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AN UNUSUAL REACTION OF TRICHLOROMETHANE WITH ACYLALS IN THE INTERPHASE CATALYSIS CONDITIONS.

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Summary. Aldehyde diacetates react with trichloromethane in the standard interphase catalysis conditions to form α-trichloromethylcarbinols or their acetates depending on temperature and time of the reaction.

The two-phase NaOH/$CHCl_3$/catalyst system provides both trichloromethylide anion and dichlorocarbene. Depending on the substrate the reaction may proceed by various paths and give rise to gem-dichlorocyclopropanes, adduct of trichloromethane across double bond or products of the insertion of dichlorocarbene into C-H, C-N bonds[1]. Here we report about one new unusual path of the reaction i.e. a substitution of one acetoxy group in aldehyde diacetates which takes place by the reaction of trichloromethane with these compounds and leads depending on the reaction conditions to the formation of α-trichloromethylcarbinols or their acetates. The reaction may be represented by the scheme:

$$RCH(OCOCH_3)_2 \xrightarrow[\text{BTEAC, r.t.}]{CHCl_3\text{, 50\% NaOH}} \underset{\underline{1}}{RCH(CCl_3)OCOCH_3} \longrightarrow \underset{\underline{2}}{RCH(CCl_3)OH}$$

R=Me (1a); n-Pr (1b); CH_2=CH (1c);
MeCH=CH (1d); Me_2C=CH (1e); CCl_2=CH (1f);
PhCH=CH (1g); $Me(CH{=}CH)_2$ (1h); $Ph(CH{=}CH)_2$ (1i)

Yields and constants of compounds 1 and 2 are given in Table 1.

The reaction proceeds easily and smoothly with diacetates of saturated aldehydes such as acetaldehyde or butyraldehyde and diacetates of conjugated mono- and dienals such as acrolein, crotonaldehyde, 3,3-dimethylacrolein, 3,3-dichloroacrolein, cinnamaldehyde, sorbic aldehyde, 5-phenylpenta-2,4-dienal[2]. The following general experimental procedure is typical for this reaction: 50% aqueous solution of 0.2 mole of sodium hydroxide is added dropwise to a stirred cooled (5-10°C) mixture of 0.1 mole of corresponding diacetate, 0.2 mole of trichloromethane and a catalytic amount of benzyltriethylammonium chloride (BTEAC) with such velocity that the temperature does not exceeded 25-30°C. The mixture is stirred at room temperature for one hour more and then it is extracted with ether. The combined extracts are dried ($MgSO_4$) and the residue after evaporation of solvent is distilled.

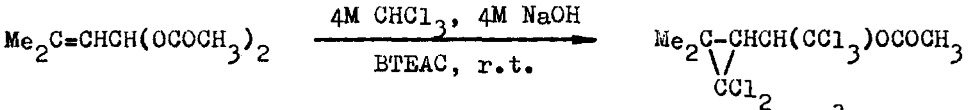
When the reaction is carried out at 40-45°C during four-six hours α-trichloromethylcarbinols 2 are formed with good yields (see Table 1) on account of hydrolysis of initially formed acetates 1 (the transformation was observed by GLC).

$$RCH(OCOCH_3)_2 \xrightarrow[\text{BTEAC},40\text{-}45^\circ C]{CHCl_3,50\%\ NaOH} \underline{1} \longrightarrow \underset{\underline{2}}{RCH(CCl_3)OH}$$

R=Ph (2a);
R=MeCH=CH (2b)

2a was obtained earlier by the action of trichloromethane on benzaldehyde in the interphase catalysis conditions[3]. However the reaction between crotonaldehyde and trichloromethane in the same conditions was accompanied by an extensive resinification and did not led to the desired α-trichloromethylcarbinol 2b.

It should be noted that it is possible to realize the substitution of an acetoxy group as well as the addition of dichlorocarbene across double bond if the reaction is carried out between trichloromethane and 3,3-dimethylacrolein diacetate with a fourfold excess of trichloromethane and sodium hydroxide at room temperature during three hours. As a result compound 3 was obtained (see Table 1).



$$Me_2C{=}CHCH(OCOCH_3)_2 \xrightarrow[BTEAC,\ r.t.]{4M\ CHCl_3,\ 4M\ NaOH} \underbrace{Me_2C-CH}_{CCl_2}CH(CCl_3)OCOCH_3$$

3

Acrolein and crotonaldehyde diacetates do not form products of dichlorocarbene addition across double bond even with big excess of reagents. This fact may be reasonable explained by lower electron density on double bond of these diacetates in comparison with 3,3-dimethylacrolein diacetate.

Table 1

Yields and constants of obtained compounds

Compound	Yield,%	B.p.°C(mm)	n_D^{20}
1a	72	62-63 (10)	1.4574
1b	57	84-86 (10)	1.4585
1c	61	89-90 (21)	1.4657
1d	57	86-88 (10)	1.4705
1e	58	103-105 (10)	1.4805
1f	65	115-117 (10)	1.4995
1g	62	133-135 (0.5)	1.5590
1h	58	74-75 (0.25)	1.5100
1i	50	179-180 (0.8)	1.6030
2a	75	140-142 (10)	1.5670
2b	61	96-98 (30)	1.5045
3	57	135-140 (10)	1.4970

So far as the substitution of acetoxy group in aldehyde diacetates proceeds with saturated and aromatic aldehyde diacetates as well as with conjugated mono- and dienal diacetates we think that this reaction belongs to the S_N2 type substitution process. Such transformation was not known before and is observed for the first time.

The structure of all obtained compounds was proved by ^1H NMR, ^{13}C NMR and mass spectra. Data of elemental analysis (C,H,Cl) of all new compounds are also in accordance with accepted formulas.

In ^{1}H NMR spectra of 1[4] proton shifts of all structure units typical for corresponding aldehyde diacetates are present with the exception of acylal group proton $C\underline{H}(OCOCH_3)_2$ which is shifted by ~1.3 ppm to a high field: from 7.2 ppm to 5.9 ppm. In ^{13}C NMR spectra the maximal change of chemical shifts is observed for carbon atom in $\underline{C}H(OCOCH_3)_2$. For instance signals of this carbon in 1d-1g are shifted to a high field by 6.2-9.7 ppm.

Mass-spectra[5] of all 1 are characterized by the presence of the corresponding molecular ions and fragment ions forming by cleavage of hydrogen chloride, acetoxy group and trichloromethyl group from initial molecule.

References and Notes

1. E.V.Dehmlov, S.S.Dehmlov, Phase Transfer Catalysis, Verlag Chemie, Weinheim, 1980.
2. A **part** of this work was presented at the Conference on Chemistry and Technology of Acetals and their Analogues, Ufa, November, 1980, Theses, p. 25.
3. A.Merz, R.Tomahogh, Chem.Ber., 110, 96 (1977).
4. ^{1}H NMR (100 MHz, δ ppm, CCl_4), 1a: 1.5 (3H, d, J=6 Hz), 2.06 (3H, s), 5.4 (1H, q, J=6 Hz); 1b: 0.9-1.65 (7H, m), 2.1 (3H, s), 5.4 (1H, dd, J=10 Hz, J=3 Hz); 1c: 2.1 (3H, s), 5.1-6.1 (4H, m); 1d: 1.64 (3H, d, J=6.5 Hz), 2.02 (3H, s), 5.4-6.2 (3H, m); 1e: 1.8 (6H, s), 2.02 (3H, s), 5.2 (1H, d,J=9 Hz), 5.7 (1H, d, J=9 Hz); 1f: 2.1 (3H, s), 5.8-6.4 (2H, m); 1g: 2.05 (3H, s), 5.9 (1H, d, J=7 Hz), 6.3 (1H, d, J=7 Hz), 6.75 (1H, d, J=7 Hz), 7.2-7.4 (5H, m); 1h: 1.74 (3H, d, J=6 Hz), 2.06 (3H, s), 5.8-7.3 (5H, m); 1i: 2.04 (3H,s), 5.66-5.86 (2H, m), 6.3-6.6 (3H, m); 2a: 3.74 (1H, s), 4.95 (1H, s), 7.1-7.6 (5H, m); 2b: 1.74 (3H, d, J=7 Hz), 3.56 (1H, s), 4.34 (1H, d, J=7 Hz), 5.45-6.1 (2H, m); 3: 1.35 (6H, s), 1.8 (1H, d, J=10 Hz), 2.1 (3H, s), 5.3 (1H, d, J=10 Hz).
5. For instance: mass-spectrum for $Me_2C{=}CHCH(CCl_3)OCOCH_3$ contains the following peaks: M^+, m/e 245; M^+-HCl, m/e 209; M^+-COCH_3, m/e 202; $M^+-HCl-OCOCH_3$, m/e 150.

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