5-Ethyl-5′-methyl-5,5′-(oxydimethylene)bis(2,2-dimethyl)-*m*-dioxane) (16).—A stirred solution of 17 g (0.1 mol) of **12** in 75 ml of dry toluene was refluxed with 1.6 g (0.07 g-atom) of sodium until it was completely reacted. Then 22 g (0.07 mol) of dry **3** was added. After 1-hr reflux, a precipitate (sodium tosylate) was apparent. After 80-hr reflux there was no further change in the glc spectrum as monitored by a 6-ft 30% silicone grease on 45/55 Chromosorb P column at 200° and 85-ml/min helium flow. This spectrum showed the two symmetrical ethers **4** and **14** at 6.4- and 12-min retention times, respectively, and the major unsymmetrical product **16** at 8.8-min retention. The product was twice fractionated to obtain the colorless oil, bp 102–115° (0.15 mm). Acid hydrolysis of **16** gave the crystalline 2-ethyl-2′-methyl-2,2′-(oxydimethylene)di-1,3-propanediol (**17**) which was converted to the tetrabutyrate **27** by butyric anhydride. The tetrabutyrate showed a retention time of 15.5 min on the 6-ft silicone grease column at 275°, 85-ml/min flow.

Reaction of Trimethylolethane with Thionyl Chloride.—To a stirred mixture of 24 g (0.2 mol) of trimethylolethane in 150 ml benzene at 50° was added dropwise 29 ml (0.4 mol) of thionyl chloride. The homogeneous solution was refluxed 2 hr, then the solvent was removed, and the residue was poured into ice water, yielding 15 g of water-insoluble product. Recrystallization from aqueous isopropyl alcohol yielded shiny crystals of the trisulfite **18**, mp 101–103°.

Anal. Calcd for $C_{10}H_{10}O_9S_3$: C, 31.74; H, 4.79; S, 25.42. Found: C, 31.30; H, 4.75; S, 25.04.

Dineopentyl Ether 25.—A stirred mixture of 22 g (0.25 mol) of neopentyl alcohol and 5.8 g (0.25 g-atom) of sodium in 150 ml of toluene was refluxed until homogeneous; then a solution of 55.3 g (0.23 mol) of neopentyl tosylate in 70 ml of toluene was added. After a reflux period of 1 week, 84% of the tosylate had reacted as determined by glc analysis on the 6-ft silicone grease column which showed the formation of dineopentyl ether (3.7-min retention, 75°, 85-ml/min flow) and disappearance of the tosylate (4.5-min retention time, 200°, 85-ml/min flow). The pure dineopentyl ether was obtained by preparative gas chromatography as a colorless liquid: $n^{25}D$ 1.3931; nmr (toluene) δ 0.94 (s, 9, CH_3) and 2.94 ppm (s, 2, CH_2); mass spectrum (70 eV) *m/e* (ion) 158 (molecular ion), 101 (neopentyloxymethyl), 71 (neopentyl ion).

Anal. Calcd for $C_{10}H_{22}O$: C, 75.88; H, 14.01. Found: C, 76.26; H, 13.77.

Bis(1-methylcyclohexylmethyl) Ether (26).—This dineoalkyl ether was obtained similarly as a colorless oil: bp 81° (0.25 mm); $n^{25}D$ 1.4690; T_D 552°F; d^{0}°F 0.9381; viscosity, cSt (°F), 5114, (−40), 283 (0), 10.65 (100), 2.49 (210).

Anal. Calcd for $C_{16}H_{30}O$: C, 80.60; H, 12.68. Found: C, 80.50; H, 12.34.

Registry No.—**2,** 3663-46-5; **3,** 34541-77-0; **4,** 34578-24-0; **5,** 21139-47-9; **6,** 34541-79-2; **10,** 5898-79-3; **11,** 21398-92-5; **12,** 20761-68-6; **13,** 34541-83-8; **14,** 34541-84-9; **15,** 23235-61-2; **16,** 34541-86-1; **18,** 11098-52-5; **19,** 34541-87-2; **20,** 34541-88-3; **21,** 34541-89-4; **22,** 34578-25-1; **23,** 34541-90-7; **24,** 34541-91-8; **25,** 28509-24-2; **26,** 34541-92-9.

Preparation of Some Methylenecycloalkenes *via* a Novel 1,4 Hofmann Elimination Reaction[1]

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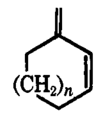
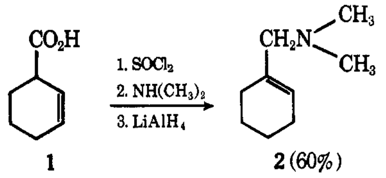
In the course of photochemical studies of conjugated dienes in this laboratory, the preparation of significant quantities of several s-trans dienes of general structure A was required. Historically, two routes that have

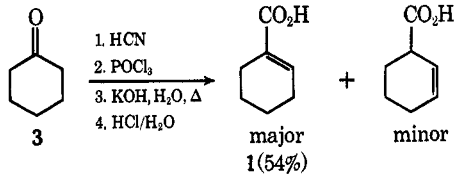


A

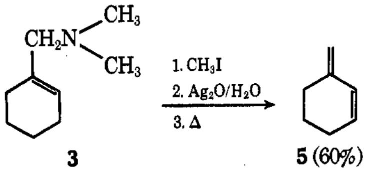
been used are acetate pyrolysis[2] and the Wittig reaction,[3] but in our hands these reactions have given variable results (both in quantity and quality); hence it was deemed desirable to explore another method.

Since one of the better methods for the preparation of olefinic compounds is the Hofmann elimination, attention was turned to the availability of suitable amines. One possibility that immediately came to mind was a novel 1,4 Hofmann elimination sequence using a β,γ-unsaturated amine such as *N*,*N*-dimethyl-*N*-cyclohexenylmethylamine (**2**), which in turn is readily available from cyclohexene-1-carboxylic acid (**1**) *via* the sequence outlined below. Acid **1**, in turn, is readily prepared from the corresponding ketone, cyclohexanone (**3**), by cyanohydrin formation, followed by dehydration and hydrolysis. Some double-bond migration was observed, but, as both isomers should give the same product when converted to their respective amines and subjected to the Hofmann degradation sequence, the presence of minor amounts of the Δ^2 isomer did not present a synthetic problem.





Reaction of **2** with iodomethane in hexane solution gave the quaternary ammonium salt, which was treated with freshly precipitated, alkaline-free silver oxide to give the quaternary ammonium hydroxide, which on pyrolysis yielded methylenecyclohexene (**5**). Methylenecycloheptene (**6**), methylenecyclooctene (**7**), and 3,5-dimethylmethylenecyclohexene (**8**) were also prepared by this method. Their yields[4] (from the respec-



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[1] Abstracted in part from the Ph.D. Dissertation of M. R. S., The University of Texas at Austin, Austin, Texas, 1971.

[2] C. H. Depuy and R. W. King, *Chem. Rev.*, **60**, 431 (1960); W. G. Dauben, C. D. Poulter, and C. Suter, *J. Amer. Chem. Soc.*, **92**, 7048 (1970).

[3] W. G. Dauben and J. S. Ritscher, *ibid.*, **92**, 2925 (1970).

[4] Analysis of the dienes for isomeric purity was accomplished using a Perkin-Elmer Model F-11 capillary chromatograph with a 50 ft × 0.01 in. column packed with *m*-bis(*m*-phenoxy)benzene plus Apiezon L (8:2). Purity in all cases was >95%.

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) 234 (21,000)	1.5079
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, $=\mathrm{C}<^{\mathrm{H}}$), 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.

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

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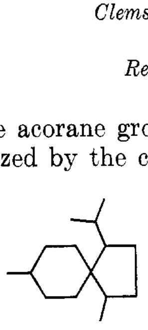
The acorane group of bicyclic sesquiterpenes, characterized by the carbon skeleton **1**, is typified by the acorones, stereoisomeric diketones represented by structure **2**,[1] and the two acorenones, stereoisomers of **3**.[2]



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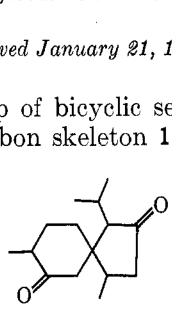

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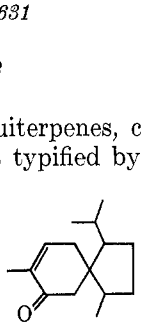

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(5) O. H. Wheller, and I. Leiner, *J. Amer. Chem. Soc.*, **78**, 64 (1956).

(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.

(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).