# REACTION OF ACYLALS WITH SOME CARBANIONS UNDER TWO-PHASE

CATALYSIS CONDITIONS

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This paper is devoted to a study of the reaction of various gem-diacetates with compounds that are capable of generating carbanions under two-phase catalysis conditions. Previously [1] we had shown that acylals (I) react with chloroform in the presence of 50% aqueous NaOH solution and catalytic amounts of tribenzylammonium chloride (TEBA) to give  $\alpha$ -trichloromethyl-substituted acetates (II), and we postulated that the (II) compounds are obtained by the nucleophilic replacement of one of the acetate groups of the acylal by CCl<sub>3</sub> anion.

 $\begin{array}{rl} \operatorname{RCH}(\operatorname{OAc})_2 \xrightarrow{\operatorname{CHCh}, \ 50\% \ \operatorname{NaOH}, \ \mathrm{TEBA}} & \operatorname{RCH}(\operatorname{CCl}_3)\operatorname{OAc} \\ (I) & (II) \\ \mathrm{R} = \operatorname{CH}_3 (a), \ \operatorname{Ph} (b), \ \operatorname{CH}_2 = \operatorname{CH} (c), \ \operatorname{CH}_3 \operatorname{CH} = \operatorname{CH} (d), \ (\operatorname{CH}_3)_2 \operatorname{C} = \operatorname{CH} (e). \end{array}$ 

However, the end product (II) can also be formed in a different way. Thus, in the case of (Ia),the formation of vinyl acetate in the first step is possible, which, as is known [2], easily adds CCl<sub>3</sub> anion to give (IIa). However, when control experiments were run with acylals (Ia, d), i.e., when their CH<sub>2</sub>Cl<sub>2</sub> solutions were mixed with 50% NaOH solution in the presence of TEBA, we were unable to detect the presence of the corresponding enol esters. Benzaldehyde was obtained when benzaldehyde acylal (Ib) was mixed with alkali and TEBA. This fact permitted us to assume that the reaction of acylals with CHCl<sub>3</sub> could be effected in another way, specifically by the initial hydrolysis of the starting acylal (I) to the corresponding aldyhyde, the addition of CHCl<sub>3</sub> to the carbonyl group [3], which leads to  $\alpha$ -trichloromethylcarbinol, and acylation of the latter by the starting diacetate.

In order to refine the scheme for the reaction of acylals (I) with CHCl<sub>3</sub> we studied the reaction of crotonaldehyde and cinnamaldehyde with CHCl3 and 50% NaOH solution under twophase catalysis conditions and respectively obtained CH<sub>3</sub>CH=CHCH(CCl<sub>3</sub>)OH (III) and PhCH=CHCH-(CCl<sub>a</sub>)OH (IV). As a result, even such a labile aldehyde as crotonaldehyde is capable of reacting with CHCl3. In the reaction of 2 equiv. of CHCl3 and alkali, when a mixture of equimolar amounts of cinnamaldehyde and crotonaldehyde acylal (Id) are added, two products are formed, specifically PhCH=CHCH(CCl<sub>3</sub>)OH (IV) and CH<sub>3</sub>CH=CHCH(CCl<sub>3</sub>)OAc (IId), i.e., transacylation does not occur in this case. When we ran the conjugated reaction with closely related compounds such as benzaldehyde and anisaldehyde acylal, and also anisaldehyde and benzaldehyde acylal (the reaction course with time was checked by GLC analysis), we found that in both cases the first products to appear in the reaction mixture are two acetates, that of  $\alpha$ -trichloromethylbenzyl alcohol and of  $\alpha$ -trichloromethyl-p-methoxybenzyl alcohol, in which connection the amount of PhCH(CCl<sub>3</sub>)OAc formed greatly exceeds the amount of  $p-CH_3OC_6H_4CH(CCl_3)-$ OAc in the first case and, conversely, the amount of p-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>CH(CCl<sub>3</sub>)OAc exceeds the amount of PhCH(CCl<sub>3</sub>)OAc in the second case. In both cases the appearance of the  $\alpha$ -trichloromethylcarbinols occurs only after the corresponding acetates have accumulated in the reaction mixture, i.e., the α-trichloromethylcarbinols are apparently formed by the hydrolysis of the acetates. Here we were unable to detect the initial formation of the carbinols from the corresponding aldehydes. Since we were unable to show by special experiments that transacylation of the starting compounds does not occur under the reaction conditions, it must be assumed that the sole possible way to form the end products is for the conjugated reaction to proceed by our proposed scheme.

The probability that in the studied reaction the (I) acylals are capable of acylating their conjugated  $\alpha$ -trichloromethylcarbinols was also checked by us. We observed examples of

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Compound	Yield, %	bp, C(p, mm Hg)	$n_D^{20}$	Found Calculated <sup>5</sup> ⁄				PMR spectrum, S, ppm
				с	н	Hal	N	(J, Hz)
(III) *	20	96—98 (30)	1,5045					1,7d (3H, CH <sub>3</sub> , $J=6$ ); 3,92 s (1H, OH); 4,4d (1H, CH, $J=7$ ); 5,4-6,1 m (2H, CH=CH)
(IV) †	44	126–128 (0,7)	1,5965					3,5s (1H, OH); 4.6d (1H, CH, $J=6$ ); 6,22 d. d (1H, CH= J=16 and 6); 6,75 d (1H, CH=, $J=16$ ); 7,2m (5H, Ph)
(Va) ‡	32	128–130 (30)	1,5355					1,59 d (3H, CH <sub>s</sub> , <i>J</i> =6) 2,01 s (3H, CH <sub>3</sub> CO); 5,4 q (1H, CH, <i>J</i> =6)
(Vb) **	37	mp 76-77 (hexane)						2,22 s (3H, CH <sub>3</sub> CO); 7,2-7,7 m (6H, CH, Ph
<b>∢</b> ¥¢)	25	77–78 (0,7)	1,5464	21,03 20,53	2,22 2,00	68,40 68,35		$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$
(Vd)	36	90–92 (0,7)	1,5445	22,62 23,02	2,38 2,48	65,95 65,72		1,9 d (3H, CH <sub>3</sub> , <i>J</i> =7); 2,2 s (3H, CH <sub>3</sub> CO); 5,8-6,5 m (3H, CH=CH-CH)
(Ve)	26	112-114 (0,8)	1,5560	25,02 25,34	2,88	65,28 65,30		$ \begin{array}{c c} 1.76 \text{ s, } 1.8 \text{ s} (6\text{H}, \\ (\text{CH}_3)_2\text{C}=); 2.1 \text{ s} \\ (3\text{H}, \text{CH}_3\text{CO}); 5.15 \text{ d} \\ (4\text{H}, \text{CH}=, J=9); \\ 5.66 \text{ d} (4\text{H}, \text{CH}=, \\ J=9) \end{array} $
(VIIa) ‡	60	100-102 (0,5)	1,4980					$ \begin{array}{c} 1,06 \ d, 1,3 \ d (3H, CH_3 \\ J=6); 1,67 \ s (3H, CH_3); 1,7 \ s, 1,9 \ s (3H, CH_3); 1,7 \ s, 1,9 \ s (3H, CH_3CO); 5,1 \ q (1H, CH, J=6); 7,2-7,5m \\ (5H, Ph) \end{array} $
(VIIb)	38	mp 97-98 (alcohol)		76,92	6,11 6,13		4,68	1,55 s (3H, CH <sub>3</sub> ); 1,8 2,1 s (3H, CH <sub>3</sub> CO); 5,8 s (1H, CH); 6,8-7,4 m (10 H, 2Ph
(IXd)	67	103-104 (0,5)	1,6110	85,26 85,17	6,44 6,55		7,83	$ \left\{ \begin{array}{c} 1,87 \text{ d } (3\text{H},\text{CH}_3,J=6) \\ 5,9-6,3 \text{ m } (1\text{H},\text{CH}=) \\ 6,45-6,75 \text{ m } (1\text{H},\\\text{CH}=); 7,0-7,6 \text{ m} \\ (6\text{H},\text{CH}=,\text{Ph}) \end{array} \right. $

TABLE 1. Yields and Characteristics of Obtained Products

such acylation when phenyltrichloromethylcarbinol was mixed with either benzaldehyde acylal (Ib) or anisaldehyde acylal in the presence of 50% NaOH solution and TEBA, as a result of which we obtained either PhCH(CCl<sub>3</sub>)OAc or p-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>CH(CCl<sub>3</sub>)OAc and their corresponding aldehydes. It is interesting to mention that as a result of mixing such systems as  $\alpha$ -trichloromethylphenylcarbinol and anisaldehyde acylal, and also  $\alpha$ -trichloromethyl-p-methoxybenzyl alcohol and benzaldehyde acylal, with 50% caustic solution and TEBA we were able to detect (checked by GLC) in the reaction mixture in both cases the compounds: PhCH0, p-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>CH0,

\*\*Corresponds to the literature data [6].

PhCH(CCl<sub>3</sub>)OAc, and p-CH<sub>8</sub>OC<sub>6</sub>H<sub>4</sub>CH . As a result, it is possible to exchange the acetate group in CCL

such compounds by the CCl<sub>3</sub> grouping. Consequently, the possibility of the direct nucleo-

philic substitution of the acetate group by  $CCl_3$  anion in acylals when the latter are reacted with  $CHCl_3$  and caustic in the presence of TEBA cannot be rejected.

As a result, our experiments do not give as yet a basis for unequivocally choosing between the two schemes proposed for accomplishing the reaction of gem-diacetates with CHCl<sub>3</sub> under two-phase catalysis conditions.

In order to expand the concept of the preparative possibilities of using acylals, we decided to study their reaction with other carbanions. We found that bromoform under two-phase catalysis conditions (50% NaOH solution,  $CH_2Cl_2$ , TEBA) reacts with the acylals of acetaldehyde (Ia), benzaldehyde (Ib), acrolein (Ic), crotonaldehyde (Id), and  $\beta$ , $\beta$ -dimethylacrolein (Ie) and, like CHCl<sub>3</sub>, leads to the acetates of  $\alpha$ -tribromomethylcarbinols (V).

RCH(OAc)2-	CHBr <sub>3</sub> , 50% NaOH, TEBA	→ RCH(CBr <sub>3</sub> )OAc
(I a-e)	•	(V a - e)

However, even when using a fourfold excess of  $CHBr_3$ , the yields of the end products (Va-e) are considerably lower (Table 1) than in the case of  $CHCl_3$ , which can apparently be explained by the greater tendency of the  $CBr_3$  anion to hydrolyze. Varying the reaction conditions (temperature and time), and also the ratio of the reactants, disclosed that it is optimum to use a fourfold excess of  $CHBr_3$  and alkali, and run the reaction at 25-35°C for 4-5 h.

Phenylmethylacetonitrile (VI) reacts with (Ia, b) under two-phase catalysis conditions to give products (VIIa, b) that formally correspond to the replacement of one acetate group in (Ia, b) by the carbanion that is generated from (VI), in which connection (VIIa) was obtained previously [2] under the same conditions by reacting (VI) with vinyl acetate.



The reaction of the unsubstituted phenylacetonitrile (VIII) with (Ib, d) respectively leads to (IXb, d), which apparently can be explained by the exceeding ease of cleavage an acetate group in the initially formed acetates when the latter contain a labile  $\alpha$ -hydrogen atom. Product (IXb) was also obtained previously [2] by adding (VIII) to vinyl acetate.



It is obvious that another scheme can also be proposed for the formation of the end products (IXb, d), specifically by the initial hydrolysis of the starting acetals (Ib, d) to the corresponding aldehydes and condensation of the latter with (VIII) based on the Knoevenagel reaction.

The structure of all of the obtained compounds was proved via the PMR spectra and elemental analysis data. The purity of the products was verified by GLC; the reaction course was checked by the same method.

#### EXPERIMENTAL

The GLC analysis was run on an LCM-8 MD-5 instrument equipped with a flame-ionization detector, and using nitrogen as the carrier gas and a  $1.4 \times 0.003$  m glass column packed with 5% of SE-30 deposited on Chromaton N-AW-DMCS. The PMR spectra were obtained on a Tesla BS-497 instrument (100 MHz) using CCl<sub>4</sub> as the solvent and TMS as the internal standard.

Preparation of (Va-e), (VIIa, b), and (IXb, d). To a mixture of 0.05 mole of acylal (I), either 0.1 mole of the CH acid component (VI) or (VIII) or 0.2 mole of CHBr<sub>3</sub>, and 0.05 mmole of triethylbenzylammonium chloride (TEBA) in 20 ml of  $CH_2Cl_2$  was added 6 ml of 50% NaOH solution, and the temperature of the vigorously stirred mixture was kept within 25-35° for 4 h by cooling with ice. The reaction mass was diluted with water, the organic layer was separated, the aqueous layer was additionally extracted with  $CH_2Cl_2$ , and the combined ex-

tracts were washed with water and dried over MgSO4. After evaporating the solvent the residue was either distilled or recrystallized (the yields and characteristics of the obtained products are given in Table 1).

Preparation of (III) and (IV). With vigorous stirring and cooling with ice, to a mixture of 0.1 mole of CHCl<sub>3</sub> and 0.05 mole of TEBA in 20 ml of CH<sub>2</sub>Cl<sub>2</sub>, cooled to 5-7°, were simultaneously added dropwise 0.05 mole of the aldehyde and 5 ml of 50% aqueous NaOH solution, after which the mixture was stirred at  $\sim 20^{\circ}$  for 0.5 h and then worked up as described above (the yields and characteristics of (III) and (IV) are given in Table 1).

#### CONCLUSIONS

1. gem-Diacetates react with CHBr<sub>3</sub>, PhCH<sub>2</sub>CN, and PhCHMeCN under two-phase catalysis conditions to give products that formally correspond to the exchange of one acetate group of the acylal by the corresponding carbanion.

2. The possible schemes for the reaction of acylals with CHCl<sub>3</sub> under the conditions of a two-phase catalytic system are discussed.

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### REACTION OF N-( $\gamma$ -HALOALKYL)-N-NITRAMIDES WITH BASES

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 $N-(\beta-Haloalkyl)-N-nitramides$  when treated with bases are converted to 4,5-dihydro-1,2,-3-oxadiazole 2-oxides [1]. In order to determine if the 4,5(5,6)-dihydro-1,2,3-oxadiazine 2-oxides can be obtained by a similar scheme, we studied the reaction of the following N-(y-haloalky1)-N-nitramides with bases: N-(y-bromopropy1)-N-nitro-m-nitro-p-toluenesulfonamide (I), N-(Y,Y-dichloropropyl)-N-nitro-m-nitro-p-toluenesulfonamide (II), and methyl N- $(\beta, \gamma-dibromopropy1)-N-nitrocarbamate (III).$ 

Compounds (I)-(III) were respectively obtained by the nitration of N-( $\gamma$ -bromopropy)-ptoluenesulfonamide (IV) with HNO3, the chlorination of N-(m-nitro-p-tosyl)-N-nitro-β-aminopropionaldehyde (V) with PCl<sub>5</sub>, and the bromination of methyl N-allyl-N-nitrocarbamate (VI).

We found that the reaction of (I) with KOH actually gives 4,5(5,6)-dihydro-1,2,3-oxadiazine 2-oxide (VII) in 46% yield. The structure

 $\underbrace{ \underset{(1)}{\text{Me}} SO \ N(NO_2)CH_2CH_2CH_2Br} \xrightarrow{KOH} K^+N^-(NO_2)CH_2CH_2CH_2Br}_{(1)} \rightarrow \underbrace{ \underset{(1)}{\overset{\parallel}{N}} N^-}_{O}$ 

of (VII) was confirmed by the elemental analysis data and the IR and PMR spectra. In the IR spectrum of (VII) the N=N group has absorption bands (1270 and 1595 cm<sup>-1</sup>) in the same re-

gion as the cis form of the O-methyl ester of methylnitramine [2]. The formation of (VII) is evidently explained by the nucleophilic attack of the sulfo group in (I) by hydroxyl ion,

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