carbodiimide in 100 ml. of dry 1-butanol was refluxed 120 hr. The reaction mixture was distilled to dryness. A 5-ml. aliquot of the distillate was allowed to react with 2,4-dinitrophenylhydrazine. A reddish-orange precipitate formed which after recrystallization from ethanol had m.p. 123–123.5°. A 5-ml. sample of 1-butanol gave no precipitate with 2,4-dinitrophenylhydrazine. The 2,4-dinitrophenylhydrazone obtained above showed melting point depressions when mixed with authentic samples of the 2,4-dinitrophenylhydrazones of acetone and *n*-butyraldehyde. The m.p. 123–123.5° compares favorably with those reported for the 2,4-dinitrophenylhydrazone of 2-ethyl-2-hexenal,[8,9] m.p. 123° and m.p. 124–125°. The ultraviolet spectrum in ethanol was identical to that reported in the literature.[8]

The residue obtained from the distillation was triturated with hexane to yield 7.3 g. (90%) of crude N-cyclohexylbenzamide. The amide was purified by crystallization from acetone–hexane to yield pure material, m.p. 147–148.5°.

The hexane extracts were evaporated to give a residue which was sublimed at 49° (bath) and 0.01 mm. By this procedure there was isolated 3.51 g. (44%) of *n*-butyl N-cyclohexylcarbamate which was crystallized from pentane m.p. 51.5–54°.

Anal. Calcd. for $C_{11}H_{21}NO_2$: C, 66.29; H, 10.62. Found: C, 66.50; H, 10.63.

***t*-Butyl Perbenzoate and N,N′-Dicyclohexylcarbodiimide in Isopropyl Alcohol.**—A solution of 3.88 g. (0.020 mole) of *t*-butyl perbenzoate and 4.12 g. (0.020 mole) of N,N′-dicyclohexylcarbodiimide in 50 ml. of isopropyl alcohol was refluxed for 98 hr. The isopropyl alcohol was removed by distillation and the residue was recrystallized from ethanol to yield 3.28 g. (81%) of N-cyclohexylbenzamide, m.p. 147–150°, no depression with an authentic sample.

A 5-ml. portion of the distillate yielded a yellow 2,4-dinitrophenylhydrazone, m.p. 120–123°. A mixed melting point determination with the 2,4-dinitrophenylhydrazone of acetone showed no depression.

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[8] E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, 498 (1945).

[9] S. G. Powell and D. A. Ballard, THIS JOURNAL, **60**, 1914 (1938).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF PURDUE UNIVERSITY]

Factors Influencing the Direction of Elimination in the Chugaev Reaction

BY ROBERT A. BENKESER AND JAMES J. HAZDRA

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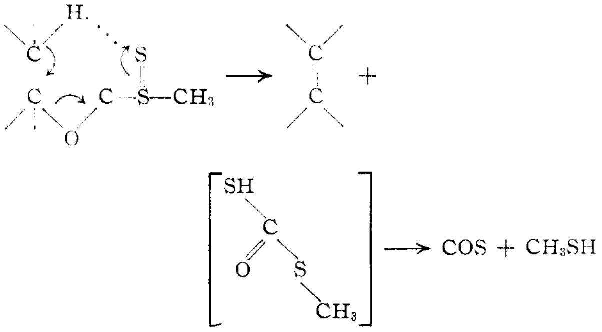
The xanthate esters of a series of 1-alkylcyclohexanols and alkylcyclohexylcarbinols were pyrolyzed (Chugaev reaction) and the resulting olefin mixtures analyzed by gas chromatography. In every instance isomers containing double bonds *exo* to the six-membered ring were disfavored. In two of the five eliminations studied, the system followed the Hofmann rather than the Saytzeff rule. In three cases, a primary or secondary hydrogen was removed, rather than the expected tertiary. It is concluded that the unifying feature underlying all of these reactions is the preferred formation of the more thermodynamically stable olefin. In this respect the Chugaev reaction closely resembles acetate pryolyses. In keeping with this observation (but contrary to published reports) it was noted that pyrolysis of 1-methylcyclohexylacetate produced a ratio of 1-methylcyclohexene/methylenecyclohexane of approximately 4. A very similar isomer distribution was noted when 1-methylcyclohexylcarbinol was dehydrated by the Chugaev procedure. Evidence is presented to indicate that steric factors are very likely of importance in controlling the direction of Chugaev elimination.

It is well known that acid-catalyzed dehydrations of alcohols frequently result in bond or group migrations.[1] This complication can be avoided if the alcohol is dehydrated *via* the Chugaev reaction,[2] which involves the thermal decomposition of its xanthate ester. Invariably this reaction proceeds by the preferential removal of hydrogen from an adjacent carbon atom, resulting in the formation of an unrearranged olefin.[3] The stereochemistry[4–6] of the Chugaev reaction has received much attention, and it is generally conceded that the preferred reaction path involves the elimination of a *cis*-hydrogen.[7] This observation, together with the demonstration of first-order kinetics,[8] lends credence to the belief the reaction proceeds by an intramolecular cyclic process.[9] However no systematic study has been made to determine how the nature of the hydrogen to be removed influences the course of the reaction. However, based upon rather numerous examples (but of widely different types of compounds), it now seems accepted that the preference for hydrogen removal in the Chugaev reaction[10] is 3° > 2° > 1°. Stated another way, the Saytzeff rule is normally followed in Chugaev eliminations. Curiously, the opposite sequence of hydrogen perference (*i.e.*, 1° > 2° > 3°) (Hofmann



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[1] E. E. Royals, "Advanced Organic Chemistry." Prentice–Hall Inc., New York, N. Y., 1954, p. 230.

[2] L. A. Chugaev, *Ber.*, **32**, 332 (1899), and subsequent papers.

[3] This fact seems well established despite a recent statement to the contrary (W. J. Bailey and J. J. Hewitt, *J. Org. Chem.*, **21**, 543 (1956)). A classic example of the utility of the Chugaev is the dehydration of pinacolyl alcohol to *t*-butylethylene (W. Fomin and N. Sochanski, *Ber.*, **46**, 244 (1913)). Acid dehydration of this compound leads to extensive rearrangement (F. C. Whitmore and H. S. Rothrock, THIS JOURNAL, **55**, 1106 (1933)).

[4] W. Hückel, W. Tappe and G. Legutke, *Ann.*, **543**, 191 (1940).

[5] D. J. Cram, THIS JOURNAL, **71**, 3883 (1949).

[6] E. R. Alexander and A. Mudrak, *ibid.*, **72**, 1810, 3194 (1950).

[7] See F. G. Bordwell and P. S. Landis, *ibid.*, **80**, 2450 (1958), where an interesting example of a *trans* elimination is disclosed.

[8] G. L. O'Connor and H. R. Nace, *ibid.*, **74**, 5454 (1952); **75**, 2118 (1953).

[9] P. G. Stevens and J. H. Richmond, *ibid.*, **63**, 3132 (1942).

[10] J. A. Mills, *J. Chem. Soc.*, 260 (1953); see also "Steric Effects in Organic Chemistry," edited by M. S. Newman, John Wiley and Sons, Inc., New York, N. Y., 1956, p. 313.

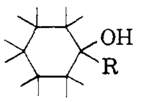
TABLE I

PHYSICAL CONSTANTS OF THE ALKYLCYCLOHEXANOLS AND ALKYLCYCLOHEXYLCARBINOLS[a]

Compound	Yield, %	Constants (this paper) B.p. °C.	Mm.	$n^{20}\text{D}$	Reported constants B.p. °C.	Mm.	$n^{t}\text{D}$	t, °C.
1-Methylcyclohexanol	71	63–64	20	1.4606	56.5	10[b]	1.4610[b]	20
1-Ethylcyclohexanol	65	78–79	20	1.4640	78	20[b]	1.4642[b]	20
1-Isopropylcyclohexanol	37	76–78	10	1.4683	76–79	10[c]	1.4683[c]	19
Methylcyclohexylcarbinol	51	82–83	12	1.4658	82	12[d]	1.4635[d]	25
Dimethylcyclohexylcarbinol	46	85–86	14	1.4695	85–86	14[e]	1.4720[e]	12

[a] In every case the alcohols in this table were prepared by methods described in the literature. Each of these literature sources is listed in the column "Reported Constants." [b] W. A. Mosher, THIS JOURNAL, **62**, 552 (1940). [c] K. Auwers and P. Ellinger, *Ann.*, **387**, 200 (1912). [d] P. Sabatier and A. Mailhe, *Compt. rend.*, **139**, 344 (1904). [e] P. Sabatier and A. Mailhe, *Bull. soc. chim.*, **33**, 74 (1905).

rule) has been claimed for acetate pyrolysis,[11] despite the fact that this reaction, like the Chugaev, is thought to proceed through an intramolecular cyclic process.[12,13] In the hope of resolving this puzzling discrepancy, it was decided to investigate the xanthate pyrolysis of a closely related series of alcohols (Table I), consisting of 1-alkylcyclohexanols (I) and alkylcyclohexylcarbinols (II).



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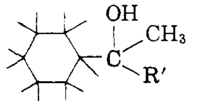
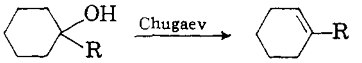


II

Since the Chugaev reaction does not result in rearrangements,[3] only two possible olefins can form from each dehydration. It will be noted that, in each of the five alcohols (Table I) chosen for study, one of these two possible olefins would have a double bond *exo* to the six-membered ring. Since such a situation is often thermodynamically disfavored,[14] this series of eliminations provides a severe test for the generalization that the Chuagev reaction normally obeys the Saytzeff rule.

1-Alkylcyclohexanols.—It will be seen from Table II that all three alkylcyclohexanols, when subjected to xanthate pyrolysis, gave a mixture of olefins, the preponderant component being a 1-alkylcyclohexene.



It should be noted, however, that in the case of 1-isopropylcyclohexanol a secondary hydrogen was removed in preference to a tertiary, a mode of elimination contrary to the presently accepted concept. In all three cases the more thermodynamically stable olefin was formed (see isomerization experiments).

There are two points of experimental procedure worthy of mention in connection with the 1-alkylcyclohexanols. In no case were the xanthate esters isolated, since they proved to be quite thermally unstable. In order to be certain, however, that the olefin mixtures were indeed arising from pyrolysis of the xanthate esters and not perhaps from the dehydration of unreacted alcohol, an infrared spectrum of the crude reaction mixture was taken just prior to pyrolysis. In every case there was less than 5% free alcohol remaining at this point.

TABLE II

XANTHATE PYROLYSES OF ALCOHOLS CONTAINING THE CYCLOHEXANE RING

Compound	Yield of olefin, %	B.p. of olefin mixt., °C.	Temp., °C., xanthate pyrolysis	% *exo* isomer[d,e]
1-Methylcyclohexanol	49	100–110	200	21
1-Ethylcyclohexanol	52	133–136	200	12
1-Isopropylcyclohexanol	46[a]	151–165	100	22
Methylcyclohexylcarbinol	52[a]	125–135	250[b]	38
Dimethylcyclohexylcarbinol	51	151–155	150[c]	21

[a] In this case the Chugaev was also run employing the Whitmore modification, *i.e.*, sodium hydroxide, rather than potassium, was used to form the salt of the alcohol. No essential difference in yield or isomer distributions of the olefin were noted. [b] The xanthate ester was actually isolated by fractionation in this instance (57% yield) prior to its pyrolysis. Its physical constants were b.p. 124–126° (2 mm.), $n^{20}\text{D}$ 1.5440. [c] The xanthate ester was isolated by fractionation (57% yield) prior to its pyrolysis. It boiled at 57–59° (0.1 mm.). [d] The values listed indicate what percentage of the total olefin obtained contained the double bond *exo* to the ring. The difference between these values and 100% would represent the percentage of the total olefin which constitutes the other possible isomer. [e] These values were obtained by gas chromatography employing fire brick (C22)-impregnated with either tri-*m*-tolyl phosphate or di-*n*-butyl phthalate.

In the case of 1-isopropylcyclohexanol (and also with methylcyclohexylcarbinol) the Chugaev procedure was repeated using a modification suggested by Whitmore.[15] In this case the alkoxide was prepared by equilibrating the alcohol with finely powdered sodium hydroxide rather than by using potassium metal directly. In the two cases where this modification was employed, no appreciable difference in olefin yield or isomer distribution was noted.

At one point in the investigation, it was deemed desirable to obtain an authentic sample of methylenecyclohexane so that its retention time could be measured by gas chromatography. Since this compound was reported (56% yield) as the sole product of the pyrolysis of 1-methylcyclohexylacetate at 450°,[16] this method of preparation seemed ideal. Unfortunately, however, the method failed in our hands. We attempted the pyrolysis at four dif-

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(11) See W. J. Bailey and C. King, Abstracts of the 122nd Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1952, p. 3M; W. J. Bailey and C. King, *J. Org. Chem.*, **21**, 858 (1956).

(12) C. D. Hurd and F. H. Blunck, THIS JOURNAL, **60**, 2419 (1938).

(13) The recent elegant work of DePuy and Leary (*ibid.*, **79**, 3705 (1957)) has demonstrated that, at least in some cases of acetate pyrolysis, relative hydrogen acidities are unimportant. The elimination in the cases studied proceeded so as to form the more thermodynamically stable olefin.

(14) H. C. Brown, J. H. Brewster and H. Shechter, THIS JOURNAL, **76**, 467 (1954).

(15) F. C. Whitmore and C. T. Simpson, *ibid.*, **55**, 3809 (1933).

(16) W. J. Bailey, J. J. Hewitt and C. King, *ibid.*, **77**, 357 (1955).

ferent temperatures (see Table III), but in every instance analysis by gas chromatography showed a ratio of 1-methylcyclohexene/methylenecyclohexane of approximately 4. Thus, in the case of 1-methylcyclohexanol at least, both the Chugaev and acetate pyrolysis give amazingly similar isomer distributions. The latter reaction, in complete accord with the findings of DePuy,[13] seems governed by the stability of the final olefin and *not* by any particular hydrogen preference.

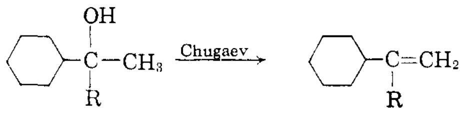
TABLE III

PYROLYSIS OF 1-METHYLCYCLOHEXYL ACETATE

Temp., °C.	Yield,[a] %	% *Exo* isomer[b,c]	B.p. of olefin mixt., °C.
250	17; 16	18	95–110
350	87; 81.5	23	100–118
430	88; 81	22	100–110
500	92; 90	19.5	101–108

[a] The first value is the yield based upon titration of the acetic acid produced in the pyrolysis. The second value is the yield based on the actual weight of olefin obtained. [b] The values listed indicate what percentage of the total olefin obtained was methylene-cyclohexane. The remainder was *endo* isomer—1-methylcyclohexene. [c] These values were obtained by gas chromatography employing fire brick (C-22) impregnated with tri-*m*-tolyl phosphate as the packing.

Alkylcyclohexylcarbinols.—Both methylcyclohexylcarbinol and dimethylcyclohexylcarbinol (see Table II) were dehydrated by the Chugaev reaction, and again an olefin mixture was obtained. This time, however, the predominant isomer had the double bond in the terminal position. These two examples are particularly interesting, since in both cases the Hofmann rather than Saytzeff rule is being followed, and in both cases a primary hydrogen is removed in preference to a tertiary.



R = H; CH_3

Discussion

It will be noted that in the five examples of the Chugaev reaction studied, there is one underlying feature all have in common. In every case the reaction proceeds so as to avoid forming a bond *exo* to the six-membered ring. In at least two cases it achieves this by proceeding in accord with the Hofmann rather than the Saytzeff rule, and in three cases it proceeds opposite to the accepted order for hydrogen removal ($3^\circ > 2^\circ > 1^\circ$). The only unifying feature in these five cases is that the more thermodynamically stable olefin predominates. It has been suggested that steric considerations constitute the ultimate reason why bonds *exo* to six-membered rings are disfavored.[14,17] If true, our results would indicate that steric factors play an important role in controlling the direction of elimination in xanthate pyrolyses. Additional evidence pointing in this direction can be gleaned from our results with methyl- and dimethylcyclohexylcarbinol (Table II) wherein the amount of *exo* isomer formed is less in the latter case. Steric interaction between the two methyl groups in dimethylcyclohexylcarbinol and adjacent axial hydrogens probably prevent the xanthate grouping from becoming *cis* and planar with the 3° hydrogen in the cyclic transition state. Since removal of 1° hydrogens from the two methyl groups is not so hindered, the rate of the latter reaction is faster. Additional work designed to demonstrate the influence of steric factors on the Chugaev reaction is presently under way in our laboratory.

The isomer distributions obtained in the five reactions studied do not represent equilibrium distributions. To demonstrate this point, a representative series of olefins (Table IV) which form as products in the various reactions were refluxed 24 hours in a glacial acetic acid solution containing catalytic amounts of *p*-toluenesulfonic acid. In every case (see Table IV) the olefins were isomerized almost completely to 1-alkylcyclohexenes, in agreement with the observations of Turner.[17]

TABLE IV

ISOMERIZATION OF VARIOUS OLEFINS UNDER THE CATALYTIC INFLUENCE OF *p*-TOLUENESULFONIC ACID

Starting olefin	% *endo* Isomer after 24 hr.
Methylenecyclohexane (87%)	98
1-Methylcyclohexene	100
Cyclohexylethylene	96
1-Isopropylcyclohexene	100
44%-Isopropylidenecyclohexane 56%-2-Cyclohexylpropylene	94

Generally speaking, our results are in accord with the findings of De Puy[13] on acetate pyrolysis, and have the consoling feature of thus providing a uniform viewpoint for these two reactions. It is of interest that the earlier generalization concerning the preferential removal of tertiary hydrogens during xanthate pyrolysis is, by coincidence, often true, since this type of hydrogen abstraction will lead frequently to the more thermodynamically stable of two possible olefin products. Thus pyrolysis of the xanthate ester of menthol results (by tertiary hydrogen removal) in a 70% yield of Δ^3-*p*-menthene[4] (a compound which is very likely more thermodynamically stable than Δ^2-*p*-menthene).

Experimental

Preparation of Alcohols.—All the alcohols employed in this study were prepared by known literature methods. Table I lists the physical constants, yields and literature sources for these alcohols.

Preparation and Pyrolysis of 1-Alkylcyclohexyl-S-methyl Xanthates.—The 1-alkylcyclohexanol (0.175 to 0.36 mole) was added to an equivalent amount of potassium suspended in 150–250 ml. of pure toluene or *p*-cymene at 65°. The mixture was stirred for two hours. Anhydrous ethyl ether (300–600 ml.) was added along with an equivalent amount of carbon disulfide. During this addition the temperature was kept below 40°. The mixture was stirred overnight and an equivalent amount of methyl iodide was added dropwise, after which the entire mixture was stirred for another 24 hours. It was then filtered and the ether removed *in vacuo*. Infrared spectra of the solutions at this point showed less than 5% of the free alcohol remaining.

The xanthate esters were pyrolyzed between 100–200°. The olefins were distilled off as they formed and were redistilled from sodium (it was demonstrated that such treatment did not result in isomerization). The isomeric olefin mixtures were analyzed by gas chromatography. The particular retention time of each olefin was identified by comparison with authentic samples whose structures were verified by ozonolysis. Table II lists the results of these pyrolyses.

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(17) R. B. Turner and R. H. Garner, THIS JOURNAL, **80**, 1424 (1958).

Preparation and Pyrolysis of Alkylcyclohexylcarbinyl-S-methyl Xanthates.—Generally these xanthates were prepared by the same method described above for the 1-alkylcyclohexyl-S-methyl xanthates. In these cases, however, the xanthates were actually isolated and purified by fractionation prior to pyrolysis (see Table II). The dimethylcyclohexylcarbinyl-S-methyl xanthate was prepared by the Whitemore[15] modification. In this variation the salt of the alcohol is obtained through the use of finely divided sodium hydroxide rather than potassium (see Table II).

Preparation and Pyrolysis of 1-Methylcyclohexyl Acetate.—1-Methyl-cyclohexyl acetate was prepared by a method similar to that described for the preparation of *t*-butyl benzoate.[18] Pure acetyl chloride (0.22 mole) was added slowly to equimolar amounts of 1-methylcyclohexanol and dry pyridine at 0°. The mixture was allowed to stand overnight, then washed with ice-water, and extracted with ethyl ether. The ether solution was dried over clacium sulfate. Subsequently the solvent was removed *in vacuo*. The acetate was obtained in 47% yield after distillation from a Todd column, b.p. 60–61° (8 mm.), $n^{20}\mathrm{D}$ 1.4402 (reported constants[19] b.p. 182–187°, $n^{18}\mathrm{D}$ 1.4386.)

Anal. Calcd. for $C_9H_{16}O_2$: C, 69.25; H, 10.25. Found: C, 69.00; H, 10.31.

The acetate (14 g.) was pyrolyzed according to the procedure of Bailey[16] at four different temperatures. The pyrolysis product in each case was washed free of acetic acid with distilled water. The washings were combined and an aliquot was titrated with standard base (see Table III).

Identification of Olefins. Xanthate Pyrolysis of Dimethylcyclohexylcarbinol.—Dimethylcyclohexyl-carbinol was dehydrated with iodine.[20] Of the olefin obtained, 35% was isopropylidenecyclohexane (b.p. 163°, $n^{20}\mathrm{D}$ 1.4720) and 65% was pure 2-cyclohexylpropylene (b.p. 151°, $n^{20}\mathrm{D}$ 1.4586). The constants reported[21] for the former compound were b.p. 164°, $n^{20}\mathrm{D}$ 1.4728.

The 2-cyclohexylpropylene (0.5 g.) was treated with ozone in 50 ml. of methylene dichloride. After hydrolysis, and working up in the usual fashion, a 2,4-dinitrophenylhydrazone was prepared. After crystallization from ethanol it melted at 140° (in agreement with the literature value[22] for methyl cyclohexyl ketone). The infrared spectrum of this olefin showed strong absorption at 6.2 and 11.2 μ, thus confirming the presence of a non-vinyl terminal olefin.[23]

Anal. Calcd. for $C_{14}H_{18}N_4O_4$: C, 54.90; H, 5.89; N, 18.3. Found: C, 54.76; H, 5.98; N, 18.00.

By gas chromatography, the retention time for the above sample of 2-cyclohexylpropylene was found to be identical to that of the component comprising 80% of the mixture obtained from the xanthate pyrolysis of dimethylcyclohexylcarbinol. Ozonolysis of the latter mixture, and the preparation of a 2,4-dinitrophenylhydrazone from the hydrolysate produced a dinitrophenylhydrazone of methyl cyclohexyl ketone.

An authentic sample of isopropylidenecyclohexane (obtained from the iodine dehydration described above) was ozonized, and a 2,4-dinitrophenyl-hydrazone of the hydrolysate gave no melting point depression with authentic 2,4-dinitrophenylhydrazone of cyclohexanone. The retention time (gas chromatography) of this authentic isopropylidenecyclohexane was identical to that of the component comprising 20% of the olefin mixture obtained from the xanthate pyrolysis of dimethylcyclohexylcarbinol (see Table II).

Xanthate Pyrolysis of Methylcyclohexylcarbinol.—Fractional distillation of the olefin mixture obtained from the xanthate pyrolysis of methyl-cyclohexylcarbinol gave a pure olefin (gas chromatography yielding only one peak) boiling at 127–128° ($n^{20}\mathrm{D}$ 1.4470). Ozonolysis of this material and the preparation of a benzylthiouronium salt from the hydrolysate produced a compound melting at 160.5°, which gave no melting point depression with the benzylthiouronium salt of cyclohexylcarboxylic acid. Thus the olefin was cyclohexylethylene. This conclusion was corroborated by the infrared spectrum of this material which showed strong absorption bands at 6.2, 10.95 and 11.2 μ which are characteristic of a vinyl terminal olefin.

The other olefin fraction from the distillation had an identical retention time to one of the products obtained from the pyrolysis of 1-ethylcyclohexyl-S-methyl xanthate. Since no rearrangements occur this material must be ethylidenecyclohexane.

Xanthate Pyrolysis of 1-Isopropycyclohexanol.—Fractional distillation of the olefin product produced pure 1-isopropylcyclohexene (one peak by gas chromatography) boiling at 154–156° ($n^{20}\mathrm{D}$ 1.4590). The reported constants[21] are b.p. 156°, $n^{20}\mathrm{D}$ 1.4593. The other olefin had the identical retention time of authentic isopropylidenecyclohexane (see above).

Xanthate Pyrolysis of 1-Ethylcyclohexanol.—Fractionation of the olefin mixture yielded pure 1-ethylcyclohexene (gas chromatography) boiling at 136° ($n^{20}\mathrm{D}$ 1.4562). Ozonolysis of this cut yielded a material which gave a qualitative test for *both* an acid and a ketone. The reported constants[21] for 1-ethylcyclohexene are: b.p. 136°, $n^{20}\mathrm{D}$ 1.4563. The other olefin fraction had the same retention time as ethylidenecyclohexane produced in the pyrolysis of ethylcyclohexyl-S-methyl xanthate.

Xanthate and Acetate Pyrolysis of 1-Methylcyclohexanol.—Fractionation of the olefin mixture obtained from the pyrolysis of the xanthate yielded a material boiling at 101–102° ($n^{20}\mathrm{D}$ 1.4502). The reported[21] constants for methylenecyclohexane are b.p. 104°, $n^{20}\mathrm{D}$ 1.4502. This fraction showed strong absorption in the infrared at 6.15 and 11.25μ (non-vinyl terminal olefin) and upon ozonolysis yielded a 2,4-dinitrophenylhydrazone which gave no depression in melting point when admixed with the same derivative prepared from cyclohexanone. Gas chromatography indicated this fraction (*i.e.*, b.p. 101–102°) was 87% pure.

The second fraction from the distillation boiling at 108° ($n^{20}\mathrm{D}$ 1.4500) proved to be pure 1-methylcyclohexene. The reported[21] constants for this material are b.p. 109° $n^{20}\mathrm{D}$ 1.4497.

Isomerization Experiments.—Samples (1.0 g.) of methylenecyclohexane, 1-methylcyclohexene, cyclohexylethylene, 1-isopropylcyclohexene and a mixture containing 56% 2-cyclohexylpropylene and 44% isopropylidene cyclohexane were dissolved in 2-ml. portions of glacial acetic acid containing a catalytic amount of *p*-toluenesulfonic acid. Each was refluxed for 24 hr. The olefin was separated from acetic acid by water dilution and analyzed by gas chromatography (see Table IV for results). The use of ethanol and sulfuric acid as the isomerizing agent caused extensive polymerization.

Control Experiments.—Samples of olefins were passed through a pyrolysis tube at 430° and subsequently analyzed by gas chromatography. No change in olefin composition was detected. Similar samples were also refluxed with sodium and ethanol for 30 hr. The mixtures were washed with water and the olefins extracted and analyzed by gas chromatography. Again no change in olefin compositions was detected.

Lafayette, Ind.

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[18] J. F. Norris and G. W. Rigby, This Journal, **54**, 2088 (1932).

[19] W. Ipatiew and N. Matow, *Ber.*, **45**, 3217 (1912).

[20] W. A. Mosher, This Journal, **62**, 552 (1940).

[21] K. Auwers and P. Ellinger, *Ann.*, **387**, 200 (1912).

[22] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd ed., J. Wiley and Sons, Inc., New York, N. Y., 1948, p. 262.

[23] H. Gilman, "Treatise of Organic Chemistry," Vol. III, J. Wiley and Sons, Inc., New York, N. Y., 1953, p. 144.