m. p. 133–134° after recrystallization from benzene–petroleum ether.

Anal. Calcd. for $C_{14}H_{20}O_3$: C, 72.55; H, 8.12. Found: C, 72.97; H, 8.25.

The ethyl ester was prepared by the acetyl chloride procedure, yield 84%, b. p. 167–168° (2 mm.). The ester was iodinated by method *I* and a 70% yield of iodo ester was obtained, m. p. 85.5–86° after recrystallization from benzene–petroleum ether.

Anal. Calcd. for $C_{17}H_{23}O_3I$: C, 50.75; H, 5.76; I, 31.6. Found: C, 50.70; H, 5.96; I, 31.9.

Acknowledgment.—The authors wish to express their appreciation to Miss Margaret Sherlock, Mrs. Hilda Breiger, Miss Virginia Paterson and Mrs. Anna Klingsberg for their assistance and to Dr. Richard Tislow and Mrs. Annette LaBelle for the pharmacological data on the compounds.

Summary

1. A series of iodinated alkoxyaryl aliphatic acids and esters have been prepared and examined as X-ray diagnostic agents for visualization of the gall bladder and body cavities, respectively.

2. Four iodination procedures were studied; namely, mercuric acetate–iodine, iodine chloride, silver acetate–iodine, and silver salt of alkoxyaryl aliphatic acid and iodine. The latter two procedures yielded the iodinated acids and esters in good yield under extremely mild conditions.

BLOOMFIELD, N. J. RECEIVED OCTOBER 8, 1949

[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Copper–Chromium Oxide Catalyst for Hydrogenation[1]

BY HOMER ADKINS,[2] EDWARD E. BURGOYNE AND HENRY J. SCHNEIDER

The preferred catalyst for the hydrogenation of esters to alcohols and for certain other reactions contains copper, chromium, barium and oxygen. Recent physical data[3] have shown that the catalyst contains copper oxide and copper chromite, but that it is neither a simple copper chromite, nor a mechanical mixture of copper oxide and copper chromite.

That the true catalyst is not copper chromite has now been clearly established in this Laboratory and others[4] by the fact that the catalyst mass, after removal of cupric oxide either by reduction or by solution, is not active for the hydrogenations of ketones or esters at temperatures up to 275°. On the other hand, while copper chromite is certainly not the catalyst, it is an essential constituent since cupric oxide alone is rendered ineffective by its reduction to copper. Furthermore, the work now reported shows that the activity of the catalyst is dependent upon the ratio of copper oxide to copper chromite.

In order to improve the catalyst and to correlate activity with composition we have tested various samples of catalyst. The basis of comparison involved the hydrogenation of 0.10 mole of methyl laurate or palmitate in 100 ml. of pure, dry methanol, with 5 g. of catalyst, under a pressure of hydrogen so adjusted that it was approximately 6000 p. s. i. at the temperature of reaction.[5] The extent of hydrogenation, after three hours at the specified temperature, was determined by saponification of the residual ester. The results of representative hydrogenations are given in Table I. The catalysts differed principally in the method of decomposition of the basic copper ammonium chromate.

TABLE I

COMPARISON OF COPPER–CHROMIUM OXIDE CATALYSTS BY % HYDROGENATION OF ESTERS AT 175° FOR THREE HOURS

Catalyst	Methyl laurate	Methyl palmitate
C and E[a]	38	
REB[b]	34	
EEB 1[c]	37	
DW and A[d]	32	
TWR[e]	55	
HJS 1[f]	53	66
HJS 2[f]	62	78

[a] Prepared in 1934 by Calingaert and Edgar.[8] [b] Prepared by Robert E. Burks, Jr., by a modification of the procedure of Lazier and Arnold.[10] The decomposition of the basic copper ammonium chromate was carried out in small batches (40–50 g.) in a porcelain crucible of 40-ml. capacity surrounded by air at 350–375°. [c] Prepared as described in footnote 2, Adkins and Burgoyne, THIS JOURNAL, 71, 3528 (1949). [d] Prepared by Drake, Walton and Anspon. The decomposition was carried out as follows: "Three tablespoonfuls of copper ammonium chromate. . . is sprinkled on the bottom of a 2-l. casserole previously heated to a dull red heat and resting on a transite board. Additional material is sprinkled on the black patches where decomposition has taken place at such a rate as is necessary to maintain decomposition of the chromate without excessive violence or additional application of heat. When the casserole is half-full. . . it is stirred to red heat for ten to fifteen minutes while the powder is thoroughly stirred" (N. L. Drake, personal communication). [e] Prepared by T. W. Riener.[9] [f] See Experimental section.

It is not implied that a comparison of catalysts under any one set of conditions will show the relative value of these preparations under any other set of conditions. However, such a comparison as now reported has enabled us to prepare

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[1] Supported in part by the Research Committee of the Graduate School from funds supplied by the Wisconsin Alumni Research Foundation.

[2] Deceased August 10, 1949.

[3] (a) Stroupe, THIS JOURNAL, **71**, 569 (1949); (b) Selwood, Hill and Boardman, *ibid.*, **68**, 2055 (1946), and personal communications.

[4] T. W. Riener, personal communication.

[5] Adkins and Billica, THIS JOURNAL, **70**, 3121 (1948).

catalysts of higher activities than those previously used in this Laboratory; they may enable others to ascertain the quality of catalyst available to them.

A critical step in the preparation of the copper–chromium oxide catalyst is the decomposition of the basic copper ammonium chromate. It has been shown repeatedly[6,7,8] that the decomposition should be carried out at the lowest possible temperature. Various techniques have been used to achieve a reasonably complete decomposition without heating the catalyst above 400°. The simple procedure recently reported by Riener,[9] appears to be quite superior to any other proposed.[6,7,8,10,11]

As may be seen from Table I, catalyst HJS 2 gave considerably more hydrogenation than one of the earlier standard catalysts such as EEB 1. This enhanced activity is due to (a) the use of Riener's procedure for carrying out the decomposition of the basic copper ammonium chromate and (b) to increasing the ratio of chromium to copper in the catalyst. Possibly, there is also a slight advantage in using sodium rather than ammonium dichromate.

The analysis of the catalyst EEB 2, which contained no barium, but which had an activity similar to the EEB 1 catalyst showed that there was a molecular excess of cupric oxide over cupric chromite. This deficiency of cupric chromite is not present in HJS 2, in which the ratio of cupric oxide to $CuCr_2O_4$ is less than unity. It is significant that while catalyst HJS 2 contains about 20% of the presumably inert barium chromate, added to stabilize the divalent copper against reduction, it has the highest catalytic activity per unit weight. Moreover, it has been found that if the catalysts EEB 2 and HJS 2 were compared in a hydrogenation of methyl laurate on the basis of equal weights of cupric oxide the catalyst HJS 2 exhibited approximately 2.5 times the catalytic activity of EEB 2. The compositions of these two catalysts are given in Table II.

All copper–chromium oxide catalysts absorb considerable hydrogen under pressure. In fact, if the catalyst under alcohol is exposed to hydrogen at 200 atm. above 100°, and the vessel quickly cooled and opened, the catalyst is pyrophoric. This absorption of hydrogen by the catalyst has two important consequences. First, if a high ratio of catalyst is used the apparent absorption of hydrogen will be greater than required for a particular hydrogenation. A comparison of the observed drop in pressure during the hydrogenation of methyl 2-naphthyl ketone over copper–chromium oxide with the calculated drop in pressure for the quantitative hydrogenation of this compound showed that approximately 150 ml. of hydrogen (0°, 760 mm.) was absorbed per gram of an active catalyst. The absorption of this amount of hydrogen by 10 g. of catalyst in a bomb of 150-ml. hydrogen capacity corresponds to a drop of 150 p. s. i., a discrepancy that may be quite significant in a hydrogenation requiring careful control. The other important consequence of the hydrogen absorption is the activation of the catalyst. In general it has been necessary to use temperatures above 120° with the copper–chromium oxide catalyst. However, with this hydrogen-activated catalyst aldehydes and ketones have been hydrogenated at room temperature and certain esters at 80°.

The activated catalyst was effective in successive hydrogenations. Methyl 2-naphthyl ketone over a previously activated catalyst, was quantitatively hydrogenated to methyl-2-naphthylcarbinol within eight minutes at 25° under about 4000 p. s. i. of hydrogen. The hydrogenation was repeated on two successive batches of ketone, using the same sample of catalyst. The time required for the second complete hydrogenation increased to ten minutes and to twelve minutes for the third. The catalyst was then removed and dried in the air overnight and used again. It had some activity but not enough to complete a hydrogenation at room temperature, although it was sufficiently active to bring about the hydrogenation of the ketone within forty-five minutes at 80°.

Cinnamaldehyde and crotonaldehyde were hydrogenated at room temperature over an activated catalyst under 4000–4500 p. s. i. of hydrogen. Crotonaldehyde adsorbed a little more than a mole of hydrogen per mole of aldehyde in three and one-half hours, while cinnamaldehyde required about twenty minutes for a similar degree of hydrogenation. Crotonaldehyde absorbed practically a mole of hydrogen per mole of compound during twenty-five hours at room temperature under only 40–45 p. s. i. of hydrogen.

The recovery of products from these hydrogenations, in which one mole of hydrogen per mole of aldehyde was absorbed, was poor and in each case there was a mixture of saturated and unsaturated aldehydes and saturated and unsaturated alcohols. Attempts to modify the conditions and extent of hydrogenation to obtain selective hydrogenation to cinnamyl and crotonyl alcohols were unsuccessful. However, in the case of cinnamaldehyde the yield of cinnamyl alcohol, as determined from the index of refraction of the product obtained after removal of the aldehydic component with sodium bisulfite, was 26% of theoretical.

The hydrogenation of the unsaturated aldehydes to the saturated alcohols is easily achieved at 24°, particularly if triethylamine is added to

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(6) Adkins and Connor, THIS JOURNAL, **53**, 1091 (1931).

(7) Adkins, Connor and Folkers, *ibid.*, **54**, 1138 (1932).

(8) Calingaert and Edgar, *Ind. Eng. Chem.*, **26**, 878 (1934).

(9) Riener, THIS JOURNAL, **71**, 1130 (1949).

(10) Lazier and Arnold, "Org. Syntheses," Vol. 19, p. 31, and Coll. Vol. II, p. 142, John Wiley and Sons, Inc., New York, N. Y., 1939; U. S. Patent 1,964,000 (1934).

(11) Other methods have been suggested in private communications and the catalysts evaluated in this Laboratory.

the reaction mixture.[5] Crotonaldehyde in methanol, with triethylamine and activated catalyst absorbed two moles of hydrogen so rapidly within twenty minutes at 4000 p. s. i. that the temperature rose 13°.

Hydrogenation of ethyl 1-naphthoate to 1-naphthylcarbinol was attempted at 80, 88, 100 and 125° using the activated catalyst. However, it was difficult to prevent hydrogenolysis of the alcohol to the 1-methylnaphthalene. The best results were obtained by hydrogenation at 88° for a period of three and one-half hours at 300 atmospheres. Under these conditions 40% of the ester was reduced to yield a mixture of five parts of hydrocarbon and one part of carbinol. A 65–72% reduction of methyl 2-naphthoate was obtained at 97° and 300 atmospheres. Over a period of three hours, the ester in methanol absorbed 1.5 moles of hydrogen per mole of ester. The products consisted of a mixture of three parts of 2-naphthylcarbinol and one part of 2-methylnaphthalene; the actual yield of carbinol isolated was 33%. In a similar experiment at 108° for one and one-half hours a 58% yield of 2-naphthylcarbinol was obtained with no increase in the total reduction, indicating that higher temperature and shorter contact time favored the selective reduction to the carbinol.

Experimental Part

The hydrogenations were made in a chrome–vanadium steel reaction vessel 1.45 i. d. × 9.75 inches, having a thermocouple well in the wall. It was rocked at 58 cycles per minute. The methanol and ethanol used were dry and were freed from catalyst poisons by distillation from Raney nickel.

Methyl laurate, methyl myristate and methyl palmitate were prepared by methanolysis of coconut oil and fractionation of the esters.[12] The weight of methyl laurate (m. p. 5°, n^{25}D 1.4302) was 32%, of methyl myristate (m. p. 17.5°, n^{25}D 1.4350) was 12% and of methyl palmitate (m. p. 26.5°) was 5% of the weight of oil subjected to methanolysis. Each of those esters was distilled from Raney nickel. Methyl 2-naphthyl ketone (m. p. 53–55°), crotonaldehyde (b. p. 102–103°, n^{25}D 1.4332) and cinnamaldehyde (n^{25}D 1.6212) were obtained from commercial sources.

The drops in pressure (250–500 p. s. i.) under the conditions used in testing the catalysts against esters were not sufficiently large so that comparisons of catalyst could be based upon them. The determination of the extent of hydrogenation was made by saponification of the residual ester. The reaction mixture was made up to 250 ml. in methanol and the ester in a 5-ml. aliquot was saponified for thirty minutes at 130° in 10 ml. of ethylene glycol containing 6 g. of potassium hydroxide per 100 ml. The solution was then acidified with 0.3 *N* hydrochloric acid and the hot acid solution titrated with 0.1 *N* sodium hydroxide against phenolphthalein.

The catalyst HJS 2 was prepared in the following manner. A solution (900 ml. at 80°) containing 260 g. of copper nitrate trihydrate and 31 g. of barium nitrate was poured with stirring into 900 ml. of a solution (at 25°) containing 178 g. of sodium dichromate dihydrate and 225 ml. of 28% ammonium hydroxide. The orange precipitate was collected on a filter, washed with 200 ml. of water in two portions, pressed and sucked as dry as possible, dried at 75–80° for twelve hours and pulverized. This product was decomposed in a 4-necked liter flask held in a Woods metal-bath at 350°. The flask was provided with a wide air condenser, a funnel for introducing a solid, a thermometer, and a stainless steel stirrer with a crescent blade 1.25 cm. wide and 10 cm. long, so shaped that it conformed to the bottom of the flask. The material to be decomposed was added through the funnel during a period of fifteen minutes with rapid stirring. The product was heated with stirring at a bath temperature of 350° for twenty minutes after all of the material had been added. The temperature registered by a thermometer in the powder rose to 310° during the period of addition and then fell to 278° during the subsequent twenty-minute period.

The product from the decomposition was leached by stirring for thirty minutes with 600 ml. of 10% acetic acid at room temperature. The powder was washed with 600 ml. of water in 100-ml. portions, dried at 125° for twelve hours and pulverized. The catalyst so obtained was brownish-black in color and amounted to 160–170 g.

Catalyst HJS 1 was prepared by the above procedure except that 151 g. of ammonium dichromate was substituted for the sodium dichromate.

Analyses for copper, chromium and barium were made by standard procedures.[13] The results given in Table II are the average of two analyses which agreed within less than 0.05% of each other. The figures given on loss in weight at 800° were obtained by using the standard apparatus and procedures for organic combustions. The sample of catalyst, EEB 2 lost 3.16% water, 0.05% nitrogen and 0.83% of an undetermined gas, presumably oxygen, when it was heated at 800–850°. The water was very firmly bound, as the amount evolved after sixteen hours at 200° was only 60% of that lost at 800–850°. The color of the catalysts and the fact that nitrogen was evolved at 850° suggest that it contained undecomposed basic copper ammonium chromate. Dumas nitrogen analyses showed 1.2% of undecomposed complex remaining in the catalyst HJS 2, while EEB 1 contained *ca.* 0.05%. Incidentally, it may be noted that the better catalysts have a slightly brownish tinge and that the jet black products generally are inferior catalysts. Catalysts which have been deactivated by overheating may be greenish-black.

TABLE II

ANALYSIS OF COPPER–CHROMIUM OXIDE CATALYSTS

Catalyst	Percentages								Moles CuO Moles $CuCr_2O_4$
	Cu	Cr	Ba	H_2O	Etc.	Cu-Cr_2O_4	Ba-CrO_4	CuO	
EEB 2	41.2	29.3	0	3.2	0.9	65.1	0	28.9	1.29
HJS 2	27.8	29.5	9.7	6.1	1.3	54.4	18.0	14.8	0.76

In the removal of copper oxide the catalyst EEB 1 (10 g.) was heated on a steam-bath with 75 ml. of concentrated hydrochloric acid for twenty minutes, under which conditions the cupric oxide is rapidly dissolved. The residue was separated by filtration and washed with 10% acetic acid and water and dried at 125° for twelve hours. The product (4.3 g.) was tested for catalytic activity against methyl 2-naphthyl ketone at both 80 and 150°; it caused no absorption of hydrogen at either temperature in contrast to a rapid hydrogenation at 80° when 1 g. of the standard catalyst was used. The failure of hydrogenation was apparently not due to a catalyst poison for the hydrogenation of methyl 2-naphthyl ketone proceeded at 80° when 1 g. of the EEB 1 catalyst was added to 1 g. of the inactivated catalyst and 17 g. of the ketone in methanol.

The material from which copper oxide had been removed also proved to be inactive for the hydrogenation of ethyl laurate at 250°. Riener[4] also has found that after the removal of cupric oxide from a catalyst (10 g.) with hydrochloric acid at room temperature, the residue (5 g.) was inactive as a catalyst for the hydrogenation of esters at 275°.

In the hydrogenation of crotonaldehyde under 4000–4500 p. s. i. of hydrogen, 21 g. of the aldehyde in methanol was used with 5 g. of an activated catalyst. In the

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[12] Sauer, Hain and Boutwell, "Org. Syntheses," John Wiley and Sons, Inc., New York, N. Y., 1940, Vol. 20, p. 67.

[13] Smith, "Quantitative Chemical Analyses," 3rd ed., Macmillan Company, New York, N. Y., 1933, pp. 141, 148.

hydrogenation at 40–45 p. s. i., 5 g. of activated catalyst for 7 g. of the aldehyde was used. In the hydrogenation to butanol-1 at room temperature, 5 ml. of triethylamine, 100 ml. of methanol, 21 g. of crotonaldehyde and 10 g. of the activated catalyst were used under 4000 p. s. i. of hydrogen. In the attempts to selectively hydrogenate cinnamaldehyde to cinnamyl alcohol the ratio of aldehyde to catalyst was 2.6:1.

The copper–chromium oxide catalyst was activated by shaking the catalyst, suspended in methanol, under approximately 4000 p. s. i. of hydrogen at 100° for five minutes. The reaction vessel was then cooled to room temperature and the compound to be hydrogenated was added.

In the hydrogenation of methyl 2-naphthyl ketone, 17 g. was used with 10 g. of activated catalyst in 100 ml. of methanol, under 4000 p. s. i. of hydrogen. The yield of methyl-2-naphthylcarbinol,[14] m. p. 74–75°, from five such hydrogenations was 80.8 g. In the hydrogenations of the naphthoate esters 0.1 mole of the ester was employed with 10 g. of activated catalyst in 100 ml. of methanol, under 300 atmospheres of hydrogen.

Summary

Procedures have been given for the preparation of the copper–chromium oxide catalyst, having a higher activity than previously described. A method for determining the activity of samples of the catalyst has been described and illustrated by application to samples of catalyst prepared by various procedures.

The catalyst if properly prepared adsorbs approximately 150 ml. of hydrogen per gram of catalyst in the temperature range 80–100° under 4000 p. s. i. The catalyst is thereby activated so that it is effective, even at room temperature, for the hydrogenation of alkene and carbonyl linkages. This catalyst is active for the hydrogenation of carboalkoxy groups of the naphthoic esters from 80° upward.

It has been demonstrated that the copper chromite is not a catalyst for the hydrogenation of aldehydes, ketones, alkenes and esters, at temperatures below 250°, at which the copper–chromium oxide catalyst is normally used.

MADISON, WISCONSIN RECEIVED DECEMBER 5, 1949

[14] Lund, *Ber.*, **70**, 1520 (1937).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Cleavage of Some Organosilanes

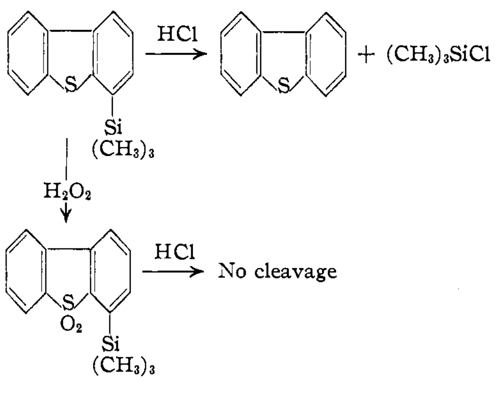
BY HENRY GILMAN AND JOHN F. NOBIS[1]

In connection with some studies on the introduction of functional groups into alkyl- and arylsilanes, it was found desirable to examine the cleavage of the Si–C linkage. This examination involved treatment of the organosilicon compounds with anhydrous hydrogen chloride in refluxing glacial acetic acid.[2] Table I (Experimental part) shows the products obtained when some selected silanes were subjected to this treatment.

The isolation of hexaphenyldisiloxane from the cleavage of triphenylphenylethynyl-silane was not entirely unexpected since the triphenylsilyl chloride formed by the cleavage reaction would be converted to triphenylsilanol when poured into water and in the presence of the acetic and hydrochloric acids this silanol would condense to form the disiloxane.[2b] It has not been definitely established, however, whether the acetophenone obtained in this same cleavage came as a result of cleavage of the Si–C bond followed by addition of hydrogen chloride to the phenylacetylene formed, with subsequent hydrolysis to acetophenone or whether addition of hydrogen chloride to the acetylenic linkage preceded cleavage.

Hexaphenyldisiloxane was the only product identified from the cleavage of triphenyl-β-styrylsilane.

The Si–C bond in 4-trimethylsilyldibenzothiophene is apparently quite unstable toward acidic reagents, as evidenced by the 87% yield of dibenzothiophene obtained when this compound was treated with hydrogen chloride. When this silane was oxidized to 4-trimethylsilyldibenzothiophene-5-dioxide, however, the silicon–carbon linkage was stabilized to a considerable extent, since the dioxide was completely resistant to hydrogen chloride treatment under corresponding conditions.



Further evidence of the stabilizing effect of the $-SO_2-$ group was noted when 4-trimethylsilyldibenzothiophene-5-dioxide was treated with fuming nitric acid and a mononitro-4-trimethylsilyldibenzothiophene-5-dioxide was isolated. A way may have been opened to the direct substitution of other sulfur-containing aryl-alkylsilanes.

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[1] Department of Chemistry, Xavier University, Cincinnati, Ohio.

[2] For other cleavage studies see: (a) Kipping and Blackburn, *J. Chem. Soc.*, 1085 (1935); (b) Gilman and Marshall, THIS JOURNAL, **71**, 2066 (1949). Numerous references to cleavage reactions are given in this article.