[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Synthesis of the Geometrical Isomers of 1,2,3-Trimethylcyclohexane[1]

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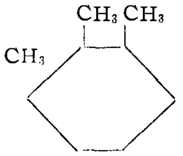
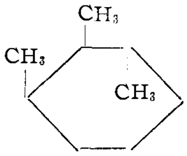
The three possible geometrical isomers of 1,2,3-trimethylcyclohexane have been synthesized individually and characterized by definitive physical properties; purities were estimated by cryoscopic methods, when possible. Co-incidentally it was necessary to study the stereospecificity of certain Diels–Alder reactions, lithium aluminum hydride reductions and hydrogenations.

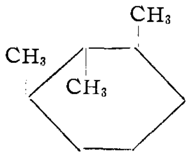
There are three possible geometrical isomers of 1,2,3-trimethylcyclohexane. By the conventional planar representation these may be designated as



cis,cis,cis



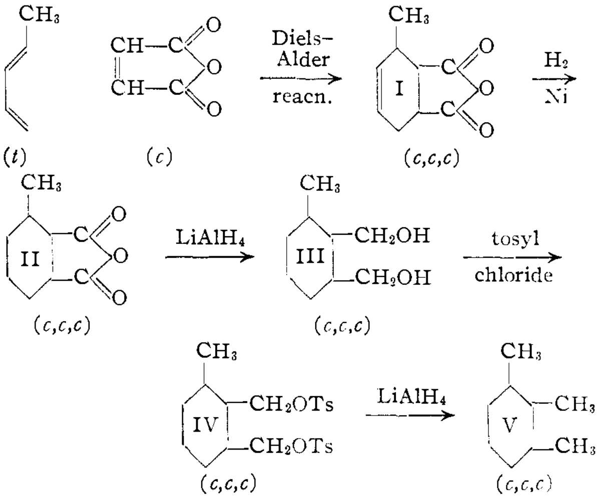
cis,cis,trans
(*d,l*-mixture)



cis,trans,cis

Reports[2] of 1,2,3-trimethylcyclohexane resulting from aluminum chloride catalyzed rearrangements of alkylcycloalkanes have been made, but identification work was sorely limited by lack of definitive physical properties. Only two references exist in the literature on preparative methods for the 1,2,3-trimethylcyclohexanes. Zelinski[3] in 1903 accomplished the first synthesis by hydrogenation of the cycloölefin(s) obtained by dehydrating the carbinol resulting from the reaction of methyl Grignard reagent and 2,6-dimethylcyclohexanone. No reference was made to the geometrical configuration of the product obtained (b.p. 141° (736 mm.), d^{20}_4 0.7898). Eisenlohr and Gorr[4] hydrogenated hemimellitene over a colloidal platinum catalyst at 70° to obtain a hydrocarbon material boiling 144 to 146°. Hydrogenation of the same aromatic over nickel at 180° gave a different hydrocarbon material (b.p. 142–143.5°). Eisenlohr followed the convention of Skita and Schneck[5] and designated the former "*cis*" and latter "*trans*"-1,2,3-trimethylcyclohexane. He apparently ignored the fact that there are actually two possible "*trans*" forms.

In the present work all three of the 1,2,3-trimethylcyclohexanes were synthesized individually, their common physical properties and infrared spectra were measured, and purities were estimated (cryoscopically, when possible). The known stereospecificity of Diels–Alder reactions[6–15] suggested a convenient and logical starting point for the syntheses. The stereochemical assignments depend on the presumption that the *trans*-piperylene–maleic anhydride adduct (I) has an "all *cis*" configuration, as predicated by the literature.[10,12–15] The following equations illustrate the synthesis of *cis,cis,cis*-1,2,3-trimethylcyclohexane.



Craig[15] reported that the Diels–Alder adduct I can be hydrogenated with retention of configuration. The next step was thought to be feasible, in view of the known stereospecificity of such lithium aluminum hydride reductions.[16,17] Tosylation of the resulting diol reputedly occurs with retention of configuration,[18] and reduction of the ditosylate IV by means of lithium aluminum hydride would not be expected to change the configuration.[19,20] The *cis,cis,cis*-1,2,3-trimethylcyclohexane (30% yield from ditosylate) obtained by this route had the following physical properties: b.p. 151.43° (760 mm.), $n^{20}\text{D}$ 1.4403, d^{20}_4 0.8021. It would not crystallize, but supercooled to a viscous glass; the physical properties of successive fractions during distillation, indicated a purity of 95 mole %.

In order to confirm the stereospecificity of the sequence, the same series of reactions was carried out, starting with hexahydrophthalic anhydride. Since the *cis* and *trans* isomers of the resulting 1,2-dimethylcyclohexane are well known (as are each of the intermediates), the terminal product served as a

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(2) G. Chiurdoglu, *Bull. soc. chim. Belg.*, **60**, 39 (1951).

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(4) F. Eisenlohr and G. Gorr, *Fortschr. Chem. Physik.*, **18**, No. 9, 10 (1925).

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(6) E. C. Coyner and R. T. Arnold, THIS JOURNAL, **66**, 1542 (1944).

(7) H. L. Holmes and R. M. Husband, *ibid.*, **70**, 141 (1948).

(8) W. E. Bachmann and L. B. Scott, *ibid.*, **70**, 1458 (1948).

(9) J. S. Meek and J. W. Ragsdale, *ibid.*, **70**, 2502 (1948).

(10) K. Alder, M. Schumacher and O. Wolff, *Ann.*, **570**, 230 (1950).

(11) H. L. Holmes, *Can. J. Res.*, **26B**, 248 (1948).

(12) K. Alder, M. Schumacher and O. Wolff, *Ann.*, **564**, 79 (1949).

(13) K. Alder and M. Schumacher, *ibid.*, **571**, 87 (1951).

(14) K. Alder and W. Vogt, *Ann.*, **571**, 87 (1950); **565**, 135 (1949).

(15) D. Craig, THIS JOURNAL, **72**, 1678 (1950).

(16) P. Karrer and A. R. Naik, *Helv. Acta. Chim.*, **31**, 1617 (1948).

(17) W. G. Brown, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 469.

(18) L. N. Owens and G. A. Haggis, *J. Chem. Soc.*, 380 (1953).

(19) P. Karrer and H. Schmid, *Helv. Chim. Acta*, **32**, 1371 (1949).

(20) D. S. Noyce and D. B. Denny, THIS JOURNAL, **74**, 5912 (1952).

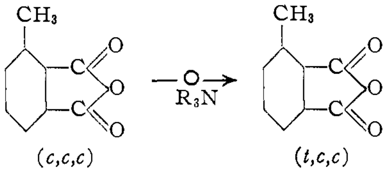
criterion of stereospecificity. The physical properties for the two isomers[21] together with those of the experimental hydrocarbon product are listed in Table I. These showed that the experimentally obtained hydrocarbon was practically pure *cis*-1,2-dimethylcyclohexane. Further support was given by the infrared spectrogram which agreed quite closely with one reported[22] for a sample estimated to be 99.89% pure.

TABLE I

PHYSICAL PROPERTIES OF THE 1,2-DIMETHYLCYCLOHEXANES

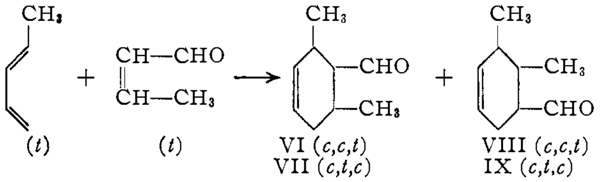
Hydrocarbon	Boiling point °C. (760 mm.)	Refractive index $n^{20}D$
trans-1,2-Dimethylcyclohexane[21]	123.42	1.4270
cis-1,2-Dimethylcyclohexane[21]	129.73	1.4360
Experimental hydrocarbon	129.5 (uncor.)	1.4361

In the synthesis of *cis,cis,trans*-1,2,3-trimethylcyclohexane the first step was to rearrange *cis*-3-methyl-*cis,cis*-hexahydrophthalic anhydride (obtained as above) to *trans*-3-methyl-*cis,cis*-hexahydrophthalic anhydride by a modification of the method of Craig,[15] which consisted of heating it with a tertiary amine. *cis,cis,trans*-1,2,3-Trimethylcyclohexane was then obtained by the same sequence used in the preparation of the *cis,cis,cis* isomer. The physical properties of the resulting isomer were: b.p. 150° (uncor.), $n^{20}D$ 1.4393; yield from the ditosylate was 36%.



cis,trans,cis-1,2,3-Trimethylcyclohexane was also prepared through *cis*-3-methyl-*cis,cis*-hexahydrophthalic anhydride. The anhydride was boiled with water[14] to obtain *cis*-3-methylcyclohexane-*cis,cis*-1,2-dicarboxylic acid which was subsequently isomerized to the *cis,trans,cis* isomer (*cis*-3-methylcyclohexane-*cis,trans*-1,2-dicarboxylic acid) by heating it with concentrated hydrochloric acid in a sealed tube at 180° for seven hours. One-half of the isomerizate was reduced directly with lithium aluminum hydride to the corresponding diol. During this reduction a putty-like precipitate came out of solution; it was assumed that this was due to salt formation and indicated that further reduction would take place only in a heterogeneous fashion. This was not considered desirable so the remainder of the rearranged diacid was esterified with ethanol (sulfuric acid catalyst), and the resulting diester was reduced with lithium aluminum hydride to the expected diol. This was tosylated, and reduction of the ditosylate was done as before to obtain *cis,-trans,cis*-1,2,3-trimethylcyclohexane: b.p. 145.6°, $n^{20}D$ 1.4343, d^{20}_4 0.7842; yield from the tosylate was 54%.

cis,cis,trans- and *cis,trans,cis*-1,2,3-trimethylcyclohexanes were also obtained by an alternate route dependent on other stereospecific reactions. *trans*-Piperylene was condensed with crotonaldehyde (*trans*[23]) in a steel bomb at 210°. The mixture of adducts was subjected to a modified Wolff–Kishner type reduction and the product was distilled at better than 100-plate efficiency to yield the two expected olefins, *cis,cis,trans*- and *cis,trans,cis*-3,4,5-trimethylcyclohexene, in the ratio of about 1:2; there was no indication of the presence of a third isomer which might have been expected if stereospecificity had not been retained throughout the reactions.



The *cis,cis,trans* isomer was hydrogenated over Raney nickel at 150° for ten hours. The hydrogenate was treated exhaustively with aqueous potassium permanganate, steam distilled, dried and fractionated at atmospheric pressure. There was obtained a slight forerun of *cis,trans,cis*-1,2,3-trimethylcyclohexane (2% of distillate, b.p. 145.2°, $n^{20}D$ 1.4356) followed by the *cis,cis,trans*-1,2,3-trimethylcyclohexane. The infrared spectrogram of this isomer was virtually identical with that of the *cis,cis,trans*-1,2,3-trimethylcyclohexane obtained before.

The *cis,trans,cis*-3,4,5-trimethylcyclohexene was hydrogenated over nickel-on-kieselguhr catalyst at 150° for three hours. The hydrogenate was treated as previously described and was distilled. Thereby the product was separated into 60% *cis,trans,cis*-1,2,3-trimethylcyclohexane and 40% *cis,cis,trans*-1,2,3-trimethylcyclohexane. The spectrogram of the *cis,trans,cis* isomer compared closely with that of the same isomer prepared previously. Since the starting olefin was the *cis,trans,cis*-3,4,5-trimethylcyclohexene isomer, it is apparent that some equilibration of isomers took place during the course of the hydrogenation in the presence of nickel-on-kieselguhr catalyst; this probably would have been much less had the Raney catalyst been used.

Table II lists the best physical properties determined for each of the isomers.

TABLE II

PHYSICAL PROPERTIES OF THE GEOMERS OF 1,2,3-TRIMETHYLCYCLOHEXANE

Isomer	B.p. °C. (760 mm.)	$n^{20}D$	d^{20}_4	M.p., °C.	Purity (mole %)
cis,trans,cis	145.61	1.4333	0.7870	−66.86	99.8
cis,cis,trans	151.21	1.4401	.8029	−85.73	96.4
cis,cis,cis	151.43	1.4403	.8021	.....	95(estd.)

On the basis of modern concepts of strain and conformation in the cyclohexane system,[24] the following conformations may be assigned: the *c,t,c* isomer would be eee, the *c,c,c* isomer eae, and the *c,c,t* iso-

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[21] F. D. Rossini, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, 1953, Pittsburgh, Pa.

[22] American Petroleum Institute Research Project 44, Infrared Absorption Spectrogram Serial No. 299, Carnegie Institute of Technology, Pittsburgh, Pa.

[23] W. G. Young, THIS JOURNAL, **54**, 2498 (1943).

[24] C. W. Beckett, K. S. Pitzer and R. Spitzer, THIS JOURNAL, **69**, 2488 (1947).

Table III

Properties of Intermediates and Derivatives Not Listed Elsewhere

Compound	Yield, %	M.p. or b.p. °C.	Mm.	$n^{20}D$	Carbon, % Calcd.	Carbon, % Obsd.	Hydrogen, % Calcd.	Hydrogen, % Obs.
Isomeric 3-methyl-1,2-dihydroxymethylcyclohexanes								
cis-3-Methyl-*cis,trans*-	52[a]	109–111	0.4	1.4891	68.31	68.10	11.46	11.56
trans-3-Methyl-*cis-cis*-	55[a]	124	1	1.4885	68.31	67.60	11.46	12.08
Isomeric diethyl 3-methylcyclohexane-1,2-dicarboxylates								
cis-3-Methyl-*cis-trans*-	50[a]	94–97	0.5	1.4519	64.43	64.62	9.15	9.34
trans-3-Methyl-*cis,cis*-	70[a]	110–111	1	1.4543	64.43	64.52	9.15	9.07
Isomeric 3-methylcyclohexane-1,2-dicarbinyl tosylates[c]								
cis-3-Methyl-*cis,trans*-	86[b]	119–120 m.p.		(S 12.35%)[d]	59.18	55.14	6.48	6.78
trans-3-Methyl-*cis,cis*-	92[b]	79–80 m.p.		(S 13.99%)[d]	59.18	59.08	6.48	6.53

[a] From rearranged anhydride. [b] From corresponding dihydroxy compound. [c] Crude products. [d] Calcd.: S, 13.72.

mer, aee. These assignments are in general agreement with past experience that more highly strained isomers have higher boiling points.

Experimental

Typical procedures are described here. These also are applicable to the sequences of the *cis,cis,trans*-, *cis,trans,cis*-1,2,3-trimethylcyclohexane and *cis*-1,2-dimethylcyclohexane which were prepared by the same route.

Piperylene.—This diolefin was synthesized by treating freshly distilled crotonaldehyde with methyl Grignard reagent and dehydrating the resulting 3-pentene-2-ol. The Grignard reaction was carried out on the large scale in the all-metal apparatus previously described,[25] the average yield of 3-pentene-2-ol being 66%. The carbinol was dehydrated by passage through a Pyrex tube packed with 4–8 mesh alumina and heated to 250°; the yields of piperylene averaged 80%. The product (b. 41.5–41.9°) consisted of 85% *trans*/15% *cis* isomer, on the average, according to the refractive index ($n^{20}D$ 1.4292–1.4306) of the main portion of the product.

***cis*-3-Methyl-4-cyclohexene-*cis,cis*-1,2-dicarboxylic Anhydride** (I).—The method used for the synthesis of this compound was that of Frank, Emmick and Johnson.[26] In a typical run 500 g. (5.1 moles) of maleic anhydride was condensed with 450 g. of piperylene, the equivalent of 5.7 moles of the *trans* isomer (the *cis* isomer does not react), to obtain 832 g. (58% yield) of crude *cis*-3-methyl-4-cyclohexene-*cis,cis*-1,2-dicarboxylic anhydride (I). The crude product melted at 61–62°; recrystallization from ether raised this to 63.0–63.5° (lit.[15] m.p. 63°).

The corresponding *cis*-3-methyl-4-cyclohexene-*cis,cis*-1,2-dicarboxylic acid was obtained in 76% yield by boiling 1 g. of adduct with water for 15 minutes; the acid melted at 153–154° (lit.[27] 155°).

***cis*-3-Methylcyclohexane-*cis,cis*-1,2-dicarboxylic Anhydride** (II).—In a typical run, 332 g. (2 moles) of the piperylene–maleic anhydride adduct (I) was dissolved in 700 ml. of ethyl acetate and hydrogenated at room temperature over 35 g. of Raney nickel. At 1000 p.s.i.g. the hydrogenation was completed within one hour. After removal of catalyst and solvent, there was obtained 318 g. (95% yield) of crude *cis*-3-methylcyclohexane-*cis,cis*-1,2-dicarboxylic anhydride (II).

A portion of anhydride II was esterified with ethanol, yielding the diester (b.p. 95–103° (0.5 mm.), $n^{20}D$ 1.4536) in 84% yield. *Anal.* Calcd. for $C_{13}H_{20}O_4$: C, 64.97; H, 8.39. Found: C, 64.89; H, 8.50.

***cis*-3-Methyl-*cis,cis*-1,2-dihydroxymethylcyclohexane** (III).—Three hundred and eighteen grams (1.9 moles) of anhydride II was dissolved in 700 ml. of dry ether and reduced with lithium aluminum hydride (60 g., 1.3 moles) in the usual fashion.[17,18] Distillation of the crude diol at reduced pressure yielded 180 g. (60% yield) of good product (b.p. 124–126° (1 mm.), $n^{20}D$ 1.4870). *Anal.* Calcd. for $C_9H_{18}O_2$: C, 68.31; H, 11.46. Found: C, 68.22; H, 11.41.

***cis*-3-Methylcyclohexyl-*cis,cis*-1,2-dicarbinyl Tosylate** (IV).—Diol III (180 g., 1.14 moles) was dissolved in an equal volume of pyridine and added dropwise to a stirred mixture of 450 g. (2.37 moles) of *p*-toluenesulfonyl chloride and 400 ml. of pyridine, cooled by an ice–salt-bath. The reaction temperature was maintained below 5° throughout the addition, and for an additional period of 4–5 hours. The mixture was stored in a refrigerator overnight, allowed to come to room temperature, and poured into a mixture of 500 ml. of concentrated hydrochloric acid and one liter of crushed ice, at which point the ditosylate appeared as a highly colored viscous oil. The aqueous layer was extracted twice with ether (300-ml. portions) and the ether extracts added to the bulk of the ditosylate. The resulting ether solution was washed with water, saturated sodium bicarbonate solution, and water, after which it was dried by percolation through a column of anhydrous sodium sulfate, and the solvent was evaporated. There was obtained 500 g. (a 93% yield) of *cis*-3-methylcyclohexyl-*cis,cis*-1,2-dicarbinyl tosylate (IV). This material was not purified further.

***cis,cis,cis*-1,2,3-Trimethylcyclohexane** (V).—An amount (250 g.) of the crude ditosylate IV was dissolved in 500 ml. of dry tetrahydrofuran, and then added dropwise to a stirred mixture of 50 g. (1.3 moles) of lithium aluminum hydride in the same solvent. The mixture was refluxed for 18 hours, allowed to cool, and hydrolyzed with: (1) 50 ml. of ethyl acetate (to destroy excess hydride), (2) 300 ml. of water and 1 liter of ethyl ether and (3) 200 ml. of 10% hydrochloric acid. The ether solution was decanted and the precipitate was stirred twice with 300-ml. portions of fresh ether. The ether extracts were combined and washed several times with water. The solution was now percolated through anhydrous sodium sulfate and distilled to obtain 25 g. of hydrocarbon (b.p. 151–153° (uncor.)). This material was treated exhaustively with an aqueous solution of potassium permanganate, steam distilled, dried and fractionally redistilled to produce 20 g. (29.5% yield from ditosylate) of *cis,cis,cis*-1,2,3-trimethylcyclohexane with the following physical properties: b.p. 151.43° (760 mm.), d^{20}_4 0.8021, $n^{20}D$ 1.4403; the sample supercooled to form a viscous glass. *Anal.* Calcd. for C_9H_{18}: C, 85.63; H, 14.37. Found: C, 85.48; H, 14.38.

There was also obtained 50 g. of material (b.p. 186–189° (750 mm.) (uncor.), $n^{20}D$ 1.4960), presumably *cis*-4-methyl-*cis,cis*-octahydroisobenzofuran formed during the lithium aluminum hydride reduction of the anhydride,[28] and/or during the formation of the tosylate.[29] *Anal.* Calcd. for $C_9H_{16}O$: C, 77.10; H, 11.51. Found: C, 77.05; H, 11.52.

***cis*-1,2-Dimethylcyclohexane.**—*cis*-Hexahydrophthalic anhydride (154 g., 1 mole) was reduced with lithium aluminum hydride, by the method described, to obtain 105 g. (0.74 mole) of crude *cis*-1,2-di-(hydroxymethyl)-cyclohexane. A portion (50 g., 0.34 mole) of the crude diol was tosylated by the procedure used for *cis*-3-methylcyclohexyl-*cis,cis*-1,2-dicarbinyl tosylate; there resulted 91 g. (59% yield) of crude cyclohexane-*cis*-1,2-dicarbinyl tosylate (m.p. 80–82°, lit.[18] 84–85°). This crude ditosylate was reduced with lithium

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[25] C. E. Boord, A. L. Henne, K. W. Greenlee, W. L. Perilstein and J. M. Derfer, *Ind. Eng. Chem.*, **41**, 609 (1949).

[26] R. Frank, R. Emmick and R. S. Johnson, This Journal, **69**, 2313 (1947).

[27] K. Alder and W. Vogt, *Ann.*, **564**, 120 (1949).

[28] P. Karrer and A. R. Naik, *Helv. Acta Chim.*, **31**, 1617 (1948).

[29] W. E. Bachman and A. S. Dreiding, This Journal, **71**, 3222 (1948).

aluminum hydride (see procedure under *cis,cis,cis*-1,2,3-trimethylcyclohexane) to obtain 8 g. (36% yield) of *cis*-1,2-dimethylcyclohexane, b.p. 129.5° (uncor.), $n^{20}\text{D}$ 1.4361.

***trans*-3-Methylcyclohexane-*cis,cis*-1,2-dicarboxylic Anhydride.**—Four moles (668 g.) of *cis*-3-methylcyclohexane-*cis,cis*-1,2-dicarboxylic anhydride was distilled (b.p. 94–100° (0.3 mm.)). This material was divided into six equal parts and sealed in glass ampoules together with 3 ml. of diethylaniline per ampoule and was heated at 145° for 22 hours. The tubes were then cooled and opened. The quantitative yield of *trans*-3-methylcyclohexane-*cis,cis*-1,2-dicarboxylic anhydride was not purified further.

A small portion of this anhydride (5 g.) was boiled 30 minutes with water (35 ml.) and the resulting clear solution deposited white crystals of *trans*-3-methylcyclohexane-*cis,cis*-1,2-dicarboxylic acid on standing 2 days at room temperature, m.p. 124–127° (lit.[15] 129°).

The rearranged anhydride (144 g., 0.86 mole) was esterified with ethanol, and the diethyl ester (145 g., 0.6 mole), b.p. 110–111° (1 mm.), $n^{20}\text{D}$ 1.4543, was obtained in 70% yield after distillation. *Anal.* Calcd. for $C_{13}H_{22}O_4$: C, 64.43; H, 9.15. Found: C, 64.52; H, 9.07.

3,4,5-Trimethylcyclohexene.—Piperylene and crotonaldehyde were caused to undergo the Diels–Alder reaction by the procedure of Tom.[30] In a typical 5-mole run there was obtained 3.8 moles (a 76% yield) of adduct (b.p. 80–82° (20 mm.), $n^{20}\text{D}$ 1.4669). The piperylene–crotonaldehyde adduct (690 g., 5 moles) was then reduced by means of the Huang-Minlon[31] modification of the Wolff–Kishner reaction, except that dihydrazine sulfate was used along with enough additional sodium hydroxide to liberate the hydrazine; thereby there was produced 405 g. (65% of theory) of crude 3,4,5-trimethylcyclohexene. The combined product of several such runs (3160 g.) was distilled at better than 100-plate efficiency to give 1707 g. of *cis,trans,cis*-3,4,5-trimethylcyclohexene (b.p. 144.36° (760 mm.), $n^{20}\text{D}$ 1.4484, d^{20}_4 0.8114) and 850 g. of *cis,cis,trans*-3,4,5-trimethylcyclohexene (b.p. 148.25° (760 mm.), $n^{20}\text{D}$ 1.4511). *Anal.* Calcd. for C_9H_{16}: C, 87.03; H, 12.97. Found for the *cis,trans,cis* isomer: C, 87.24; H, 13.03. Found for the *cis,cis-trans* isomer: C, 87.08; H, 12.89.

***cis,trans,cis*-1,2,3-Trimethylcyclohexane.**—The *cis,trans,cis*-3,4,5-trimethylcyclohexene (1707 g., 13.78 moles) was hydrogenated in a steel bomb at 150° over nickel (Ni(K)) catalyst for a period of 3 hours (1500 p.s.i.g. hydrogen). The catalyst was removed by filtration, and the hydrogenate was treated exhaustively with aqueous potassium permanganate solution to remove any unsaturates. The hydrocarbon material was then steam distilled, dried, and fractionated at about 35-plate efficiency. There was obtained a 60/40 mixture of *cis,trans,cis-/cis,cis,trans*-1,2,3-trimethylcyclohexane (b.p. 151.15° (760 mm.), $n^{20}\text{D}$ 1.4394). The physical properties of the *cis,trans,cis*-1,2,3-trimethylcyclohexane were b.p. 145.61, $n^{20}\text{D}$ 1.4333, d^{20}_4 0.7870, m.p. −66.86°. Its purity was determined cryoscopically as 99.8 ± 0.2 mole per cent. *Anal.* Calcd. for C_9H_{18}: C, 85.63; H, 14.37. Found: C, 85.50; H, 14.51.

***cis,cis,trans*-1,2,3-Trimethylcyclohexane.**—The *cis,cis,trans*-3,4,5-trimethylcyclohexene was hydrogenated over Raney nickel at 150° for a period of 10 hours (1500 p.s.i.g. hydrogen). The hydrogenate was treated precisely as in the purification of the *cis,trans,cis* isomer, and final distillation at high efficiency gave principally *cis,cis,trans*-1,2,3-trimethylcyclohexane (b.p. 151.21, $n^{20}\text{D}$ 1.4401, d^{20}_4 0.8029, m.p. −85.73°). Its purity was determined cryoscopically as 96.4 ± 0.5 mole per cent. *Anal.* Calcd. for C_9H_{18}: C, 85.63; H, 14.37. Found: C, 85.51; H, 14.21.

***cis*-3-Methylcyclohexane-*cis,trans*-1,2-dicarboxylic Acid.**—*cis*-3-Methylcyclohexane-*cis,cis*-1,2-dicarboxylic acid was prepared by heating anhydride II and water at 100° for 1 hour. An amount of this product (250 g.) was placed in a glass liner within a steel bomb together with 500 ml. of concentrated hydrochloric acid (Baker C.P.), and was heated at 180° for seven hours to effect the desired isomerization.[14] The yield of crude *cis*-3-methylcyclohexane-*cis,trans*-1,2-dicarboxylic acid was 245 g. (96%). A small sample (4 g.) was recrystallized from water for analysis. This diacid (m.p. 162–163°) when mixed with the "all-*cis*"-diacid (m.p. 165–167°) gave a mixed m.p. of 139–140°, indicating it was a different species. *Anal.* Calcd. for $C_9H_{14}O_4$: C, 58.05; H, 7.58. Found: C, 58.23; H, 7.56.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NORTHWESTERN UNIVERSITY]

α- *versus* β-Elimination in the Cleavage of Ethers by Organoalkali Metal Compounds

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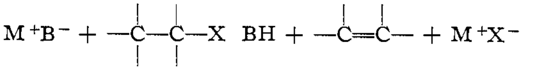
The purpose of this work was to determine whether elimination reactions which occur when ethers are treated with organoalkali metal compounds are α- or β-elimination processes. It was found by use of deuterium labeled compounds that the ethylene obtained from the reaction of propylsodium with ethyl aryl ethers originated by β-elimination. When an α-position of an ether was activated by a phenyl group, as in ethyl benzyl ether, the principal initial step of the elimination was α-metallation. No case could be found, however, in which α-metallation was followed by α-elimination. In the course of this work a new reaction was observed, the cleavage of 2-phenyltetrahydrofuran by organoalkali metal compounds to give high yields of ethylene and acetophenone. Furthermore, it was found that ethyl benzhydryl ether underwent a Wittig rearrangement when treated with propylsodium. Ethyl groups have not previously been observed to migrate in this type of rearrangement.

The work described in this paper was undertaken with the object of learning more about the course of reactions in which ethers are converted to olefins by organoalkali metal compounds. These processes are of particular interest since, as formal analogs to the elimination reactions (E2) effected by bases such as sodium alkoxide and sodium amide (see reaction I), they test the limits to which the concepts developed from the homogeneous reactions of the weaker bases can be extended. We have previously reported a stereochemical study which revealed a significant difference in the mech-



$$M^+B^- + -\overset{H}{\underset{|}{\overset{|}{C}}}-\overset{H}{\underset{|}{\overset{|}{C}}}-X \quad BH + -\overset{|}{C}=\overset{H}{\overset{|}{C}}- + M^+X^- \qquad (I)$$

For ether cleavages B is a carbanion; X, alkoxyl. For E2 reactions B is hydroxide, alkoxide, etc.; X, halide, quaternary ammonium, etc. M is a metal cation.