oxide, the material balance being 96–97%. From the reaction in refluxing acetone containing acetic acid the products were similar and the material balance was 94%. The main products of the reaction in methanol in the presence of acetic acid were methyl trityl ether and triphenylphosphine oxide. These products accounted for 88% of the starting material, but there was also formed about 3% of an unknown material, melting at 190–210°.

Decomposition of the triarylmethyl azide-triphenylphosphine complexes in glacial acetic acid. From 1.85 g. of the trityl azide–triphenylphosphine complex decomposed in 5 cc. of glacial acetic acid under nitrogen were obtained, after distillation of the solvent and chromatography on alumina, 0.66 g. of triphenylcarbinol and 0.82 g. of triphenylphosphine oxide. Elution of the column with water gave ammonium acetate. A similar experiment with 2.0 g. of the 9-phenyl-9-fluorenyl azide–triphenylphosphine complex gave 0.60 g. of 9-phenyl-9-fluorenyl acetate, 0.61 g. of triphenylphosphine oxide, and 0.63 g. of *N*-(9-phenyl-9-fluorenyl)triphenylphosphineimine, m.p. 223–224°.

Anal. Calcd. for $C_{37}H_{28}NP$: C, 85.9; H, 5.45; N, 2.7. Found: C, 85.9, H, 5.13; N, 2.68.

The other products were identified by their infrared spectra and mixed melting points. Similar experiments in the presence of excess triarylmethyl azide gave similar results; the excess azide was recovered unchanged.

Trapping of triphenylphosphineimine. A solution of 10 cc. of benzoyl chloride and 4.4 g. of the trityl azide–triphenylphosphine complex in benzene was refluxed for 24 hr., washed with K_2CO_3, and concentrated by distillation. *N*-Benzoyltriphenylphosphineimine, which crystallized from the residual oil in good yield, was identified by a mixed melting point. Other products were triphenylcarbinol, triphenylphosphine oxide, trityl chloride, and benzoic anhydride.

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Study of the Chromium(VI) Oxide–Pyridine Complex

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The chromium(VI) oxide–pyridine complex was found to be a good oxidizing agent at room temperature for the conversion of primary benzylic and allylic alcohols to their corresponding aldehydes. Data for twenty-one compounds are presented. Simple aliphatic and aromatic secondary alcohols are converted to ketones in fair to good yields; data for six are presented.

The chromium(VI) oxide–pyridine complex was introduced as an oxidant for the conversion of primary and secondary alcohols to aldehydes and ketones by Poos, Arth, Beyler, and Sarett.[1] They reported that the reagent, in a pyridine dispersion at room temperature, did not attack such readily oxidized groups as olefinic double bonds and thiol ether linkages. Acetal groups were not affected by the reagent, for the medium was basic. First applied in the steroid field, the reported use of the reagent has been almost entirely in that area since.[2] In most cases, the application has been to the conversion of a secondary alcohol to a ketone, and it has been routinely observed that olefinic linkages and acetal groups are little affected by the reagent.

Aldehyde syntheses *via* the reagent have been seldom reported. Mazur, Danieli, and Sondheimer reported the conversion of 3,16-biscycloethylenedioxybisnor-5α-cholan-22-ol, a primary aliphatic alcohol, to the corresponding C-22 aldehyde in 83% yield by employing the reagent at a moderately elevated temperature (37°) for a briefer than normal reaction time.[2h] The few reports of attempts to accomplish the same type of aldehyde synthesis by using the reagent at room temperature have been discouraging. (*cf.* ref. 2a, 2m) Zimmerman, Singer, and Thyagarajan, for example, did not obtain aldehyde by action of the reagent on the epoxyalcohol, 2,3-*cis*-diphenyl-2,3-epoxypropan-1 ol.[3] α,β-Epoxy secondary alcohols, however, readily yielded ketones.[3,4] In the present study, citronellol was converted to citronellal by the chromium(VI) oxide–pyridine complex in pyridine in only 25%

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[1] G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *J. Am. Chem. Soc.*, **75**, 425 (1953).

[2] The following list of references does not constitute an exhaustive search of the literature. (a) L. F. Fieser, T. Goto, and B. K. Bhattachoryya, *J. Am. Chem. Soc.*, **82**, 1704 (1960). (b) J. A. Zderic, E. Batres, D. C. Limon, H. Carpio, J. Lisci, G. Monroy, E. Necoechea, and H. J. Ringold, *J. Am. Chem. Soc.*, **82**, 3404 (1960). (c) W. S. Johnson, W. A. Vredenburgh, and J. E. Pike, *J. Am. Chem. Soc.*, **82**, 3409 (1960). (d) S. Bernstein and R. H. Lenhard, *J. Am. Chem. Soc.*, **82**, 3683 (1960). (e) S. Bernstein, M. Heller, L. I. Feldman, W. S. Allen, R. H. Blank, and C. E. Linden, *J. Am. Chem. Soc.*, **82**, 3685 (1960). (f) H. E. Kenney, S. Serota, E. A. Weaver, and M. E. Wall, *J. Am. Chem. Soc.*, **82**, 3689 (1960). (g) W. S. Allen, S. Bernstein, L. I. Feldman, and M. J. Weiss, *J. Am. Chem. Soc.*, **82**, 3696 (1960). (h) Y. Mazur, N. Danieli, and F. Sondheimer, *J. Am. Chem. Soc.*, **82**, 5889 (1960). (i) J. C. Sheehan, R. L. Young, and P. A. Cruickshank, *J. Am. Chem. Soc.*, **82**, 6147 (1960). (j) D. N. Kirk and V. Petrow, *J. Chem. Soc.*, 4667 (1960). (k) R. Neher and A. Wettstein, *Helv. Chim. Acta*, **43**, 1191 (1960). (l) E. S. Rothman and M. E. Wall, *J. Org. Chem.*, **25**, 1396 (1960). (m) See also B. E. Cross, *J. Chem. Soc.*, 3032 (1960), who applied the reagent with little success in working with derivatives of gibberellic acid. (n) J. Fishman, E. R. H. Jones, G. Lowe, and M. C. Whiting, *J. Chem. Soc.*, 3948 (1960) applied the reagent in studying the stereochemistry of tricothecin. (m) K. Heusler, J. Kalvoda, C. Meystre, P. Wieland, G. Anner, A. Wettstein, G. Cainelli, D. Arigoni, and O. Jeger, *Helv. Chim. Acta*, **44**, 502 (1961).

[3] H. E. Zimmerman, L. Singer, and B. S. Thyagarajan, *J. Am. Chem. Soc.*, **81**, 108 (1959).

[4] H. H. Wasserman and N. E. Aubrey, *J. Am. Chem. Soc.*, **77**, 590 (1955).

yield after twenty-one hours at room temperature, but the conversion occurred to the extent of 47% after only four and one-half hours at 40°.

The desirable features of the chromium(VI) oxide–pyridine complex as an oxidizing agent for alcohols, when other easily oxidized groups or acid-labile groups are present, have been sought in other systems. Snatzke, who reviewed these efforts, found that a solution of chromium(VI) oxide in dimethylformamide, containing a trace of sulfuric acid, was a good alternative.[5] In spite of the presence of a trace of acid, Snatzke's reagent system left ketal groups and the readily oxidized 7-methylene group in Δ^5-steroids intact.

Alkaline hypochlorite has been used by Meyers to convert benzyl alcohols to aldehydes.[6] Good yields of benzaldehyde and *o*-methoxybenzaldehyde were reported, but the method failed with *o*-hydroxybenzaldehyde. Instead, formaldehyde and 2,4,6-trichlorophenol were obtained.

The present work was undertaken to determine the effectiveness of the chromium(VI) oxide–pyridine complex for converting allylic and benzylic alcohols to aldehydes and to determine its limitations in a limited number of other structural situations. An immediate objective was the conversion of the 2-hydroxymethyl group of kojic acid (2-hydroxymethyl-5-hydroxy-4-pyrone) to the corresponding aldehyde, a goal that was not realized.[7]

The results of experiments in which the conditions and relative proportions of reactants were essentially the same as those reported by Poos *et al.*[1] are summarized in Table I. These conditions include use of a mole ratio of complex to alcohol of 3:1; room temperature; pyridine as the dispersing medium for the complex; and a reaction time varying from fifteen to twenty-two hours. In nearly all cases where good yields of aldehydes were obtained, the slurry of the complex in pyridine darkened rapidly as soon as the alcohol was added. Where yields were poor, the slurry usually darkened slowly. Yields were determined for each case in one of three ways: direct weighing of product; use of the method of Smith and Mitchell, which involves titration of the hydrochloric acid liberated when hydroxylamine hydrochloride reacts with aldehydes and ketones[8]; and determination *via* the yield of semicarbazone.

TABLE I

Alcohol	Product	Yield, %
Allylic, primary		
Geraniol	Geranial	66[a]
Nerol	Neral	83[a]
Cinnamyl alcohol	Cinnamaldehyde	81[a]
Benzylic, primary		
Benzyl alcohol	Benzaldehyde	63[a]
p-Isopropylbenzyl alcohol	*p*-Isopropylbenzaldehyde	83[a]
o-Methoxybenzyl alcohol	*o*-Methoxybenzaldehyde	89[b]
m-Methoxybenzyl alcohol	*m*-Methoxybenzaldehyde	60[a]
p-Methoxybenzyl alcohol	*p*-Methoxybenzaldehyde	76[a]
o-Hydroxybenzyl alcohol	*o*-Hydroxybenzaldehyde	17[b]
m-Hydroxybenzyl alcohol	*m*-Hydroxybenzaldehyde	75[c]
p-Hydroxybenzyl alcohol	*p*-Hydroxybenzaldehyde	50[a]
o-Nitrobenzyl alcohol	*o*-Nitrobenzaldehyde	30[b]
m-Nitrobenzyl alcohol	*m*-Nitrobenzaldehyde	50[b]
p-Nitrobenzyl alcohol	*p*-Nitrobenzaldehyde	28[c]
3,4-Methylenedioxybenzyl alcohol (piperonyl alcohol)	Piperonal	85[b]
3,4-Dimethoxybenzyl alcohol (veratryl alcohol)	Veratraldehyde	41[b]
Miscellaneous		
Furfuryl alcohol	Furfural	46[a]
Citronellol	Citronellal	25[a,d]
2-Hydroxymethyl-5-bicyclo-[2.2.1]heptene	5-Bicyclo[2.2.1]hepten-2-carboxaldehyde	34[a]
1-Heptanol	Heptanal	10[a]
1-Dodecanol	Dodecanal	18[a]
Cyclopentanol	Cyclopentanone	21[a]
Cyclohexanol	Cyclohexanone	45[a]
Cycloheptanol	Cycloheptanone	63[a]
Cyclooctanol	Cyclooctanone	72[b]
2-Octanol	2-Octanone	18[a]
Benzhydrol	Benzophenone	71[c]

[a] The method of Smith and Mitchell was used to determine the yield of aldehyde (or ketone).[8] [b] The yield was determined *via* the weight of semicarbazone obtained.[10] [c] The yield was determined by direct isolation of the product. [d] At 40° after 4.5 hours, the yield of citronellal was 47%.

In general, it was found that the chromium(VI) oxide–pyridine complex was a good reagent for the conversion at room temperature of benzyl and allyl alcohols to their corresponding aldehydes (or ketones). Low-formula-weight (and, accordingly, volatile and water-soluble) aldehydes and ketones are not readily accessible by the reagent and conditions employed. Carbonyl compounds were not isolated when the reagent was allowed to react with kojic acid or its 5-methyl ether, with vitamin-A alcohol, 3-(1-hydroxyethyl)aniline, or α-hydroxyacetophenone.

Experiments with ammonium dichromate in aqueous pyridine indicated that it is inferior to the chromium(VI) oxide–pyridine complex. Benzaldehyde was obtained in yields of 33% and 41% as compared with 63% using the pyridine complex of chromium(VI) oxide.

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(5) G. Snatzke, *Ber.*, **94**, 729 (1961).

(6) C. Y. Meyers, *J. Org. Chem.*, **26**, 1046 (1961).

(7) Y. Obata and T. Yamanishi [*J. Agr. Chem. Soc., Japan*, **24**, 334 (1951); *Chem. Abstr.*, **46**, 11475*b* (1952)] were unable to effect this oxidation using mild oxidizing agents such as phenylhydroxylaminesulfonic acid, nitrosodimethylaniline, hydrogen peroxide and iron(II) sulfate, methylene blue, and sunlight.

(8) D. M. Smith and J. Mitchell, Jr., *Anal. Chem.*, **22**, 750 (1950).

Acetone was studied as an alternative dispersing medium to pyridine in an effort to find a way to make isolation of products easier. (The chromium(VI) oxide–pyridine complex is only slightly soluble in acetone. It is insoluble in dimethyl sulfoxide, nitromethane, ethyl acetate, ethyl bromide, chloroform, nitrobenzene, and carbon disulfide.) Under conditions where a pyridine dispersion gave 63% benzaldehyde (from benzyl alcohol) and 71% benzophenone (from benzhydrol), an acetone dispersion gave, respectively, 41% benzaldehyde and 45% benzophenone (with 49% recovery of benzhydrol).

EXPERIMENTAL

The alcohols used in this study were the purest materials that were commercially available. Furfuryl alcohol and benzyl alcohol were freshly distilled. Pyridine and chromium(VI) oxide were both Mallinckrodt AR compounds, and they were used without further purification.

General procedure. As indicated previously, chromium(VI) oxide must be added *to* pyridine. The reverse addition causes the mixture to enflame. Preparation of the reagent may be hastened considerably, however, by the use of vigorous stirring with a Hershberg stirrer. *Care must be exercised to prevent accumulation of localized pockets of solid chromium* (VI) *oxide.*

A slurry of the complex in anhydrous pyridine was prepared by adding chromium(VI) oxide (6.2×10^{-2} mole) to vigorously stirred, chilled (ice bath) pyridine (70 cc.) over a period of 10 to 15 min. The alcohol (2×10^{-2} mole), in pyridine (5–10 cc.), was added to the slurry in one portion. The mixture was stirred for approximately 30 min., and then it was allowed to remain undisturbed at room temperature for 15–22 hr. The mixture was poured into water (300 cc.) and extracted with three portions of ether (total, 250 cc.). In only a few instances were emulsions a serious problem. The combined ether extracts were washed successively with 10% hydrochloric acid (three portions; total 150 cc.), 10% sodium carbonate (25 cc.),[9] and water (25 cc.). The sodium carbonate extract was acidified and examined for carboxylic acid. Usually, only trace amounts were found. They were identified by melting points where they were solids. The following acids (with yields in parentheses) were obtained from corresponding alcohols: piperonylic acid (3%), cinnamic acid (5%), *p*-isopropylbenzoic acid (6%), *m*-methoxybenzoic acid (7%), *p*-nitrobenzoic acid (9%), and benzoic acid (10%). The ether layer was dried (sodium sulfate), and the ether was removed. The residue, or an aliquot portion thereof, was analyzed for aldehyde (or ketone) by one of three ways: directly, by isolation of the aldehyde (or ketone); conversion to semicarbazone[10]; or the method of Smith and Mitchell.[8] Products were identified usually by conversion to semicarbazones or 2,4-dinitrophenylhydrazones.

Experiments with ammonium dichromate in aqueous pyridine. To a solution of ammonium dichromate (7.56 g., 3×10^{-2} mole) in water (20 cc.) and pyridine (30 cc.), benzyl alcohol (2.2 g., 2×10^{-2} mole) was added. The mixture remained at room temperature for 17 hr. It was worked up in the usual way. The crude product was a colorless oil (2.11 g.) that contained 41% benzaldehyde by Smith and Mitchell determination.[8] Acidification of the sodium carbonate extracts produced no benzoic acid. Identification of the remainder of the oily product was not attempted; presumably, however, it was unchanged starting material. In another experiment, a yield of 33% benzaldehyde was obtained.

Experiments with acetone dispersions of the chromium (VI) *oxide-pyridine complex.* The complex was prepared by adding chromium (VI) oxide (50 g.) to vigorously stirred pyridine (600 cc.) over a period of 1 hr. The temperature of the mixture was not permitted to rise above 30°. The precipitate was collected on a filter and washed twice with anhydrous, thiophene-free benzene and twice with anhydrous ether. The product was dried *in vacuo*, and there was obtained 74 g. of a slightly tannish, mustard colored powder. It was stored in a dry atmosphere; over a period of a few weeks it gradually darkened. For purposes of succeeding experiments, it was assumed that it was pure $CrO_3 \cdot 2C_5H_5N$.

A slurry of the dry complex (7.7 g., 3×10^{-2} mole) in acetone (50 cc.) was mixed with benzyl alcohol (1.1 g., 1×10^{-2} mole). The mixture remained at room temperature for 17 hr. It was filtered, and the filtrate was concentrated to a volume of about 5 cc. The liquid was taken up in ether (60 cc.), washed with water (six 15-cc. portions), and dried (magnesium sulfate). Removal of the ether left an oil (0.80 g.) which contained 41% benzaldehyde (Smith and Mitchell determination[8]).

When the same procedure and conditions were applied to benzhydrol (1.84 g., 1×10^{-2} mole), the yield of crude product was 1.75 g. This was chromatographed from petroleum ether (b.p. 30–60°) containing a trace of benzene onto activated alumina (Alcoa, F-20, 19 g.). Elution with petroleum ether (b.p. 30–60°) gave benzophenone (0.82 g.; m.p. 45–48°; 45% yield), and elution with ether gave benzhydrol (0.90 g.; m.p. 67–68°; 49% recovery). In another experiment, where the reaction time was extended to 45 hr., a quantitative yield of benzophenone was obtained.

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(9) Sodium bicarbonate (5%) was used when the experiment involved a phenolic material.

(10) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds*, 4th ed., Wiley, New York, 1956, p. 218.