

and VI are similar to one another, and show a decrease in complexity and intensity in the C=C region compared with the tetraenes. The presence of ester carbonyl is clearly indicated, but it is difficult to assign an unconjugated/conjugated ratio. (3) The octanes VII and VIII are similar to one another, and have lost all C=C absorptions. (4) The spectra of the acids show very strong OH stretches but no anhydride bands.

High Pressure Reactions.—Reactions of the gaseous monomers listed in Table I were all carried out in similar fashion. A 280-ml. glass-lined autoclave was charged with solid $\text{Ni}(\text{PCl}_2)_4$ catalyst and 100 ml. of cyclohexane. The autoclave was then flushed with nitrogen and gaseous monomer was condensed into the chilled reaction vessel, either from a weighed transfer bomb or from the storage tank. Monomer to catalyst ratios were about 700:1 in all cases. The autoclave was then sealed and allowed to warm to 20°, where shaking and a temperature-time program were begun. With acetylene (12 g.), 4.5 hours at 85° produced 0.4 g. of an unidentified aromatic-smelling yellow oil. This product contained no nickel or cyclooctatetraene derivatives, but showed infrared absorption bands at 3380s, 1635m, 1665m, 1175m and 1025s. cm^{-1} .

With ethylene no reaction was achieved after 4 hours of contact at 120°.

With allene (14.5 g.), 5 hours of contact at 80° produced a bright yellow solution. Absolute ethanol (50 ml.) was added to decompose the remaining catalyst, after which the solution was filtered and evaporated at 25° under high vacuum. As the evaporation proceeded, a yellow solid and a yellow oil were deposited. The combined weight of these products was 3.5 g., or 24%, based on allene. The infrared spectra of both were the same, and were identical with the spectra of the mixture of trioxomethylenecyclohexane and tetraoxomethylenecyclooctane reported by Benson and Lindsay.⁵

With butadiene (69 g.), a 36-hour contact at 115° followed by a further 36 hours at 150° produced 68.2 g. of a homogeneous yellow oil. After centrifugation to remove inorganic solids, the oil was fractionated at reduced pressure, giving 22.9 g. of the thermal dimer 4-vinylcyclohexene and 22.8 g. of the g. thermal high polymer polybutadiene. The remaining 22.5 g. consisted of three fractions containing (by mass spectroscopy) butadiene dimer (25%), trimer (50%) and tetramer (25%). The composition of these oligomers is unknown, but it appears they are different from those obtained by Reed³² and Wilke³³ with other catalyst systems.

(32) W. H. B. Reed, *J. Chem. Soc.*, 1931 (1954).

(33) G. Wilke, *J. Polymer Sci.*, **38**, 45 (1959).

COMMUNICATIONS TO THE EDITOR

THE CHROMIC ACID OXIDATION OF ORGANO-BORANES—A CONVENIENT PROCEDURE FOR CONVERTING OLEFINS INTO KETONES via HYDROBORATION

Sir:

The hydroboration of olefins, with subsequent oxidation of the resulting organoboranes with alkaline hydrogen peroxide, provides a convenient procedure for the conversion of olefins into alcohols.¹ These alcohols can be taken up in ether and converted, without isolation, into the corresponding ketones, by chromic acid oxidation.²

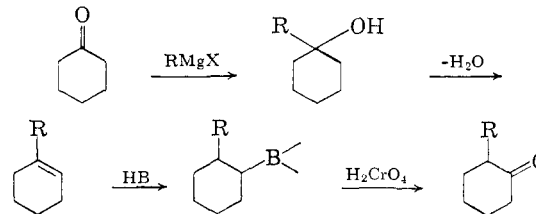
It has been reported that the hydroboration of conessine followed by chromic acid oxidation³ in aqueous acetic acid⁴ yielded 3 β -dimethylaminocononanin-6-one. Since organoboranes are susceptible to protonolytic cleavage in the presence of acetic acid, but are stable to aqueous mineral acids,⁵ we undertook to explore the utility of aqueous chromic acid as a general procedure for the conversion of organoboranes into ketones.

Cyclohexene, hydroborated in diglyme, tetrahydrofuran, or ethyl ether, was treated with aqueous chromic acid. After two hours at 25–35°, 60–65% yields of cyclohexanone were realized. Since the use of ethyl ether greatly facilitated the isolation of the ketone, later studies emphasized

this medium. 1-Methylcyclopentene was converted into 2-methylcyclopentanone in 83% yield, and 1-methylcyclohexene was converted into 2-methylcyclohexanone in 87% yield. Similarly, 1-phenylcyclohexene produced 2-phenylcyclohexanone in 63% yield and α -pinene was converted into isopinocampone in 72% yield (several per cent. of the epimer, pinocampone was indicated in the gas chromatogram).

The procedure is exceedingly simple. The olefin is hydroborated in ethyl ether with boron trifluoride-etherate and lithium borohydride or with sodium borohydride in the presence of catalytic quantities of zinc chloride.^{6,7} A slight excess (10%) over the theoretical quantity of aqueous chromic acid is added over 15 minutes, the mixture refluxed (35–37°) for two hours, and the product isolated as an ether solution.

This ready oxidation of organoboranes to ketones makes available a convenient general synthesis of 2-alkyl- and 2-arylcycloalkanones:



(6) H. C. Brown, K. J. Murray, L. J. Murray, J. A. Snover and G. Zweifel, *ibid.*, **82**, 4233 (1960).

(7) Alternatively, the lithium aluminum hydride procedure of Sondheimer and his co-workers may be employed to achieve hydroboration in this solvent: S. Wolfe, M. Nussim, Y. Mazur and F. Sondheimer, *J. Org. Chem.*, **24**, 1034 (1959).

(1) H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **78**, 5694 (1956); *J. Org. Chem.*, **22**, 1135 (1957); H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **81**, 247 (1959).

(2) H. C. Brown and C. P. Garg, *ibid.*, **83**, 2952 (1961).

(3) R. Pappo, *ibid.*, **81**, 1010 (1959).

(4) R. Pappo, private communication as reported in L. F. Fieser and M. Fieser, "Steroids," Reinhold Publishing Corporation, New York, N. Y., 1959, p. 864.

(5) H. C. Brown and K. Murray, *J. Am. Chem. Soc.*, **81**, 4108 (1959).

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).

Acknowledgment.—This study was made possible by contracts DA-33-008-ORD-992 and 2002 supported by the Office of Ordnance Research. This assistance is gratefully acknowledged.

(8) A. Skita, *Ber.*, **56**, 1014 (1923).

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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.

(1) E. Beckmann, *Ann.*, **250**, 322 (1889); L. T. Sandborn, "Organic Syntheses," Coll. Vol. I, 340 (1941).

(2) B. Gastamide, *Ann. chim. Paris*, **9**, 257 (1954).

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

(4) H. C. Brown and C. P. Garg, *J. Am. Chem. Soc.*, **83**, 2951 (1961).

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

(5) O. Zeitschel and H. Schmidt, *Ber.*, **59**, 2298 (1926).

(6) J. Read and G. J. Robertson, *J. Chem. Soc.*, 2209 (1926).