[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF OKLAHOMA]

Chromyl Chloride Oxidation of Saturated Hydrocarbons[1]

BY CHARLES C. HOBBS, JR.,[2] AND BRUCE HOUSTON

RECEIVED AUGUST 26, 1953

The action of chromyl chloride on saturated hydrocarbons has been further examined using ten paraffins and cycloparaffins. All types used formed solid complexes with the chromyl chloride. A marked difference was noted in the rate of complex formation between those possessing tertiary carbons and those which did not. A number of the products obtained on the hydrolysis of these complexes have been identified. A reaction mechanism has been proposed.

Tillotson and Houston[3] found that chromyl chloride reacted readily with methylcyclohexane to give a solid complex of the formula $C_7H_{14}\cdot 2CrO_2Cl_2$ provided that a trace of olefin was added to the saturated hydrocarbons. On hydrolysis of this complex, hexahydrobenzaldehyde was isolated in 25% yield.

Étard[4] had reported the formation of such complexes with pentane, hexane and heptane many years before. The hydrocarbons used were of uncertain structure and the isolated hydrolytic products in each case were incompletely characterized chloroketones. Cristol and Eilar[5] reported the slow formation of a complex between chromyl chloride and cyclohexane and the isolation of cyclohexyl chloride from its hydrolysis products.

We have now investigated the action of this reagent with ten saturated hydrocarbons and identified a number of the hydrolytic products from the complexes thus formed. From these results we have formulated a tentative reaction mechanism for these reactions. We have also checked the value of traces of olefins as initiating materials in the one case where rigorous purification methods were used to remove them from the starting material. A summary of the results obtained is shown in Table I.

TABLE I

CHROMYL CHLORIDE COMPLEXES FORMED AND HYDROLYSIS PRODUCTS ISOLATED

Hydrocarbon	Yield of complex	Time, days	Chromium, % Found	Chromium, % Calcd. RH·2CrO₂Cl₂	Chromium, % Calcd. RH·3CrO₂Cl₂	Hydrolysis products
2-Methylbutane	Near quant.	3				3-Me-2-butanone, $C_5H_{11}OCl$
n-Hexane	31.5	7	28.9, 29.0, 28.9	26.3	28.3	2-Hexanone, 3-hexanone
2-Methylpentane	Near quant.	3				2-Me-3-pentanone, 4-Me-2-pentanone
3-Methylpentane	Near quant.	3	25.7	26.3		3-Me-2-pentanone, chloroketone
2,2-Dimethylbutane	19	90	27.2, 27.0	26.3	28.3	Carbonyl compounds
2,3-Dimethylbutane	Near quant.	3	26.5, 26.6, 26.5	26.3		Acetone, 3,3-dimethyl-2-butanone, 2,3-dimethylbutanoic acid
Cyclohexane	90	90	27.3, 27.3	26.4	28.4	Cyclohexanone
2,2,3-Trimethylpentane	Near quant.	3	24.8, 24.9, 24.7	24.5		2,4,4-Trimethylpentanal, 2,4,4-trimethylpentanoic acid, 4,4-dimethyl-2-pentanone
2,5-Dimethylpentane	Near quant.	3	26.5, 26.5, 26.4	23.7	26.3	Undetermined
Bicyclohexyl	Near quant.	3				Undetermined

Experimental

Material.—The first six hydrocarbons listed in Table I were Phillips Pure Grade guaranteed to be not less than 99 mole per cent. pure. The cyclohexane was Eastman White Label ($n^{20}D$ 1.4261) and the 2,2,4-trimethyloctane was Eastman (practical grade indicated to be 99.5+% pure. The bicyclohexyl was from Matheson Co., Inc. The 2,5-dimethylheptane was prepared by the method of Boord, *et al.*,[6] using isoamyl iodide and methyl ethyl ketone as starting materials. The final product distilled between 133-136°, $n^{20}D$ 1.4043; reported values[7] b.p. 136°, $n^{20}D$ 1.4038.

Chromyl chloride was prepared according to the directions of Sisler.[8] It was promptly diluted with twice its volume of carbon tetrachloride and stored in brown bottles. One batch was purified by extraction with concentrated sulfuric acid as described by Slack and Waters[9] instead of by distillation. This left the chromyl chloride cloudy and all other runs were purified by distillation. No difference was noted in either the reactivity of the reagent or in the products formed by the chromyl chloride in either case.

Analyses of the Complexes.—Chromium analyses were run by an adaptation of the method given by Hillebrand and Lundell.[10] The method was checked with several known mixtures of potassium dichromate, concentrated hydrochloric acid and acetone under varying conditions.

Preparation of Hydrocarbon-Chromyl Chloride Complexes.—In those cases in which the hydrocarbon possessed a tertiary carbon the method was as follows. One mole of chromyl chloride diluted with twice its volume of carbon tetrachloride was added over a 3-hour period to one mole of the hydrocarbon in twice its volume of carbon tetrachloride. The reaction mixture was kept between 30° and 35°. The brown precipitate began to form immediately. Stirring and heating were continued for 6 hours after the addition of the chromyl chloride at which time the reaction was approximately two-thirds complete. The mixture was allowed to stand for 3 more days and the red color of the

---

[1] Taken from the M.S. and Ph.D. theses of Charles C. Hobbs, Jr. A portion of this work was presented before the Southwest Regional Meeting of the American Chemical Society on December 6, 1951, at Austin, Texas.

[2] Pan American Refining Corporation Fellow, 1950-1952.

[3] A. Tillotson and B. Houston, THIS JOURNAL, **73**, 221 (1951).

[4] A. Étard, *Compt. rend.*, **84**, 128, 951 (1877).

[5] B. J. Cristol and K. R. Eilar, THIS JOURNAL, **72**, 4353 (1950).

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

[7] M. Tuot, *Compt. rend.*, **197**, 1434 (1933).

[8] H. H. Sisler, "Inorganic Syntheses," Vol. 11, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 205.

[9] R. Slack and W. A. Waters, *J. Chem. Soc.*, 594 (1949).

[10] W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1929, p. 410.

chromyl chloride was gone. The product was filtered, washed with carbon tetrachloride and dried *in vacuo*. The extremely hygroscopic nature of these complexes made it desirable to have a stream of dried air playing over the surface of the funnel during the filtration and washing. The final yield in these cases was essentially quantitative, based on the chromyl chloride. The fact that carbon tetrachloride was isolated from some of the hydrolysis mixtures indicated that the drying period used was not enough for its complete removal. Samples which were used for analyses were kept under low pressure for at least a week at room temperature or in some cases for 2 days in a vacuum oven at 40°.

For those hydrocarbons not possessing a tertiary carbon the reactions were much slower. In the case of *n*-hexane considerable chromyl chloride was unused at the end of 3 days. After one week the solid was filtered and a yield of 30–35% (depending on the formula chosen for the complex) was obtained. It is noteworthy in this case that after the excess chromyl chloride was washed from the precipitate the stream of dry air passing over the complex carried hydrogen chloride vapor. Calcd. for $C_6H_{13}(Cr_2O_4Cl_3)$: Cr, 28.9. Found: Cr, 28.9, 29.0, 28.9.

With 2,2-dimethylbutane and cyclohexane the reactions were much slower. After 3 months time the former gave an approximate yield of 19%, whereas the cycloparaffin in the same period gave a yield of about 90%. In each of these last three cases small amounts of amylene were added to the starting materials as an initiator without noticeable effect.

Effect of Olefins on Reaction between Hydrocarbons and Chromyl Chloride.—With the hydrocarbons used in the main experiments described in this paper the addition of an olefin as an initiating agent as described by Tillotson and Houston[3] was either unnecessary or ineffective. It was concluded that the samples used probably contained traces of unsaturated hydrocarbons as impurities.

This was tested in the case of 2-methylpentane. The method described in reference 11 for the determination of small percentages of olefins in low molecular weight hydrocarbons was used with slight modification on the 2-methylpentane. This indicated that it contained 0.03 mole per cent. of olefin. By successive treatments of the hydrocarbon with aluminum chloride followed by distillation a sample was obtained which showed no test for olefin (claimed limit 0.0001 mole per cent.). Five ml. of this material was placed in a test-tube and 5 ml. of the chromyl chloride solution added. This sample required 4 minutes to become cloudy and 20 minutes to show a definite precipitate. A sample of the original hydrocarbon gave a considerable quantity of precipitate in 2 minutes.

An 80-ml. sample of the purified 2-methylpentane was mixed with 5 ml. of chromyl chloride solution and allowed to stand 10 minutes. It was then twice distilled through the 24-inch column. The distillate was definitely more reactive than the purified hydrocarbon.

Hydrolysis of the Complexes.—Several different methods of hydrolysis were tried with no great difference noted in the amounts of organic materials recovered. It was found, however, that in the case of the 3-methylpentane (the first hydrocarbon studied) the relative amount of chlorinated to unchlorinated ketone was lowered when a reducing agent was present in the mixture. The method used in most cases was as follows. The hygroscopic complex was slowly added to a stirred water solution of sodium sulfite in such a manner as to minimize contact with moist air. The concentration of the hydrolytic solution was such that by using 2 ml. of it for each gram of complex enough sodium sulfite would be present to complete the reduction of the chromium to the trivalent state and to neutralize the acids formed. The reaction flask was immersed in a refrigerated bath and the solid added at such a rate that the temperature in the flask did not exceed 8°.

In the case of 3-methylpentane and of 2-methylbutane the organic products were obtained from the hydrolytic mixtures by ether extraction. In these cases also, as with 2-methylpentane, sulfur dioxide was the reducing agent used.

In the other cases studied the hydrolysis mixture was subjected to steam distillation, allowed to stand 24 hours, acidified with sulfuric acid and again steam distilled to obtain any volatile acids formed.

Hydrolysis Products. 2-Methylbutane.—The ether extract from the hydrolysis of 100 g. of the complex was dried with anhydrous sodium sulfate and distilled. Seven grams of a ketone boiling between 91 and 95° was obtained. This yielded a 2,4-dinitrophenylhydrazone, m.p. 117.5–118.5°, and a semicarbazone, m.p. 111–112.5°; reported for 3-methyl-2-butanone: b.p. 94°,[12] m.p. of 2,4-dinitrophenylhydrazone 117°,[13] m.p. of semicarbazone 113°.[14] A second fraction of 8 g. boiled between 111 and 114°. It was mildly lachrymatory, gave a precipitate with alcoholic silver nitrate and an oily precipitate with 2,4-dinitrophenylhydrazine; reported b.p. for 3-chloro-3-methyl-2-butanone 117.2°.[15] No other materials of definite character were obtained. The higher boiling liquids rapidly decolorized bromine in carbon tetrachloride.

3-Methylpentane.—The dried ethereal extract from the hydrolysis of 100 g. of the complex yielded 8.5 g. of material which distilled between 114 and 164°. Decomposition took place at the higher temperatures. On redistillation, we obtained a ketone boiling between 115 and 117° which yielded a 2,4-dinitrophenylhydrazone, m.p. 69–70°, and a semicarbazone, m.p. 93.5–95°; reported for 3-methyl-2-butanone: b.p. 118°,[16] 2,4-dinitrophenylhydrazone m.p. 71.2°,[17] semicarbazone m.p. 95.[16] A second fraction which appeared to be a chlorinated ketone boiled between 133 and 136°. It yielded a derivative with 2,4-dinitrophenylhydrazine melting at 94–95° which had no chlorine, and a precipitate with semicarbazide which did have chlorine and melted at 253–256°. The compound gave the following analyses: C, 54.3, 54.3; H, 8.46, 8.49. No ketone can be found in the literature to fit the above data.

2-Methylpentane.—The resultant mixture from the hydrolysis of 133 g. of the complex in a small amount of water and refluxing sulfur dioxide was steam distilled. Thirty-six and seven-tenths grams of organic material was collected. On redistilling some of this liquid a few drops came over at 60°, the boiling point of the hydrocarbon. The bulk distilled between 114–119°; recorded for 4-methyl-2-pentanone, b.p. 117°,[18] and for 2-methyl-3-pentanone, b.p. 115–116°.[18] Negative chlorine and aldehyde tests were noted. Part of the distillate was allowed to react with 2,4-dinitrophenylhydrazine and a solution of the resulting derivatives passed through a column of bentonite as outlined by White.[19] No satisfactory bands were obtained. Alumina was substituted for the bentonite and a saturated solution of the reaction mixture in hexane passed through a 24-inch column. The solvent came through colorless and a dark green band formed at the top of the column. On development with a 10% solution of ether in hexane two major bands and five minor ones developed. The two major bands eluted first. One minor band was eluted, but the others were too diffuse to recover individually. As the solution containing the first band eluted was evaporated, reddish crystals formed on the surface of the liquid which melted at 116.5–118°. As the evaporation proceeded, yellow needles formed in the body of the hexane. These underwent a change to a reddish color between 80 and 84° and melted at 116.5–118°. Discherl and Nahm[20] record such behavior for the 2,4-dinitrophenylhydrazone of 2-methyl-3-pentanone; reported temp. of color change 84–88°, m.p. 111–113°. Other melting points recorded for this hydrazone are 109–109.5°[21] and 168–169°.[22] The material from the second band melted at 95–96°; reported for the 2,4-dinitrophenylhydrazone of 4-methyl-2-pentanone 95°.[18]

Only a liquid from which no crystals were obtained re-

---

[11] "UOP Laboratory Methods for Petroleum and its Products," Method G-158-4, Universal Oil Products Co., Chicago, Ill.

[12] J. C. Rintelen, Jr., J. H. Saylor and P. M. Gross, THIS JOURNAL, **59**, 1129 (1937).

[13] C. F. H. Allen, *ibid.*, **52**, 2957 (1930).

[14] F. C. Whitmore and W. L. Evers, *ibid.*, **55**, 815 (1933).

[15] P. Delbaerse, *Bull. soc. chim. Belg.*, **51**, 1 (1942); *C.A.*, **37**, 5018^2 (1943).

[16] S. B. Lebedev and S. M. Orlov, *ibid.*, **30**, 2169^4 (1936).

[17] N. L. Drake and F. P. Veitch, Jr., THIS JOURNAL, **57**, 2623 (1935).

[18] I. M. Heilbron, "Dictionary of Organic Compounds," Vol. II, Eyre and Spottiswoode, London, 1936, p. 751.

[19] J. W. White, Jr., *Anal. Chem.*, **20**, 726 (1948).

[20] W. Discherl and H. Nahm, *Ber.*, **73B**, 448 (1940).

[21] H. Burton, C. W. Shopee and C. L. Wilson, *J. Chem. Soc.*, **136**, 720 (1933).

[22] M. S. Kharasch, E. Sternfeld and F. R. Mayo, *J. Org. Chem.*, **5**, 362 (1940).

sulted on evaporation of the solution containing the third band. Efforts to separate the mixed *p*-nitrophenylhydrazones chromatographically were unsuccessful.

***n*-Hexane.**—Approximately 150 g. of the complex was hydrolyzed in sodium sulfite solution. Steam distillation yielded 19.9 g. of neutral substances. No acidic material was obtained. About 8 g. boiling between 120–130° and n^{20}D varying from 1.4046 to 1.4063 was obtained by distillation. This appeared to be a mixture of hexanones. Attempts to separate this mixture chromatographically failed. What remained from this fraction was treated with a saturated solution of sodium bisulfite. The solid formed was filtered, washed with hexane and the hexane washing reserved for further investigation. The bisulfite addition product was decomposed with dilute hydrochloric acid and the organic layer separated. It yielded a 2,4-dinitrophenylhydrazone which melted after purification at 109–109.5° and a semicarbazone melting at 124.5–125.5°; reported for 2-hexanone; b.p. 127–128°,[13] n^{20}D 1.40069,[23] m.p. of 2,4-dinitrophenylhydrazone 106°,[13] m.p. of semicarbazone 122°.[20] The hexane solution from above gave a 2,4-dinitrophenylhydrazone melting at 146.5–149°; reported for 3-hexanone: b.p. 123–123.5,[18] n^{20}D 1.39899, m.p. of 2,4-dinitrophenylhydrazone 146.5–148°,[18] 149–151°.[18] The higher boiling material gave tests which indicated a mixture of unsaturated ketones.

2,3-Dimethylhexane.—This hydrocarbon as supplied contained 0.0068 weight per cent. of du Pont No. 6 inhibitor. When a small amount of the hydrocarbon with the inhibitor was treated with chromyl chloride the initial reaction was vigorous and the temperature rose rapidly. The inhibitor was removed by distillation and a fraction of the hydrocarbon boiling at 56.8° was used for the formation of the complex. Approximately 350 g. of the complex was hydrolyzed in sodium sulfite solution and the mixture steam distilled. The organic layer weighed 55.3 g. and was slightly denser than water. The water layer was extracted with ether and this solution added to the water-insoluble organic material. Approximately 1 g. of acidic material was obtained from this by extractions with sodium bicarbonate. The amide and the *p*-toluidide of this acid were prepared. The former melted at 128.5–130.5° and the latter at 111–112.5°; reported for 2,3-dimethylbutanoic acid: m.p. of amide 131.5°,[24] m.p. of *p*-toluidide 112.5–113°.[25] From the neutral ether solution a small quantity of acetone was obtained, b.p. 55°, 2,4-dinitrophenylhydrazone m.p. 123.5–125°, mixed m.p. with authentic sample of acetone 2,4-dinitrophenylhydrazone 123–124.5°. One other product identified from this mixture was 8.5 of pinacolone, b.p. 105–106°, n^{20}D 1.4002, 2,4-dinitrophenylhydrazone m.p. 121–124°, semicarbazone m.p. 153–156°; reported for pinacolone: b.p. 106°, n^{20}D 1.3956,[26] m.p. of semicarbazone 157°.[27] Ten grams of material boiling between 106 and 110° gave tests which indicated it to be chiefly pinacolone but which was contaminated with small amounts of unsaturated compounds.

2,2-Dimethylbutane.—Most of the 38 g. of complex was hydrolyzed as in the previous cases. Not enough oxygenated material was obtained for fractionation and identification.

Cyclohexane.—Ninety grams of the complex was hydrolyzed, using a mixture of sodium bisulfite and magnesium hydroxide instead of sodium sulfite. The hydrolysis mixture was steam distilled and the distillate extracted with ether. About 2.5 g. distilled between 146–152° (most between 150 and 151°). This gave a precipitate with alcoholic silver nitrate but had the odor of cyclohexanone and yielded a 2,4-dinitrophenylhydrazone melting at 160–162.5° and a semicarbazone melting at 166–169°, n^{20}D 1.4495; reported for cyclohexanone: b.p. 155°,[28] m.p. of 2,4-dinitrophenylhydrazone 162°,[28] m.p. of semicarbazone 166,[28] n^{20}D 1.4507.[28] Apparently this fraction was chiefly cyclohexanone. The residue also contained chlorine and polymerized on standing.

2,2,4-Trimethylpentane.—Approximately 565 g. of the complex from this hydrocarbon was hydrolyzed as in the case of the *n*-hexane. Steam distillation gave 89 g. of organic material from the alkaline solution. On acidification of the remaining hydrolysis mixture with sulfuric acid, an additional 6 g. was obtained by further steam distillation. The combined organic layers were extracted with sodium carbonate solution and this alkaline layer twice extracted with ether. After heating to remove the ether, the alkaline layer was acidified with sulfuric acid and 7.7 g. of organic acid obtained. Approximately 6 g. boiled between 200 and 216°; 2 g. of this appeared to be reasonably pure 2,2,4-trimethylpentanoic acid, b.p. 213.5–216°, n^{20}D 1.4232, neut. equiv. 145, m.p. of the anilide 117–117.5°; reported for 2,4,4-trimethylpentanoic acid, b.p. 217.4°,[29] n^{20}D 1.4233, m.p. of anilide 117.5°, calcd. for neutral equivalent 144.2.

The non-acidic material from the steam distillation was yellow and had a camphor-like odor. It was combined with the ether extracts from the alkaline solution of the acid, dried and distilled. Carbon dioxide was slowly bubbled through the flask during the distillation. After the removal of the ether and carbon tetrachloride the fractionation was complicated by what appeared to be polymerization reactions even at low pressures.

Most of the subfractions were obviously impure, the refractive indices changing as each drop came over. However, one fraction was obtained which appeared to be of reasonably constant composition. The following data were obtained on it: b.p. 125–128° (atm. pressure), n^{20}D 1.4063, m.p. of 2,4-dinitrophenylhydrazone 96–99°, m.p. of semicarbazone 171–174°. It gave a positive iodoform test; reported for 4,4-dimethyl-2-pentanone: b.p. 120–124°,[30] 124–124.5°,[31] 126°,[32] n^{20}D 1.4130,[30] 1.4030[31], 1.4030–1.4036[32]; m.p. of semicarbazone 176^0,[31] 176,[31] 173–173.5[32]; m.p. of 2,4-dinitrophenylhydrazone 100°,[30] 101–102°,[33] 90–92°.[34] Attempts to purify the 2,4-dinitrophenylhydrazone chromatographically were unsuccessful. Another definite fraction distilled between 144–146.5° at atmospheric pressure; other data obtained n^{20}D 1.4158, m.p. of 2,4-dinitrophenylhydrazone 143.5–144.5°, m.p. of semicarbazone 112.5–114°. The substance gave negative tests with Schiff and with Tollens reagents (these reagents were tested with a known sample of heptanal and gave strong positive tests) reported for 2,4,4-trimethylpentanal: b.p. 149–151°,[35] n^{20}D 1.4180,[35] m.p. of 2,4-dinitrophenyhydrazone 143–145°,[32] m.p. of semicarbazone 116–117°[32]; reported for 1,2-epoxy-2,4,4-trimethylpentane: b.p. 140–141°, n^{20}D 1.4157.[32] According to Byers and Hickenbottom[31] this epoxide rearranges to the aldehyde in acid solution. They also state that it yields the corresponding glycol (m.p. 62–63°) when refluxed 36 hours with aqueous alcohol. This test gave no crystalline material with our substance. It also gave a negative periodic test with tested reagents.

A drop of the known heptanal was added to a few drops of the unknown and the Schiff test repeated. Again the test was negative. The Tollens test applied to this mixture of known aldehyde and unknown resulted in the formation of a small lump of solid. This lump appeared to have a black deposit on its surface. It is suggested that this fraction is the aldehyde containing some impurity which inhibits the Schiff test and that it polymerizes too readily in the alkaline Tollens reagent to give a satisfactory reduction of the silver ion.

The higher boiling fractions yielded precipitates with 2,4-dinitrophenylhydrazine but were not identified.

2,5-Dimethylheptane.—As indicated in Table I this hydrocarbon gave a complex which appeared to have the formula $C_9H_{20}\cdot 3CrO_2Cl_2$. One hundred and twelve grams

---

(23) P. Ceuterick, *Bull. soc. chim. Belg.*, **45**, 777 (1936); *C. A.*, **31**, 919^5 (1937).

(24) F. Reindel and H. Kipphan, *Ann.*, **493**, 181 (1932).

(25) R. A. Barnes and W. M. Budde, THIS JOURNAL, **68**, 2341 (1946).

(26) F. C. Whitmore, C. I. Noll and V. C. Meunier, *ibid.*, **61**, 684 (1939).

(27) H. Gilman and J. F. Nelson, *Rec. trav. chim.*, **55**, 529 (1936).

(28) E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 382.

(29) F. C. Whitmore, C. I. Noll, J. W. Heyd and J. D. Surmatis, THIS JOURNAL, **63**, 2028 (1941).

(30) L. Schmerling, U. S. Patent 2,481,157, Sept. 6, 1949; *C. A.*, **44**, 651^h (1950).

(31) A. Byers and W. J. Hickenbottom, *J. Chem. Soc.*, 1336 (1948).

(32) G. W. Moersch and F. C. Whitmore, THIS JOURNAL, **71**, 820 (1949).

(33) H. Baldock, N. Levy and C. W. Scaife, *J. Chem. Soc.*, 2627 (1949).

(34) M. Mugdan and D. P. Young, *ibid.*, 2988 (1949).

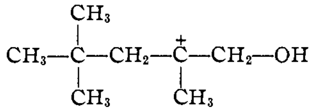
(35) W. J. Hickenbottom, *ibid.*, 1333 (1948).

of it on hydrolysis and steam distillation yielded 16.9 g. of water-insoluble organic products.

Bicyclohexyl.—In this case it was established that the hydrocarbon readily formed a complex with chromyl chloride.

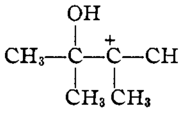
Discussion

An examination of the results obtained indicates that the hydrocarbons studied divide themselves into two classes. Those which possess one or two tertiary hydrogen atoms react with chromyl chloride at a far more rapid rate than those which do not. Furthermore, those which have this structural feature gave complexes of the composition $RH\cdot 2CrO_2Cl_2$ with the exception of 2,5-dimethylheptane which formed $C_9H_{20}\cdot 3CrO_2Cl_2$ and the earlier described 2,7-dimethyloctane[36] which formed $C_{10}H_{22}\cdot 4CrO_2Cl_2$. The other hydrocarbons gave complexes whose chromium analyses indicated mixtures. An examination of the substances identified among the hydrolysis products of the Étard complexes in the first class will show that each could be accounted for as either a rearrangement product or oxidative fission product of a glycol. Thus Byers and Hickenbottom[37] found that 2,4,4-trimethyl-1,2-pentanediol would rearrange to 2,4,4-trimethylpentanal and would yield 4,4-dimethyl-2-pentanone on oxidation. Those substances together with some of the acid corresponding to the aldehyde were found among the hydrolysis products of the 2,4,4-trimethylpentane complex. Similarly, the glycol 2,3-dimethyl-2,3-butanediol or pinacol, rearranges to 3,3-dimethyl-2-butanone and gives acetone on oxidative fission. These were the products isolated from the chromyl chloride oxidation of 2,3-dimethylbutane. The formation of trace amounts of the 2,3-dimethylbutanoic acid from this hydrocarbon would correspond to the oxidized rearrangement product of the 1,2-glycol. Since no glycols were found among the hydrolysis products, it is not assumed that they were present. But the unstable intermediate obtained on the hydrolysis of the hydrocarbon–chromyl chloride complex should be similar to that assumed to precede the rearrangement of the glycols. Thus the intermediate assumed to account for the products from the 2,2,4-trimethylpentane would have the form of



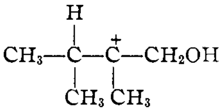
$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{+}{\underset{CH_3}{C}}-CH_2-OH$$

and from the 2,3-dimethylbutane would be



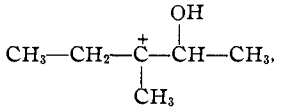
$$CH_3-\overset{OH}{\underset{CH_3}{C}}-\overset{+}{\underset{CH_3}{C}}-CH_3$$

together with a smaller quantity of



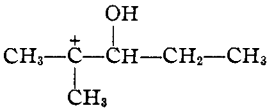
$$CH_3-\overset{H}{\underset{CH_3}{C}}-\overset{+}{\underset{CH_3}{C}}-CH_2OH$$

From the 3-methylpentane it would be



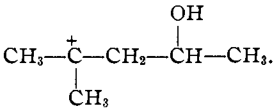
$$CH_3-CH_2-\overset{+}{\underset{CH_3}{C}}-\overset{OH}{CH}-CH_3,$$

The preferential migration of hydrogen to methyl in 2-methylpentane-2,3-diol where such migration would cause the formation of a quaternary carbon has been demonstrated.[38] In the case of the 2-methylpentane it would be necessary to assume two intermediates



$$CH_3-\overset{+}{\underset{CH_3}{C}}-\overset{OH}{CH}-CH_2-CH_3$$

and



$$CH_3-\overset{+}{\underset{CH_3}{C}}-CH_2-\overset{OH}{CH}-CH_3.$$

A rearrangement of the type postulated here has been reported in the case of one 1,3-glycol, trimethylene glycol, which has been found to rearrange to propionaldehyde.[39] It is assumed that in the formation of the complex the first molecule of chromyl chloride attaches itself to the hydrocarbon in place of the tertiary hydrogen. This presumably activates a hydrogen on an adjacent for carbon so that a second chromyl chloride molecule combines with it. The insolubility of this complex in non-polar solvents indicates that this second residue causes one of the linkages—presumably on the tertiary carbon—to assume the ionic character suggested.

In the case of those hydrocarbons not having a tertiary hydrogen the reaction is much slower. Since no rearrangement products were found it may be assumed that two chromyl chloride molecules are attached to the same carbon as in the case of the Étard complex with toluene.

NORMAN, OKLAHOMA

---

(36) K. E. Crook, M.S. Thesis, Univ. of Okla., 1926.

(37) A. Byers and W. J. Hickenbottom, *J. Chem. Soc.*, 1328 (1948).

(38) K. A. Kraskuii and M. M. Movsumzade, *J. Gen. Chem.* (*U.S.S.R.*), **7**, 2909 (1937); *C. A.*, **32**, 5610^6 (1938); I. N. Nazarov and A. N. Elizarova, *Bull. Acad. Sci.*, *U.S.S.R.*, *Classe Sci. Chim.*, 189^9 (1940); *C. A.*, **36**, 743^4 (1942); C. M. Suter and H. D. Zook, THIS JOURNAL, **66**, 738 (1944).

(39) C. Neuberg and B. Rewald, *Biochem. Z.*, **71**, 158 (1915).