extract was concentrated and distilled to separate 24.947 g. of clear distillate, b.p. 67–79° (0.6 mm.). The residue, 33.249 g., was again subjected to a similar pyrolysis and isolation procedure to afford an additional 14.425 g. of distillate, b.p. 68–80° (0.6 mm.). Gas chromatographic analysis[33] of the combined distillates indicated the presence of the octalones *1* and *2* in a ratio of 1 to 5 as well as decalone and its enol acetates. A mixture of the combined distillates (39.371 g.), 200 ml. of 5% aqueous sulfuric acid, and sufficient dioxane to effect homogeneity was refluxed for 1.5 hr. and then cooled, neutralized with aqueous sodium bicarbonate, and extracted with petroleum ether. After the organic extract had been concentrated, distillation of the residue afforded 31.462 g. of colorless distillate, b.p. 60–74° (0.65 mm.), which contained[33] tetralin (~1%), 1-decalone (17%), the $\Delta^{8,9}$-octalone *2* (64%), the $\Delta^{9,10}$-octalone *1* (12%), and a number of minor components (total 6%). Fractional distillation through a 90-cm. spinning-band column served to separate the mixture into fractions containing primarily each of the three main components. The fractions containing high concentrations of the $\Delta^{8,9}$-octalone *2* were collected in the range 53–58° (0.08 mm.), n_D^{25} 1.5156–1.5166.

$\Delta^{8,9}$-*Octal-1-one* (*2*). A sample of this ketone, collected from the gas chromatographs[33] of appropriate fractions, was redistilled under reduced pressure in a short path still to obtain a sample of the ketone, a colorless liquid n_D^{27} 1.5157 (lit.,[12] n_D^{25} 1.5161), whose purity was greater than 95% the principal contaminant being the isomeric octalone *1*. The product exhibits infrared absorption[31] at 1678 cm.$^{-1}$ (conj. C=O) and 1623 cm.$^{-1}$ (conj. C=C) with an ultraviolet maximum[32] at 246 mμ (ϵ 6170) [lit.,[12] 246 mμ (ϵ 7300)] The infrared spectrum[37] of the material is identical with the spectrum of the sample prepared previously.[12] The NMR spectrum (60 mc.)[38] exhibits a doublet (or a partially resolved quartet) centered at 3.43 τ $(\overset{\diagdown}{\underset{\diagup}{}}\mathrm{C}{=}\mathit{CH}{-}\mathrm{CH_2}{-})$ with intense, partially resolved absorption in the region 7.20 to 9.25 τ ($-\mathrm{CH_2}-$). Reaction of a 19.6-mg. sample of the ketone with 2,4-dinitrophenylhydrazine yielded, after several recrystallizations from ethanol-ethyl acetate mixtures, the *2,4-dinitrophenylhydrazone* as deep red needles, m.p. 226–226.5° dec. [lit.,[12] m.p. 223.5–224° dec.], yield 17 mg. (38%). Reaction of a 35-mg. sample of the ketone with semicarbazide yielded, after several crystallizations from aqueous ethanol, 8 mg. (15%) of the *semicarbazone* as white crystals, m.p. 197.5–199.5° dec. [lit.,[12] m.p., 197.5–198.5° dec.].

$\Delta^{9,10}$-*Octal-1-one* (*1*). A sample of this ketone, collected from gas chromatographs[34] of appropriate fractions and distilled under reduced pressure in a short path still, was obtained as a colorless liquid n_D^{25} 1.5267 (lit.[12] n_D^{25} 1.5263), whose purity was approximately 95%, the principal contaminant being the octalone *2*. The material has infrared absorption[31] at 1664 cm.$^{-1}$ (conj. C=O) and 1634 cm.$^{-1}$ (conj. C=C) with an ultraviolet maximum[32] at 245.5 mμ (ϵ 12,400) [lit.,[12] 245 mμ (ϵ 12,300)]. The NMR spectrum (60 mc.)[38] of the ketone has a series of partially resolved bands in the region 7.45 to 8.65 τ ($-\mathrm{CH_2}-$) with no absorption attributable to a vinyl hydrogen atom. Reaction of a 15.5-mg. sample of the ketone with 2,4-dinitrophenylhydrazine yielded, after several recrystallizations from an ethanol-ethyl acetate mixture, 26.5 mg. (80%) of the 2,4-dinitrophenylhydrazone as red needles m.p. 266–266.5° dec. [lit., m.p. 264.5–265.5°,[11] 264–266°,[9] 265.5–266° dec.[12]].

CAMBRIDGE 39, MASS.

---

[37] Determined as a solution in chloroform.

[38] Determined as a solution in deuterochloroform.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

Synthesis of 1,2,3,4-Tetramethylcyclopentanes. I[1,2]

HAROLD N. MILLER[3] AND KENNETH W. GREENLEE

Received March 20, 1961

Synthesis of none of the six isomeric 1,2,3,4-tetramethylcyclopentanes has previously been reported, though one of them (1-*trans*-2-*cis*-3-*trans*-4-tetramethylcyclopentane) has been found in a crude petroleum. Now, three have been synthesized by methods which clearly establish their configurations; they are 1-*cis*-2-*cis*-3-*cis*-4- and 1-*trans*-2-*trans*-3-*cis*-4- and 1-*cis*-2-*trans*-3-*cis*-4-tetramethylcyclopentane. The three geometrically isomeric 2,3-dimethyl-5-norbornenes were oxidized to three dimethylcyclopentanedicarboxylic acids, which were reduced in four steps to tetramethylcyclopentanes of high purity. Their properties compare reasonably well with the predicted values.

The tetramethylcyclopentanes include seven structural isomers, or sixteen geometric isomers of which only seven have been synthesized[4,5] and four of these were obtained as pairs which were not separated and characterized. One of the structural isomers, 1,2,3,4-tetramethylcyclopentane has six possible geometric isomers representing an especially difficult problem in synthesis and identification: A. 1-*cis*-2-*cis*-3-*cis*-4-Tetramethylcyclopentane; B. 1-*cis*-2-*cis*-3-*trans*-4-Tetramethylcyclopentane; C. 1-*cis*-2-*trans*-3-*cis*-4-Tetramethylcyclopentane; D. 1-*cis*-2-*trans*-3-*trans*-4-Tetramethylcyclopentane; E. 1-*trans*-2-*cis*-3-*trans*-4-Tetramethylcyclopentane; F. 1-*trans*-2-*trans*-3-*cis*-4-Tetramethylcyclopentane. Only one of these (E) has been characterized[6] and it was not synthesized but isolated from petroleum.

The present paper is a report on the stereospecific synthesis of three of these hydrocarbons, A, C, and

---

[1] This paper is based on the Ph.D. thesis of Harold N. Miller, The Ohio State University, 1959.

[2] Financial support for this research was provided by the American Petroleum Institute Research Projects 45 and 58A.

[3] Present address: Esso Research and Engineering Co., Linden, N. J.

[4] G. Slomp, M. Inatome, C. E. Bowers, J. M. Derfer, K. W. Greenlee, and C. E. Boord, *J. Org. Chem.*, **25**, 514 (1960).

[5] J. F. Eykman, *Chem. Weekblad*, **3**, 685 (1906).

[6] M. B. Epstein, C. B. Willingham, B. J. Mair, and F. D. Rossini, *Anal. Chem.*, **28**, 1924 (1956).

F, as listed above. The syntheses were based on the preparation of the three isomeric 2,3-dimethyl-5-norbornenes according to Alder, Roth, and Grell[7,8] in a series of reactions depicted in Plate I. The norbornenes were converted by oxidative cleavage to three different dimethylcyclopentanedicarboxylic acids which were reduced to the corresponding tetramethylcyclopentanes in four chemical steps as outlined in Plate II. The norbornenes obtained were pure (better than 99%) and, according to their properties (Table V) and infrared spectra, were identical to those of the literature. The tetramethylcyclopentanes were highly pure, as proved by accepted cryoscopic procedures,[9] and their properties (Table X) correspond well with predicted values.[10] The identifications of the products are firmly based on the known or predicted stereo-specificity of the many reactions involved; at the same time, the demonstrated purity of the final products and many of the intermediates affords additional proof of the stereospecificity of the reactions.

DISCUSSION

Schematic outlines of the reaction sequences used are given in Plates I and II, with a code number given to each compound. The nomenclature of these compounds is given in Tables I and II. For brevity, the code numbers are generally used in the following. Procedures are given in the experimental section only if new or significantly improved.

TABLE I

Nomenclature of Compounds Depicted on Plate I

Code	Name
Ia	*endo-cis*-5-Norbornene-2,3-dicarboxylic anhydride
Ib	*exo-cis*-5-Norbornene-2,3-dicarboxylic anhydride
Ic	*trans*-5-Norbornene-2,3-dicarbonyl chloride
IIa	*endo-cis*-Dimethyl 5-norbornene-2,3-dicarboxylate
IIb	*exo-cis*-Dimethyl 5-norbornene-2,3-dicarboxylate
IIc	*trans*-Dimethyl 5-norbornene-2,3-dicarboxylate
IIIa	*endo-cis*-5-Norbornene-2,3-dimethanol
IIIb	*exo-cis*-5-Norbornene-2,3-dimethanol
IIIc	*trans*-5-Norbornene-2,3-dimethanol
IVa	*endo-cis*-5-Norbornene-2,3-dimethanol-di-*p*-toluenesulfonate
IVb	*exo-cis*-5-Norbornene-2,3-dimethanol-di-*p*-toluenesulfonate
IVc	*trans*-5-Norbornene-2,3-dimethanol-di-*p*-toluenesulfonate
Va	*endo-cis*-2,3-Dimethyl-5-norbornene
Vb	*exo-cis*-2,3-Dimethyl-5-norbornene
Vc	*trans*-2,3-Dimethyl-5-norbornene

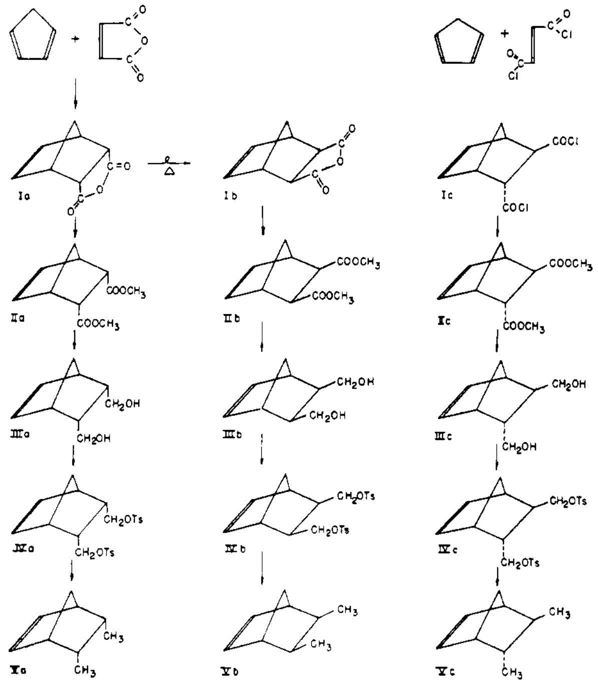

Plate I

Cyclopentadiene was made to react with maleic anhydride after the manner of Diels and Alder[11] to give 96% yield of *endo-cis* anhydride, Ia. Some of this anhydride was thermally isomerized (70% yield) to the *exo-cis* form (Ib) by the method of Craig.[12] Condensation of cyclopentadiene and fumaryl chloride yielded 99% of the *trans*-dicarbonyl chloride, Ic. The two anhydrides and one

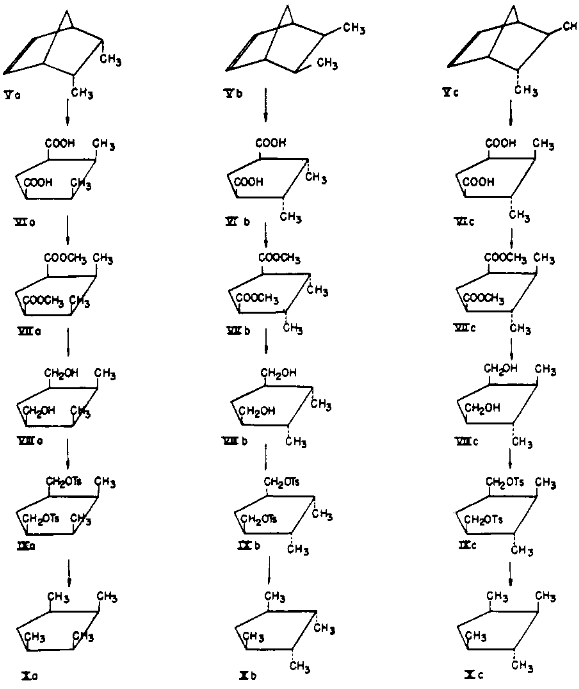

Plate II

---

[7] K. Alder, W. Roth, and A. Grell, *Chem. Ber.*, **88**, 407 (1955).

[8] K. Alder and W. Roth, *Chem. Ber.*, **87**, 161 (1954).

[9] B. J. Mair, A. R. Glasgow, and F. D. Rossini, *J. Research Natl. Bur. Standards*, **26**, 591 (1941).

[10] Estimates, published in *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds*, Table 33a, April 30, 1955; American Petroleum Institute Research Project 44, Carnegie Institute of Technology, Pittsburgh, Pa.

[11] O. Diels and K. Alder, *Ann.*, **460**, 98 (1928).

[12] D. Craig, *J. Am. Chem. Soc.*, **73**, 4889 (1951).

TABLE II

NOMENCLATURE OF COMPOUNDS DEPICTED ON PLATE II

Code	Name
Va	*endo-cis*-2,3-Dimethyl-5-norbornene
Vb	*exo-cis*-2,3-Dimethyl-5-norbornene
Vc	*trans*-2,3-Dimethyl-5-norbornene
VIa	*cis*-4,*cis*-5-Dimethyl-1,*cis*-3-cyclopentanedicarboxylic acid
VIb	*trans*-4,*trans*-5-Dimethyl-1,*cis*-3-cyclopentanedicarboxylic acid
VIc	*cis*-4,*trans*-5-Dimethyl-1,*cis*-3-cyclopentanedicarboxylic acid
VIIa	Dimethyl *cis*-4, *cis*-5-dimethyl-1,*cis*-3-cyclopentanedicarboxylate
VIIb	Dimethyl *trans*-4,*trans*-5-dimethyl-1,*cis*-3-cyclopentanedicarboxylate
VIIc	Dimethyl *cis*-4,*trans*-5-dimethyl-1,*cis*-3-cyclopentanedicarboxylate
VIIIa	*cis*-4,*cis*-5-Dimethyl-1,*cis*-3-cyclopentanedimethanol
VIIIb	*trans*-4,*trans*-5-Dimethyl-1,*cis*-3-cyclopentanedimethanol
VIIIc	*cis*-4,*trans*-5-Dimethyl-1,*cis*-3-cyclopentanedimethanol
IXa	*cis*-4,*cis*-5-Dimethyl-1,*cis*-3-cyclopentanedimethanol-di-*p*-toluenesulfonate
IXb	*trans*-4,*trans*-5-Dimethyl-1,*cis*-3-cyclopentanedimethanol-di-*p*-toluenesulfonate
IXc	*cis*-4,*trans*-5-Dimethyl-1,*cis*-3-cyclopentanedimethanol-di-*p*-toluenesulfonate
Xa	1,*cis*-2,*cis*-3,*cis*-4-Tetramethylcyclopentane
Xb	1,*trans*-2,*trans*-3,*cis*-4-Tetramethylcyclopentane
Xc	1,*cis*-2,*trans*-3,*cis*-4-Tetramethylcyclopentane

dichloride were converted to dimethyl esters in 84–95% yields by conventional methods.

Reduction of the diesters (IIa, IIb, and IIc) by the literature procedure[7] was incomplete because of sludging, unless about 100% excess of lithium aluminum hydride was used. However, substitution of tetrahydrofuran (for diethyl ether) as solvent gave a stoichiometric reaction and high yields of the desired diols. (See Table III and the Experimental.)

TABLE III

5-NORBORNENE-2,3-DIMETHANOLS

	IIIa	IIIb	IIIc
Yield, %	93.4 (purif.)	90 (crude)	100 (crude)
M.p.	84.5–86.2	52.6–53.4	—
M.p., lit.[a]	86	—	—
B.p./mm.	—	130–134/1	132–136/3
B.p., lit.[a]	170–175/25	95/0.035	103–6/0.15
n_D^{20}	—	—	1.5154–6

[a] Ref. 8.

The 5-norbornene-2,3-dimethanols (IIIa, IIIb, and IIIc) were tosylated with *p*-toluenesulfonyl chloride and pyridine, a reaction known to occur with retention of carbinol configuration. Excellent yields were obtained by using a procedure as published[13] except that the reaction temperature was maintained at 0° or below. (See Table IV).

TABLE IV

5-NORBORNENE-2,3-DIMETHANOL DITOSYLATES

	IVa	IVb	IVc
Yield, %	86–95	81–91	91
M.p.	102.9–3.9[b]	172.0–0.6[b,d]	89.8–92.0[b]
	103.6–4.6[c]	172.9–3.4[c,d]	92.3–93.1[c]
M.p., lit.[a]	90–91	173	91
Solvent used	CH_3OH	$C_2H_5OAc—C_6H_6$	CH_3OH

[a] Ref. 8. [b] Crude. [c] Recrystallized. [d] Decomposes.

The reductive hydrogenolysis of the ditosylates (IVa, IVb, and IVc) was accomplished by Alder *et al.*, with lithium aluminum hydride in refluxing tetrahydrofuran. However, numerous attempts to reduce IVa to Va by their procedure failed. Use of longer reaction times and higher boiling solvents (dioxane, ethyl *n*-butyl ether, and di-*n*-butyl ether) did not help. This problem was solved by an expedient of Johnson, Blizzard, and Carhart[14] who reduced alkyl halides with lithium hydride together with a little aluminum hydride, as lithium aluminum hydride, to act as a carrier. With this modification, good yields of the dimethylnorbornenes were obtained (see Table V and Experimental).

TABLE V

5,6-DIMETHYL-2-NORBORNENES

	endo-cis (Va)	*exo-cis* (Vb)	*trans* (Vc)
Yield, %	71–86	73–78	74
B.p./mm.	143.31/760	144.04/760	132.53/760
	(61.5/50)[a]	(61.4/50)[a]	(53/50)[a]
n_D^{20}	1.4650	1.4680	1.4552
	(1.4673)[a]	(1.4679)[a]	(1.4555)[a]
d_4^{20}	—	—	0.8550
	(0.8782)[a]	(0.8776)[a]	(0.8554)[a]
F.p. (m.p.)	+25.32	−72.32	−56.83
	(+25)[a]	—	—
t_1: °C.[b]	+26.05	−72.13	−56.65
A, M.fr./°C.[c]	0.0024	0.0220	0.0049
Purity, mole %	99.8	99.6	99.9

[a] Literature value (reference 7). [b] Calculated true freezing point (reference 9). [c] Cryscopic constant, mole fraction/°C. (reference 9).

The oxidation of dimethylnorbornenes (Va, Vb, and Vc) was obviously a crucial step, as yield could be diminished by either over- or under-severe conditions, and both yield and purity could be affected by isomerization. Birch, Oldham, and Johnson[15] converted norbornene (by treatment with peracetic acid) to a glycol which, when further oxidized with chromic acid, gave a mixture including tricarboxylic acids; however, by direct oxidation of norbornene with sodium or potassium permanganate they obtained the desired 1-*cis*-3-cyclopentanedicarboxylic acid only. Subsequently,

---

(13) C. S. Marvel and V. C. Sekera, *Org. Syntheses*, **20**, 50 (1940).

(14) J. E. Johnson, R. H. Blizzard, and H. W. Carhart, *J. Am. Chem. Soc.*, **70**, 3664 (1948).

(15) S. F. Birch, W. J. Oldham, and E. A. Johnson, *J. Chem. Soc.*, 818 (1947).

others[16,17] have shown that the glycol formed by hydroxylation of norbornene with peracids is not the expected vicinal diol but a 1,3-type diol evolved through skeletal rearrangement. Other recent work[18,19] emphasizes that the norbornene system is prone to undergo carbonium ion-type rearrangements.

Birch *et al.*[15] found that yields of the expected diacid were low when norbornene was oxidized with potassium permanganate; however, excellent yields were had when sodium permanganate was used and *p*H was carefully controlled near the neutral point. In the present work, the Birch procedure and many variations of it were unsatisfactory as applied to the oxidation of dimethylnorbornene Va. Yields were sometimes low and sometimes as high as 70% in small-scale (0.02 to 0.10 mole) experiments, but were always low or nil in runs of 0.5 mole or over. This was at least partly explained in the discovery that the desired diacid (VIa) itself is susceptible to attack by dilute permanganate solutions. This suggested the need of a catalyst or conditions which would promote the formation of the dicarboxylic acid without speeding its degradation.

Birch *et al.*[15] had reported that in their most successful experiments (with sodium permanganate) there possibly were "traces of nitrate present in the permanganate, since red fumes were sometimes observed." This suggested to one of us that the oxidation might be promoted by nitrate ion or by nitrogen oxides, and this was proved true by experiment. When potassium nitrate (1–2 mole %) was added to pure potassium permanganate, or sodium nitrate to the nitrate-free sodium permanganate previously used, 30–35% yields of the desired diacid (VIa) were consistently obtained. (See Experimental) (See Table VI).

TABLE VI

4,5-DIMETHYL-1,3-CYCLOPENTANEDICARBOXYLIC ACIDS

	VIa	VIb	VIc
Yield %	30–35	56–66	74–85
M.p.	202.5–203.5	101.6–102.6	149.0–149.7
M.p. lit.[a]	200	103	148
% C[b]	58.47	58.23	57.83
% H[c]	7.86	7.49	7.68

[a] Ref. 7. [b] Calcd. 58.05%. [c] Calcd. 7.58%.

The second dimethylnorbornene (Vb) was more readily oxidized, and work with it was completed before the nitrate promoter was discovered. However, it was found that at ambient temperatures only about one-third of the theoretical amount of permanganate reacted and that it was necessary to heat the mixture on a steam bath to make the reaction complete. Yields of 56–66% were obtained.

The third dimethylnorbornene (Vc) showed an even greater tendency toward underoxidation and another expedient was tried. It was found that when *tert*-butyl alcohol was added to the reaction mixture, the oxidation proceeded rapidly (permanganate color instantly discharged), exothermally and completely, giving high yields (74–85%) of the desired diacid (see Experimental and Table VI). Small scale oxidations (0.02 mole) of Va and Vb indicated that this method would be equally successful with them, but this was not proved on the large scale.

The conversion of the diacids to the dimethyl esters (VIIa, VIIb and VIIc) was done by the method of Clinton and Laskowski[20] with excellent results (Table VII). The first two esters were purified by distillation and the third by crystallization from ether at low temperatures. Reduction of these esters (by lithium aluminum hydride in tetrahydrofuran) to the corresponding diols (VIIIa, VIIIb, and VIIIc) was done by essentially the same procedure as used earlier for converting ester IIa to diol IIIa (see Experimental). Diol VIIIa would not crystallize and was taken as a crude product to the next stage since decomposition during distillation was feared; however, a small sample was distilled for property determination and analysis (Table VIII). Diol VIIIb (m.p. 39.6–40.6°) was purified by crystallization from ether and had almost the same melting point as diol VIIIc (m.p. 41.0–42.2°) which was purified in the same way. However, the nonidentity of these two diols was shown by the melting point of their mixture (mixture m.p. 28°).

TABLE VII

4,5-DIMETHYL-1,3-CYCLOPENTANEDICARBOXYLATES

	VIIa	VIIb	VIIc
Yield %	94.5	97.4	88.1
B.p./mm.	120–121/2	121/2	—
n_D^{20}	1.4594	1.4540	1.4516
d_4^{20}	1.0913[c]	1.0736	1.065
M.p.	26.4–27.4	−27.17	−3.81
% C[a]	62.06	61.12	61.87
% H[b]	8.60	8.81	8.72

[a] Calcd. 61.66%. [b] Calcd.. 8.47%. [c] Supercooled.

The diols were converted to ditosylates (IXa, IXb, and IXc) in excellent yield, through reaction with *p*-toluenesulfonyl chloride in pyridine by the procedure[13] already used on the series III diols. The ditosylates were purified by crystallization

---

(16) H. M. Walborsky and D. F. Lonerini, *J. Am. Chem. Soc.*, **76**, 5396 (1954).

(17) H. Kwart and W. G. Vosburgh, *J. Am. Chem. Soc.*, **76**, 5400 (1954).

(18) J. D. Roberts and C. C. Lee, *J. Am. Chem. Soc.*, **73**, 5009 (1951).

(19) S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, **74**, 1147 (1952).

(20) R. O. Clinton and S. C. Laskowski, *J. Am. Chem. Soc.*, **70**, 3135 (1948).

TABLE VIII

4,5-DIMETHYL-1,3-CYCLOPENTANEDIMETHANOLS

	VIIIa	VIIIb	VIIIc
Yield %	97 (crude)	92.4	96.3
M.p.	[a]	40.4–41.2	41.0–42.2
% C[b]	67.97	68.08	67.90
% H[c]	11.46	11.81	11.28

[a] Would not crystallize: b.p. 156–160/2 n_D^{20} 1.4908 d_4^{20} 1.030. [b] Calcd. 68.31%. [c] Calcd. 11.46%.

from ethyl acetate, and small samples were recrystallized for use in determination of melting points, analyses (Table IX) and infrared spectra.

TABLE IX

4,5-DIMETHYL-1,3-CYCLOPENTANEDIMETHANOL DITOSYLATES

	IXa	IXb	IXc
Yield %	71–87	97.0	86.7
M.p.	138.8–139.6	64.8–65.8	83.1–83.9
Solvent used	C_2H_5OAc	CH_3OH	CH_3OH
% C[a]	59.01	59.11	58.82
% H[b]	6.59	6.67	6.32
% S[c]	13.35	13.88	13.92

[a] Calcd. 59.19%. [b] Calcd. 6.49%. [c] Calcd. 13.74%.

The final step in the long sequence was the reductive hydrogenolysis of the ditosylates by lithium hydride and lithium aluminum hydride to give the tetramethylcyclopentanes (Xa, Xb, and Xc), a process similar to that used earlier on ditosylates IVa, *etc.* A detailed procedure is given for Xa in the Experimental section. Yields for the three ranged from 70 to 89%. The products were distilled through a Nester-Faust spinning band column, capable of 40 theoretical plates but operated at only about 10-plate efficiency, before determination of their properties and purities (see Table X). Thus, the high purities of Xa and Xb (99.6 and 99.1%) must be attributed to stereospecific synthesis rather than to purification occurring in the final distillation. The purities of Xa and Xb were easily calculated[9] from their experimentally determined cryoscopic constants (A = mole fraction/degree lowering of freezing point) and their extrapolated true freezing points (t_1) derived from their freezing point curves. The purity of hydrocarbon Xc could not be determined precisely because its supercooling prevented determination of a suitable freezing curve. The uncertainty was compounded by its occurrence in two crystalline forms with different freezing (or melting) points. However, it was possible to estimate for Xc a minimum purity of 96%.

TABLE X

1,2,3,4-TETRAMETHYLCYCLOPENTANES

	Xa (*cis,cis,-cis,cis*)	Xb (*cis,trans,-trans,cis*)	Xc (*cis,cis,-trans,cis*)
Yield, %	89.2	83.1	70.6
Purity, mole %	99.6	99.1	96+[a]
B.p./760	147.32	133.86	134.53
n_D^{20}	1.4332	1.4208	1.4219
d_4^{20}	0.7924	0.7669	0.7687
F.p. (m.p.)	−100.32	−110.71	−109.63 (I) −113.82 (II)
t_1	−100.22	−110.52	−113.1[a] (II)
A, m.Fr./°C.	0.040	0.044	0.04
% C[b]	85.64	85.70	85.58
%H[c]	14.25	14.63	14.63

[a] Estimated. [b] Calcd. 85.63%. [c] Calcd. 14.37%.

Infrared spectra were determined for all products of series V through IX and were found concordant with comparable spectra in the literature (where known) or with spectra of similar compounds. Carbon and hydrogen analyses (and sulfur analyses, where appropriate) were obtained for all new compounds isolated in this work, and they were found consistent with the calculated values within acceptable limits.

It should be noted that in the three 1,2,3,4-tetramethylcyclopentanes here synthesized, methyl groups 1 and 4 were held to the *cis* relationship while 2 and 3 were given all geometric variations. In work to be reported in paper II of this series, methyls 2 and 3 will be held fixed (*cis* or *trans*) while methyls 1 and 4 (or their precursors) will be varied to produce the other three isomers.

EXPERIMENTAL

IIa→IIIa. Lithium aluminum hydride (5.5 moles or 209 g.) and dry tetrahydrofuran (4.5 l.) were charged into a three-neck, 12-l. flask equipped with a stainless steel Hershberg stirrer, an efficient aluminum-coil reflux condenser (fitted with an overflow trap and a nitrogen inlet), a dropping funnel, and an electric heating mantle. Five moles of diester IIa (1051 g.) dissolved in 1.5 l. of dry tetrahydrofuran was added at a rate maintaining vigorous reflux, and the reaction solution was refluxed an additional hour. The tetrahydrofuran solvent was stripped under reduced pressure and replaced with 2 l. of diethyl ether and the excess lithium aluminum hydride was decomposed with cold water followed by cold, dilute sulfuric acid. The ether-diol layer was separated, the aqueous layer was extracted repeatedly with ether and all extracts were combined, washed once with cold water, then dried over magnesium sulfate and magnesium carbonate (7:1). The ether solution of diol was concentrated to a small volume and chilled with Dry Ice, whereupon diol crystallized. The crystals were filtered on a cold Buchner, washed with ether, cooled to −80°, and vacuum desiccated. The filtrate, concentrated to a smaller volume, yielded a second crop of diol crystals. A total of 4.67 moles (720 g.) of diol was obtained. The procedure and results for IIIb and IIIc were similar (Table III); likewise for the VIII series (Table VIII).

IVa→Va. To a three neck, 5-l. flask equipped as in the preceding section was added 8 g. (0.21 mole) of lithium aluminum hydride and 24 g. (3.0 moles) of 100-mesh lithium hydride. Dry tetrahydrofuran (3.5 l.) was added and stirred vigorously to effect solution of the lithium aluminum hydride and suspend the lithium hydride. This mixture was heated at reflux and 694 g. (1.50 moles) of powdered, crystalline ditosylate IVa was added portionwise through a powder funnel. The reaction was only mildly exothermic, and continuous heating was necessary to maintain reflux conditions. The reaction mixture was refluxed an additional 4 hr. and stirred at room temperature overnight. The tetrahydrofuran solvent and some of the hydrocarbon formed was stripped under reduced pressure and condensed in Dry Ice–cooled traps. The stripped solvent was replaced with 1 l. of ether and the excess hydrides and inorganic residues were decomposed with cold water, followed with cold, dilute sulfuric acid. The ether-hydrocarbon layer was separated and the aqueous layer was extracted with ether. The combined ether solutions of product were dried over magnesium sulfate and magnesium carbonate and then stripped of ether with a fractionating column. The hydrocarbon product was washed with water and dilute sodium hydroxide, then was dried over magnesium sulfate. The washed and dried hydrocarbon was fractionated at atmospheric pressure through a Nester-Faust spinning band column operated at about 20-plate efficiency and 1.19 moles (146.0 g.) of pure hydrocarbon Va was obtained. Vb and Vc were made by essentially the same procedure. Data for all three comprise Table V.

Va→VIa. To a 12-l., three neck flask which was equipped with a stirrer, reflux condenser, thermometer, and dropping funnel, and was partially submerged in a tap-water cooled bath, were added 2000 ml. of water, 41.5 g. of potassium carbonate, 100 ml. of isooctane, and 61.1 g. (0.50 mole) of Va. To the vigorously stirred mixture was added a solution of the theoretical amount (211.0 g., 1.335 moles) of potassium permanganate (Baker's analytical, 99.6% potassium permanganate) and 2.7 g. (0.0267 mole) of potassium nitrate dissolved in 4000 ml. of water, at such a rate that the temperature of the reaction mixture never exceeded 35°. Upon complete discoloration of the permanganate in the reaction mixture—*i.e.* almost immediately on final addition of the permanganate solution—the reaction products were filtered from the manganese dioxide on a Büchner funnel. The filter cake was washed three times with 500-ml. portions of water. The clear, straw-yellow filtrate was concentrated to a small volume on a steam bath and acidified with concd. hydrochloric acid. The diacid (VIa) which precipitated was filtered and washed with water on a Büchner funnel. Ether extraction of the resulting filtrate yielded a dark viscous oil which would not crystallize and when resubjected to permanganate oxidation yielded none of the desired diacid. The crude diacid obtained was immediately recrystallized from water yielding 31.1 g. (0.166 mole or 33.3%) of white crystalline product (Table VI).

Vc→VIc. To a 12-l., three neck flask, which was equipped with stirrer, reflux condenser, thermometer, and dropping funnel and was partially immersed in an ice water bath, were added 1250 ml. of water, 500 ml. of *t*-butyl alcohol, and 61.0 g. (0.50 mole) of Vc. The mixture was vigorously stirred and the theoretical amount of sodium permanganate (1.334 moles or 223 g. of 85% sodium permanganate) dissolved in 1250 ml. of water was added at such a rate that the reaction temperature never exceeded 30°. The oxidation reaction was highly exothermic. The *p*H of the reaction mixture was controlled by suffusing it continuously with gaseous carbon dioxide, thus maintaining a mildly basic medium. The last of the permanganate solution to be added was discolored almost immediately, whereupon the reaction products were filtered from the manganese dioxide on a Buchner funnel. The filter cake was washed three times with 500-ml. portions of water and the clear filtrate was evaporated to a small volume on a steam bath, then was acidified with concd. hydrochloric acid. The diacid which precipitated was filtered and washed with cold water on a Buchner funnel, then immediately recrystallized from water; yield, 0.381 mole (71.0 g. or 76.2%) of white crystals (Table VI).

IXa→Xa. To a three neck, 3-l. flask equipped with a stirrer, an efficient reflux condenser (provided with an overflow trap and a nitrogen inlet), and an electric heating mantle were added 0.11 mole (4.0 g.) of powdered lithium aluminum hydride and 2.0 moles (16 g.) of 100-mesh lithium hydride. Dry tetrahydrofuran (800 ml.) was added and stirred vigorously and then was heated at reflux while 0.606 mole (283 g.) of crystalline ditosylate IXa was added portion-wise during 1 hr. The reaction mixture was refluxed for 4 hr. more, cooled to room temperature, and stirred overnight. The tetrahydrofuran solvent and some of the hydrocarbon formed were stripped out of the reaction mixture (mildly heated under reduced pressure) and condensed in Dry Ice–acetone cooled traps. One liter of ether was added to the stripped residue and the excess hydrides and salt residues were decomposed with cold water followed by cold, dilute sulfuric acid. The ether-hydrocarbon solution was separated and the aqueous layer extracted with ether. Solution and extracts were combined and stripped of ether with a fractionating column. The product, combined with that obtained from the stripped tetrahydrofuran, was washed with 10% sodium hydroxide solution and with cold water, then was dried over magnesium sulfate. It was distilled on a Nester-Faust spinning band column operated at about 10-plate efficiency, and 0.541 mole (68.3 g.) of Xa was obtained with properties as listed in Table X. Hydrocarbons Xb and Xc were similarly obtained from ditosylates IXb and IXc.

COLUMBUS, OHIO