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# γ-HALOGENATION OF α,β-UNSATURATED ALDEHYDES

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We wish to report here a new synthesis of γ-halo-α,β-unsaturated aldehydes, which we have applied succesfully to the preparation of γ-chloro-(IV, R=H, X=Cl) and γ-bromo-crotonaldehyde (IV, R=H, X=Br) and γ-chloro-(IV, R=$CH_3$, X=Cl) and γ-bromo-β-methylcrotonaldehyde (IV, R=$CH_3$, X=Br). This synthesis operates according to the following sequence of reactions:

$$\underset{\mathrm{I}}{\mathrm{CH_3\text{-}CR{=}CH\text{-}CHO}} \xrightarrow{1} \underset{\mathrm{II}}{\mathrm{CH_2{=}CR\text{-}CH{=}CHOCOCH_3}} \xrightarrow{2}$$

$$\underset{\mathrm{III}}{\mathrm{XCH_2\text{-}CR{=}CH\text{-}CH(OCOCH_3)X}} \xrightarrow{3} \underset{\mathrm{IV}}{\mathrm{XCH_2\text{-}CR{=}CH\text{-}CHO}}$$

1.- $AcOCH(CH_3){=}CH_2$, $(AcO)_2Cu$, p-TsOH; 2.- $X_2$; 3.- $H_2O$.

A typical preparation was as follows: Chlorine (6,92 g) dissolved in carbon tetrachloride (70 ml) was added dropwise to an hexane solution (50 ml) of 1-acetoxybutadiene (II, R=H) (10,94 g) containing a small amount (0,019 g) of barium carbonate; throughout the addition (40 min.), the temperature was mantained at about -70ºC. After 10 min., the solution was allowed to warm up to room temperature, sodium bicarbonate (18 g) and water (100 ml) were added and the heterogeneous mixture was shaked during 4 hr. Conventional working up led to trans-γ-chlorocrotonaldehyde (IV, R=H, X=Cl), $b_{25}$ 45-7ºC (6,27 g, 62% yield) (Required for $C_4H_5ClO$: C: 45,97; H: 4,83; Cl: 33,43. Found C: 45,80 and 46,10; H: 4,94 and 4,98; Cl: 33,69 and 33,70). IR: $\nu_{max}(CS_2)$: 2810, 2720, 1713, 974 $cm^{-1}$.

The acetoxybutadienes (II, R=H and R=$CH_3$) were prepared by the method of Bayley and Barclay (1) and were shown (n.m.r. monitoring) to be mixtures of trans- and cis-isomer in a ratio of ca. 9:1.

In preparative reactions, it was found unnecessary to isolate the intermediate γ-halogenated mixed acylals (III); only compound III (R=H, X=Br) was isolated and identified.

The resulting γ-haloaldehydes (IV) are rather unstable but their solutions in organic solvents are stable. The solutions obtained in the preparative sequence can be used directly for further reactions, as, for instance, for the preparation of the corresponding phosphonium salts (2).

The γ-haloaldehydes IV (R=H, X=Cl, and R=H, X=Br) were isolated and identified as the pure trans isomers. The other two γ-haloaldehydes (R=$CH_3$, X=Cl, and R=$CH_3$, X=Br) decomposed upon elimination of the solvent and were shown by n.m.r. to be trans-cis mixtures in a ratio of ca. 3:1.

NMR assignments (spectra registered in $CCl_4$ solutions)

| IV | CHO | α-H | β-H | $XCH_2$ | $CH_3$ | $J_{1,2}$ | $J_{2,3}$ | $J_{3,4}$ |
|---|---|---|---|---|---|---|---|---|
| (R=H, X=Cl) | 0,32 | 3,67 | 3,05 | 5,66 | - | 6,8 | 15,4 | 5,6 |
| (R=H, X=Br) | 0,38 | 3,79 | 3,10 | 5,85 | - | 7,0 | 13,1 | 7,5 |
| (R=$CH_3$, X=Cl) (trans) | -0,06 | 3,90 | - | 5,74 | 7,68 | 7,2 | | |
| (R=$CH_3$, X=Cl) (cis) | -0,01 | 4,00 | - | 5,42 | 7,85 | 6,7 | | |
| (R=$CH_3$, X=Br) (trans) | -0,13 | 3,85 | - | 5,92 | 7,68 | 7,7 | | |
| (R=$CH_3$, X=Br) (cis) | -0,14 | 3,98 | - | 5,53 | 7,85 | 7,7 | | |

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## References

1.- W. J. Bayley and R. Barclay, Jr. J. Org. Chem. 1956, 21, 328.

2.- M. J. Berenguer, J. Castells, R. M. Galard, and M. Moreno-Mañas. Following paper.