Tetrahedron Letters No. 36, pp 3119 - 3120, 1977. Pergamon Press. Printed in Great Britain.

HETEROGENEOUS REACTIONS. IV. THE HIGH TEMPERATURE REDUCTION OF 3-BROMOTRICYCLO [2.2.1.$0^{2,6}$] HEPTANE WITH SODIUM METHOXIDE.

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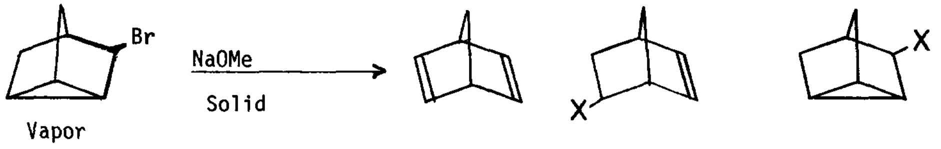
(Received in USA 26 May 1977; received in UK for publication 14 July 1977)

We have recently reported an efficient heterogeneous system which employs alkoxide bases as the solid phase substrate in reactions with vapor phase alkyl halides.[1] In these previous systems the alkyl halides reacted almost exclusively with β-elimination, and the complication of solvolytic reactions was eliminated. In this communication we wish to report an unusual reaction involving sodium methoxide and the alkyl halide 3-bromotricyclo [2.2.1.$0^{2,6}$]-heptane (I), which as a result of the geometric constraints imposed by its carbon framework is precluded from reaction via β-elimination. This alkyl halide was found to be inert to the reaction conditions at temperatures below 200°C, however at temperatures in excess of 200°C the reaction summarized in the equation below became significant. The major products isolated were bicyclo [2.2.1] hept-2-ene (IIIa) and tricyclo [2.2.1.$0^{2,6}$] heptane (IVa) in a ratio of 2:3 respectively. Some bicyclo [2.2.1] hept-2,5-diene (II), and trace amounts of 5-methoxybicyclo [2.2.1] hept-2-ene (IIIb) and 3-methoxytricyclo-[2.2.1.$0^{2,6}$] heptane (IVb) were observed in all reactions. In each case IVb was found in excess of IIIb. The reduction products, IIIa and IVa, and their isomeric distribution are identical with the results reported for the reduction of 3-chlorotricyclo-



I

II

III
a. X = H
b. X = OMe

IV
a. X = H
b. X = OMe

[2.2.1.$0^{2,6}$] heptane with sodium biphenyl,[2a] and for the reduction of I using tri-n-butyltin hydride.[2b].

The basic design of our reaction system and the methods of handling the reagents have been described previously.[1,3,4] A specific feature of the heterogeneous system which we had not explored previously is the possibility of diluting the concentration of the gaseous alkyl halide by the simultaneous addition of a hydrocarbon solvent or secondary reagent. The results of several reactions with I and sodium methoxide at 260°C, both neat and diluted with several hydrocarbon solvents are shown in the Table.

TABLE[a]

SOLVENT	TOTAL HYDROCARBON YIELD[b]	SOLVENT	TOTAL HYDROCARBON YIELD[b]
none	5 - 10%	toluene	30 - 40%[c]
cyclohexane	10 - 20%	mesitylene	40 - 60%[c]
pentane	20 - 30%	pentamethylbenzene	70 - 90%[c]

a. All reactions reported at 260°C using 0.10 mole NaOMe, 0.01 mole I, and 0.04 mole solvent. b. The total yield of II, IIIa and IVa, the relative yields of these products were constant in a 1:2:3 ration respectively, all yields were determined utilizing glpc internal standard yield analysis. c. In these reactions there was a suppression of the relative amount of II formed.

The improvement in yield with the addition of solvents having a higher hydrogen donating ability and the concurrent reduction in the relative amount of II would imply that a radical process is operating. It would also appear that the methoxide is initiating this radical process. Control experiments with I and several hydrocarbons in the absence of sodium methoxide gave no reaction and good recovery of unreacted I. It is possible that the sodium methoxide is serving as a source of electrons in a radical anion-free radical process.[5] We are continuing to investigate the specifics of this reduction process.

Acknowledgments: Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, and to the Research Corporation for support of this work.

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