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Rearrangement. IV.[1] Pyrolysis and Acetolysis of Some Sulfonic Esters

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The pyrolysis of cyclohexanemethyl methanesulfonate and 1-methylcyclohexanemethyl *p*-toluenesulfonate has been investigated, yielding predominantly rearranged cycloalkenes, with lesser amounts of cycloalkanes. The experiments support the suggestion that the pyrolysis may proceed, at least in part, through a free radical process. The methanesulfonic ester, on acetolysis in a 50% aqueous acetic acid solution, gave rearranged-unrearranged cycloalkenes and alcohols, and an unrearranged acetate, whereas the *p*-toluenesulfonic ester gave exclusively rearranged cycloalkenes, alcohols and acetates.

The availability of a *cis*-β-hydrogen in cyclohexanemethyl derivatives of acids or amines suggests that the pyrolysis of these compounds could involve a cis elimination,[2] giving predominantly methylenecyclohexane. Indeed, the pyrolysis of cyclohexanemethyl acetate[3] and *N*, *N*-dimethylcyclohexanemethylamine oxide[3,4] gave exclusively methylenecyclohexane; in contrast, however, cyclohexanemethyl borate[5] underwent pyrolytic change, chiefly into rearranged cycloalkenes, the formation of which was interpreted in terms of a carbonium ion-type rearrangement. Previous work in this

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[1] Part III: R. Kotani, *J. Chem. Eng. Data*, **11**, 248 (1966).

[2] G. H. DePuy and R. W. King, *Chem. Revs.*, **60**, 431 (1960).

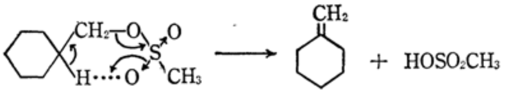
[3] H. E. Baumgarten, F. A. Bower and T. T. Okamoto, *J. Am. Chem. Soc.*, **79**, 3145 (1957).

[4] A. C. Cope, C. L. Bumgardner and E. E. Schweizer, ibid., **79**, 4729 (1957).

[5] O. L. Chapman and G. W. Borden, *J. Org. Chem.*, **26**, 4193 (1961).

series⁶⁾ has shown that the pyrolysis of cyclohexanemethyl *p*-toluenesulfonate (I) at 200°C under reduced pressure gave predominantly rearranged cycloalkenes. The saturated hydrocarbon methylcyclohexane was also formed in a fairly high yield, whereas it was not mentioned as a pyrolytic product of the above acetate, amine oxide or borate. The nature of the pyrolysis of the sulfonate, however, remained to be determined, and such is the purpose of the present study.

Cyclohexanemethyl methanesulfonate (II) was pyrolyzed in the manner described earlier for I. No solvent was used. The crude product was analyzed by gas chromatography. Each component was separated by preparative-scale gas chromatography and identified by comparing its relative retention time and NMR spectrum with those of an authentic sample. The products were methylcyclohexane, 1-methylcyclohexene, 3-methylcyclohexene, methylenecyclohexane, cycloheptene, and cyclohexene. Except for the absence of toluene⁷⁾ the product composition was essentially the same as that obtained from I.

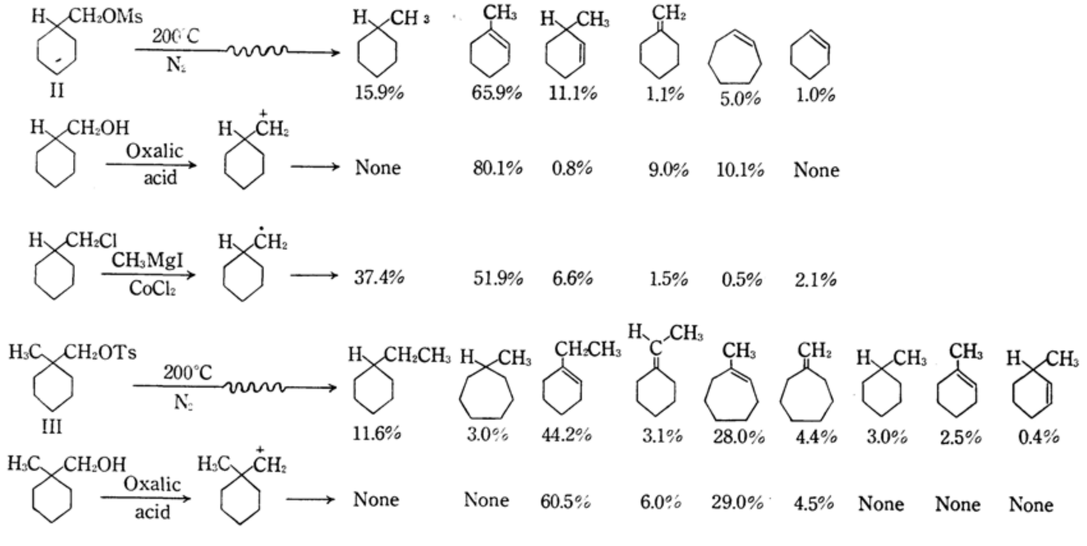


IV

It would not be unreasonable to expect that II might decompose predominantly, with the elimination of a *cis*-β-hydrogen through a quasi, six-membered ring (IV) as a transition state,⁸⁾ to give methylenecyclohexane, as has been observed in the runs with the acetate and amine oxide. That it does not do so is, however, evident from a consideration of the following facts: (1) the relative yield of methylenecyclohexane was only 1.1%; (2) rearranged cycloalkenes predominated (82.0%), and (3) a control experiment showed that the isomerization of exocyclic to endocyclic double bonds scarcely occurred under the experimental conditions employed.

1-Methylcyclohexanemethyl *p*-toluenesulfonate (III) was selected for study because it has no β-hydrogen for any possible participation in a cis elimination mechanism. Since III is a neoalkyl type of ester, it was expected that its pyrolysis would involve a complicated rearrangement of the carbon skeleton. Indeed, this was found. The product was separated into six fractions by preparative-scale gas chromatography; each fraction was characterized as has been described above under II. The products were methylcyclohexane, ethylcyclohexane, methylcycloheptane, 1-ethylcyclohexene, ethylidenecyclohexane, 1-methylcycloheptene, methylenecycloheptane, 1-methylcyclohexene, 3-methylcyclohexene, and an unidentified saturated compound (1.7%).⁹⁾

The dehydration of cyclohexanemethanol and 1-methylcyclohexanemethanol was carried out at 150°C in the presence of oxalic acid to obtain an indication of the product ratios in a simple carbonium ion reaction. The dehydration of cyclohexanemethanol¹⁰⁾ gave 1-methylcyclohexene, 3-



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6) R. Kotani and S. Satoh, ibid., **30**, 3245 (1965).

7) The nonformation of toluene with II, but its formation with III, support the previous conclusion⁶⁾ that it arose from the *p*-toluenesulfonate group.

8) C. D. Hurd and F. H. Blunk [*J. Am. Chem. Soc.*, **60**, 2419 (1938)] first proposed a cyclic, concerted mechanism for stereospecific cis elimination.

9) A small amount of toluene was also formed. It obviously arose from the *p*-toluenesulfonate group, as has been discussed elsewhere.⁶⁾

10) Chapman and Borden⁵⁾ reported that the dehydration of cyclohexanemethanol at 135°C in the presence of oxalic acid gave 1-methylcyclohexene (82.2%), methylenecyclohexane (10.2%), and cycloheptene (7.6%).

methylcyclohexene, methylenecyclohexane and cycloheptene, while that of 1-methylcyclohexanemethanol gave 1-ethylcyclohexene, ethylidenecyclohexane, 1-methylcycloheptene and methylenecycloheptane. No saturated hydrocarbon was formed from either alcohol; its nonformation was in contrast to its formation in the pyrolysis of the sulfonic esters.

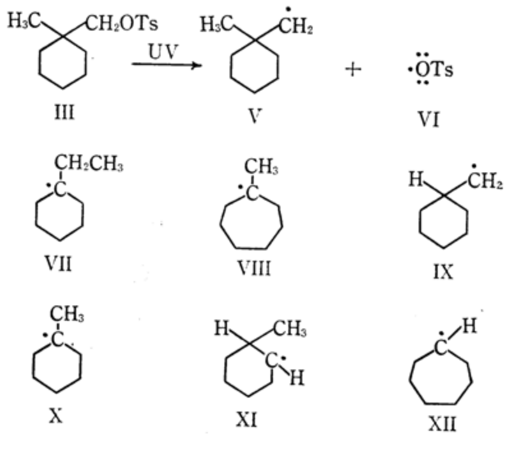
A carbonium ion mechanism would account readily for the formation of cycloalkenes; it may, indeed, account for many of these products. It is questionable, however, if a carbonium ion intermediate participates in the formation of the observed cycloalkanes (16—20% yields), since this would require the unreasonable assumption of the abstraction of hydride ions from some other part of the reacting system.[6] The latter conclusion is supported experimentally by the absence of acetylenes or dienes in the products and by the nonformation of the cycloalkanes during the dehydration of the alcohols with oxalic acid.

The cycloalkanes could be explained readily by way of a radical mechanism; this idea was next explored. Some pyrolytic elimination reactions suggestive of or proceeding through a radical-chain process have been reported,[8,11] namely, the pyrolysis of carboxylic esters with no β-hydrogen and certain sorts of xanthates and sulfoxides.

The reaction of cyclohexanemethyl chloride with methylmagnesium iodide in the presence of cobalt(II) chloride was carried out in order to obtain an indication of the product ratios in a simple free radical process.[12] This reaction gave methylcyclohexane, 1-methylcyclohexene, 3-methylcyclohexene, methylenecyclohexane, cycloheptene, and cyclohexene. This composition was virtually the same as those obtained from I and II.

In an attempt to learn if free radicals participated in the present reactions, I, II and III were heated in the presence of a free radical inhibitor, and then in that of a free radical initiator. The addition of *p*-benzoquinone to I or II caused a change in the ratio of cycloalkane to cycloalkene (approximately 1 : 6.8 and 1 : 8.5 compared to 1 : 3.7 and 1 : 5.3, respectively), and also a decrease in the yield of the product (it was reduced by approximately 30% in both instances). The addition of *p*-benzoquinone to III exerted no appreciable influence on the product composition, but caused a decrease in its yield (approximately a 40% decrease). The decrease in yield and the change in product composition suggest that the free radicals formed would partially be trapped by the quinone. I, II or III, when heated with benzoyl peroxide at 100—105°C for a few minutes, yielded small amounts of cycloalkenes and cycloalkanes, whereas heating the sulfonic ester alone under the same conditions gave no product. No free radical chain reaction, however, was initiated by the addition of benzoyl peroxide.

III was selected for electron spin resonance (ESR) study because the nonavailability of a β-hydrogen would make its ESR spectrum simple. III was irradiated with ultraviolet rays for 1 hour at room temperature, and then it was cooled by liquid nitrogen. The ESR spectrum of its primary product showed a triplet with a relative intensity ratio of about 1 : 2 : 1. The spectrum suggests a free radical whose unpaired electron interacts equally with two protons; it was identified as the free radical V. The supperposed spectrum appearing in the central peak of V may be due to the free radical VI. When the irradiated III was taken out of the liquid nitrogen and kept at room temperature for a few minutes, the triplet spectrum changed into a poorly-resolved complex spectrum consisting of 15 hyperfine lines. The ESR spectrum of the free radical VII may consist of 7 hyperfine lines, and that of the free radical VIII, of 8 hyperfine lines. The observed change in the ESR spectrum suggests the rearrangement of the less stable primary free radical, V, to the more stable tertiary free radicals, VII and VIII. The above ESR study also suggests indirectly, if not directly, the fate of the primary product of the pyrolysis of III.



III V VI

VII VIII IX

X XI XII

The experimental data described above support the suggestion that the pyrolysis of I, II and III proceeds, at least in part, through a free radical process. I and II, on pyrolysis, would give a presumably less stable primary free radical (IX), which would predominantly rearrange to a presumably more stable tertiary free radical (X) by a 1, 2-hydrogen shift. Part of IX would give

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11) a) E. M. Bilger and H. Hibbert, *J. Am. Chem. Soc.*, **58**, 823 (1936); b) C. A. Kingsbury and D. J. Cram, ibid., **82**, 1810 (1960); c) H. R. Nace, D. G. Manly and S. Fuso, *J. Org. Chem.*, **23**, 687 (1958); d) D. G. Botteron and G. P. Shulman, ibid., **27**, 2007 (1962).

12) M. S. Kharasch and W. H. Urry [*J. Org. Chem.*, **13**, 101 (1948)] investigated the reaction of alkylmagnesium halides with alkyl halides in the presence of cobalt(II) chloride.

methylenecyclohexane by the loss of a hydrogen. X would lose a hydrogen, thus yielding 1-methylcyclohexene and methylenecyclohexane, the former predominating. Part of X would subsequently rearrange to a presumably less stable secondary free radical (XI) through a 1, 2-hydrogen shift, which by the loss of hydrogen would yield 1-methylcyclohexene and 3-methylcyclohexene. The abstraction of hydrogen by IX, X or XI would give the saturated hydrocarbon methylcyclohexane. Another secondary free radical (XII) would also come from IX, but by ring enlargement rather than by hydrogen shift, and it would lead to cycloheptene. The primary product of III on pyrolysis would be the presumably less stable primary free radical V, which would subsequently rearrange to the presumably more stable tertiary free radicals, VII and VIII; this would be followed by the loss of hydrogen atoms, leading to the formation of the corresponding unsaturated hydrocarbons. The abstraction of hydrogen atoms by VII and VIII would yield the corresponding saturated hydrocarbons.

The acetolysis of II, III and 1-methylcyclohexanemethyl methanesulfonate (XIII) was carried out in a 50% aqueous acetic acid solution containing catalytic amounts of sodium acetate at reflux temperatures. From II there was formed 1-methylcyclohexene (27.3%), 3-methylcyclohexene (0.5%), methylenecyclohexane (0.5%), cycloheptene (1.5%), 1-methylcyclohexanol (15%), cyclohexanemethanol (7.0%), cycloheptanol (3.6 %), cyclohexanemethyl acetate (44.2%), and 1-methylcyclohexyl acetate (a trace). Bly and Dryden13) have reported that II, when acetolyzed in the presence of acetic anhydride and an excess of sodium acetate, gave exclusively the unrearranged cyclohexanemethyl acetate, free from any cycloalkenes, alcohols or rearranged acetates. In contrast to this, the addition of water to the solvolysis system of II caused the formation of rearranged-unrearranged cycloalkenes and alcohols in about 30 and 26% yields. The formation of alcohols may be expected from the fact that water is much more nucleophilic than acetic acid.14) The rearranged alcohols may be formed through rearrangement of the unstable primary carbonium ion initially formed to the more stable tertiary or secondary carbonium ions. The formation of the rearranged alcohols from the corresponding cycloalkenes and water in the presence of an acid may not be negligible.15) The predominance of 1-methylcyclohexene among the cycloalkenes formed may be due to the relative stabilities of carbonium ions involved and to the acid-catalyzed exocyclic-endocyclic olefin isomerization. The experimental conditions used are quite favorable to such an isomerization.15) No explanation is, however, apparent to account for cycloalkene formation in the presence of water, but its failure to be formed in the absence of water. It seems unlikely that the unrearranged acetate (44%) arose predominantly from the cyclohexanemethyl carbonium ion, because the unstable primary carbonium ions would mainly rearrange to the more stable tertiary or secondary carbonium ions, as evidenced by the formation of the rearranged alcohols (rearranged: unrearranged=2.7 : 1). The absence of rearranged acetate is in keeping with this suggestion. In view of these facts, the most probable conclusion is that two processes are competitively operative in the acetolysis of II under the conditions employed: (1) the S_N1 reaction, followed by rearrangement and elimination, and (2) the S_N2 displacement of the methanesulfonate group by solvents.

The products from III and XIII had essentially the same product composition; the products were 1-ethylcyclohexene (42.2 and 44.6%), ethylidenecyclohexane (1.3 and 0.6%), 1-methylcycloheptene (38.9 and 40.1%), methylenecycloheptane (1.3 and 1.4%), 1-ethylcyclohexanol (8.5 and 6.7%), 1-methylcycloheptanol (7.8 and 6.6%), and trace amounts of acetates of the above alcohols. Unrearranged alcohol or its acetate was not found in the products within the limits of detectability by gas chromatography under the conditions used. The addition of acetic anhydride and an excess of sodium acetate to III and XIII eliminated the formation of alcohols and acetates, but it gave exclusively rearranged cycloalkenes; the products were 1-ethylcyclohexene (52.5 and 50.0%), ethylidenecyclohexane (1.0 and 1.5%), 1-methylcycloheptene (45.5 and 47.5%), and methylenecycloheptane (1.0 and 1.0%).16) The exclusive formation of the rearranged compounds in the acetolysis of III and XIII, neoalkyl-type esters, was in accord with that observed in the Demjanov rearrangement of 1-methylcyclohexanemethylamine, a neoalkyl-type amine.17) The lack of unrearranged product may be explained in a manner similar to that presented in connection with the above amine.

Experimental18)

Gas Chromatographic Analysis of Products.—The analysis was carried out using 500×0.35 cm. (A, B and D) and 1100×0.35 cm. (C) columns packed with 80—100 mesh Celite which was coated with the appropriate stationary phase. The stationary phases

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13) R. S. Bly, Jr., and H. L. Dryden, Jr., *Chem. Ind. (London)*, **1959**, 1287.

14) C. G. Swain, R. B. Mosely and D. E. Bown, *J. Am. Chem. Soc.*, **77**, 373 (1955).

15) A. C. Cope, D. Ambros, E. Ciganek, C. F. Howell and Z. Jacura, ibid., **82**, 1750 (1960).

16) Bly and Dryden13) have reported that XIII, when acetolyzed under the same conditions, gave ethylcyclohexane and methylcycloheptane (after the hydrogenation of the product cycloalkenes).

17) R. Kotani, *J. Org. Chem.*, **30**, 350 (1965).

employed were: (A) 30% (by weight) of a 40% solution of silver nitrate in tetraethylene glycol, (B) 25% (by weight) of octyl phthalate, (C) 30% (by weight) of polyethylene glycol, and (D) 30% (by weight) of Apiezon grease L. Columns A, B and C were used to analyze hydrocarbons at 60, 100 and 110°C respectively. Alcohols and acetates were analyzed using a column, D, at 150°C. The helium outlet flow rates were 45 (A), 55(B), 60(C), and 60(D) cc./min. The relative retention time is the ratio of the retention time of a substance to the retention time of benzene as measured from an air peak. Quantitative analysis was done as follows; the relative thermal conductivity cell response per mole of the authentic samples of the compounds under discussion was determined using benzene as an internal standard, following the procedure of Messner et al.(19) The mole ratio of the compounds in the product was determined from the above relative response and from the apparent peak area, which was obtained by half-width and peak-height measurements. The relative response of the unidentified compound obtained from the pyrolysis of III (1.7%) was arbitrarily assigned the value of 145 (100 for benzene, 145 for ethylcyclohexane, and so on).

NMR Analysis of Products.—The analysis was run at 25°C for cycloalkenes and at 70°C for alcohols in carbon tetrachloride (5—10%) on a Varian Associates Model V-4311 high resolution spectrometer operating at 60 Mc., using tetramethylsilane (τ 10.00) as an internal standard, unless otherwise noted. The resonance line shapes and chemical shifts (τ-value) used for the structural assignments(20) were as follows: cyclohexene (a triplet, 4.43 J=1.5 c. p. s., olefinic protons), 1-methylcyclohexene (an incompletely resolved multiplet,(21) 4.71, an olefinic proton; an incompletely resolved doublet, 8.40, methyl protons), 3-methylcyclohexene (a complex multiplet, three main lines, 4.44, 4.47 and 4.53, olefinic protons; an asymmetrical doublet, 9.00 and 9.11, J=6.6 c. p. s., methyl protons), methylenecyclohexane (a quintet, 5.47, terminal methylene protons), cycloheptene (a triplet, 4.30, J=3.7 c. p. s., olefinic protons), 1-ethylcyclohexene (an incompletely resolved multiplet, 4.65, an olefinic proton; a triplet, 9.03, methyl protons), ethylidenecyclohexane (two lines,(22) 4.90 and 4.99, an olefinic proton), 1-methylcycloheptene (a triplet, 4.51, an olefinic proton; an incompletely resolved doublet, 8.35, methyl protons), methylenecycloheptane (a quintet, 5.37, terminal methylene protons), methylcyclohexane (an asymmetrical doublet,(23) 9.07 and 9.14, J=4.2 c. p. s., methyl protons), cyclohexanemethanol (a doublet, 6.66, methylene protons of the $-CH_2OH$), 1-methylcyclohexanol (a singlet, 8.85, methyl protons), cycloheptanol (a broad absorption, 6.25, a methine proton), 1-ethylcyclohexanol(24) (a triplet, 9.14, methyl protons), and 1-methylcycloheptanol(24) (a singlet, 8.83, methyl protons).

ESR Analysis.—The ESR spectra were measured with a Varian x-band EPR spectrometer, Model V-4566, using field modulation at 100 kc./sec.

1-Methylcyclohexanemethyl *p*-toluenesulfonate was irradiated under nitrogen with ultraviolet rays for 1 hr. at room temperature, using a Toshiba SHLS-100 2B ultraviolet lamp set at the distance of 5 cm. from the sample. During the irradiation, the sample was dipped in liquid nitrogen to prevent heating, and then subjected to ESR spectroscopy.

Pyrolysis of Sulfonic Esters.—The pyrolysis was conducted in a 100-ml. flask equipped with a side arm for introduction of nitrogen. The flask was connected to a 40-cm. distilling column, which was connected in turn to a trap immersed in a dry ice-methanol bath, and then to a water pump. The flask was then charged with the sulfonic ester (0.03 mol. each), evacuated to 40 mmHg, and immersed in an oil bath. The bath was heated rapidly to 200—205°C. After a few minutes, the sulfonic ester began to decompose; this decomposition continued for 30—45 sec. The product in the trap was then taken up with ether, washed with a dilute sodium hydroxide solution and water, and dried over anhydrous magnesium sulfate, and the ether was removed, leaving a hydrocarbon mixture weighing between 1.92—2.19 (I), 1.71—1.98 (II), and 2.11—2.42 g. (III). Considerable amounts of tar-like substances remained in the reaction flask, but no attempt was made to identify them.

I, II and III (0.03 mol. each) were similarly pyrolyzed at 80 mmHg in the presence of *p*-benzoquinone (0.01 mol.), giving 1.15—1.40, 1.20—1.38, and 1.30—1.45 g. of hydrocarbons, respectively. I and II gave cyclohexene (2.1% and a trace), 1-methylcyclohexene (66.1 and 74.3%), 3-methylcyclohexene (9.7 and 9.3%), methylenecyclohexane (1.2 and 1.2%), cycloheptene (4.1 and 4.8%), methylcyclohexane (12.3 and 10.5%), and toluene (4.7% and none).

A mixture of I (0.03 mol.) and benzoyl peroxide (0.01 mol.) was rapidly heated to 100—105°C at 40 mmHg under nitrogen. II and III were treated in this way also. After 2 min. benzoyl peroxide began to decompose; this decomposition continued for several minutes. The heating was then discontinued. The products collected in the trap immersed in a dry ice-methanol bath weighed 0.38—0.42, 0.35—0.40, and 0.57—0.62 g., respectively. The residues consisted mainly of the unreacted sulfonic ester. I and II gave cyclohexene (a trace), 1-methylcyclohexene (5.5 and 5.3%), 3-methylcyclohexene (a trace), methylenecyclohexane (0.3 and 0.3%), methylcyclohexane (1.3

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18) All melting points and boiling points are uncorrected.

19) A. E. Messner, D. M. Rosie and P. A. Argabright, *Anal. Chem.*, **31**, 230 (1959).

20) Signals due to the ring methylene protons are not described.

21) The signal determined at 40 Mc. was reported to be a triplet by G. V. D. Tiers, "Table of Characteristic NMR Shielding Values."

22) Since a sufficient quantity of ethylidenecyclohexane could not be isolated, its NMR spectrum was determined using a mixture of ethylidenecyclohexane and 1-ethylcyclohexene. The olefinic proton of the former would be expected to show a quartet by spin-spin coupling with methyl protons with the relative intensities of 1 : 3 : 3 : 1, but only two lines were detected. The proton showed a sharp single line (τ 4.95) when the spin-decoupling technique was applied.

23) The signal determined at 40 Mc. was reported to be a singlet.(21)

24) The NMR spectra of 1-ethylcyclohexanol and 1-methylcycloheptanol were determined at 120°C without a solvent and using cyclohexane (τ 8.56) as an internal standard.

and 1.1%), and benzene (92.7 and 93.3%), respectively. III gave 1-methylcyclohexene (a trace), 1-ethylcyclohexene (3.2%), 1-methylcycloheptene (2.5%), ethylcyclohexane (0.9%), and benzene (93.4%).

Evidence for the saturated compounds was obtained as follows: (1) the whole reaction product was treated with bromine in ether at 0°C, and then gas chromatographed; (2) the whole reaction product was analyzed on a 30 cm. column of 30% concentrated sulfuric acid on 40—60 mesh silica gel, which was connected to the end of the above octyl phthalate column; (3) by a comparison of the relative retention times with those of authentic samples (using an authentic sample alone and in admixture), and (4), in the case of the isolated methylcyclohexane or ethylcyclohexane, the NMR spectrum of each compound was exactly identical with that of an authentic sample, showing the absence of any resonance line due to olefinic protons.

Oxalic Acid-Catalyzed Dehydration of Cyclohexanemethanol and 1-Methylcyclohexanemethanol.—The dehydration was conducted following the procedure of Chapman and Borden.[5] A mixture of cyclohexanemethanol (0.05 mol.) or 1-methylcyclohexanemethanol (0.05 mol.) and oxalic acid (0.4 mol.) was heated to 150°C. The olefinic product was dried over anhydrous magnesium sulfate, and then analyzed by gas chromatography.

Cobalt(II) Chloride-Catalyzed Reaction of Cyclohexanemethyl Chloride.—In a 500-ml. three-necked flask fitted with a mechanical stirrer, a dropping funnel and a reflux condenser, there were placed magnesium (0.1 mol.) and 30 ml. of dry ether. Methyl iodide (0.1 mol.) in 20 ml. of dry ether was then added dropwise into the flask with stirring. Cyclohexanemethyl chloride (0.1 mol.) in 50 ml. of dry ether was then added. Cobalt(II) chloride (0.05 mol.) was added in portions into the reaction mixture with stirring. After the exothermic reaction had ceased, 20 ml. of water was added, and the ether layer was separated and dried over anhydrous magnesium sulfate. Distillation gave 3.5 g. of a hydrocarbon mixture. The mixture was analyzed by gas chromatography and NMR spectroscopy.

Acetolysis of Sulfonic Esters.—In a 500-ml. flask equipped with a reflux condenser, the top of which was connected to a trap immersed in a dry ice-methanol bath, there were placed the sulfonic ester (0.05 mol. each), sodium acetate (0.05 mol.), glacial acetic acid (1 mol.), and water (1 mol.). The flask was heated for 48 hr. in an oil bath under gentle reflux, and then cooled to 0—5°C. The contents were neutralized with a dilute sodium hydroxide solution and extracted with ether. The trap and condenser were rinsed with ether. The combined extracts were dried over anhydrous magnesium sulfate, and then fractionally distilled into 2 fractions. II gave 0.93 g. of a low-boiling fraction (b. p. 90—113°C) and 3.2 g. of a high-boiling fraction (b. p. 55°C at 20 mmHg to 85°C at 15 mmHg), while III gave 3.2 g. (b. p. 110—139°C) and 0.6 g. (b. p. 70—80°C at 20 mmHg) portions, and XIII, 3.6 g. (b. p. 110—139°C) and 0.6 g. (70—80°C at 20 mmHg) portions, respectively. No attempt was made to identify the residue.

III and XIII (0.05 mol. each) were similarly solvolyzed in glacial acetic acid (1 mol.) containing acetic anhydride (0.035 mol.) and sodium acetate (0.1 mol.); they gave 3.4 and 3.1 g. of cycloalkenes, respectively.

Preparation of Sulfonic Esters.—Cyclohexanemethyl *p*-toluenesulfonate, m. p. 32—33°C (lit.[25] m. p. 32—33°C), cyclohexanemethyl methanesulfonate, m. p. 43—44°C, 1-methylcyclohexanemethyl *p*-toluenesulfonate, m. p. 37—38°C (lit.[25] m. p. 37—38°C), and 1-methylcyclohexanemethyl methanesulfonate,[26] were prepared from the corresponding alcohols and methanesulfonyl or *p*-toluenesulfonyl chlorides in pyridine at room temperature. The crude products were then recrystallized twice from hexane, in 65—70% yields.

Preparation of Alcohols.—1-Methylcyclohexanol, b. p. 68°C at 20 mmHg (lit.[27] b. p. 72°C at 22 mmHg), 1-ethylcyclohexanol, b. p. 76.5°C at 20 mmHg (lit.[28] b. p. 77°C at 20 mmHg), and 1-methylcycloheptanol, b. p. 83—85°C at 20 mmHg (lit.[27] b. p. 82—85°C at 20 mmHg) were prepared following the directions of Mosher.[29] Cyclohexanemethanol, b. p. 91—92°C at 18 mmHg (lit.[30] b. p. 88—93°C at 18 mmHg), cycloheptanol, b. p. 184—185°C (lit.[31] b. p. 184—187°C), and 1-methylcyclohexanemethanol, b. p. 88°C at 17 mmHg (lit.[32] b. p. 85°C at 14 mmHg), were prepared by the methods of Gilman and Catlin, Matthews and Becker, and Koch and Haaf respectively.

Preparation of Acetates. — Cyclohexanemethyl acetate, b. p. 83—85°C at 15.5 mmHg (lit.[33] b. p. 199—201°C) at 740 mmHg, 1-methylcyclohexyl acetate b. p. 177°C (lit.[34] b. p. 178—179°C), 1-ethylcyclohexyl acetate, b. p. 190—192°C, and cycloheptyl acetate, b. p. 199°C (lit.[35] b. p. 199—200.5°C) were prepared from the corresponding alcohols and an excess of acetic anhydride in the presence of anhydrous sodium acetate.

Preparation of Cycloalkenes.— 1-Methylcyclohexanol, 1-ethylcyclohexanol, and 1-methylcycloheptanol were dehydrated following the method of Traynelis et al.,[36] thus yielding mixtures of 1-methylcyclohexene and methylenecyclohexane, (94 : 6), 1-ethylcyclohexene and ethylidenecyclohexane (95 : 5), and 1-methylcyclohexene and methylenecycloheptane (90 : 10) respectively. 1-Methylcyclohexene, b. p. 110°C (lit.[37] b. p. 110.2°C), methylenecyclohexane, b. p. 102°C (lit.[37] b. p. 102.5°C), 1-ethylcyclohexene,

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[25] C. F. Wilcox, Jr., and S. S. Chibber, *J. Org. Chem.*, **27**, 2332 (1962).

[26] The methanesulfonate was solvolyzed without purification.

[27] M. Barbier and M. F. Hügel, *Bull. Soc. Chim. France,* **1961**, 951.

[28] H. B. Williams and W. R. Edwards, Jr., *J. Am. Chem. Soc.*, **69**, 336 (1947).

[29] W. A. Mosher, ibid., **62**, 552 (1940).

[30] H. Gilman and W. E. Catlin, "Organic Syntheses," Coll. Vol. I, 188 (1961).

[31] D. N. Matthews and E. I. Becker, *J. Org. Chem.*, **21**, 1317 (1956).

[32] H. Koch and W. Haaf, *Ann.*, **618**, 251 (1958).

[33] A. Fawarsky and I. Borgmann, *Ber.*, **40**, 4865 (1907).

[34] J. G. Traynham and O. S. Pascual, *J. Org. Chem.*, **21**, 1362 (1956).

[35] N. A. Nelson, J. H. Fassnacht and J. U. Piper, *J. Am. Chem. Soc.*, **83**, 206 (1961).

[36] V. J. Traynelis, W. L. Hergenrother, H. T. Hanson and J. A. Valicenti, *J. Org. Chem.*, **29**, 123 (1964).

[37] R. B. Turner and R. H. Garner, *J. Am. Chem. Soc.*, **79**, 253 (1957).

b. p. 136°C (lit.[37] 136.2°C), 1-methylcycloheptene. b. p. 137°C (lit.[37] b. p. 136°C), and methylenecycloheptane, b. p. 136°C (lit.[37] b. p. 135°C), were isolated in the pure form by preparative-scale gas chromatography, and their structures were confirmed by their NMR spectra. Cycloheptanol and a mixture of *cis*- and *trans*-3-methylcyclohexanols were dehydrated by the method of Mosher,[29] thus yielding cycloheptene, b. p. 115°C (lit.[38] b. p. 115°C), and an olefinic mixture, respectively. Gas chromatographic analysis showed the olefinic mixture to consist of four components. The component corresponding to 3-methylcyclohexene was isolated by gas chromatography; its b. p. was 103°C (lit.[39] b. p. 104°C), and its structure was proved by NMR spectroscopy.

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[38] R. Willstätter, *Ann.*, **317**, 221 (1901).

[39] N. D. Zelinsky, *Ber.*, **57**, 2055 (1924).