

A representative procedure is given. 1-Methylcyclohexene, 4.8 g. (50 mmoles), and 22.5 mmoles of lithium borohydride in 30 ml. ethyl ether were placed in a 200-ml. flask fitted with a stirrer, condenser, addition funnel and thermometer. To the reaction mixture was added 0.95 ml. (7.5 mmoles) of boron trifluoride etherate in 4 ml. of ether over a period of 15 minutes at 25–30°. After two hours, excess hydride was destroyed with 5 ml. of water. The chromic acid solution, prepared from 11.0 g. (36.9 mmoles) of sodium dichromate dihydrate and 8.25 ml. (147.4 mmoles) of 96% sulfuric acid and diluted with water to 45 ml., was added to the stirred solution over a period of 15 minutes, maintaining the temperature at 25–30°. After heating under reflux for two hours, the upper layer was separated, and the aqueous layer extracted with two 10-ml. portions of ether. Gas chromatographic examination indicated an 87% yield of 2-methylcyclohexanone. Distillation gave 4.36 g., 78% yield, of 2-methylcyclohexanone, b.p. 63–64° at 24 mm., n_D^{20} 1.4487 (lit.⁸ n_D^{20} 1.4483).

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A SIMPLE PROCEDURE FOR THE CHROMIC ACID OXIDATION OF ALCOHOLS TO KETONES OF HIGH PURITY

Sir:

We wish to report a simple, convenient procedure for chromic acid oxidations which converts secondary alcohols into ketones in excellent yields and high purities. This procedure offers especial promise for the synthesis of ketones capable of undergoing epimerization under the more usual oxidation conditions.

The oxidation of secondary alcohols to ketones with aqueous chromic acid at 50–55° has long been a standard synthetic procedure.¹ Improved procedures have been proposed, based upon the use of organic solvents, such as acetic acid² and acetone,³ solvents which are miscible with water and resist oxidation by chromic acid.

In the course of studying the direct chromic acid oxidation of organoboranes to ketones⁴ in the usual hydroboration solvents, diglyme, tetrahydrofuran and ethyl ether, we observed that the latter immiscible solvent offered advantages for the oxidation of the organoboranes and were thereby led to explore its utility for the oxidation of alcohols. An exceedingly simple procedure was developed.

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(3) K. Bowden, I. M., Heilbron, E. R. H. Jones and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

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In this procedure the theoretical quantity of chromic acid (from sodium dichromate and sulfuric acid) is added over 15 minutes to a stirred solution of the alcohol in ether at 25–30°. After two hours, the ether layer is separated and the product isolated. The yields realized in representative cases are summarized in Table I.

TABLE I

OXIDATION OF REPRESENTATIVE ALCOHOLS IN ETHER WITH AQUEOUS CHROMIC ACID

Alcohol	Ketone yield, %	
	G.C.	Isolated
3-Methyl-2-butanol	85	
Cyclopentanol	87	
Cyclohexanol	92	
Cyclooctanol	93	
2-Methylcyclohexanol	97	87 ^a
<i>l</i> -Menthol	97	84 ^b
Isopinocampheol	94	80 ^c

^a B.p. 64–65° at 23 mm., n_D^{20} 1.4490. ^b B.p. 66–67° at 4 mm., n_D^{20} 1.4500, $[\alpha]_D$ -29.9°. ^c B.p. 62–63° at 3 mm., n_D^{20} 1.4745, α_D +10.04°.

The gas chromatographic analysis of the *l*-menthone and isopinocampheol produced in this procedure indicated very high purities for the products. Accordingly we applied the usual oxidation procedures^{1–3} to the oxidation of *l*-menthol and isopinocampheol and compared the products (Table II).

The results indicated that this new procedure offers major advantages for the preparation of ketones capable of undergoing epimerization under the usual oxidation conditions. Evidently the immiscible ether layer extracts the ketone as it is formed and protects it from further oxidation.

We attempted to replace the ethyl ether with *n*-pentane and with benzene in the oxidation of *l*-menthol. However, in each case, severe emulsions were formed, hindering the isolation of the product.

The following procedure is representative.

Ethyl ether, 20 ml., and 7.80 g. (50 mmoles) of *l*-menthol were placed in a 100-ml. flask fitted with a stirrer, condenser and addition funnel. The chromic acid solution, prepared from 5.00 g. (16.8 mmoles) of sodium dichromate dihydrate and 3.75 ml. (67 mmoles) of 96% sulfuric acid diluted to 25 ml., was added to the stirred solution over 15 minutes, maintaining the temperature at 25°. After two hours, the upper ether layer was separated, and the aqueous phase extracted with two 10-ml. portions of ether. The combined extracts were washed with saturated sodium bicarbonate, then water. Gas chromatographic analysis on a Carbowax 4000 column indicated 97% *l*-menthone, a trace of isomenthone and 1.5% of menthol. Distillation gave 6.45 g., 84% yield, of *l*-menthone, b.p. 66–67° at 4 mm., n_D^{20} 1.4500, $[\alpha]_D$ -29.9° (lit. n_D^{20} 1.45038,⁵ $[\alpha]_D$ -29.6°⁶).

Acknowledgment.—This study was made possible by Contracts DA-33-008-ORD-992 and 2002

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TABLE II
OXIDATION OF *l*-MENTHOL AND ISOPINOCAMPHEOL BY VARIOUS PROCEDURES

	Procedure	<i>l</i> -Menthol		Isopinocampheol	
		Products	%	Products	%
1 ^a	Aqueous chromic acid at 50-55°	Menthone	90	Isopinocampheone	86
		Isomenthone	3	Pinocampheone	4
		Menthol	trace	Isopinocampheol	1
2 ^b	Chromic acid in 90% acetic acid at 25°	Menthone	71	Isopinocampheone	78
		Isomenthone	3	Pinocampheone	3
		Menthol	0	Isopinocampheol	0
3 ^c	Chromic acid in acetone at 5-10°	Menthone	86	Isopinocampheone	84
		Isomenthone	4	Pinocampheone	4
		Menthol	2	Isopinocampheol	1
4 ^d	Aqueous chromic acid with alcohol in ether at 25-30°	Menthone	97	Isopinocampheone	94
		Isomenthone	trace	Pinocampheone	trace
		Menthol	1.5	Isopinocampheol	0

^a Ref. 1. ^b Ref. 2. ^c Ref. 3. ^d Present study.

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TECHNETIUM CARBONYL

Sir:

We wish to report the synthesis and properties of a new carbonyl, and its derivatives with iodine. This work for technetium fills in the last missing member of the manganese sub-group metal carbonyls which had been more elusive to obtain¹ than those of the neighboring groups. The difficulties were heightened in the case of technetium because of its rarity.

In a typical preparation, ammonium pertechnetate² (0.85 g., 4.70 mmole) was pyrolyzed at 400° in a Vycor tube, the pressure being reduced to 1 mm. after the salt turned black. The contents were then treated with excess dry oxygen at 600°. Upon cooling, the reaction tube containing pale yellow hygroscopic technetium heptoxide was inserted into a copper-plated autoclave (350 ml. capacity), insuring minimum contact with atmospheric moisture. After flushing with 800 psig. of Matheson research grade carbon monoxide, the bomb was pressurized to 3,000 psig./25° and then heated for twenty hours at 220°, pressure rising to 5,100 psig.

After cooling, the autoclave was outgassed slowly through a trap at -78°. Only traces of material later identified as the carbonyl were found in the trap, but, in particular, no evidence in the infrared (4,000-650 cm.⁻¹) was obtained which might have indicated volatile Tc-H containing materials.³ The autoclave and contents were rinsed with diethyl ether which subsequently was evaporated at water

pump vacuum. A residue was deposited which upon sublimation (50°, 10⁻²mm.) yielded 50-100 mg. of colorless crystals (I). There was evidence of some decomposition when solutions of this product were extensively handled in air, in accordance with the behavior of some other metal carbonyls, particularly that of manganese. Recrystallization from pentane followed by two sublimations yielded material which melted (sealed capillary) at 159-160° (corr.). The spectrum of I in the carbonyl stretching region of the infrared consisted of three bands, listed in the table below, closely paralleling in position and intensity those of Mn₂(CO)₁₀ and Re₂(CO)₁₀.

Analysis of I for carbon monoxide was carried out on the vacuum line by slowly heating 46.8 mg. of compound, below the softening point of Pyrex glass. Carbon monoxide thus evolved was identified by infrared spectrum: found, 21.5 cc.; required for [Tc(CO)₅]_n, 21.9 cc.

In a micromolecular weight apparatus adapted to high vacuum techniques from that described by Gysel, *et al.*,⁵ 12.5 mg. of I was mixed with 300.9 mg. of diethyl ether resulting in a vapor pressure depression of 3.08 mm. at 22°. Molecular weight: required for Tc₂(CO)₁₀, 478; found,⁶ 465 ± 26.

Magnetic susceptibility for I was determined by nuclear magnetic resonance, using the method described by Evans,⁷ adapted by us for use with coaxial sample tubes of Zimmerman and Foster.⁸ The separation for neat liquids between the resonance of methyl protons of toluene in the inner tube and protons of cyclohexane in the annular space was found to be 13.3 cps. at 40 mc. and 31°.

(4) All cc. are given for S.T.P.

(5) H. Gysel, W. Padowetz and K. Hamberger, *Mikrochim. Acta*, 192 (1960).

(6) Accuracy of our method, to be fully described in a forthcoming paper, depends on tensimetric homogeneity of solvent. Need for accurate temperature measurement or for reproducing vapor pressures quoted for the solvent in the literature is avoided. Actual vapor pressure of solvent is measured during molecular weight run, in the same constant temperature bath. For the measurement reported here, diethyl ether, purified by distillation from LiAlH₄, exerted a vapor pressure of 468 mm. (handbook value, 462 mm.). Tensimetric homogeneity was demonstrated for two successive 0.5 ml. samples as no difference in vapor pressure was noted to within 0.02 mm.

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(2) Technetium, synthetically produced, consisting mainly of isotope ⁹⁹Tc, *t*_{1/2} = 2.12 × 10⁵ y., β = 0.29 mev., is obtained as NH₄TcO₄ from Oak Ridge National Laboratories, Oak Ridge, Tenn.

(3) Re(CO)₅H has been isolated in the preparation of rhenium carbonyl from the heptoxide or the heptasulfide for cases where the starting material was known not to be rigorously dry, cf. W. Hieber and H. Fuchs, *Z. anorg. Chem.*, **248**, 256 (1941).