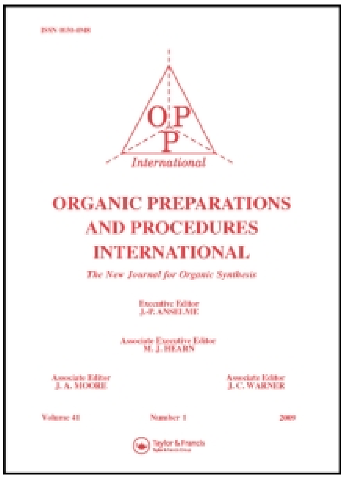

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A PRACTICAL PROCEDURE FOR THE PREPARATION OF HINDERED α-HALOEPOXIDES AND α-HALOALDEHYDES

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A PRACTICAL PROCEDURE FOR THE PREPARATION OF HINDERED α-HALOEPOXIDES AND α-HALOALDEHYDES

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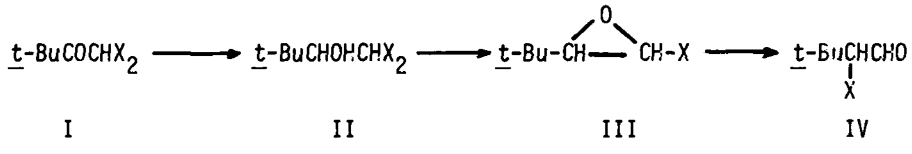
This paper describes a practical procedure for the preparation of hindered α-haloepoxides IIIa and IIIb directly from α,α-dihaloketones Ia and Ib in a one-pot reaction. Base-promoted cyclisation of β,β-dihaloalcohols easily obtained from α,α-dihaloketones, is commonly used for the preparation of α-haloepoxides.[1] The α,α-dihaloketones (Ia or Ib) were converted directly to the corresponding α-haloepoxides III by treatment with sodium borohydride, in a $NaOH-H_2O-MeOH-Et_2O$ solution, [2] without isolation of the intermediate alcohols.



a) X = Cl b) X = Br

The technique offers the advantage that large scale reactions can be performed and epoxide formation is favored by partial homogeneity of the reaction medium. In addition, the superior selectivity of sodium borohydride suppresses halogen reduction, a side-reaction often observed with lithium aluminium hydride. Finally the hindered aldehydes IVa and IVb may be obtained in large scale by heating the corresponding epoxides IIIa and IIIb.

EXPERIMENTAL

1-Chloro-3,3-dimethyl-1,2-epoxybutane IIIa

(a) From 1,1-Dichloro-3,3-dimethyl-2-butanone, Ia.- To a stirred solution of sodium hydroxide (120 g, 3 moles) in a mixture of water (600 ml) and methanol (250 ml) at 10-15°, was added over ca. 10 min., a solution of dichloropinacolone Ia (338 g, 1.976 mole) in 800 ml ether. To the well stirred heterogeneous solution was then added at 10°, sodium borohydride (40 g, 1.05 mole) by portions so as to control excessive foaming. The mixture was stirred at room temperature for 24 hrs. The organic layer was decanted, dried over $MgSO_4$ and concentrated in the cold on a rotatory evaporator under reduced pressure. Distillation of the residue gave 159 g (59 %) of 1-chloro-3,3-dimethyl-1,2-epoxybutane, bp. 45-46°/28mm. No decomposition was observed for a sample stored four years at room temperature.

(b) From 1,1-Dichloro-3,3-dimethyl-2-butanol, IIa.- To a solution of sodium hydroxide (160 g, 4 moles) in a mixture of 600 ml water and 200 ml methanol was added a solution of 1,1-dichloro-3,3-dimethyl-2-butanol IIa (prepared from α,α-dichloropinacolone Ia in 70 % yield 1)) (370 g, 2.26 moles) in 800 ml ether. The solution was stirred at room temperature for 20 hours and worked up as above : bp. 44-48°/30mm; yield : 79 %.

1-Bromo-3,3-dimethyl-1,2-epoxybutane IIIb

(a) From 1,1-Dibromo-3,3-dimethyl-2-butanone, Ib[3].- The procedure described above provide epoxide IIIb from Ib (516 g, 2 moles) in

63 % yield, bp. 55-58°/28mm.

The epoxide is labile and should be stored at -30° to minimize contamination by traces of α-brominated aldehyde IVb.

Isomerisation of Epoxide IIIa to 2-chloro-3,3-dimethylbutanal IVa.- Epoxide IVa (130 g, 0.966 mole) was gradually heated up to reflux (∿ 140°) for 25-30 hrs. The formation of aldehyde IVa was followed by the decrease in the characteristic absorptions of the epoxide (1240-1290 and 930-940 cm^{-1}) and the increase of the carbonyl (1730 cm^{-1}). The crude aldehyde was distilled under reduced pressure to give 87 g (67 %) of aldehyde IVa, bp. 50-53°/28mm.

Isomerisation of Epoxide IIIb to 2-bromo-3,3-dimethylbutanal IVb.- The following technique was used for the isomerisation of IIIb (226 g, 1.26 mole). Epoxide IIIb (30-40 g) was refluxed until the isomerisation started (the reaction can be vigorous with evolution of hydrogen bromide).

The remaining brominated epoxide then was added dropwise at reflux temperature and the mixture was heated at 142-143°. The formation of the aldehyde was followed by IR as above. After 10-14 hrs the reaction mixture was cooled to room temperature and distilled under reduced pressure to yield 161 g (71 %) of 2-bromo-3,3-dimethylbutanal IVb, bp. 58-60°/28mm, lit.[4] bp. 96°/100 mm.

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