Anal. Calcd. for $C_8H_{17}NO$: C, 67.09; H, 11.96. Found: C, 67.36; H, 11.73.

The N-acetyl derivative was prepared by allowing a solution of 640 g. (0.00447 mole) of the amino alcohol XXIV and 541 mg. (0.00530 mole) of acetic anhydride in 6.4 ml. of absolute methanol to stand at room temperature for 18 hours. After removal of the solvent the amide was recrystallized from benzene to yield 790 mg. (95%) of an analytical sample, m.p. 126.5–127.5°.

Anal. Calcd. for $C_{10}H_{19}NO_2$: C, 64.83; H, 10.34. Found: C, 64.74; H, 10.68.

Reduction of 1-Oxaspiro[2.5]octane-2-carbonitrile (XV) with Lithium Aluminum Hydride in the Presence of Aluminum Chloride.—To 1.38 g. (0.0364 mole) of lithium aluminum hydride dissolved in 150 ml. of absolute ether was added 19.42 g. (0.1456 mole) of aluminum chloride. Stirring was commenced and 5.00 g. (0.0364 mole) of glycidonitrile XV in 50 ml. of absolute ether was added over a 15-minute period. The reaction mixture was allowed to stir for 12 hours at room temperature. Decomposition of the reaction mixture was accomplished by dropwise addition of water and then addition with cooling of 110 ml. of 10% sulfuric acid. The solution was extracted with ether, the ether layer was washed with water and the combined water layers were saved for further processing. The ether extract was dried and evaporated yielding 1.02 g. of neutral material. The infrared spectrum indicated the presence of hydroxyl (3.0 μ) and carbonyl (5.85 μ) groups. Treatment of this mixture with 2,4-dinitrophenylhydrazine reagent yielded after several recrystallizations a 2,4-dinitrophenylhydrazone, m.p. 171–172°. It was shown to be identical with the 2,4-dinitrophenylhydrazone of cyclohexanecarboxaldehyde (reported[20] m.p. 172°) by mixed melting point.

The combined aqueous acid fractions were made basic with concentrated sodium hydroxide solution and extracted with ether. The ether was washed with saturated sodium chloride solution, dried and evaporated. The crude product weighed 4.04 g. Distillation yielded 1.11 g. (21%) of **α-(aminomethyl)-cyclohexanemethanol (XXVI)**, b.p. 130–133° (12 mm.), and a residue which could not be distilled up to 190°. The amino alcohol solidified and had m.p. 55–70°. On recrystallization from ligroin 0.95 g. was obtained with m.p. 80–85°. The melting point was not depressed by admixture with an authentic sample of XXVI, prepared as described later on.

The N-acetyl derivative was formed by the reaction of 0.17 g. (0.0012 mole) of XXVI and 0.15 g. (0.0015 mole) of acetic anhydride in 2 ml. of absolute methanol. After standing overnight at room temperature the solvent was removed and the crude amide was recrystallized three times from benzene to yield 0.17 g. (77%) of pure **N-acetyl-α-(aminomethyl)-cyclohexanemethanol**, m.p. 107–108°. Mixed melting point with an authentic sample (see below) gave no depression.

Authentic α - (Aminomethyl) - cyclohexanemethanol (XXVI).—To a stirred solution of 28.1 g. (0.460 mole) of nitromethane and 0.93 ml. of 10 *N* sodium hydroxide solution in 25.5 ml. of absolute ethanol kept at 30–35° was added 51.5 g. (0.467 mole) of 3-cyclohexene-1-carboxaldehyde. After the addition of approximately two-thirds of the aldehyde over a 1-hour period, 0.93 ml. of 10 *N* sodium hydroxide and 3.4 ml. of water were added. The remainder of the aldehyde was added over a half-hour. The mixture was then stored at 37° for 5 days. Concentrated hydrochloric acid (1.5 ml.) was added and the reaction mixture was shaken vigorously. After discarding the aqueous layer the solution was extracted with ether and the ether layer was washed three times with saturated sodium chloride solution. The ether was dried and evaporated. Distillation yielded 39.9 g. (51%) of **1-(3-cyclohexen-1-yl)-2-nitroethanol**, b.p. 116–126° (1 mm.).

A solution of 10.0 g. (0.058 mole) of the above nitro alcohol in 5 ml. of glacial acetic acid and 100 ml. of absolute ethanol was hydrogenated under a pressure of two atmospheres in the presence of 1.0 g. of 10% palladium-on-charcoal. There was an uptake of 4 moles of hydrogen. The solution was filtered to remove the catalyst and was concentrated to dryness. The residue was taken up in water and extracted with ether. The water layers were concentrated practically to dryness, made basic with 40% sodium hydroxide solution, and extracted with ether. The ether was washed with a small amount of water, dried and evaporated. There was obtained 5.9 g. (72%) of the amino alcohol **α-(aminomethyl)-cyclohexanemethanol (XXVI)**, m.p. 73–82°. On recrystallization from ligroin the melting point remained in the range 70–80°. Only when heated at 70° for several hours did the melting point gradually rise to 85–86°. On crystallization from ligroin the melting point again dropped to 70–80°. The compound is probably dimorphic. A sample, sublimed twice at 100° (15 mm.), had m.p. 85–86°.

Anal. Calcd. for $C_8H_{17}NO$: C, 67.09; H, 11.96; N, 9.78. Found: C, 66.81; H, 11.90; N, 9.78.

The N-acetyl derivative was prepared by allowing a mixture of 1.00 g. (0.0070 mole) of α-(aminomethyl)-cyclohexanemethanol (XXVI), 0.71 g. (0.0070 mole) of acetic anhydride and 10 ml. of absolute methanol to stand at room temperature for 18 hours. The solvent was removed and the residue was dissolved in chloroform. The chloroform was extracted with dilute hydrochloric acid, washed with water, dried and evaporated. The crude product weighed 1.03 g. (79%) and had m.p. 107–108°. Several recrystallizations from benzene gave an analytical sample, m.p. 107.5–108.0°.

Anal. Calcd. for $C_{10}C_{19}NO_2$: C, 64.83; H, 10.34. Found: C, 64.62; H, 10.57.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE UNIVERSITY, AMES, IOWA]

Stereochemistry of Hydrogen Halide Addition to 1,2-Dimethylcyclopentene

BY GEORGE S. HAMMOND[1] AND CAROL H. COLLINS

RECEIVED DECEMBER 12, 1959

Addition of hydrogen chloride to 1,2-dimethylcyclopentene gives predominantly (perhaps exclusively) *trans*-1,2-dimethylcyclopentyl chloride. The product isomerizes, even in pentane solution, to a mixture which is richer in the *cis*-chloride. Addition of hydrogen bromide to the same alkene gives mixtures which are apparently equilibrated. This is attributed to instability of the halide, which is evidenced by the fact that elimination of hydrogen bromide occurs rapidly in non-polar solvents.

In an earlier study of the addition of hydrogen bromide to 1,2-dimethylcyclohexene in pentane or glacial acetic acid, the product was shown to be *trans*-1,2-dimethylcyclohexyl bromide.[2] Because of the flexibility of cyclohexene systems the mechanistic significance of the *trans*-addition is slightly clouded. Assumption of diaxial attack on the double bond leads to the conclusion that hydrogen and bromine are widely separated at the time they enter the molecule. The first product of such an addition would be I, the stable conformer of *trans*-1,2-dimethylcyclohexyl bromide.

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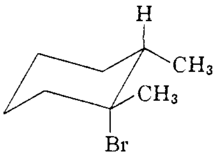
[1] Division of Chemistry, California Institute of Technology, Pasadena, Calif.

[2] G. S. Hammond and T. D. Nevitt, THIS JOURNAL, **76**, 4121 (1954).



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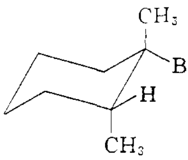

II

An alternative mode of attack can, however, be visualized. Attack by hydrogen bromide by approach in the alkene plane could give *trans*-bromide in conformation II. Although such a mechanism would not accord with usual assumptions[3,4] concerning the stereochemistry of electrophilic attack on unsaturated systems, in-plane attack might be favored in media of low dielectric as a way to avoid charge separation. The present study was carried out with a more rigid system, 1,2-dimethylcyclopentene. We felt that decreasing the flexibility of the ring system should substantially increase the activation energy for in-plane attack. If such an unexpected path were involved with the cyclohexene system the reactions of cyclopentenes would be slower and might well be diverted to some other steric course such as *cis*-addition. We hasten to point out that no evidence has arisen to sustain such a view.

Results and Discussion

Because of their instability, pure halides could not be isolated. Attempts were made to determine the composition of mixtures by means of selective reaction with sodium ethoxide in ethanol as was done in the earlier study.[2] However, the rates of solvolysis of the halides in absolute ethanol were so rapid[5] that the rates of bimolecular reactions with ethoxide could not be measured. Therefore, a partial analysis of the products was carried out by treating them with a solution of sodium *sec*-butoxide in mesitylene. Mesitylene was chosen as a solvent in preference to benzene or toluene in order to facilitate separation of olefinic products by gas chromatography.

Elimination occurred very rapidly when pentane solutions of the halides were added to the solution of alkoxide in mesitylene. We presume that reaction occurred by the E_2 mechanism since qualitative observation showed that, although hydrogen halides were released in neutral mesitylene solution, the reactions were much slower than those which occurred in the basic media. Halides formed by addition of hydrogen chloride and hydrogen bromide to 1,2-dimethylcyclopentene underwent elimination to give mixtures of 1,2-dimethylcyclopentene and 2,3-dimethylcyclopentene. The results are summarized in Tables I and II. Yields of halides were measured by solvolysis[5] of aliquots from the reaction mixtures after the unreacted hydrogen halides were extracted with water. In runs in which yields were not measured in this manner they were estimated by comparison with other experiments carried out under similar or identical reaction conditions. The yields of olefin given in the tables have been corrected for the amount of unreacted 1,2-dimethylcyclopentene remaining in the solution at the end of the addition reaction.

Table I

Composition of Alkene Mixtures Produced by Action of Sodium *sec*-Butoxide in Mesitylene on Bromides Prepared from 1,2-Dimethylcyclopentene and Hydrogen Bromide

Reaction	Reaction temp., °C.	Reaction time, min.	Yield of bromides,[a] %	1,2-Dimethylcyclopentene,[b] %	2,3-Dimethylcyclopentene,[b] %
1	0	5	68[c]	68	32
2	0	10	69	67	33
3	0	15	70[c]	64	36
4	0	30	70	62	38
5	0	60	73	63	37
6	0	4320	80[d]	67	33
7	−78	60	95[d]	80	20
8	−196 to −78	60	95[d]	92	8
9	25	60	?	84[e]	16[e]

[a] From solvolysis data. [b] Corrected for unreacted starting material. [c] Estimated by comparison with runs 2, 4 and 5; see text. [d] Estimated from data for runs, not reported in detail, in which degradative studies were not completed. [e] Uncorrected.

Table II

Composition of Alkene Mixtures Produced by Action of Sodium *sec*-Butoxide in Mesitylene on Chlorides Prepared from 1,2-Dimethylcyclopentene and Hydrogen Chloride

Reaction	Reaction temp., °C.	Reaction time, min.	Yield of chlorides,[a] %	1,2-Dimethylcyclopentene,[b] %	2,3-Dimethylcyclopentene,[b] %
10	0	5	25[c]	92	8
11	0	15	25[c]	92	8
12	0	30	28	93[d]	7[d]
13	0	60	40[c]	82	18
14	0	120	55[c]	74	26
15	0	4320	80[c]	75	25
16	−78	30	78	76[e]	24[e]
17	−78	4320	95[c]	80	20
18	−196 to −78	30	75	65[e]	36[e]
19	−196 to −78	60	78[c]	69	31

[a] From solvolysis data. [b] Corrected for unreacted starting material. [c] Estimated; see text. [d] Average of three runs. [e] Average of two runs.

Halide mixtures were also prepared by reaction of *cis*- and *trans*-1,2-dimethylcyclopentanol with hydrogen halides. Tables III and IV show composition of the alkene mixtures produced by elimination from the products of such substitution reactions.

Two assumptions must be made in rendering a qualitative interpretation of the data. First, it must be assumed that "spontaneous" elimination of hydrogen halides is not so accelerated by the presence of sodium alkoxide in mesitylene that it predominates over E_2 elimination. Second, it must be assumed that the E_2 reaction is stereospecifically *trans* as has been repeatedly demonstrated in other cases.[6-8]

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(3) J. E. Leffler, "The Reactive Intermediates of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1956, Chapt. VII.

(4) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, Chapt. 9.

(5) C. H. Collins and G. S. Hammond, *J. Org. Chem.*, in press.

(6) W. Hückel, W. Tappe and G. Legutke, *Ann.*, **543**, 191 (1940).

(7) S. J. Cristol, This Journal, **69**, 340 (1947), and subsequent papers.

(8) For a review see, D. J. Cram, "Steric Effects in Organic Chemistry," M. S. Newman, Editor, John Wiley and Sons, Inc., New York, N. Y., 1956, Chapt. 6.

TABLE III

COMPOSITION OF ALKENE MIXTURES PRODUCED BY THE ACTION OF SODIUM *sec*-BUTOXIDE IN MESITYLENE ON BROMIDES PRODUCED FROM 1,2-DIMETHYLCYCLOPENTANOLS AND HYDROGEN BROMIDE

Reaction	Substrate alcohol	Reaction temp., °C.	Reaction time, min.	1,2-Dimethylcyclopentene, %	2,3-Dimethylcyclopentene, %
20	*cis*-	0	5	79	21
21	*cis*-	0	60	69[a]	31[a]
22	*cis*-	−78	60	77	23
23	*cis*-	−196 to −78	60	78	22
24	*trans*-	0	5	84	16
25	*trans*-	0	60	70[a]	30[a]
26	*trans*-	−78	60	82	18
27	*trans*-	−196 to −78	60	80	20

[a] Average of two runs.

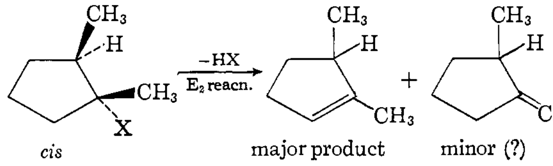
TABLE IV

COMPOSITION OF ALKENE MIXTURES PRODUCED BY ACTION OF SODIUM *sec*-BUTOXIDE IN MESITYLENE ON CHLORIDES PRODUCED FROM 1,2-DIMETHYLCYCLOPENTANOLS AND HYDROGEN CHLORIDE

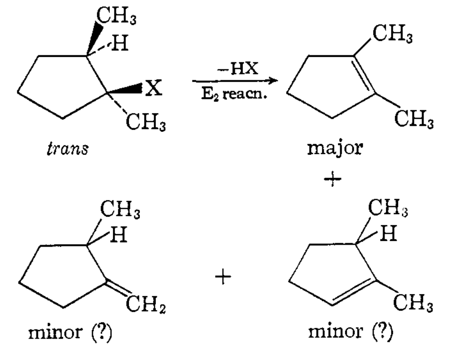
Reaction	Substrate, alcohol	Reaction temp., °C.	Reaction time, min.	1,2-Dimethylcyclopentene, %	2,3-Dimethylcyclopentene, %
28	*cis*-	0	30	83[a]	17[a]
29	*cis*-	0	60	79	21
30	*cis*-	−78	30	86[b]	14[b]
31	*cis*-	−196 to −78	30	83	17
32	*trans*-	0	30	89	11
33	*trans*	0	60	83	17
34	*trans*-	−78	30	81[b]	19[b]
35	*trans*-	−196 to −78	30	73	27

[a] Average of three runs. [b] Average of two runs.

One would expect that *cis*-1,2-dimethylcyclopentyl halides would eliminate to give predominantly 2,3-dimethylcyclopentene and that 1,2-dimethylcyclopentene would be specifically excluded from the products of such a reaction. On the other hand, *trans*-1,2-dimethylcyclopentyl halides should give predominantly 1,2-dimethylcyclopentene and, possibly, minor amounts of isomeric alkenes (see eq. 1 and 2). No detectable amount of 2-methylmethylenecylopentane was observed in any of the gas chromatograms although the compound was found in alkene mixtures prepared by pyrolysis of dimethylcyclopentyl acetates.[9]



(1)



(2)

Examination of the data in Tables I–IV, in the light of these assumptions, indicates that *trans*-halides must have predominated strongly in all product mixtures. However, the data of Table I indicate that an equilibrated mixture of bromides probably gives somewhere between 60 and 70% 1,2-dimethylcyclopentene. This follows from the fact that the results of addition at 0° in pentane are essentially independent of the reaction time. Two runs carried out at lower temperature gave mixtures which apparently contained larger amounts of *trans*-bromide. The result may indicate that *trans*-addition predominates at low temperatures and that isomerization is relatively slow. Alternatively, it may indicate that equilibrium favors the *trans* isomer more at low temperatures. Run 8, in which the reactants were frozen in the reaction cell at liquid nitrogen temperature and allowed to warm up in a Dry Ice–acetone-bath, gives a curious result. Addition of hydrogen bromide to 1,2-dimethylcyclohexene under similar conditions gave a significant amount of *cis*-halide as does the addition of hydrogen chloride to 1,2-dimethylcyclopentene (*vide infra*). We hesitate to attach any mechanistic significance to these limited observations. The value for *trans*-addition indicated by run 9 is a maximum which is uncorrected for any 1,2-dimethylcyclopentene which had not reacted with hydrogen bromide.

Bromide mixtures produced from the 1,2-dimethylcyclopentanols also showed little variation in their behavior when subjected to the elimination reaction. The results shown in Table III indicate that the products from both alcohols contained more *trans*-bromide than those prepared by addition to the alkene. Since long contact time in pentane at 0° tended to reduce the amount of symmetrical alkene produced on elimination, one might conclude that the substitution reactions are not sterically random. Very similar results are obtained with both isomeric alcohols as substrates, perhaps indicating that the two alcohols may react by way of a common intermediate. However, the great lability of dimethylcyclopentyl bromides again discourages any very serious interpretation of the results.

Experiments with hydrogen chloride as the reagent were more definitive. The data of Table II show that the product formed from 1,2-dimethylcyclopentene and hydrogen chloride, with short contact times, undergoes elimination to regenerate 92–93% of the parent alkene. This result indicates that *the initial product is at least 92% trans-1,2-dimethylcyclopentyl chloride.* Since it is likely that *trans*-chloride would undergo elimination to give some 2,3-dimethylcyclopentene,[10] it is entirely possible that addition shows exclusive, *trans* stereospeci-

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(9) D. H. Froemsdorf, C. H. Collins, G. S. Hammond and C. H. De Puy, THIS JOURNAL, **81**, 643 (1959).

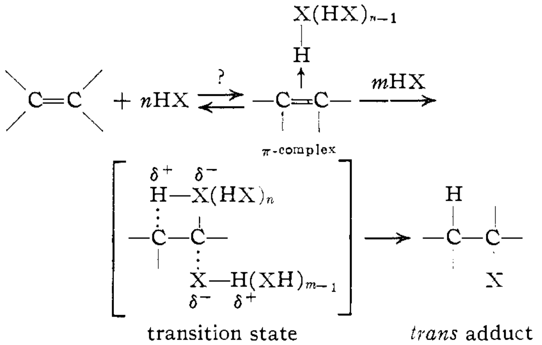
(10) For example, re-examination, using gas chromatography, shows that *trans*-1,2-dimethylcyclohexyl bromide gives 89% 1,2-dimethylcyclohexene and 11% 2,3-dimethylcyclohexene when treated with 1 *N* sodium ethoxide in ethanol.[4]

ficity. The extreme lability of these systems is clearly demonstrated by the results of experiments involving longer contact times. It is probable that the equilibrium mixture of chlorides is such as to produce about 75% symmetrical alkene in the elimination reaction. If this is true, the experiments beginning at liquid nitrogen temperature produced slightly more than the equilibrium (at 0°) amount of *cis*-chloride.

Hydrogen chloride reacts with the stereoisomeric alcohols to produce mixtures which, with one exception, apparently contain more than the equilibrium amount of *trans*-chloride. Since *trans*-alcohol gives more *trans*-chloride than does its *cis* isomer, we may conclude that substitution occurs by way of a mixed mechanism with one path involving retention of configuration. Similar results were obtained in the reaction of 1,2-dimethylcyclohexanols with hydrogen bromide.[11] Reactions at low temperatures show no indication of preferential retention of configuration, in contrast to the reactions of hydrogen halides with other alcohols such as α-phenylethanols[12] and 1,2-diphenylethanol.[13]

The lability of the halides in pentane was demonstrated in several experiments. If hydrogen halide was removed from any of the reaction mixtures and the residual pentane solutions were allowed to stand for periods of hours (bromides) or days (chlorides), substantial vapor pressures of hydrogen halide were developed. In one experiment hydrogen chloride was added to dimethylcyclopentene (−78° for 30 minutes). Hydrogen chloride was then pumped off and replaced by hydrogen bromide and the reaction vessel was sealed off and stored at 0° for three days. At the end of this time the flask was opened, the solution was washed with water and an aliquot was solvolyzed in ethanol.[5] Analysis of the data by the differential kinetic method[14,15] showed that only 8% of the residual halide was chloride, the rest had been converted to bromide.

Mechanism.—The experiments with hydrogen chloride and dimethylcyclopentene show that *trans* addition persists, even with a rigid substrate. Since hydrogen and chlorine are held far apart in the *trans*-chloride, it seems evident that out-of-plane, *trans* attack must have occurred. As has been pointed out previously,[2] such an attack may be visualized as being either completely concerted or as involving a π-complex as an intermediate (see eq. 3). In either case the product-determining step must involve some charge separation. Association of the ions being produced with hydrogen halide is consistent with the high-order kinetics reported by Mayo and Katz[16] for the reaction of hydrogen chloride with isobutene.



(3)

The reason for preferential *trans* attack is somewhat obscure. The phenomenon is no doubt stereoelectronic in origin and one is intuitively led to associate it with the well established steric preference for *trans* elimination in E_2 reactions. In both instances the transition state resembles an alkene double bond which is trying to maintain or establish its integrity and at the same time form or maintain bonds to two other groups. Perhaps the preference for *trans* orientation is due to minimization of electron–electron repulsion between the four electrons which are trying to bind the attached groups. The picture of the transition state arising from this view is essentially one in which one pair of electrons is left in the bonding π-orbital and a second pair is placed in the anti-bonding π-orbital and then both are partially drained off by the loosely-attached entering (or leaving) groups. The preferred configuration is then determined by the symmetry of the anti-bonding π-orbital.

Experimental

Materials.—Ethyl cyclopentanone-2-carboxylate was prepared by minor modification of published procedures[17] involving the Dieckmann reaction of diethyl adipate using excess sodium hydride with toluene as solvent. Yields averaged 75%. Ethyl 2-methylcyclopentanone-2-carboxylate was prepared by methylation of the sodium salt of ethyl cyclopentanone-2-carboxylate, formed from the ester and sodium hydride, with methyl iodide in benzene or toluene[18]; average yield 81%. The keto ester was decarboxylated[19] by refluxing with dilute hydrochloric acid in yields averaging 65%. After pilot runs, the entire sequence was carried out without isolation of products and gave an average yield of 45% of 2-methylcyclopentanone based upon diethyl adipate. The product was distilled through an 18-inch column packed with nichrome helices. The major fraction boiled at 135.0–139.0°, n^{20}D 1.4353. A further fraction, b.p. 139.0–142.0°, n^{20}D 1.434, had nearly an identical infrared spectrum, gave a semicarbazone, m.p. 167–170°, identical to that from the main fraction, and gave good yields when used in the following step. A mixture of 1,2-dimethylcyclopentanols was prepared from the reaction of 2-methylcyclopentanone with methylmagnesium chloride.[20] Yields with the chloride were much higher than those obtained with the other methyl Grignard reagents. Reaction in ether was carried out at the reflux temperature for 15–20 hours. The product mixture was hydrolyzed with saturated, aqueous ammonium chloride. Distillation gave the mixed alcohols in an average yield of 50%. The isomeric alcohols were separated by fractionation with either a 50-plate concentric tube column

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[11] T. D. Nevitt and G. S. Hammond, THIS JOURNAL, **76**, 4124 (1954).

[12] P. A. Levene and A. Rothen, *J. Biol. Chem.*, **127**, 237 (1939).

[13] D. Y. Curtin and D. B. Kellom, THIS JOURNAL, **75**, 6011 (1953).

[14] J. S. Fritz and G. S. Hammond, "Quantitative Organic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 158.

[15] The rate of solvolysis of the bromide is 60 times that of the chloride.[5]

[16] F. R. Mayo and J. J. Katz, THIS JOURNAL, **69**, 1339 (1947).

[17] M. van Rysselberge, *Bull. sci. acad. roy. Belg.*, [5] **12**, 171 (1926); G. Chiurdoglu, *Bull. soc. chim. Belg.*, **41**, 152 (1932); R. P. Linstead and E. M. Meade, *J. Chem. Soc.*, 935 (1934); and P. S. Pinkney, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1934, p. 116.

[18] M. van Rysselberge, ref. 17; F. H. Case and E. E. Reid, THIS JOURNAL, **50**, 3062 (1928); and G. Chiurdoglu, *Bull. soc. chim. Belg.*, **44**, 527 (1935).

[19] M. van Rysselberge, ref. 17; G. Chiurdoglu, *ibid.*, **41**, 152 (1932); F. H. Case and E. E. Reid, ref. 18; and J. B. Umland and M. I. Jefraim, THIS JOURNAL, **78**, 2788 (1956).

[20] M. van Rysselberge, ref. 17; and G. Chiurdoglu, *Bull. soc. chim. Belg.*, **44**, 527 (1935).

or a 20-plate spinning brush column. The *cis:trans* ratio in the mixture was 7:3, physical constants, *cis*-**1,2-dimethylcyclopentanol**, b.p. 59.5–61.0° at 17 mm., $n^{20}\mathrm{D}$ 1.4541; *trans*-**1,2-dimethylcyclopentanol**, b.p. 50.0–51.2° at 16 mm., $n^{20}\mathrm{D}$ 1.4506. The alcohol was dehydrated[21] by heating it with oxalic acid.[22] The alkene mixture was dried over barium oxide and distilled giving a mixture of dimethylcyclopentenes in 62% average yield. Gas chromatography showed that the mixture contained 90% 1,2-dimethylcyclopentene. Distillation with a spinning brush column gave **1,2-dimethylcyclopentene**, b.p. 103.2–104.0° at 740 mm., $n^{20}\mathrm{D}$ 1.4442, and **2,3-dimethylcyclopentene**, b.p. 96–99° at 740 mm., $n^{20}\mathrm{D}$ 1.4358. Gas chromatography showed that the lower boiling fraction was always contaminated with a small amount of the higher boiling isomer. Infrared spectra of none of the fractions showed terminal methylene absorption, indicating the absence of 2-methylmethylenecyclopentane.

1,2-Dimethylcyclopentene deteriorated rapidly on storage. After one month at room temperature gas chromatograms showed the appearance of substantial amounts of impurities, and the infrared spectrum showed many new bands, including carbonyl absorption. The deterioration was retarded, but not completely stopped, by storing the material in a refrigerator over barium oxide.

Hydrogen bromide, Matheson 99.9%, was condensed in the vacuum line and distilled once before use. ***n*-Pentane**, Phillips Pure Grade 99 mole per cent. minimum, was dried over sodium before use.

Sodium ethoxide solutions (2 *N*) were prepared by dissolving freshly cut sodium in reagent grade ethanol which had been purified by 24 hours reflux over sodium hydroxide followed by distillation.

Sodium *sec*-butoxide solutions (1*N*) were prepared by dissolving equimolar amounts of *sec*-butyl alcohol and freshly cut sodium in mesitylene. Reflux periods of 12–24 hours were necessary for complete reaction. Although the sodium alkoxide was not completely soluble at room temperatures, hot solutions could be transferred readily.

Procedures were essentially the same as those described by Hammond and Nevitt.[2] Hydrogen halide was introduced into the vacuum system and stored in a 1-liter storage bulb and in liquid air traps. The substrates, 1,2-dimethylcyclopentene or the alcohols, were dissolved in pentane, attached to the vacuum line in the reaction chambers and degassed. The temperature of the solution was adjusted to that desired and hydrogen halide was admitted by proper manipulation of stopcocks. After various reaction times the reaction mixtures were removed and usually poured into water. The pentane layer was separated and dried. In some experiments the reaction mixture was poured directly into a solution of sodium *sec*-butoxide in mesitylene. The amount of hydrogen halide absorbed by the pentane solutions was measured manometrically. The amounts were essentially the same in experiments carried out with different substrates at the same temperature. Since the amount of solvent was maintained constant, the result is due partly to the solubility of hydrogen halide in pentane. At 0° the amount absorbed was 1.5 millimoles of HBr (1.3 millimoles of HCl) per millimole of substrate, at −78° the amount was 4.6 millimoles of HBr (6.3 millimoles of HCl) per millimole of substrate and at −196° the amount was 18.7 millimoles of HBr (28.5 millimoles of HCl) per millimole of substrate.

During the addition of hydrogen bromide to 1,2-dimethylcyclopentene at 0° the solution became deep yellow almost immediately and, within 5 minutes, a small amount of insoluble, brown or black material deposited on the walls of the flask. These pentane-insoluble materials were water soluble. When the reaction was carried out at 25° the pentane solution rapidly became dark green and more than the usual amount of tarry material separated from the solution. The reactions with dimethylcyclopentanols showed similar behavior. When hydrogen bromide was admitted to the reaction cell at −196°, it crystallized above the frozen pentane solution. The liquid air trap was then replaced by a Dry Ice trap. Evidence of rapid reaction was noted when the hydrogen bromide began to melt. In runs begun at −78° a white solid separated immediately on introduction of the hydrogen bromide. The solid then became yellow and finally dissolved giving a yellow solution.

The addition of hydrogen chloride to 1,2-dimethylcyclopentene and the reaction of hydrogen chloride with the 1,2-dimethylcyclopentanols showed similar, although not so intense, color changes. At 0°, the solutions were initially cloudy, becoming light yellow with several small, light brown, water soluble deposits on the walls. Reactions at −78° and at liquid nitrogen temperatures were characterized by the immediate formation of a solid which slowly disappeared, leaving a yellow solution, again with small amounts of the brownish solid on the walls.

Elimination reactions in both ethanolic sodium hydroxide and mesitylene solutions of sodium *sec*-butoxide were carried out by adding 15 ml. of the reaction mixture to 50 ml. of the solution of base. Sodium halides began to precipitate immediately. The solutions were allowed to stand at room temperature for 24 hours or more and were then poured into a separatory funnel containing 25 ml. of water and 20 ml. of pentane. The pentane layer was washed twice with water, dried over anhydrous calcium sulfate and concentrated by distillation. The residues were then analyzed by gas chromatography.

Gas Chromatography.—Samples of olefin mixtures were chromatographed at 110°, using a 10 foot by 0.25 inch column with Apiezon L (40% on firebrick) as the liquid phase. The peaks for 1,2-dimethylcyclopentene and 2,3-dimethylcyclopentene were separated cleanly. Peak areas were calculated by triangulation[23] and used to calculate the relative amounts of 1,2-dimethylcyclopentene and 2,3-dimethylcyclopentene.

Controls.—Virtually all olefin mixtures produced by elimination in sodium ethoxide solution contained 91–93% 1,2-dimethylcyclopentene. Kinetic studies reported elsewhere[6] showed that unimolecular elimination probably accounted for a substantial amount of the reaction. "Spontaneous" elimination was studied by allowing a pentane solution of dimethylcyclopentyl bromide to stand at room temperature for 2 days. The solution became dark green and tar was deposited on the walls of the flask. The solution was washed with water, dried and concentrated. The residue was chromatographed, and the results showed that the composition of the alkene mixture was 79% 1,2-dimethylcyclopentene and 21% 2,3-dimethylcyclopentene. Alkene mixtures did not isomerize when treated with sodium *sec*-butoxide in mesitylene. Duplicate gas chromatographic analyses were reproducible to ± 1.5%.

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