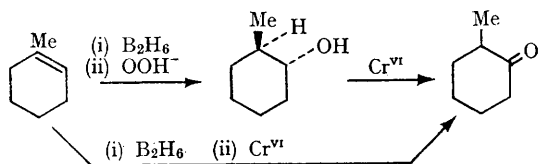


Rearrangement during Chromic Acid Oxidation of Organoboranes

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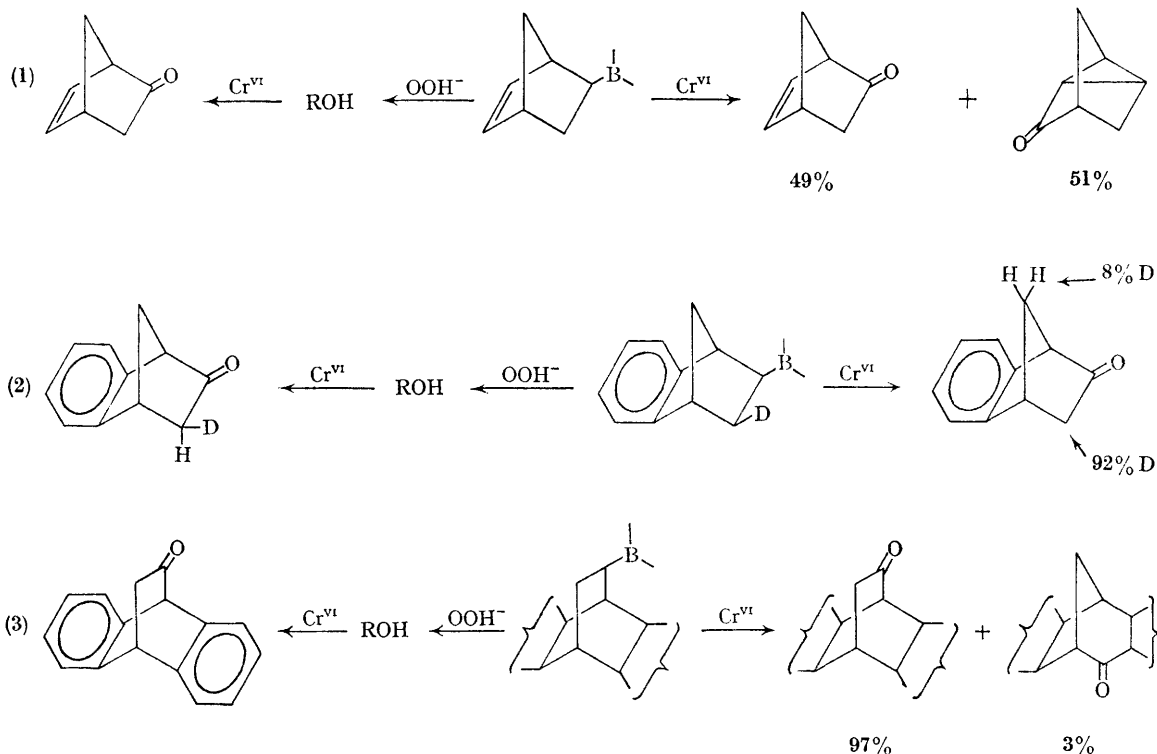
It has recently been reported that direct chromic acid oxidation of hydroborated olefins leads, in straightforward fashion, to ketones which previously were obtained¹ in two uncomplicated steps:



While the reported examples¹ are doubtless correct, we have found several exceptions to the

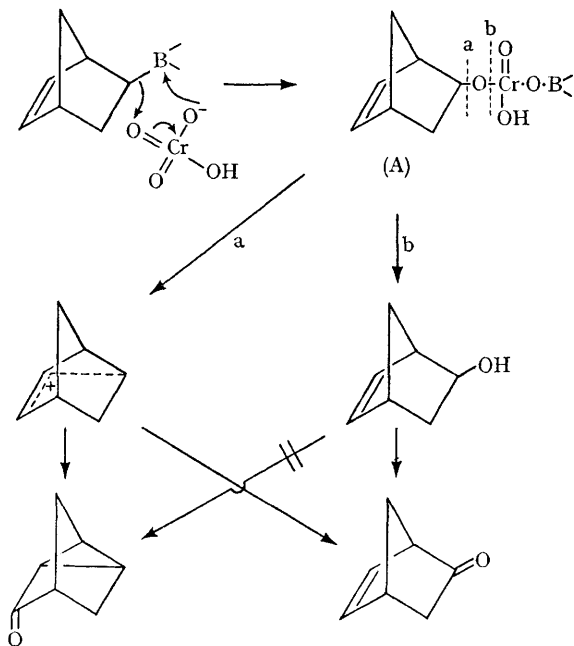
are recorded (Reactions 1—3). Product analyses in Reactions 1 and 3 were by spectroscopy and v.p.c., using authentic samples for comparison. The deuterium scrambling in Reaction 2 was determined by "washing out" enolizable deuterium and mass-spectral analysis.²

The rearrangements noted above are somewhat reminiscent of the corresponding carbonium-ion isomerizations in tosylate solvolyses,³⁻⁴ and could conceivably arise from C-O fission of an intermediate Cr^{IV} ester.⁶ Rearrangement could precede or follow formation of A, but must come before formation of alcohol, as shown in control experiments. However, the ionic mechanism fails to explain the absence of detectable *p*-anisyl migration



above scheme, wherein direct oxidation of boranes¹ leads to rearranged ketones, although the two-step oxidation sequence (borane \rightarrow alcohol \rightarrow ketone) proceeds without this occurrence. Several examples

(by n.m.r.) in the deuteroboration-oxidation of *trans*-2-*p*-anisylbut-2-ene (which gives only 3-*p*-anisyl[3-²H]butane-2-one). Perhaps the above results are due to free radicals⁷ since both



norbornenyl⁸ and β -arylalkyl⁹ radicals are known to isomerize.

Several potentially significant variables were checked in the hydroboration-oxidation of norbornadiene. It was found that the presence or absence of oxygen and of added manganous ion¹⁰ do not materially alter the ratio of nortricyclanone and dehydronorcamphor, which was *ca.* 50:50 in all cases.

More work is needed before definite mechanistic conclusions can be made. For the present, it should be realized that the direct chromic acid oxidation of organoboranes can lead to rearranged ketones, although the corresponding alcohol precursors do not give rise to this complication under the mild, standardized oxidizing conditions.¹ A "one pot" synthesis without rearrangement is possible if the initially-formed borane is treated first with alkaline hydroperoxide and then directly with chromic acid. In this way we have synthesized pure dehydronorcamphor in *ca.* 50% yield (v.p.c.) from norbornadiene.

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¹ (a) H. C. Brown and C. P. Garg, *J. Amer. Chem. Soc.*, 1961, **83**, 2951, 2952; (b) H. C. Brown, "Hydroboration", W. A. Benjamin, Inc., New York, 1962.

² Kindly performed by Dr. Norman R. Mancuso.

³ S. Winstein, H. M. Walborsky, and K. C. Schreiber, *J. Amer. Chem. Soc.*, 1950, **72**, 5795.

⁴ W. P. Giddings and J. Dirlam, *J. Amer. Chem. Soc.*, 1963, **85**, 3900.

⁵ S. J. Cristol, F. P. Parungo, D. E. Plorde, and K. Schwarzenbach, *J. Amer. Chem. Soc.*, 1965, **87**, 2879, and previous papers.

⁶ J. C. Ware and T. G. Traylor, *J. Amer. Chem. Soc.*, 1963, **85**, 3026.

⁷ In free-radical rearrangements during decarbonylation of β -aryl- β -methylbutyraldehydes, the migratory aptitude of *p*-anisyl was found to be 0.35 (phenyl=1), quite opposite from the high migration tendency of *p*-anisyl in carbonium-ion rearrangements (C. Ruchardt, *Chem. Ber.*, 1960, **94**, 2609).

⁸ D. J. Trecker and J. P. Henry, *J. Amer. Chem. Soc.*, 1963, **85**, 3204.

⁹ C. Walling, "Molecular Rearrangements", P. deMayo, ed., Interscience Publishers, New York, 1963, Vol. 1, p. 407.

¹⁰ F. H. Westheimer, J. Hampton, and A. Leo, *J. Amer. Chem. Soc.*, 1956, **78**, 306.