

since a complete reaction between $(i\text{-C}_3\text{H}_7)_2\text{Ge}(\text{NCS})_2$ and silver acetate occurs. The two systems below yield mixtures of organogermanium compounds (Table II).

$[(\text{C}_2\text{H}_5)_3\text{Ge}]_2\text{O} + 2 \text{AgOCOCH}_3 \rightleftharpoons 2 (\text{C}_2\text{H}_5)_3\text{GeOCOCH}_3 + \text{Ag}_2\text{O}$.—One hour of reflux of 0.742 g. of $[(\text{C}_2\text{H}_5)_3\text{Ge}]_2\text{O}$ and 0.732 g. of silver acetate followed by distillation under low pressure yielded a mixture containing 16.3% $-\text{OCOCH}_3$; similarly, 1.122 g. of $(\text{C}_2\text{H}_5)_3\text{GeOCOCH}_3$ and 0.595 g. of silver oxide yielded a liquid mixture containing 16.6% $-\text{OCOCH}_3$. Distillation of a combination of the two mix-

tures showed 33% $[(\text{C}_2\text{H}_5)_3\text{Ge}]_2\text{O}$ and 67% $(\text{C}_2\text{H}_5)_3\text{GeOCOCH}_3$ to be present by weight. This confirmed the composition obtained by titration, which averaged 3.12 mole of $(\text{C}_2\text{H}_5)_3\text{GeOCOCH}_3$ per mole of $[(\text{C}_2\text{H}_5)_3\text{Ge}]_2\text{O}$.

$(i\text{-C}_3\text{H}_7)_3\text{GeCl} + \text{AgNCS} \rightleftharpoons (i\text{-C}_3\text{H}_7)_3\text{Ge}(\text{NCS}) + \text{AgCl}$.—Study of this reaction from both sides, with fractional distillation of each product and with tests of the isothiocyanate contents, showed that the system required 80% $(i\text{-C}_3\text{H}_7)_3\text{GeCl}$ and 20% $(i\text{-C}_3\text{H}_7)_3\text{Ge}(\text{NCS})$.

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[CONTRIBUTION NO. 1336 FROM STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

Chromate Esters. I. Solvolysis of Di-(2,4-dimethyl-4-hexyl) Chromate¹

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RECEIVED SEPTEMBER 28, 1955

Chromate esters of simple tertiary alcohols are isolable by freeze-drying technique. A new method of preparation of such esters using chromyl chloride is described. The solvolysis of the chromate ester of optically active 2,4-dimethyl-4-hexanol in methanol yields only the parent alcohol with essentially unchanged optical activity. The general occurrence of chromium-oxygen bond formation and fission in these reactions implied by this optical result and product is related to the oxidizing power of hexavalent chromium.

The appearance of a red, crystalline compound, decomposing to menthone at 53°, was observed by Beckmann³ in 1889 during the chromic acid oxidation of menthol and is the earliest reported indication of the existence of chromate esters. Such intermediates have been observed since, during similar oxidations of a few other alicyclic alcohols⁴⁻⁶ such as cholesterol,⁶ but as a rule oxidation proceeds too rapidly to allow either the observation or isolation of chromate esters. If, however, chromic anhydride is shaken with a solution of a secondary alcohol in benzene⁷ or petroleum ether⁸ a yellow color often forms which must be due to the formation of the chromate ester, since chromic anhydride itself is insoluble in these solvents. Decomposition to a brown solid usually occurs rapidly, within one-half hour, the one exception being the ester of borneol⁹ which was isolated as a fairly stable, red liquid. The chromate esters of tertiary alcohols, however, have been isolated as solids or liquids, ranging from yellow to orange to red in color and are, in general, more stable than those derived from oxidizable alcohols.¹⁰ All esters so far isolated have been diesters of the oxyacid, $(\text{HO})_2\text{CrO}_2$, although monoesters have been proposed as transient oxidation intermediates.

In a remarkable series of papers Westheimer and his colleagues¹¹ have presented compelling evidence

for the participation of chromate ester in the oxidation of isopropyl alcohol and have shown further that the elimination of the secondary hydrogen atom of this alcohol after esterification is the rate-determining process. The lack of stability of secondary chromates is undoubtedly related to the ease of elimination of the secondary hydrogen atom. Since tertiary alcohols possess no α -hydrogen atoms, the Westheimer mechanism is inoperable; hence their esters are more stable and must decompose by a different path requiring a greater activation energy.¹²

Since Gomberg isolated the chromate of triphenylcarbinol by treating silver chromate with triphenylmethyl chloride in benzene,¹³ other chromate esters have been obtained by treating tertiary alcohols with chromic acid in suitable solvents. Thus Wienhaus and Treibs have systematically prepared a series of such chromates by this method in petroleum ether, benzene, hydrogen sulfide and carbon tetrachloride.⁸⁻¹⁰ Alternatively, chromic anhydride can be treated directly with the carbinol,¹⁴ the ester then being dissolved in solvent to remove it from the aqueous phase formed by the elimination of water during reaction. For several carbinols Fieser and Ourisson¹⁵ found that the esters resulted from shaking the alcohols with sodium dichromate dihydrate in glacial acetic acid or with chromic anhydride in acetic anhydride. Stable esters such as di-2-methylfenchyl chromate¹⁶ can be prepared by all known methods, and these esters have been prepared for the purpose of purifying tertiary alcohols⁹ such as tricyclohexylcarbinol¹⁷ and 9-deca-

(1) This work was supported by Contracts No. DA-19-059-ORD-849 and -1494 between the Office of Ordnance Research, U. S. Army, and Yale University. Taken from the doctoral dissertation submitted by C. N. Matthews to the Faculty of the Graduate School, Yale University, 1955.

(2) Monsanto Chemical Co., Dayton 7, Ohio.

(3) E. Beckmann, *Ann.*, **250**, 322 (1889).

(4) W. Dieckmann, *ibid.*, **317**, 27 (pp. 65 and 70) (1901).

(5) R. A. Plattner, Th. Petrizilka and W. Lang, *Helv. Chim. Acta*, **27**, 513 (1944).

(6) L. F. Fieser, *THIS JOURNAL*, **75**, 4377 (1953).

(7) F. Holloway, M. Cohen and F. H. Westheimer, *ibid.*, **73**, 65 (1951).

(8) H. Wienhaus and W. Treibs, *Ber.*, **56**, 1648 (1923).

(9) W. Treibs, Dissertation, Göttingen, 1917.

(10) H. Wienhaus, *Ber.*, **47**, 322 (1914).

(11) (a) F. H. Westheimer and A. Novick, *J. Chem. Phys.*, **11**, 506 (1943); (b) W. Watanabe and F. H. Westheimer, *ibid.*, **17**, 61

(12) Product and kinetic studies of this decomposition have been made and are the subject of forthcoming papers.

(13) M. Gomberg, *Ber.*, **35**, 2397 (1902).

(14) R. Oppenauer and H. Oberrauch, *Anales assoc. quim. argentina*, **37**, 246 (1949).

(15) L. F. Fieser and G. Ourisson, *Bull. soc. chim.*, 1152 (1953).

(16) D. A. Pease, Jr., Dissertation, Yale University, 1954.

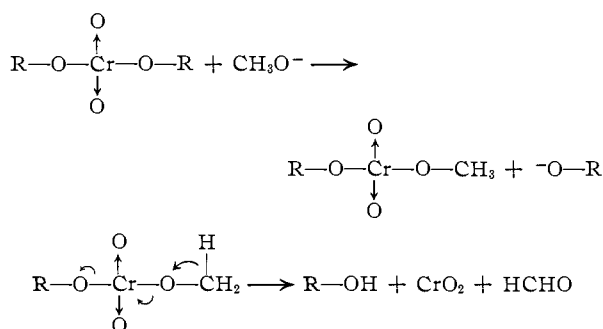
(17) O. Neunhoffer, *Ann.*, **509**, 115 (1934).

lol.¹⁸ Unstable esters such as *t*-butyl chromate have been used as agents for the specific oxidation of primary alcohols to aldehydes,¹⁴ olefins to α,β -unsaturated ketones¹⁹ and for converting aromatic hydrocarbons to quinones.²⁰

Reactions with chromate esters have been generally limited to the regeneration of parent alcohol by basic⁸⁻¹⁰ and acid¹⁶ hydrolysis, by reduction^{8-10,15-18} and by oxidation with hydrogen peroxide.¹⁵ More recently, mechanistic studies have been undertaken with the chromates of *t*-butyl alcohol,^{11d,21} triphenylcarbinol,²¹ 2-methylfenchyl alcohol and 2-methylborneol.^{16,22} In the present paper the preparation and solvolysis of the optically active chromate ester of 2,4-dimethyl-4-hexanol has been studied in order that the path by which ester formation and cleavage occurs may be defined.

The chromates of a series of aliphatic tertiary alcohols have been prepared successfully in pentane solutions over chromic anhydride and also by a new method employing chromyl chloride in carbon tetrachloride. The important part of the technique in both methods is the removal of solvent, excess alcohol and any olefin at low temperature and pressure (*ca.* -40° (0.1 mm.)) in a specially designed freeze-dry apparatus. Decomposition difficulties at this point prevented earlier workers from realizing the isolation of these esters. When pure, the esters can be stored indefinitely without appreciable decomposition at -60° in the dark. The chromates of 2,4-dimethyl-4-hexanol, 3-ethyl-3-pentanol, 2-methyl-2-butanol and *t*-butyl alcohol, as well as 2-phenyl-2-butanol, 2-phenyl-2-propanol and triphenylcarbinol, have been prepared by either or both of these methods.

Di-(2,4-dimethyl-4-hexyl) chromate, a red, liquid ester, undergoes rapid decomposition in sodium methoxide-methanol solution to pure 2,4-dimethyl-4-hexanol, formaldehyde and reduced chromium. The mechanism apparently involves displacement by methoxide ion on chromium, *i.e.*, transesterification, followed by internal oxidation-reduction of the intermediate primary-tertiary chromate.



Both steps as written involve chromium-oxygen bond fission and should lead to optically active car-

(18) W. Hüchel and M. Blohm, *Ann.*, **502**, 114 (1933).

(19) G. Dupont, R. Dulou and O. Mondou, *Bull. soc. chim.*, **60** (1953); D. Ginsburg and R. Pappo, *J. Chem. Soc.*, 516 (1951).

(20) W. J. Murray and E. P. Stevenson, U. S. Patent 2,169,368 (1939); *C. A.*, **33**, 9323 (1939).

(21) M. Anbar, I. Dostrovsky, D. Samuel and A. D. Yoffe, *J. Chem. Soc.*, 3603 (1954).

(22) F. R. Zwanzig, Dissertation, Yale University, 1955.

binol of unchanged configuration if the chromate ester be itself optically active.

The esterification of optically active 2,4-dimethyl-4-hexanol,²³ $[\alpha]_D +4.54^\circ$ (in CCl_4), with either chromic anhydride or chromyl chloride gave active chromate. However, repetition of the basic hydrolysis just described gave carbinol, $[\alpha]_D +4.27^\circ$ and $+4.33^\circ$, respectively. We conclude that the ester has the same configuration and optical purity as that of the parent alcohol and that the hydrolysis of the chromate has proceeded almost exclusively, if not totally, by chromium-oxygen bond fission.

Di-triphenylcarbinyl chromate, however, in methoxide-methanol solution does not react exclusively by the chromium-oxygen cleavage process, since a small amount of methyl ether is detectable in the reaction product. These results are in agreement with the O¹⁸ experiments reported by Dostrovsky and his colleagues,²¹ according to which alkaline hydrolysis resulted in exclusive chromium-oxygen cleavage of the chromate of *t*-butyl alcohol and partial carbon-oxygen cleavage of di-triphenylcarbinyl chromate.

In absolute methanol solvolysis of di-(2,4-dimethyl-4-hexyl) chromate was substantially complete within 24 hours. Again the sole organic products were the parent alcohol and formaldehyde. The absence of methyl ether or olefin was unexpected in view of the formation of such products in the methanolysis of tertiary carboxylic esters and, more particularly, of di-2-methylfenchyl chromate.¹⁶ In fact the methyl ether of 2,4-dimethyl-4-hexanol and the olefin mixture derived from the dehydration of the alcohol had been prepared for comparison purposes in anticipation of their formation during the solvolysis. Since mixtures of these three liquids are not at all readily separable by distillation it is considered unlikely that either ether or olefin was lost during distillation of the methanolysis product.

The occurrence of chromium-oxygen fission alone in the methanolysis of this aliphatic tertiary chromate ester was confirmed by the reaction of the optically active ester in methanol. Here solvolysis of the chromate ester prepared from carbinol, $[\alpha]_D +4.54^\circ$, gave back carbinol with 96% retention of configuration, $[\alpha]_D +4.35^\circ$. This almost complete retention of optical activity supports the hypothesis that chromium-oxygen cleavage is the sole mode of fission of alkyl chromates in such reactions and represents the first reported example of retention of configuration about a tertiary carbon atom in solvolytic reaction. By contrast, methanolyses of the optically active tertiary carboxylic esters, hydrogen 2,4-dimethyl-4-hexyl phthalate²⁴ and hydrogen 2-phenyl-2-butyl phthalate²⁵ occur with predominant inversion accompanied by racemization.

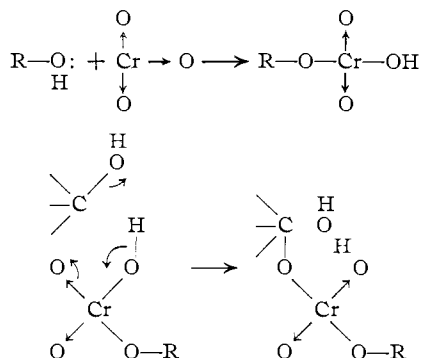
The methanolysis of di-(2-ethyl-2-pentyl) chromate likewise gave only carbinol as the solvolysis product, whereas di-triphenylcarbinyl chromate gave a much larger proportion of methyl ether than was obtained by basic hydrolysis.

(23) W. von E. Doering and H. H. Zeiss, *THIS JOURNAL*, **70**, 3966 (1948); **72**, 147 (1950).

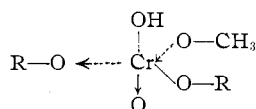
(24) W. von E. Doering and H. H. Zeiss, *ibid.*, **75**, 4733 (1953).

(25) H. H. Zeiss, *ibid.*, **75**, 3154 (1953).

These stereochemical results permit only those mechanisms which preserve configurational identity to be written for the formation and solvolysis of di-(2,4-dimethyl-4-hexyl) chromate. One such sequence is attractive to us in which the monoester is first formed, followed by a frontside nucleophilic attack on the tertiary carbon atom of the carbinol by the monoester through a six-membered cyclic transition state. Of course reaction between a



second molecule of carbinol and the monoester by a mechanism shown in the first step above is also reasonable and would lead to the same result. The simultaneous attack of two carbinol molecules on chromic anhydride is conceivable but improbable. A two-step displacement of chloride ion from chromyl chloride by carbinol is the most reasonable path for the formation of diester with this reagent. The solvolysis of the ester can then be written as a protonization of chromium oxygen with concurrent solvation of the chromium atom by methanol and separation of the tertiary alcohol with retention of configuration.



The exceptional oxidizing power of chromic acid and its esters can be rationalized by comparison with the solvolytic behavior of other oxyacids. Hydrolysis of the tertiary esters of the general structure, $MO_n(OR)_m$, where n is 1, 2 or 3, m is 1 or 2, and M is Cl, S, N or Cr, *i.e.*, the esters of perchloric, sulfuric, nitric, chromic and nitrous acids, listed in the order of decreasing acid strength in water,²⁶ will result either in C-O or M-O bond cleavage or a mixture of both in relation to the strength of the parent acid. Thus, alkaline hydrolysis causes C-O cleavage in aliphatic tertiary esters of the strong acids (perchlorate, sulfate, and nitrate) but not in the esters of the weak acids (chromate and nitrite) where M-O fission prevails.²¹ In the case of perchlorates and sulfates even the primary and secondary esters are hydrolyzed in alkali with C-O fission,²¹ whereas primary and secondary nitrates undergo substantial M-O cleavage²⁷ as do primary and secondary chromates. For neutral and acid hydrolysis essentially the same relationship is apparent between ease of removal of a

(26) R. J. Gillespie, *J. Chem. Soc.*, 2537 (1950).

(27) R. Boschan, R. T. Merrow and R. W. Van Dolah, *Chem. Revs.*, **55**, 485 (1955).

proton from the acid and the ease of C-O cleavage in its ester.

Ease of M-O cleavage is closely related to the oxidizing capacity of an ester and its parent acid. Oxidation of primary and secondary alcohols occurs if their esters can decompose by M-O cleavage, subject to the further condition that the expelled group be capable of independent, albeit temporary, existence. Thus, chromic acid and its tertiary esters exhibit excellent oxidizing properties, M-O cleavage occurring with formation of a compound of tetravalent chromium which is reduced further to the more stable trivalent state. The facileness of these reactions involving chromium compounds is of course related to the transitional character of chromium in which the number of valence electrons can be easily varied by chemical means. By contrast, perchloric acid is a poor oxidizing agent at ordinary temperatures,²⁸ while sulfuric acid and the sulfates hardly oxidize alcohols at all; indeed the use of primary sulfates for alkylating alcohols depends on their ability to undergo C-O cleavage. Nitrates are intermediate in their oxidizing properties; nitric acid oxidizes alcohols but tertiary nitrates (C-O fission) do not. Nitrous acid on the other hand is not an oxidizing agent in spite of the fact that its esters undergo M-O cleavage,²⁹ since oxidation would require the ejection of the unknown $:\ddot{N}=\ddot{O}$ ion. Similarly, carboxylic acids do not oxidize alcohols since even a highly transient existence of an intermediate anion, $R-\ddot{C}=\ddot{O}$, seems improbable.

A further consideration in the comparison of the properties of chromate esters with other esters is the powerful electron-attracting character of the hexavalent chromium atom. Nucleophilic attack is strongly directed at the chromium atom rather than at the adjacent carbon atom, whereas for carboxylates, for example, the relatively small difference between the electronegativities of the alkyl and acyl carbon atoms permits solvolytic attack on the former when its electronegativity is increased by electron-repelling groups as in tertiary esters³⁰ or in certain secondary esters.³¹ Thus one observes C-O fission in the solvolysis of tertiary carboxylates but not of the corresponding chromates. It is predicted that the solvolysis of tertiary aliphatic nitrites will be found to follow a stereochemical course similar to that of the chromates since clean M-O fission is characteristic of their reactions also.²⁹

The optical results obtained in the solvolysis of the hydrogen phthalate²⁴ and chromate of 2,4-dimethyl-4-hexanol clearly show that the original concept of invariable and extensive racemization of a tertiary carbon center in solvolytic reactions is far from true.

Experimental³²

Preparation of Di-(2,4-dimethyl-4-hexyl) Chromate and Other Tertiary Chromates. (a) Chromium Trioxide Method.

(28) H. Burton and P. F. G. Praill, *The Analyst*, **80**, 4 (1955).

(29) A. D. Allen, *J. Chem. Soc.*, 1968 (1954).

(30) S. G. Cohen and A. Schneider, *This Journal*, **63**, 3382 (1941); J. N. E. Day and C. K. Ingold, *Trans. Faraday Soc.*, **37**, 686 (1941).

(31) A. G. Davies, J. Kenyon, B. J. Lyons and T. A. Rohan, *J. Chem. Soc.*, 3474 (1954), and earlier papers.

(32) Optical rotations were measured in 0.5-dm. tubes at room temperature in carbon tetrachloride solution.

—A typical preparation using 2,4-dimethyl-4-hexanol²³ involved shaking mechanically 13 g. of the carbinol in 250 ml. of pentane (purified by shaking thrice with concentrated sulfuric acid, washing with sodium carbonate solution and water, drying over calcium chloride and distilling) with 6 g. of chromium trioxide (twice crystallized from water and dried over phosphorus pentoxide *in vacuo*) for 20 minutes. The orange-red solution was decanted from the aqueous chromic acid layer which had formed and was shaken again with 6 g. of fresh trioxide for 10 minutes. Little water was formed indicating that esterification was essentially complete. The red solution was filtered onto solid calcium chloride, shaken for 10 minutes and then filtered into the freeze-dry apparatus receiver flask (*vide infra*). Decomposition of the diester occurs after a few minutes at room temperature (brown precipitate) but if freeze-drying is carried out at once no decomposition is apparent. The diester solution was kept at -40° during the freeze-drying, the flask being submerged in a bath of Dry Ice and acetone, and after several days at 0.1 mm. pressure the infrared spectrum indicated that the diester was free of carbinol or olefin (distinctive chromate bands at 10.1 and 10.3 μ). Almost quantitative yields of the diester were obtained (90%).

The freeze-dry apparatus used consisted of a 3-l. r.b. flask sealed into a 5-l. r.b. flask fitted with openings for the attachment of the receiver flask and a vacuum line. The outer surface of the 3-l. flask served as a condenser (the flask was kept filled with Dry Ice-acetone mixture or liquid air) enabling solvent or other material to be trapped effectively. The apparatus allowed large amounts of solvent *e.g.*, 500 ml., to be removed continuously by freeze-drying while in the final stage the small volume of almost pure ester could be transferred to a small receiver fitted with a side arm allowing samples to be removed easily for analysis.

Esterification of some other tertiary alcohols was also performed using the above techniques. With *t*-butyl alcohol much lower yields were obtained because of the solubility of the ester and the carbinol in water. Extended shaking of 3-ethyl-3-pentanol with chromium trioxide in three batches was necessary before the characteristic deep red color of the pentane solution was attained. With 2-phenyl-2-butanol and 2-phenyl-2-propanol excess carbinol remained even after extended shaking (3 hours) and freeze-drying (several days).

(b) **Chromyl Chloride Method.**—The chromyl chloride esterification was carried out in carbon tetrachloride at room temperature rather than in pentane at low temperatures, the rapid reaction being more efficient than the slow, cold one in spite of some decomposition. A typical reaction with 2,4-dimethyl-4-hexanol involved adding 13 g. of the alcohol to a slight excess (7 g.) of chromyl chloride³³ dissolved in 500 ml. of carbon tetrachloride. Nitrogen, after passing through a xylene solution of benzophenone ketyl, was run into the stirred solution and on exit was passed through silver nitrate solution. No precipitation of silver chloride was observed until the carbinol addition had commenced, and this precipitation was accompanied by a slight warming of the solution. When all the alcohol had been added (10 minutes) stirring was continued for 15 minutes more, and at the end of this period only a minute deposit of the chloride was obtained in fresh silver nitrate solutions. Solid sodium carbonate was then added to the red solution with stirring for the purpose of removing traces of sulfuric acid originally present in the chromyl chloride, hydrogen chloride and excess chromyl chloride (a carbon tetrachloride solution of chromyl chloride is instantly decolorized by sodium carbonate). After filtering, the diester was obtained by the freeze-drying technique. With *t*-butyl alcohol a 90% yield of the diester was secured, but with triphenylcarbinol only a small amount of ester was recovered, the carbinol itself not being very soluble in carbon tetrachloride.

In all cases the developing purity of the ester during freeze-drying was followed by the infrared spectra of its carbon tetrachloride solutions. An ester was judged to be essen-

tially pure when the absence of hydroxyl (2.92 μ) or olefinic (6.0, 11.25 μ) bands coincided with the full development of the chromate bands at 10.1 and 10.3 μ . The rock salt cell used in obtaining these spectra soon became clouded with a yellow deposit, probably sodium chromate, and had to be cleaned periodically.

Analyses of Chromate Esters.—The combustion of the chromate esters to chromium sesquioxide gave in most cases only approximate results for chromium content due to the instability of the esters as shown by the change in weight during weighing. The analysis of the chromate diester of optically active 2,4-dimethyl-4-hexanol consisted of weighing rapidly and carefully 0.123 g. of the ester in a micro porcelain crucible, igniting slowly in a small muffle furnace (the final temperature after 2 hours was 900°) and obtaining 0.0276 g. of the green sesquioxide. The chromium content of the diester was 15.36% as compared to the calculated value of 15.19%.

Analyses for carbon, hydrogen, oxygen and chromium were performed by the Schwarzkopf Microanalytical Laboratory, Middleville, L. I., N. Y., and gave the following results on samples which had been stored in vials on Dry Ice. A violent explosion occurred in one analysis.

TABLE I
CHROMATE ESTER ANALYSES

Parent alcohol		Analyses, %			Chromium	Total, %
		Carbon	Hydrogen	Oxygen		
<i>t</i> -Butyl	Calcd.	41.73	7.88	27.79	22.59	99.99
C ₈ H ₁₈ O ₄ Cr	Found	41.99	7.65	27.07	22.05	98.76
<i>t</i> -Amyl	Calcd.	46.50	8.58	24.78	20.14	100.00
C ₁₀ H ₂₂ O ₄ Cr	Found	46.89	8.55	24.71	20.00	100.15
2,4-Dimethyl-4-hexyl	Calcd.	56.11	10.01	18.69	15.19	100.00
C ₁₆ H ₃₄ O ₄ Cr	Found	53.63	9.38	20.44	16.77	100.22
		49.99	9.15	21.99	18.29	99.42
		54.62	9.32	17.03	18.57	99.54
		53.48	9.42	15.15	21.00	99.05

Reasonable results for the esters of *t*-butyl alcohol and *t*-amyl alcohol contrast with the poor agreement between theoretical and observed values, and also between individual determinations for the branched octanol ester. The discrepancies, *i.e.*, low values for carbon and hydrogen and high values for chromium, are most likely due to the high susceptibility of this ester to decomposition at room temperature.

Spectrophotometric analysis was abandoned after the failure of efforts to improve on reproducibility of results obtained from duplicate samples.

Optically Active Di-(2,4-dimethyl-4-hexyl) Chromate.—Optically active 2,4-dimethyl-4-hexanol was obtained by fractional crystallization of the brucine salt of its acid phthalate ester and subsequent lithium aluminum hydride reduction of this salt according to procedures described fully elsewhere.³⁴ The optically active carbinol, $[\alpha]_D^{20} +2.17^{\circ}$, was treated with chromium trioxide as previously described to form the diester.

Anal. Calcd. for C₁₆H₃₄O₄Cr: Cr, 15.19. Found: Cr, 15.36.

A solution of the ester in carbon tetrachloride (*c* 0.76) gave an observed rotation of $+0.08^{\circ}$ with a red light source: $[\alpha]_{red} +10.1^{\circ}$. Preliminary attempts had shown that even a very dilute solution of the ester (less than 1%) was opaque to white light and that an observable "matching point" in the polarimeter could be obtained only if red light were used, either by passing intense white light through a monochromator³⁵ (λ 5840 Å.) or through red filters. With concentrations of about 1% rotations could just be observed, although the heating effect of the strong light source (G. E. projector lamp, 500 W.) caused fluctuations in readings. In any case the results showed that the ester is undoubtedly optically active; solutions of the ester prepared from racemic alcohol gave *no* rotation under similar conditions.

Solvolysis of Di-(2,4-dimethyl-4-hexyl) Chromate in Methanol.—Fifty drops (1.12 g.) of the red, liquid ester was added to 100 ml. of freshly distilled, absolute methanol.

(33) Chromyl chloride was prepared according to the method of H. A. Sisler, "Inorganic Syntheses," Vol. II, John Wiley & Sons, New York, 1939, p. 205, except that the final distillation step was omitted. Instead, washing with concentrated sulfuric acid was carried out to give a product of 99% purity: R. Slack and W. A. Waters, *J. Chem. Soc.*, 594 (1949). In later experiments a sample (98% pure) kindly supplied by the Mutual Chemical Company of Baltimore was used.

(34) See reference 1 and also A. Streitwieser, Ph.D. Thesis, Columbia University, 1951.

(35) Model B Monochromator, Cambridge Thermionic Corp., Cambridge, Mass.

The reaction flask was then flushed with nitrogen, stoppered and shaken occasionally. In the course of 36 hours the originally orange solution became murky, changing in color to brown, then brown-green, gray-green and finally gray (colloidal suspension). After 7 days, separation in the centrifuge (or better, in the ultracentrifuge) resulted in a fine gray precipitate and a colorless methanolic solution. This solution was extracted with pentane, the pentane evaporated and the solvolysis product distilled (40° (7 mm.)) to give 0.6 g. (75%) of a liquid which on infrared examination proved to be pure, parent alcohol, 2,4-dimethyl-4-hexanol. The methyl ether of the carbinol, 4-methoxy-2,4-dimethyl-hexane, was not detected.

The dried gray solid had a chromium content of 33.29%. Duplicate experiments gave solid in which the chromium % was 32.32 and 35.45. These values compare favorably with the calculated chromium content of chromic methoxide, $\text{Cr}(\text{OCH}_3)_2$: 35.86%.

The chromate ester besides being insoluble in water is also relatively inert toward it, requiring about 2 weeks for complete decomposition. The product is a mixture of the parent alcohol, ketonic material (5.83 μ) and olefin(s) with peaks at 6.0, 6.1 and 11.26 μ (intense).

Repetition of the methanolysis of di-(2,4-dimethyl-4-hexyl) chromate just described using optically active chromate diester prepared from 2,4-dimethyl-4-hexanol, $[\alpha]_D +4.54^\circ$ (α 0.27°, c 11.9 in CCl_4), was performed. The pure carbinol isolated from the methanolysis was also optically active: $[\alpha]_D +4.35^\circ$ (α 0.23°, c 10.58 in CCl_4). This represents 96% retention of configuration during reaction.

Reaction of Di-(2,4-dimethyl-4-hexyl) Chromate with Sodium Methoxide.—Fifty drops of the liquid diester (1.12

g.) was dropped into a solution of 10 g. of sodium in 100 ml. of methanol. After flushing with nitrogen the flask was stoppered and shaken. A yellow-green slurry formed at once which separated after 30 minutes as a deposit of yellow, crystalline sodium chromate in a green solution. An additional 50 ml. of methanol was now added, then 200 ml. of water, and the resultant green solution was extracted with four 50-ml. portions of pentane. After drying with sodium sulfate and removal of pentane by evaporation, the product was distilled (40° (7 mm.)) to give 0.65 g. (76%) of pure 2,4-dimethyl-4-hexanol (infrared comparison). The aqueous layer was shaken with dimedon solution (ρH 4.6) from which the white crystalline derivative of formaldehyde was isolated. This solid was filtered, washed with water and dried; m.p. 190°.

In a side experiment the chromate diester of triphenylcarbinol was treated with sodium methoxide by the same procedure. Although the major product was the parent alcohol, a small amount of its corresponding methyl ether (9.3 μ) was detected.

Reaction between sodium methoxide and optically active chromate ester taken from the same source as that used in the solvolysis work above resulted in the formation of optically active parent alcohol, $[\alpha]_D +4.27^\circ$ (α 0.25°, c 11.7 in CCl_4). This amounts to 94% retention of configuration.

Optically active di-(2,4-dimethyl-4-hexyl) chromate was also prepared from 2,4-dimethyl-4-hexanol, $[\alpha]_D +4.54^\circ$, and chromyl chloride. Reaction of this ester with sodium methoxide in methanol gave pure carbinol, $[\alpha]_D +4.33^\circ$ (α 0.26°, c 12.0 in CCl_4), with 95% retention of configuration.

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Branched-chained Tertiary Alcohols. I. Diisobutylethylcarbinol

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RECEIVED SEPTEMBER 6, 1955

The reaction of ethylmagnesium bromide with diisobutyl ketone yields diisobutylethylcarbinol accompanied by considerable reduction and enolization. The structure of the alcohol is confirmed through dehydration and the ozonolysis on the resulting olefins.

Our interest in the general problem of the synthesis of branched-chain tertiary alcohols was stimulated by the discovery that in a preparation involving the condensation of ethylmagnesium bromide with diisobutyl ketone the yield of the expected alcohol I was almost zero. This was a striking result in view of the fact that ethylmagnesium bromide with diisopropyl ketone is reported to give a 77% yield of the addition product.¹ Whitmore and George studied a series of ketone-Grignard reagent reactions and determined the extent of addition, reduction and enolization obtained in each case. With branched-chained ketones where the branching occurred on the α -carbon atoms the addition reaction of *n*-propyl and higher Grignard reagents ceased to be the main reaction. Whitmore and Lewis² found that the degree of enolization of the carbonyl compound in the presence of ethylmagnesium bromide depends upon the nature of the substituents on the carbon atom adjacent to the carbonyl group, and that substitution on the β -carbon atom had less effect on the reaction of the carbonyl group.

(1) F. C. Whitmore and R. S. George, *THIS JOURNAL*, **64**, 1239 (1942).

(2) F. C. Whitmore and C. E. Lewis, *ibid.*, **64**, 2964 (1942).

In order to obtain an appreciable yield of the addition product, an excess of Grignard reagent to ketone was employed. The replacement of ethyl ether by benzene in the Grignard reagent solution and the subsequent higher temperature used during the addition of the ketone had little effect upon the product distribution. Only a trace of I was obtained from the two runs in which an approximate 1:1 mole ratio of Grignard reagent to ketone was employed.

The reaction of an excess of ethylmagnesium bromide with diisobutyl ketone gave 20% enolization and reduction, 40% unreacted diisobutyl ketone and 40% I. The large amount of unreacted ketone differs from the results of Whitmore and George¹ in the study of the reaction of ethylmagnesium bromide and diisopropyl ketone.

The alcohol was easily dehydrated in the presence of oxalic acid. Ozonolysis of the olefinic material gave diisobutyl ketone and ethyl isobutyl ketone. The ketones were identified by conversion to the corresponding 2,4-dinitrophenylhydrazones. Thus, the dehydration of I gave a mixture of two new isomeric olefins, 4-ethyl-2,6-dimethyl-3-heptene and 3-isobutyl-5-methyl-2-hexene. The structure of the alcohol is established.