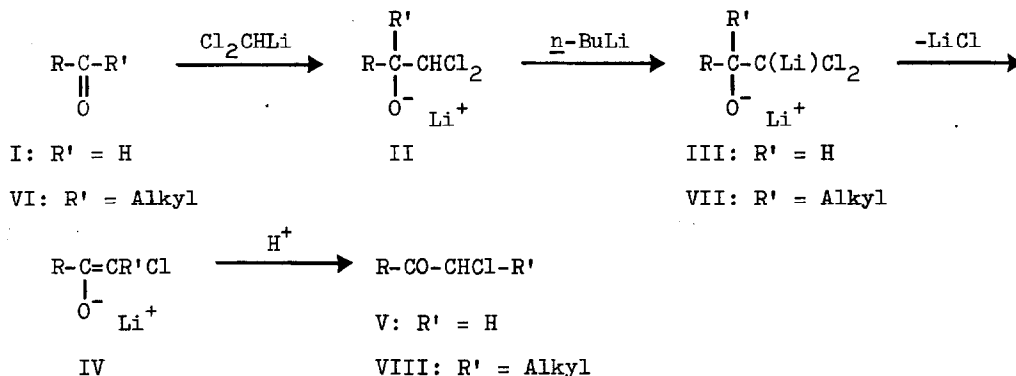


A SIMPLE SYNTHESIS OF α -HALOKETONES VIA β -OXIDO CARBENOIDS

Hiroaki Taguchi, Hisashi Yamamoto, and Hitosi Nozaki
 Department of Industrial Chemistry, Kyoto University
 Yosida, Kyoto, Japan

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A recent communication of Villieras et al¹ has prompted this publication of independent results obtained thus far on the same reaction sequence:



We wish to point out following items which have not been covered by the previous report, or alternatively, in which some discrepancies between two groups have been observed.

(1) The reaction of benzaldehyde gave exclusively phenacyl chloride (V, R = Ph) under conditions described below, whereas the French chemists claimed to have obtained a mixture of V (R = Ph) and PhCHClCHO (85:15). Benzaldehyde (1.00 equiv) was added to a solution of dichloromethylithium² (1.20 equiv) in THF at -95° and the mixture was treated with an excess of *n*-butyllithium (1.80 equiv) at -95° . The resulting colourless solution was warmed gradually to 0° (20 min) and then quenched with dil. hydrochloric acid. Preparative TLC gave phenacyl chloride (72%), mp $53-54^\circ$, mmp $53-54^\circ$, whose NMR indicated the absence of any

isomer (<2% if any) before and after TLC.

(2) The reaction of PhCDO (98% D content)³ gave PhCOCHDCl (97% D content) after recrystallization from the crude product. We believe this is a token indicating the intermediacy of the enolate IV resulting from intramolecular carbene insertion to the adjacent C-H bond of β -oxido carbenoid III.

(3) Following aldehydes reacted successfully under similar conditions to give the corresponding chloromethyl ketones V in good yields. The kind of R, yield (%) of V (after TLC purification), $\nu_{\text{C=O}}^{\text{neat}}$ in cm^{-1} , δ (CCl_4) of ClCH_2COR in ppm, mass parent in $\underline{m/e}$ are given in this order: $\underline{n}\text{-C}_8\text{H}_{17}\text{-}$, 62, 1725, 3.89, 190; 2-furfuryl, 62, 1685, 3.85, 144; $\text{Me}_2\text{C}=\text{CH}(\text{CH}_2)_2\text{CMe}=\text{CH-}$, 51, 1710, 3.84, 200.

(4) The possibility of extending this reaction sequence to ketones VI has been briefly hinted in the communication¹ without any experimental results. Sequential treatment of cyclododecanone (1.00 equiv) with dichloromethyl lithium (1.20 equiv) at -78° for 1.5 hr, at -30° for 0.5 hr and then \underline{n} -butyllithium (3.00 equiv) at -30° afforded 2-chlorocyclotridecanone (46% after TLC): $\nu_{\text{C=O}}^{\text{neat}}$ 1715 cm^{-1} ; δ (CCl_4) 4.20 (dd, 1H, COCHCl); mass $\underline{m/e}$ 230 (M^+). Similarly, cyclopentanone gave 2-chlorocyclohexanone (64%): $\nu_{\text{C=O}}^{\text{neat}}$ 1720 cm^{-1} ; δ (CCl_4) 4.32 (dd, 1H, COCHCl); mass $\underline{m/e}$ 132 (M^+).

(5) The conversion from II to IV proceeded only in the presence of excess \underline{n} -butyllithium, and when less amount of \underline{n} -butyllithium was used, for example 1.00 equiv, none of the desired 2-chloroketone was obtained. The role of this excess \underline{n} -butyllithium is being speculated. Further extension and mechanistic details also are to be reported in due course.

REFERENCES

- 1). J. Villieras, C. Bacquet, and J. F. Normant, J. Organometal. Chem., 40, Cl (1972).
- 2). G. Kübrich, Angew. Chem. Internat. Ed. Engl., 11, 473 (1972).
- 3). A. W. Burgstahler, D. E. Walker, Jr., J. P. Kuebrich, and R. L. Schowen, J. Org. Chem., 37, 1272 (1972).