

SHORT  
COMMUNICATIONS

$\gamma$ -Alkylthio- $\gamma$ -chloro- $\alpha,\beta$ -dicarbonyl Compounds

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Reactions of  $\alpha$ -chloro- $\beta$ -oxoaldehydes [1] with O-, N-, and C-anionic nucleophiles are known to involve cleavage of the C–CHO bond [2–4]. We have found that the main pathway in the reactions of  $\alpha,\alpha$ -dichloro- $\beta$ -oxoaldehydes **I** with sodium 1-propanethiolate and 2-propanethiolate is nucleophilic substitution of one chlorine atom, which leads to formation of  $\alpha$ -dicarbonyl compounds (**IV**) (Scheme 1).

The most probable reaction scheme includes attack by thiolate ion on the aldehyde group to give intermediate alkoxide ion **A**. The latter can be stabilized via cleavage of the C–C bond or intramolecular nucleophilic reaction. The first pathway leads to enolate **III** and *S*-alkyl thioformate, and the second involves intermediate formation of unstable chlorooxiranes **B** which are converted into  $\gamma$ -alkylthio- $\gamma$ -chloro- $\alpha,\beta$ -dicarbonyl compounds **IV**; the latter were synthesized by us previously by a different procedure [1]. It should be noted that in the reaction of ethoxycarbonyl derivative **Ib** (R = EtO) with 1-propanethiolate ion, only nucleophilic substitution occurred to afford  $\alpha$ -chloro sulfide **IVc** in 80% yield.

The different behaviors of  $\beta$ -oxodichloroaldehydes **Ia** and **Ib** in reactions with *S*-nucleophiles may be

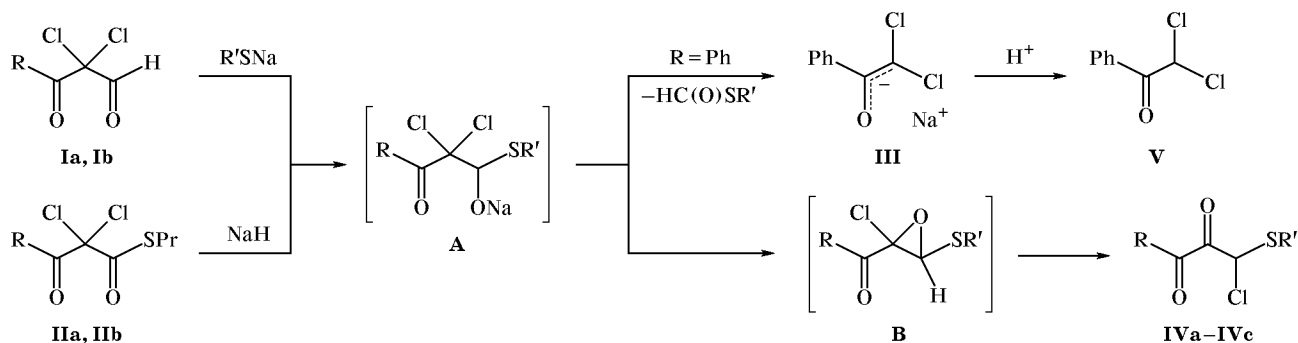
explained by different activities of the aldehyde carbonyl groups therein and different stabilities of enolates **III**. Undoubtedly, dichloroacetophenone anion **III** is more stable than the anion derived from ethyl dichloroacetate which could be formed by decomposition of intermediate **A**.

Dichloroaldehyde semithioacetal **Ib** was shown to undergo rearrangement into product **IVc** by the action of sodium hydride. Under similar conditions, benzoyl-substituted semithioacetal **Ia** gives rise to both isomerization and cleavage of the C–C bond. The ratio of the products formed along the above two pathways is 1:1, as in the reaction of aldehyde **Ia** with thiolate ion.

Compounds **IVa–IVc** are potential tricarbonyl electrophiles which can be used in the synthesis of heterocyclic compounds.

**Reaction of benzoyl(dichloro)acetaldehyde (Ia) with sodium 1-propanethiolate.** Aldehyde **Ia**, 0.2 mol, was added dropwise with stirring at  $-30$  to  $-40^\circ\text{C}$  to a suspension of freshly prepared sodium 1-propanethiolate in 70 ml of dry diethyl ether. The mixture was allowed to slowly warm up to room temperature and was then heated for 1 h under reflux.

Scheme 1.



**I, II**, R = Ph (**a**), EtO (**b**); **IV**, R = Ph, R' = Pr (**a**); R = Ph, R' = *i*-Pr (**b**); R = EtO, R' = Pr (**c**).

The mixture was acidified with 10% hydrochloric acid to pH 5–6, the organic phase was separated, and the aqueous phase was extracted with two portions of diethyl ether. The extracts were combined with the organic phase, dried over  $\text{MgSO}_4$ , and evaporated, and the residue was subjected to fractional distillation to isolate compounds **V** and **IVa**.

**Dichloroacetophenone (V)**. Yield 40%. bp 80–81°C (0.09 mm) [5].

**3-Chloro-1-phenyl-3-propylthio-1,2-propanedione (IVa)**. Yield 40%. bp 128–130°C (0.08 mm),  $n_D^{20} = 1.5784$ . IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1685 (C=O), 1750 (C=O).  $^1\text{H}$  NMR spectrum (acetone- $d_6$ ),  $\delta$ , ppm: 0.97 t (3H,  $\text{CH}_3$ ), 1.50 m (2H,  $\text{CH}_2$ ), 2.55 m (2H,  $\text{SCH}_2$ ), 7.65 m (3H,  $\text{H}_{\text{arom}}$ ), 8.20 m (2H,  $\text{H}_{\text{arom}}$ ), 9.50 s (1H,  $\text{CHCl}$ ). Found, %: Cl 13.65; S 12.65.  $\text{C}_{12}\text{H}_{13}\text{ClO}_2\text{S}$ . Calculated, %: Cl 13.84; S 12.47.

Compounds **IVb** and **IVc** were synthesized in a similar way.

**3-Chloro-3-isopropylthio-1-phenyl-1,2-propanedione (IVb)**. Yield 40%. bp 120°C (0.09 mm),  $n_D^{20} = 1.5672$  [1].

**Ethyl 3-chloro-2-oxo-3-propylthiopropionate (IVc)**. Yield 80%. bp 66–68°C (10 mm),  $n_D^{20} = 1.4607$ . IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1680 (C=O), 1755 (C=O).  $^1\text{H}$  NMR spectrum (acetone- $d_6$ ),  $\delta$ , ppm: 0.95 t (3H,  $\text{CH}_3$ ), 1.20 t (3H,  $\text{CH}_3$ ), 1.60 q (2H,  $\text{CH}_2$ ), 2.50 t (2H,  $\text{SCH}_2$ ), 4.30 q (2H,  $\text{OCH}_2$ ), 9.40 s (1H,  $\text{CHCl}$ ).  $^{13}\text{C}$  NMR spectrum (acetone- $d_6$ ),  $\delta_C$ , ppm: 16.36 and 17.28 ( $\text{CH}_3$ ), 25.02 ( $\text{CH}_2$ ), 66.88 ( $\text{SCH}_2$ ), 69.57

( $\text{OCH}_2$ ), 83.50 ( $\text{CHCl}$ ), 168.63 (OC=O), 187.69 (C=O). Found, %: Cl 15.50; S 14.37.  $\text{C}_8\text{H}_{13}\text{ClO}_3\text{S}$ . Calculated, %: Cl 15.78; S 14.25.

**Reaction of dichloroaldehyde semithioacetals IIa and IIb with sodium hydride.** 1-Propanethiol, 0.1 mol, was added dropwise with stirring at –8 to –5°C to a solution of 0.15 mol of aldehyde **Ia** or **Ib** in 50 ml of dry diethyl ether. The mixture was kept for 2 h at that temperature and cooled to –15°C, and 0.22 mol of sodium hydride was added in portions. The mixture was allowed to slowly warm up to room temperature, the precipitate was filtered off, the solvent was removed from the filtrate, and the residue was subjected to fractional distillation. The reaction of compound **IIa** with sodium hydride gave products **IVa** and **V**, and from compound **IIb** ester **IVc** was obtained.

## REFERENCES

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