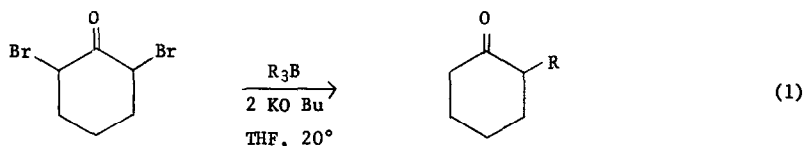


THE REACTION OF  $\alpha,\alpha'$ -DIBROMOKETONES WITH ORGANOBORANES

Rolf H. Prager\* and James M. Tippet  
 Organic Chemistry Department, University of Adelaide,  
 Adelaide, South Australia, 5000.

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Brown<sup>1</sup> has shown that  $\alpha$ -haloketones react with organoboranes in the presence of base to give  $\alpha$ -alkylketones, although the reaction is not particularly facile for cyclohexanones. We have investigated the reaction of  $\alpha,\alpha'$ -dibromocycloalkanones with organoboranes, and find that the reaction yields mono-alkylated ketones faster, and in better yield, than  $\alpha$ -bromocycloalkanones. However, the reaction (equation 1) is particularly sensitive to the substrates used.



Highest yields were obtained when two equivalents of a highly hindered base (potassium t-heptoxide was best) were used in the absence of any proton source. Some typical results are shown in the Table.

TABLE

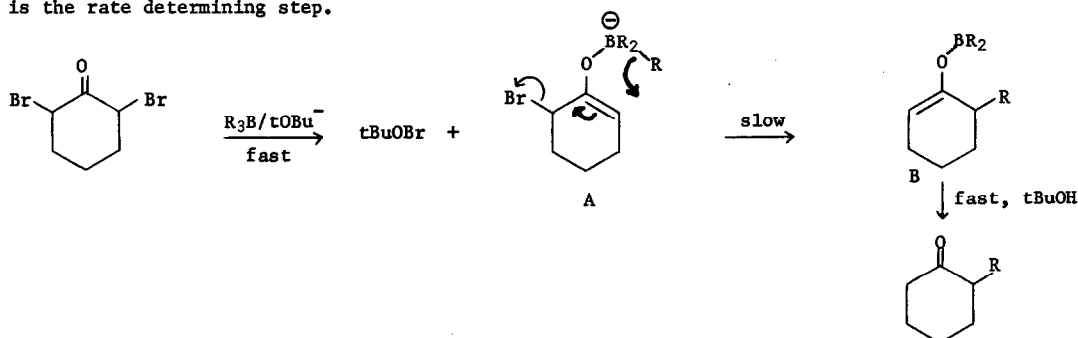
Alkylation of  $\alpha,\alpha'$ -Dibromoketones with Organoboranes

| Ketone   | Borane            | Base  | Monoalkylated Product %     |
|--|-------------------|-------|-----------------------------|
| <u>cis</u> -2,6-dibromocyclohexanone           | Et <sub>3</sub> B | KOtBu | 76                          |
| <u>cis</u> ,2,6-dibromo-4-tbutyl-cyclohexanone | Et <sub>3</sub> B | KOtBu | 95                          |
|  | Bu <sub>3</sub> B | KOiPr | 0 (55% 4-tBu cyclohexanone) |
|  |                   | KOtBu | 90                          |

| Ketone  | Borane            | Base   | Monoalkylated Product %                        |
|---|-------------------|--------|--|
|   |                   | KOtHep | 100  |
| <u>trans</u> -2,6-dibromo-4-t butyl-cyclohexanone             | Bu <sub>3</sub> B | KOtBu  | 0  |
| <u>cis</u> -2,5-dibromocyclopentanone                         | Et <sub>3</sub> B | KOBu   | 0  |
| <u>cis</u> -2,7-dibromocycloheptanone                         | Et <sub>3</sub> B | KOBu   | 0  |
| <u>cis</u> -2,6-dibromo- <u>trans</u> -3-methyl-cyclohexanone | Bu <sub>3</sub> B | KOBu   | <u>cis</u> -2-butyl-5-methyl-cyclohexanone 65% |

The reaction described, which is essentially complete in 2 hours at 20°, has several interesting mechanistic features. Two equivalents of base are necessary; use of one equivalent gives almost exclusive reduction to the parent ketone. Traces of alcohol in the alkoxide also lead to reduction becoming the major pathway. In the two unsymmetrical dibromoketones investigated, alkylation occurred exclusively on the less hindered side.<sup>2</sup> Thus only 2-butylcholestanone is obtained from the alkylation of 2,4-dibromocholestan-3-one. Furthermore, the reaction appears to have very strong configurational specificity. Several trans-dibromoketones failed to yield any alkylated product at all.

The evidence to date is consistent with the pathway below. Tetrahydrofuran, the solvent, provides the source of the additional proton. Quenching the reaction with water traps intermediate A, and leads to total reduction (cyclohexanone formation), showing that alkyl transfer is the rate determining step.



#### REFERENCES

1. Brown, H.C., Rogic, M.M., and Rathke, M.W., *J. Am. Chem. Soc.*, **91**, 6854 (1969).
2. Contrast with: Posner, G.H., and Sterling, J.J., *J. Am. Chem. Soc.*, **95**, 3076 (1973).