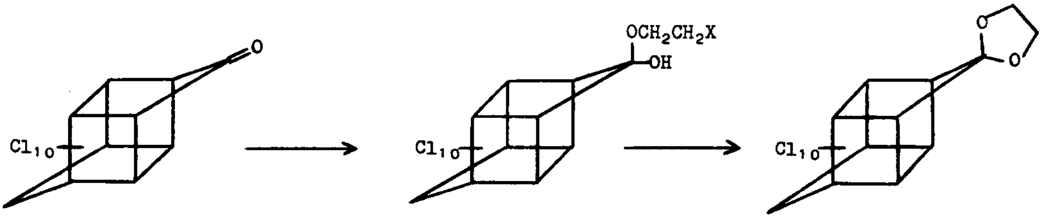
Tetrahedron Letters No.49, pp. 4915-4916, 1967. Pergamon Press Ltd. Printed in Great Britain.

CYCLIC ETHYLENE KETALS OF STRAINED α-CHLORINATED KETONES

R. John Stedman, Larry D. Davis and Libby S. Miller
Research and Development Division
Smith Kline & French Laboratories, Philadelphia, Pennsylvania

(Received in USA 21 July 1967)

Griffin and Price (1) reported that the chlorinated bis-homocubanone I ('Kepone') could not be ketalized by normal techniques; with either ethylene glycol or ethyl orthoformate under acid catalysis it gave only hemi-ketals. They explained these observations as resulting from the unusual steric and inductive effects operating in I. On the basis of these considerations, it may be assumed that other strained α-halogenated ketones would be similarly resistant to the usual ketalization procedures. Griffin and Price were able to obtain certain full ketals of I by treating the hemi-ketals with diazomethane. We now wish to report a convenient method for preparing the hitherto inaccessible cyclic ethylene ketal II through the base catalyzed cyclization of the hemi-ketals obtained from I and 2-bromo or 2-chloroethanol:



I (X = Cl or Br) II

A convenient technique is to dissolve I in an excess of the haloethanol and to add this solution to aqueous-ethanolic sodium hydroxide. The ketal II is precipitated in 93% yield while unchanged I remains in solution as its acidic hydrate. The structure of II (no m.p. below 350°) is supported by its elemental analysis and by its n.m.r. spectrum (60 Mc in $CDCl_3$) which shows a single spike 4.27 ppm downfield from TMS.

This type of ketalization procedure has previously been used in the perfluoroacetone area (2). Further studies, which will be reported in full at a later date, show that it is applicable to a variety of chlorinated cage ketones.

References

1. G. W. Griffin and A. K. Price, J. Org. Chem., **29**, 3192 (1964).
2. H. E. Simmons and D. W. Wiley, J. Am. Chem. Soc., **82**, 2288 (1960).