol was removed under reduced pressure, ~300 ml of benzene was added and the solution was filtered. The filtrate was dried over sodium sulfate and filtered again and the cyanohydrin was dehydrated by the slow addition of phosphorus oxychloride (154 g, 1 mol) in benzene–pyridine (250 ml of each) and then refluxed for 1 hr. The dark solution was poured over crushed ice; the organic phase was separated and washed five times with 500-ml portions of 10% hydrochloric acid. The benzene solution was dried over sodium sulfate and filtered and benzene was removed at reduced pressure. The residue was distilled [bp 97–103° (16 mm)] and redistilled [bp 69–75° (2 mm)] to yield 62.2 g of 1-cyano-3,5-dimethylcyclohexene, ir 2222 cm^{-1} (α,β-unsaturated nitrile).

Δ^1- and Δ^2-3,5-Dimethylcyclohexene-1-carboxylic Acid.—A mixture of 1-cyano-3,5-dimethylcyclohexene (30 g, 0.22 mol) and potassium hydroxide (60 g) in 500 ml of water was stirred under reflux for 72 hr. The solution was cooled in an ice bath and the solution was made acidic with concentrated hydrochloric acid, with the temperature being kept below 10°. The solution was extracted five times with 200-ml portions of ether, the combined ether extracts were dried over sodium sulfate and filtered, the solvent was removed, and the residue was distilled [bp 83–97° (0.1 mm)] to yield 34.8 g (98%) 3,5-dimethylcyclohexene-1-carboxylic acid. The nmr spectrum indicated a mixture of α,β- and β,γ-unsaturated acids (70:30) by the presence of absorptions at δ 6.87 and 5.45.

***N,N*-Dimethyl-*N*-(3,5-dimethylcyclohexenyl)methylamine.**—The acid mixture (96.7 g, 0.64 mol) from the previous preparation was treated with thionyl chloride (84 g, 0.70 mol) in refluxing benzene (~300 ml). The acid chloride was cooled and added dropwise to 200 ml of anhydrous dimethylamine and stirred overnight. The solution was filtered and benzene was then removed under reduced pressure. The crude amide was dissolved in 500 ml of anhydrous ether and added dropwise to a stirring slurry of lithium aluminum hydride (19.0 g, 0.50 mol) in 1 l. of anhydrous ether. The mixture was refluxed for 72 hr and then the reaction was quenched by the careful addition of water (18.0 g, 1.0 mol). Sodium sulfate (50 g) was added and the mixture was filtered. The precipitate was washed twice with 100-ml portions of ether. The ethereal solution was concentrated and distilled giving 66.5 g (63%) of the amine, bp 62–64° (4 mm), $n^{25}D$ 1.4603.

1-Methylene-3,5-dimethylcyclohex-2-ene.—The amine (57.7 g, 0.35 mol) from the previous preparation was dissolved in 500 ml of hexane and to this was added iodomethane (100 g, 0.70 mol) over a 2-hr period. The solution was then stirred overnight. Enough water was added to dissolve the salt, the aqueous solution was added to freshly prepared silver oxide (from 0.4 mol of silver nitrate), and the mixture was stirred for 4 hr at 60°. The dark solution was then filtered through a fine sintered-glass funnel. The filtrate was distilled, first at atmospheric pressure and then at reduced pressure (~40 mm), while the oil-bath temperature was allowed to rise to 180°, all distillate being collected in a receiver immersed in a Dry Ice–2-propanol bath. The distillate was thawed and extracted four times with 200-ml portions of pentane. The combined pentane washings were dried and filtered and the solvent was distilled. The residue was subjected to distillation [bp 92–96° (150 mm)] to yield 24.5 g (57%) of the diene: $n^{25}D$ 1.4852; uv max (pentane) 234 nm (ε 22,500); ir (neat) 890 cm^{-1} (=CH_2); nmr (CCl_4) δ 5.86 (s, 1 H, =C<H), 4.59 (s, 2 H, =CH_2).

Registry No.—**5**, 1888-90-0; **6**, 34564-56-2; **7**, 34564-56-2; **8**, 34564-57-3; 1-cyano-3,5-dimethylcyclohexene, 34565-58-4; Δ^1-3,5-dimethylcyclohexene-1-carboxylic acid, 34599-22-9; Δ^2-3,5-dimethylcyclohexene-1-carboxylic acid, 34564-59-5; *N,N*-dimethyl-*N*-(Δ^1-3,5-dimethyl-1-cyclohexenyl)methylamine, 34564-60-8; *N,N*-dimethyl-*N*-(Δ^2-3,5-dimethyl-2-cyclohexenyl)methylamine, 34564-61-9.

Acknowledgment.—The author expresses his gratitude to Dr. G. J. Fonken for his guidance and advice in the course of this work and to the Robert A. Welch Foundation for financial support of this work through a grant to Professor G. J. Fonken for study of photochemical and thermal reactions of unsaturated hydrocarbons.

(5) O. H. Wheller, and I. Leiner, *J. Amer. Chem. Soc.*, **78**, 64 (1956).

(6) E. A. Braude, W. F. Forbs, B. F. Gofton, R. P. Houghton, and E. S. Waight, *J. Chem. Soc.*, **171**, 4711 (1957).

(7) K. Ziegler, "Organic Syntheses, Coll. Vol. I, Wiley, London, 1941, p 314. It is strongly recommended for the worker to smoke while preparing this reagent.

Synthesis of the Spiro[4.5]decane System. An Approach to the Acorane Sesquiterpene Group

A. R. PINDER,* S. J. PRICE, AND R. M. RICE

Department of Chemistry, Clemson University, Clemson, South Carolina 29631

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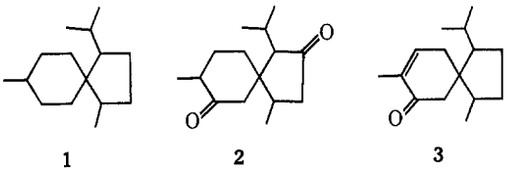
The acorane group of bicyclic sesquiterpenes, characterized by the carbon skeleton **1**, is typified by the



1 **2** **3**

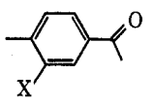
acorones, stereoisomeric diketones represented by structure **2**,[1] and the two acorenones, stereoisomers of **3**.[2]

(1) F. Šorm and V. Herout, *Collect. Czech. Chem. Commun.*, **13**, 177 (1948); **14**, 723 (1949); V. Sykora, V. Herout, J. Pliva, and F. Šorm, *Chem. Ind. (London)*, 1231 (1956); *Collect. Czech. Chem. Commun.*, **23**, 1072 (1958); V. Sykora, V. Herout, A Reiser, and F. Šorm, *ibid.*, **24**, 1306 (1959); J. Vrkoč, V. Herout, and F. Šorm, *ibid.*, **27**, 2709 (1962).

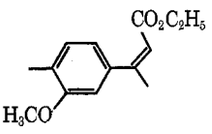
(2) J. Vrkoc, V. Herout, and F. Šorm, *ibid.*, **26**, 1021, 3183 (1961); R. J. McClure, K. S. Schorno, J. A. Bertrand, and L. H. Zalkow, *Chem. Commun.*, 1135 (1968).

We have investigated a synthetic approach to the acorones along the following lines. After we had become deeply involved in the project, we discovered that an almost identical route had already been outlined, culminating in a synthesis of acorone, though not substantiated by published details.[3]

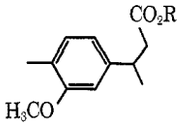
We began with *p*-methylacetophenone (**4**) which was



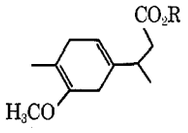
4, X = H
5, X = OCH_3



6

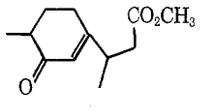


7, R = C_2H_5
8, R = H

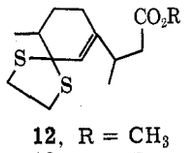


9, R = H
10, R = CH_3

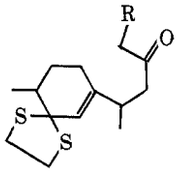
converted by successive nitration, reduction, diazotization, acid treatment,[4] and methylation[5] into a 3-methoxy-4-methylacetophenone (**5**). A Reformatsky reaction between **5** and ethyl bromoacetate[5] gave, after dehydration, the unsaturated ester **6**,[5] as a mixture of cis and trans modifications, hydrogenation of which yielded saturated ester **7**. The corresponding acid **8** was reduced with lithium and *tert*-butyl alcohol in liquid ammonia–tetrahydrofuran, under carefully defined conditions, to the dihydro acid **9**, which was quickly esterified with diazomethane to **10**, and then hydrolyzed with acid to the conjugated enone **11**. The ethylene



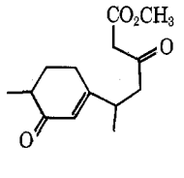
11



12, R = CH_3
13, R = H

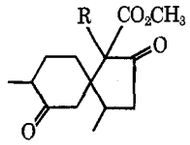


14, R = H
15, R = CO_2CH_3

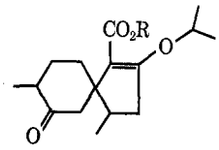


16

dithioketal **12** of the latter on hydrolysis afforded the corresponding acid **13**, which with methyllithium was converted into ketone **14**.[6] Reaction of **14** with dimethyl carbonate and sodium hydride[7] furnished the β-keto ester **15**, hydrolyzed by mercuric chloride–mercuric oxide in aqueous methanol[8] to the diketo ester **16**. The latter underwent smooth cyclization by internal Michael addition to the spiro diketo ester **17**



17, R = H
18, R = $CH(CH_3)_2$



19, R = CH_3
20, R = $CH(CH_3)_2$

on treatment with sodium methoxide. Since **17** was almost entirely crystalline, it seems likely that one of the several possible stereoisomers corresponding to this structure predominated.

The penultimate step in the sequence was isopropylation of **17** to **18**, hydrolysis and decarboxylation of which would yield acorone **2**. Unfortunately, despite claims to the contrary,[3] all efforts to C-isopropylate **17** were unsuccessful. Treatment of **17** with methanolic sodium methoxide and isopropyl iodide yielded almost entirely the enol ether **19**, while the thallous salt[9] of **17**, when heated with the same halide, afforded a complex mixture of products including the same enol ether, accompanied by isopropyl esters, possible retro-Michael reaction products, and unchanged starting material. Presumably steric factors, opposing the setting up of three contiguous groups on the same side of the cyclopentane ring,[10] are responsible for the failure of the alkylation.

Experimental Section

Melting points and boiling points are uncorrected. Nmr spectra were recorded on a Varian A-60 spectrometer, and mass spectra on a Du Pont 21-490 mass spectrometer.

Ethyl 3-(3′-Methoxy-*p*-tolyl)butanoate (7).—3-Hydroxy-4-methylacetophenone was synthesized according to a published sequence,[4] and methylated[5] to give **5**: bp 74–75° (0.25 mm); nmr ($CHCl_3$) δ 2.16 (s, 3), 2.47 (s, 3), 3.80 (s, 3), 7.24 (AB q, 2, J = 8.5 Hz), 7.33 (d, 1, J = 2 Hz). The unsaturated ester **6** was obtained, as a mixture of cis and trans forms, *via* a Reformatsky reaction[5] between ketone **5** and ethyl bromoacetate, followed by dehydration with iodine.[5] It had bp 120–121° (0.15 mm) [lit.[5] bp 132–138° (0.6 mm)]; ir (film) 1710, 1640 cm^{-1}. The ester **8** (58.25 g, 0.25 mol), methanol (200 ml), and 5% palladized carbon were mixed and shaken in hydrogen at 45 psi and room temperature until uptake of gas ceased. The catalyst was removed by filtration and the filtrate was freed of solvent. The residual saturated ester **7** distilled at 102–103° (0.2 mm) (52 g, 88%): ir (film) 1735 cm^{-1}; nmr ($CDCl_3$) δ 1.15 (t, 3, J = 7.0 Hz), 1.28 (d, 3, J = 8.0 Hz), 2.20 (s, 3), 2.55 (d, 2, J = 8.0 Hz), 3.20 (m, 1), 3.80 (s, 3), 4.05 (q, 2, J = 7.0 Hz), 6.90 (m, 3). *Anal.* Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 70.93; H, 8.53.

3-(3′-Methoxy-*p*-tolyl)butanoic Acid (8).—The foregoing ester (118 g, 0.5 mol) and 3 *N* aqueous sodium hydroxide (1 l.) were refluxed for 3 hr. The cooled, homogeneous solution was rendered acidic with 6 *N* hydrochloric acid and extracted twice with ether. Concentration of the combined, dried extracts afforded the acid **8**: bp 124–125° (0.04 mm) (103 g, 99%); ir (film) 3100–3500, 1715 cm^{-1}; nmr ($CDCl_3$) δ 1.20 (d, 3, J = 7.0 Hz), 2.15 (s, 3), 2.50 (d, broad, 2, J = 7.0 Hz), 3.20 (m, 1), 3.80 (s, 3), 6.90 (AB q, 3), 11.50 (s, broad, 1). *Anal.* Calcd for $C_{12}H_{16}O_3$:

(3) W. Parker, R. Ramage, and R. A. Raphael, quoted as a personal communication by J. M. Mellor and S. Munavalli, *Quart. Rev., Chem. Soc.*, **18**, 270 (1964), footnote 87 on p 293.

(4) O. L. Brady and J. N. E. Day, *J. Chem. Soc.*, 114 (1934); G. T. Morgan and A. E. J. Pettet, *ibid.*, 418 (1934), R. E. Lutz, *et al.*, *J. Org. Chem.*, **12**, 617 (1947).

(5) L. Ruzicka and L. Sternbach, *Helv. Chim. Acta*, **23**, 355 (1940).

(6) *Cf.* C. Tegner, *Acta Chem. Scand.*, **6**, 782 (1952); M. J. Jorgenson, *Org. React.*, **18**, 1 (1970).

(7) *Cf.* A. P. Krapcho, J. Diamanti, C. Cayen, and R. Bingham, *Org. Syn.*, **47**, 20 (1967).

(8) *Cf.* D. Seebach, N. R. Jones, and E. J. Corey, *J. Org. Chem.*, **33**, 300 (1968).

(9) E. C. Taylor, G. C. Hawks, and A. McKillop, *J. Amer. Chem. Soc.*, **90**, 2421 (1968); E. C. Taylor and A. McKillop, *Accounts Chem. Res.*, **3**, 338 (1970).

(10) *Cf.* T. G. Crandall and R. G. Lawton, *J. Amer. Chem. Soc.*, **91**, 2127 (1969).

C, 69.21; H, 7.74, neut equiv, 208.3. Found: C, 69.47; H, 7.94 neut equiv, 208.4.

Methyl 3-(4'-Methyl-3'-oxo-1'-cyclohexenyl)butanoate (11).[11]—The preceding acid (29.2 g, 0.14 mol) in purified tetrahydrofuran (600 ml) and dry *tert*-butyl alcohol (600 ml) was added gradually to distilled, stirred liquid ammonia (1500 ml). With continued stirring, lithium metal (16.7 g, 2.4 mol) was added in small pieces during 45 min. The deep blue solution was stirred for 5 hr, then quenched with methanol (150 ml) and stirred overnight during evaporation of the ammonia. Water was added and the organic solvents were removed *in vacuo*. The residue was diluted with water to 2 l., then cooled in ice, acidified with cold 4 *N* hydrochloric acid, and quickly extracted thrice with ether. The combined extracts were dried, cooled in ice, and mixed with an excess of ethereal diazomethane. The ether solution was washed with aqueous sodium bicarbonate and water, dried, and concentrated. The residue was stirred with 2.5 *N* hydrochloric acid (500 ml) for 3 hr, and organic material was isolated with ether. The extract was dried and concentrated, and the residual keto ester **11** distilled: bp 110° (0.25 mm) 22.4 g, 76%); λ_{max} (EtOH) 234 nm (ϵ 11,000); ir (film) 1735, 1720 (weak), 1665, 1635 cm^{-1}; nmr ($CDCl_3$) δ 0.90–1.30 (dd, 6), 3.60 (s, 3), 5.80 (s, 1). *Anal.* Calcd for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63. Found: C, 68.44; H, 8.60.

Ethylene Dithioketal 12.—The above keto ester (22.8 g, 0.11 mol), 1,2-ethanedithiol (10.8 g, 0.115 mol), and methanol (200 ml) were stirred and cooled in ice during the dropwise addition of boron trifluoride etherate (17 ml). After 16 hr of stirring, excess ice–water was added and the product was isolated with ether. Evaporation of the dried extract gave the desired dithioketal **12**: bp 135° (0.1 mm) (24.7 g, 80%); ir (film) 1735 cm^{-1}; nmr ($CDCl_3$) δ 1.05 (d, 3, J = 7.0 Hz), 1.20 (d, 3, J = 6.5 Hz), 3.30 (m, 4), 3.80 (s, 3), 5.75 (s, broad, 1). *Anal.* Calcd for $C_{14}H_{22}O_2S_2$: C, 58.70; H, 7.75; S, 22.46. Found: C, 58.73; H, 7.77; S, 22.35.

4-(3',3'-Ethylenedithio-4'-methyl-1'-cyclohexenyl)-2-pentanone (14).—The dithioketal **12** (38.9 g, 0.136 mol) was refluxed with 2.5 *N* aqueous sodium hydroxide (500 ml) for 2 hr, then cooled, acidified with 6 *N* hydrochloric acid, and extracted with ether. The dried extract, containing the crude acid **13**, was stirred and cooled in ice during the gradual addition, under nitrogen, of ethereal methyllithium[6] (133 ml of 2 *N*), during 1 hr. After a further 2 hr of stirring the product was poured into ice–water and the organic phase was separated. The aqueous layer was extracted twice with ether and the combined extracts were washed with water, dried, and concentrated. The residual methyl ketone **14** distilled at 125° (0.01 mm) (30.7 g, 85%): ir (film) 1710, 1360 cm^{-1}; nmr ($CDCl_3$) δ 1.00 (d, 3, J = 6.0 Hz), 1.15 (d, 3, J = 6.0 Hz), 2.15 (s, 3), 3.30 (m, 4), 5.70 (s, broad, 1). *Anal.* Calcd for $C_{14}H_{22}OS_2$: C, 62.66; H, 8.20; S, 23.68. Found: C, 62.20; H, 8.23; S, 23.67.

1-Carbomethoxy-4-(3',3'-ethylenedithio-4'-methyl-1'-cyclohexenyl)-2-pentanone (15).[7]—Sodium hydride (11.0 g of a 50% dispersion in mineral oil, 0.23 mol) was washed thrice with petroleum ether (bp 30–60°) by decantation, then mixed with dry benzene (500 ml), dimethyl carbonate (20.5 g, 0.23 mol), and the foregoing methyl ketone (30.7 g, 0.23 mol). The whole was refluxed under nitrogen for 72 hr, then cooled, acidified cautiously with glacial acetic acid, and treated with ice–water. The organic layer was separated and the aqueous layer was extracted twice with ether. The combined extracts were shaken with aqueous sodium bicarbonate and water, dried, and concentrated. The remaining β-keto ester **15** distilled at 170–180° (bath, 0.01 mm) (35.4 g, 94%). It gave a wine-red color with ferric chloride, was soluble in cold, aqueous alkali, and formed a copper complex with cupric acetate: ir (film) 1730, 1706, 1639, 1621 cm^{-1}; nmr ($CDCl_3$) δ 1.00 (d, 3, J = 6.0 Hz), 1.17 (d, 3, J = 6.0 Hz), 3.30 (m, 4), 3.80 (s, 3), 5.60 (s, broad, 1). *Anal.* Calcd for $C_{16}H_{24}O_3S_2$: C, 58.52; H, 7.37; S, 19.53. Found: C, 58.63; H, 7.41; S, 19.32.

1-Carbomethoxy-4-(4'-methyl-3'-oxo-1'-cyclohexenyl)-2-pentanone (16).—The dithioketal above (10.5 g, 0.032 mol) was refluxed with methanol (300 ml), water (24 ml), mercuric oxide (5.4 g, 0.025 mol), and mercuric chloride (183 g, 0.0675 mol) for 4 hr.[8] Inorganic material was removed by filtration, the filtrate was diluted with water, and the product was isolated with ether. The ether extract was washed with aqueous ammonium chloride and water, dried, and concentrated. The residual β-keto ester **16** distilled at 160–165° (bath, 0.04 mm) (6.2 g, 77%). It showed the usual properties of an enolic compound, forming a bluish-gray copper complex with cupric acetate: ir (film) 1748, 1712, 1669, 1629 cm^{-1}; nmr ($CDCl_3$) δ 1.10 (two d, 4), 3.50 (s, 2), 3.70 (s, 3), 5.75 (s, broad, 1). *Anal.* Calcd for $C_{14}H_{20}O_4$: C, 66.64; H, 7.99. Found: C, 66.84; H, 8.25.

4,7-Dimethyl-1-methoxycarbonylspiro[4,5]decane-2,6-dione (17).—Sodium metal (0.455 g, 0.0198 mol) was dissolved in dry methanol (200 ml) and the preceding β-keto ester **16** (5.0 g, 0.0198 mol) was added, the solution being stirred under nitrogen at room temperature for 1 hr. After acidification with glacial acetic acid the solvent was removed *in vacuo*. Ice–water was added and the product was isolated with ether. The extract was concentrated to small bulk and shaken with an excess of aqueous cupric acetate for 2 hr. The light green copper complex was collected, washed with water, and dried; it crystallized from benzene in light green prisms, mp 213–214° dec. *Anal.* Calcd for $C_{28}H_{38}O_8Cu$: C, 59.42; H, 6.72. Found: C, 59.28; H, 6.81. The copper complex (5.0 g), suspended in ether, was shaken vigorously with cold 2 *N* sulfuric acid for 45 min. The clear layers were separated and the organic phase was washed with water, dried, and concentrated. The remaining spiro keto ester **17** distilled at 150–155° (bath, 0.05 mm) (2.75 g). It crystallized almost entirely on keeping and separated from methanol in prisms: mp 113°; ir (film) 1764, 1715 cm^{-1}, with broad OH and C=O bands characteristic of enolic form; nmr ($CDCl_3$) δ 1.05 (two d overlapping, 6), 3.75 (m, 3, keto–enol mixture). *Anal.* Calcd for $C_{14}H_{20}O_4$: C, 66.64; H, 7.99; mol wt, 252.3. Found: C, 66.78; H, 8.02; mol wt, 252 (mass spectrum).

Registry No.—**7**, 34638-68-1; **8**, 34638-69-2; **11**, 34638-70-5; **12**, 34638-71-6; **14**, 34638-72-7; **15**, 34638-73-8; **16**, 34638-74-9; **16** copper complex, 34630-94-9; **17**, 34638-75-0.

(11) *Cf.* H. L. Dryden, G. M. Webber, R. R. Burtner, and J. A. Cella, *J. Org. Chem.*, **26**, 3237 (1961).

The Synthesis of Two Metabolites of (−)-Δ^8-Tetrahydrocannabinol

KENNETH E. FAHRENHOLTZ

Chemical Research Department, Hoffmann-La Roche Inc., Nutley, New Jersey 07110

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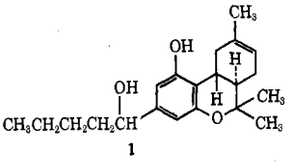
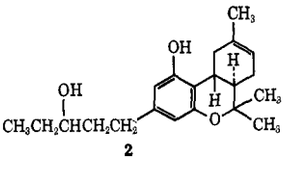
Recent studies from these laboratories have resulted in the isolation[1] of two *in vitro* dog liver metabolites of (−)-Δ^8-tetrahydrocannabinol. By inspection of their mass and nmr spectra and comparison of their nmr spectra with those of suitable monocyclic model compounds, structures **1** and **2** were established for these metabolites. The microgram quantities of these materials isolated from the metabolic mixtures were too small to allow determination of the configuration of the introduced hydroxyl groups. We now report the



1



2

unequivocal syntheses of these two metabolites as diasteromeric mixtures at the carbinol carbons.

We envisioned the synthesis of **1** as proceeding *via* an acid-catalyzed condensation of the known[2] resorcinol

(1) D. E. Maynard, O. Gurny, R. G. Pitcher, and R. W. Kierstead, *Experientia*, **27**, 1154 (1971).

(2) R. Huls and A. Hubert, *Bull. Soc. Chim. Belg.*, **65**, 596 (1956).