

layers were in evidence. The lower (acid) layer was separated and then neutralized with 322 g. of potassium hydroxide. By continuous ether extraction of this layer, 3 g. of material was recovered and added to the upper (mono- and/or diformic ester) layer. The ester material was saponified by refluxing for 5 hr. with 90 g. of potassium hydroxide and 100 ml. of water. Upon cooling to room temperature, the upper (glycol) layer solidified and weighed 199.5 g. The lower (aqueous) layer yielded 4.5 g. of additional glycol on continuous extraction with ether. The glycol (204 g.) was distilled under reduced pressure to yield 152 g., b.p.₇ 120–122° and 13 g., b.p.₇ 122–125° (combined yield 84%). A small amount of glycol from the 120–122° fraction was recrystallized from benzene, and this sample of 3,3,5-trimethylcyclohexane-1,2-diol melted at 102.4–102.8°.

Anal. Calcd. for C₉H₁₈O₂: C, 68.31; H, 11.47. Found: C, 68.11; H, 10.91.

3,5,5-Trimethylcyclohexane-1,2-diol. 3,5,5-Trimethylcyclohexene (155 g., 1.25 moles) was oxidized in exactly the same manner as its isomer, with 159.5 g. of 27% hydrogen peroxide solution (1.27 moles) in 308 ml. of 87% formic acid. There was obtained 167.3 g. (85% yield) of a mixture of geometrical isomers of the glycol (b.p.₇ 120–130°). A small amount of material from a center fraction (b.p.₇ 124–125°) was recrystallized to yield white needles; m.p. 58.3–58.7°.

Anal. Calcd. for C₉H₁₈O₂: C, 68.31; H, 11.47. Found: C, 68.77; H, 11.77.

2,2,4-Trimethyladipic acid from 3,3,5-trimethylcyclohexane-1,2-diol. 3,3,5-Trimethylcyclohexane-1,2-diol (158 g., 1.0 mole) was placed with 100 ml. of water in a 3-l. flask fitted with an efficient stirrer and a baffle to aid mixing. The mixture was warmed to 45°, and 400 g. of sodium permanganate in 1800 ml. of water was added, portionwise, with enough cooling to maintain temperature at 45–50°.

The reaction mixture was then made slightly alkaline with 20% sodium hydroxide (about 30 ml. being required), and permanganate solution was added until no more was consumed (about 90 ml. additional required). A small amount of sodium bisulfite was then added (enough to destroy the purple color), and the reaction mixture was filtered, hot, through a Buchner funnel. The filter cake (manganese dioxide) was rinsed with 100 ml. of hot water, then removed from the funnel and leached by boiling with

200 ml. more water, after which it was refiltered. Both batches of filtrate were evaporated (individually) to about one-half volume; they were then cooled and acidified to pH 2 with hydrochloric acid. A small amount of carbon dioxide was evolved and the solution became cloudy just before the desired pH was reached. The mixtures were held at –5° overnight, to crystallize. The first filtrate yielded 175.5 g. of white crystalline acid and the second filtrate, obtained by leaching the solid manganese dioxide with more water, yielded 10 g. more, corresponding to a 98.7% of crude acids having a neutralization equivalent of 101.1 (theory, 94.11). The acid was recrystallized once from water to yield 170 g. (92% yield) of 2,2,4-trimethyladipic acid; neut. equiv. 94.3, m.p. 100.1 to 100.4°, (lit.⁵, m.p. 101.1 to 101.5°).

Anal. Calcd. for C₉H₁₆O₄: C, 57.42; H, 8.57. Found: C, 57.45; H, 8.58.

2,4,4-Trimethyladipic acid from 3,5,5-trimethylcyclohexane-1,2-diol. In exactly the same manner as its isomer, 3,5,5-trimethylcyclohexane-1,2-diol (152.1 g., 0.96 mole) was oxidized to yield 120 g. of crystalline acids from the first filtrate and 15.5 g. from the second filtrate. The total yield was 65.8% of crystalline material having a neutralization equivalent of 97.0 (theory, 94.11). The aqueous layers were combined and upon continuous ether extraction yielded 51.4 g. (28.4%) of oil with a neutralization equivalent of 116.0, bringing the total yield of crude acid up to 94.2%. This oily acid did not crystallize when seeded and held at –5° for 1 week. The crystalline acids were recrystallized once from water and there was obtained 115 g. (63.7% yield) of 2,4,4-trimethyladipic acid having a neutral equivalent of 94.3, m.p. 69.7 to 70.0°, (lit.⁵, m.p. 68.6 to 69.2°).

Anal. Calcd. for C₉H₁₆O₄: C, 57.42; H, 8.57. Found: C, 57.40; H, 8.56.

Trimethylcyclopentanones from pure trimethyladipic acids. The pure 2,2,4- and 2,4,4-trimethyladipic acids were distilled, separately, with barium hydroxide and manganese carbonate as described under 2,2,4,4-tetramethylcyclopentanone. The yields of purified 2,2,4- and 2,4,4-trimethylcyclopentanone were 67% and 78%, respectively, and the properties of these samples were virtually identical with those of the corresponding ketones isolated earlier from their mixture.

COLUMBUS 10, OHIO

[CONTRIBUTION FROM THE R & E DIVISION, MONSANTO CHEMICAL COMPANY]

Methylcyclopentadiene Isomers

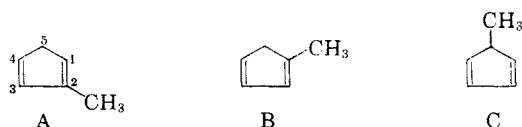
SIGMUND M. CSICSERY¹

Received October 12, 1959

The three methylcyclopentadiene isomers, 1-, 2-, and 5-methylcyclopentadiene were separated by vapor phase chromatography over 2,4-dimethylsulfolane substrate and identified *via* their ultraviolet absorption maxima. Five methylcyclopentadiene dimer isomers were separated by vapor phase chromatography over silicone oil substrate. They were identified as far as the parent monomers are concerned by dimerizing monomer mixtures of known isomer concentration. Composition of the dimer isomers approaches statistical distribution. Infrared spectra of the monomer isomers are included.

Commercial methylcyclopentadiene is a by-product of thermal cracking of petroleum hydrocarbons. Pyrolysis of the commercial methylcyclopentadiene dimer yields a mixture of isomeric methylcyclopentadienes and some cyclopentadiene. Three isomers of monomeric methylcyclopentadiene are possible: 2-methyl (A), 1-methyl (B),

and 5-methylcyclopentadiene (C). Only Diels-Alder adducts of two of these isomers, presumably those of 1-methyl and 2-methylcyclopentadiene have been separated.^{2,3} Structures were not as-



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signed with certainty to any of the parent dienes.³ Attempts to prepare 5-methylcyclopentadiene produced a mixture of the other two monomers. Separation of the pure isomers by vapor phase chromatography over dinonylphthalate substrate was reported by McLean to be unsatisfactory. In the present work the three isomers of methylcyclopentadiene monomer have been separated by vapor phase chromatography and identified.

The two monomeric isomers A and B comprising commercial methylcyclopentadiene (the by-product of thermal cracking) have been successfully resolved using 2,4-dimethylsulfolane substrate. Methylcyclopentadiene monomer obtained by the catalytic dehydrogenation of methylcyclopentane contained beside A and B the third isomer, 5-methylcyclopentadiene, representing only about 3% of the total methylcyclopentadiene monomer. The ratio of the first two isomers was the same as in the methylcyclopentadiene obtained by pyrolyzing the commercial dimer. The distribution of the monomer isomers obtained by dehydrogenating methylcyclopentane is as follows: 2-methylcyclopentadiene 51.7%, 1-methylcyclopentadiene 45.3% and 5-methylcyclopentadiene 3.0%. The three methylcyclopentadiene monomer isomers were identified via the wavelengths of the absorption maxima in their ultraviolet spectra. The absorption maximum of unsubstituted cyclopentadiene is at 240 m μ . It can be predicted on theoretical grounds that the bathochromic shifts of simple substituents in the 1- and 2- positions of the butadienyl system are in the ratio of 3:1.⁴ A methyl group in the 1- or 2- position will cause a bathochromic shift of 9 or 3 m μ respectively.⁵ Substitution on the saturated carbon atom (5-position) should not increase the wavelength of the absorption maximum. In non alternate ring systems (rings containing odd numbers of carbon atoms) inductive effects may cause a hypsochromic shift, *i.e.*, a decrease of the wavelength of the ultraviolet absorption maximum.

Maxima at 244 and 249.6 m μ were found for the first two isomers. For the third isomer, present only in minor quantities, the exact position of the maximum was obscured by impurities present in the

sample. It was between 235 and 240 m μ . Cyclopentadiene absorbed at 240 m μ . The commercial methylcyclopentadiene monomer (a mixture of the first two isomers) absorbed at 247 m μ .⁶ Ultraviolet absorptions are summarized in Table I. Infrared spectra of the three monomeric isomers are illustrated in Fig. 1. The spectrum of cyclopentadiene is included for comparison. No isomerization of the monomeric isomers was observed on standing.

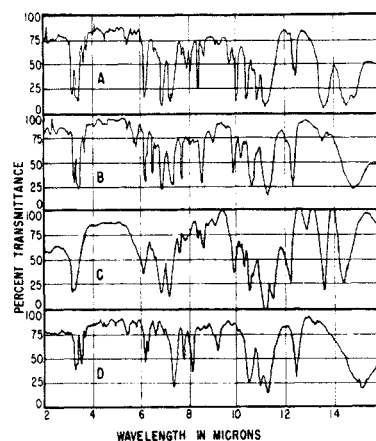


Fig. 1. Infrared spectra of the methylcyclopentadiene isomers and of cyclopentadiene monomer

A = 2-methylcyclopentadiene
B = 1-methylcyclopentadiene
C = 5-methylcyclopentadiene
D = cyclopentadiene

Dimer isomers. The dimerization tendency of methylcyclopentadiene is well known. Dimerization is measurable above 0° and it is practically completed within two hours at 60°. Above 172° dedimerization occurs and the monomers are recovered. No dimerization was observed below -20° over a prolonged time, or in very dilute alcoholic solution. A difference was noted in the rates of dimerization at room temperature of 1-methylcyclopentadiene and 2-methylcyclopentadiene; the latter dimerizes faster and the residual monomeric fraction gets richer in 1-methylcyclopentadiene. During five days the ratio of 2-methylcyclopentadiene to 1-methylcyclopentadiene in the residual monomeric fraction decreased from 1.08 to 0.46. This difference of rates was also observed by Craven.² The dimerization rate of cyclopentadiene is faster than that of the methylcyclopentadiene isomers.

Methylcyclopentadiene dimer isomers were resolved by vapor phase chromatography with D.C. 550 Silicone Oil on C₂₂ Firebrick substrate at 107°. The different dimer isomers were identified as far as the parent monomers are concerned by dimerizing monomer mixtures with known concentrations of the various isomers. By comparing the dimer compositions with the distribution of the monomer isomers in the initial mixture the

TABLE I

ULTRAVIOLET ABSORPTIONS OF THE METHYLCYCLOPENTADIENE MONOMER ISOMERS

Compound	UV Absorption Predicted	UV Absorption Measured
2-Methylcyclopentadiene	243	244
1-Methylcyclopentadiene	249	249.6
5-Methylcyclopentadiene	240	235-240
Cyclopentadiene	240	240

(2) W. J. Craven, Ph.D. Thesis, Cornell University, 1955.

(3) S. McLean, Ph.D. Thesis, Cornell University, 1958.

(4) D. Peters, *J. Chem. Soc.*, 1761 (1959).

(5) H. Booker, L. K. Evans, and A. E. Gillam, *J. Chem. Soc.*, 1453 (1940).

(6) J. S. Powell and K. C. Edson, *Anal. Chem.*, 20, 510 (1948).

TABLE II

DISTRIBUTION OF THE METHYLCYCLOPENTADIENE DIMER ISOMERS RESULTING FROM DIMERIZING MONOMER ISOMER MIXTURES OF KNOWN CONCENTRATION

Monomer Composition before Dimerization				Composition of the Dimer-Fraction after Dimerization					
Exp. No.	Mole %			Mole %					
	2-MCPD ^a (A)	1-MCPD ^b (B)	CPD ^c (D)	AA	iso-AA (or iso-AB)	BB	AB	AD, BD	DD
1	95	5	—	86.7	6.4	1.5	5.4	—	—
2	80	20	—	61.7	3.2	5.9	29.2	—	—
3	35	65	—	14.5	1.0	34.5	50.0	—	—
4	51.5	45.1	3.4	33.5	6.7	18.4	37.8	2.3	1.3
5	—	—	100.0	—	—	—	—	—	100.0
	Commercial Dimer (Enjay)			33.6	10.2	18.6	33.4	2.5	1.7

^a 2-Methylcyclopentadiene. ^b 1-Methylcyclopentadiene. ^c Cyclopentadiene.

identity of the dimer isomers was determined. The composition of the dimer isomers approaches statistical distribution. Slight deviations are due to the higher dimerization rate of 2-methylcyclopentadiene and to the formation of trimers. Five dimer isomers were characterized. They are the simple dimers of cyclopentadiene, 1-methylcyclopentadiene and 2-methylcyclopentadiene, and two "codimers" resulting from the addition of two different monomers (i.e., 2-methylcyclopentadiene + 1-methylcyclopentadiene, and cyclopentadiene + any methylcyclopentadiene isomer). The sixth dimer isomer could be either any isomeric simple dimer of 2-methylcyclopentadiene or less likely any isomeric codimer of 2-methylcyclopentadiene + 1-methylcyclopentadiene (Table II).

The dimers have the same *endo*-dicyclopentadiene skeleton: No attempts were made to locate



the positions of the methyl substituents. The dimer isomers did not have any characteristic absorption in the ultraviolet region. The available quantity of 5-methylcyclopentadiene was insufficient for dimerization studies.

Trimers and higher polymers are formed simultaneously with the dimers. They were observed during the vapor phase chromatographic analyses.

EXPERIMENTAL⁷

The monomeric isomers were separated with a Perkin-Elmer Vapor Fractometer, Model 154 over 30% tetrahydro-2,4-dimethyl thiophene-1,1-dioxide (2,4-dimethylsulfolane) on C₂₂ Firebrick (mesh 30-60) in a 6 ft. long 1/4" stainless steel column at 34°. The carrier gas was helium with 23 ml/min flow rate at 5 p.s.i. inlet pressure. The outlet line

(7) Ultraviolet spectra were obtained in ethanolic solution using a Cary Model 11 Spectrophotometer. Infrared spectra were obtained of the undiluted hydrocarbons employing a Baird Model B Infrared Spectrophotometer. Commercial methylcyclopentadiene was obtained from the Enjay Corporation.

of the instrument was equipped with small glass cold-traps cooled to -70° with Dry Ice. Twenty to twenty-five runs with sample sizes from 0.01 to 0.02 ml. gave sufficient material for infrared and ultraviolet analyses. Retention time ratios to cyclopentadiene as standard monomer of the methylcyclopentadiene monomer isomers and other conjugated diolefins over 2,4-dimethylsulfolane at 34° are listed in Table III. At temperatures above 40° the difference in

TABLE III

RETENTION TIME RATIOS OF METHYLCYCLOPENTADIENE MONOMER ISOMERS AND OTHER CONJUGATED DIOLEFINS OVER 2,4-DIMETHYLSULFOLANE AT 34°

Compound	Retention Time Ratio
Butadiene	0.22
Isoprene	0.54
1- <i>trans</i> -3-Pentadiene	0.71
1- <i>cis</i> -3-Pentadiene	0.79
Cyclopentadiene	1.00 (by definition)
2-Methylcyclopentadiene	2.52
1-Methylcyclopentadiene	2.85
5-Methylcyclopentadiene	3.29

the retention time of methylcyclopentadiene isomers decreases and the resolution declines. The same instrument with the same column and the same carrier gas was used for the separation of the methylcyclopentadiene dimer isomers. 10% D.C. Silicone Oil on C₂₂ Firebrick (mesh 40-60) substrate was used at 107° column temperature. Attempts to

TABLE IV

RETENTION TIME RATIOS OF METHYLCYCLOPENTADIENE DIMER ISOMERS OVER D.C. 550 SILICONE OIL AT 107°

Compound	Retention Time Ratio	
DD	Cyclopentadiene dimer	1.00 (by definition)
AD, BD	Cyclopentadiene-methylcyclopentadiene codimer	1.29
BB	1-Methylcyclopentadiene dimer	1.43
AB	1-Methylcyclopentadiene-2-methylcyclopentadiene codimer	1.77
AA	2-Methylcyclopentadiene dimer	2.10
iso-AA	Isomeric 2-methylcyclopentadiene dimer (?)	2.52

resolve the dimer isomers with 30% D.C. 710 Silicone Oil substrate were unsuccessful. Retention time ratios to cyclopentadiene dimer as standard, of the methylcyclopentadiene dimer isomers over D.C. 550 Silicone Oil at 107° are included in Table IV.

Dimerization. Methylcyclopentadiene monomer mixtures of desired composition were kept in a 60° waterbath. Dimerization was practically complete within 2-3 hr.

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[CONTRIBUTION FROM THE ORGANIC BASIC RESEARCH LABORATORY, THE DOW CHEMICAL COMPANY]

Preparation of Ketals from 2,2-Dimethoxypropane¹

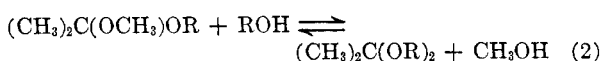
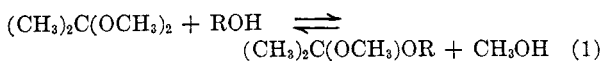
N. B. LORETTE AND W. L. HOWARD

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Methods are given for preparing symmetrical and mixed ketals by alkoxy and ketone interchanges between 2,2-dimethoxypropane and alcohols, ketones, and other ketals. Properties of twenty-one ketals are given.

Acetone dimethyl acetal (2,2-dimethoxypropane) is now readily available² and transketalization methods have been developed by which it can be used to prepare a variety of other ketals. The methods comprise interchanging the alkoxy or ketone groups in a slightly acid medium, and both kinds of groups can, in effect, be interchanged simultaneously in the same mixture. Both symmetrical and mixed ketals, RR'C(OR'')₂ and RR'-C(OR'')OR''', can be obtained in good yields by proper choice of conditions. Occasional instances of the use of alkoxy interchange are found in the literature³ but the reaction does not seem to have been studied extensively. The ketone interchanges are similar to the reactions with orthoesters studied by MacKenzie and Stocker.^{3a} Mixed ketals have been obtained previously in isolated instances.⁴ The use of 2,2-dimethoxypropane in preparing ketals avoids the necessity of obtaining the less accessible orthoesters or substituted acetylenes required by previous methods.³

Acidification of a mixture of 2,2-dimethoxypropane and an alcohol quickly establishes the equilibria (1), (2), and (3).



By distilling the methanol formed, the position of equilibrium can be shifted far in the direction of the new ketals. Methanol and 2,2-dimethoxypropane form a binary azeotrope (b.p. 61°, 56.5% dimethoxypropane by weight), but this is easily broken by using hexane or benzene as a solvent. With the methanol these hydrocarbons form lower-boiling azeotropes which are practically free of 2,2-dimethoxypropane. By their use the reactions can be brought nearly to completion at moderate temperatures without appreciable loss of 2,2-dimethoxypropane. These azeotrope relations also exist at reduced pressures so that low reaction temperatures can be maintained for preparing heat-sensitive ketals.

The mixed ketals are obtained from reaction (1) by using only one mole of alcohol per mole of 2,2-dimethoxypropane or other ketal. However, the simultaneous occurrence of reaction (3) limits the yield of the mixed ketal. If R is a lower primary alkyl radical, the methoxy and alkoxy groups will be distributed statistically as in the redistribution reaction of Calingaert and Beatty⁵ and the theoretical yield of mixed ketal will be 50%. With the alkyl radical sterically or electronically considerably different from methyl, yields of the mixed ketals can exceed 50%. The higher symmetrical ketal is a usual by-product of the preparation of the mixed ketal. Two or more moles of alcohol per mole of 2,2-dimethoxypropane give predominantly the symmetrical ketal with small amounts of mixed ketal depending on the completeness of removal of the methanol.

The redistribution in reaction (3) has been demonstrated in both directions with acetone methyl and allyl ketals. The final ratio of mixed to symmetrical ketals was 2:1:1. In a simple mixture of ketals of the same ketone the redistri-

(1) Presented in part at the Gordon Research Conference on Organic Reactions and Processes, July 1958.

(2) The Dow Chemical Company, Midland, Mich.

(3) Reviews are given in (a) C. A. MacKenzie and J. H. Stocker, *J. Org. Chem.*, **20**, 1695 (1955) and (b) R. B. Wagner and H. D. Zook, *Synthetic Organic Chemistry*, John Wiley and Sons, Inc., New York, 1953, Chap. 8.

(4) (a) C. D. Hurd and M. A. Pollack, *J. Am. Chem. Soc.*, **60**, 1905 (1938); (b) R. Alquier, *Bull. soc. chim.*, **10**, 197 (1943).

(5) G. Calingaert and H. A. Beatty, *Organic Chemistry, An Advanced Treatise*, Vol. II, 2nd ed., H. Gilman, Ed., John Wiley and Sons, Inc., New York, 1947, Chap. 24.