BRIEF COMMUNICATIONS

UNSATURATED ALDEHYDES IN THE THERMOLYSIS OF SODIUM TRICHLOROACETATE

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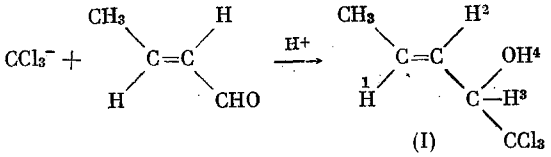
Simple methods for the preparation of cyclopropanes with aldehyde groups are lacking up to now. The easiest syntheses of cyclopropanes via the carbenes are run under alkaline conditions, where the aldehydes are polymerized. The thermolysis of CCl_3COONa in the presence of olefins was proposed as a method of obtaining cyclopropanes in a nonalkaline medium [1]. It is known that the thermolysis of CCl_3COONa in the presence of ketones [2], acrolein or 2-furaldehyde [3] gives the addition products of the CCl_3^- anion to the carbonyl group. The purpose of this paper was to study the applicability of this method to the synthesis of cyclopropanes from unsaturated aldehydes in which the C=C bond is activated toward dichlorocarbene by the presence of either a CH_3 or C_6H_5 group.

It was found that when the pyrolysis of CCl_3COONa is run in the presence of crotonaldehyde or cinnamaldehyde the starting compounds undergo intense polymerization, and the reaction mass has an alkaline character. To prevent polymerization of the aldehydes the thermolysis was run in the presence of CCl_3COOH. The minimum amount of acid, where the aldehydes do not polymerize, is determined by the ratio of 0.5 mole of acid per mole of salt. The presence of the acid does not interfere with the formation of the cyclopropanes: the thermolysis of CCl_3COONa in the presence of CCl_3COOH and styrene leads to phenyl-2,2-dichlorocyclopropane in 60% yield.

Nevertheless, the thermolysis of CCl_3COONa in the presence of crotonaldehyde and CCl_3COOH leads to 1-trichloromethyl-2-buten-1-01 (I).

$$CCl_3COONa \rightarrow CCl_3^- + Na^+ + CO_2$$


(I)

Based on the GLC analysis data, the thermolysis of CCl_3COONa in the presence of cinnamaldehyde leads to one product, which could not be isolated in the pure state.

In order to ascertain if cyclopropane aldehydes are formed even slightly during thermolysis we attempted to synthesize the aldehydes by the scheme: (see following page for scheme). Employing GLC, we were unable to detect the presence of aldehydes (IV) and (V) in the reaction mixtures in a single case. In order to exclude the possibility of aldehydes (IV) and (V) decomposing under the reaction conditions we ran the thermolysis of CCl_3COONa and CCl_3COOH in the presence of 2,2-dichloro-3-methylcyclopropanecarboxaldehyde (IV). Using an internal standard, it was shown by GLC that aldehyde (IV) is stable under the thermolysis conditions.

As a result, the thermolysis of CCl_3COONa in the presence of unsaturated aldehydes fails to give cyclopropane derivatives. Consequently, the reaction of the trichloromethyl anion with a conjugated aldehyde group is faster than its decomposition into dichloro-

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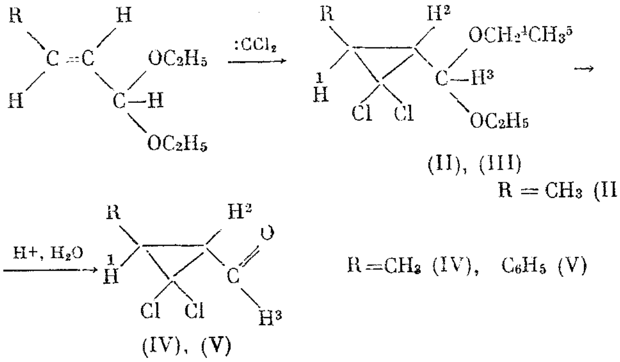
TABLE 1. NMR Spectral Data for Compounds (I)-(V)

Compound	τ, ppm						J, Hz				
	H^1	H^2	H^3	H^4	H^5	R	1–2	2–3	4–5	R-1	R-2
(I)	4,18	4,50	5,70	6,50	—	8,28	15,2	7,6	—	6,5	1,2
(II)	8,60	8,75	5,70	6,47	8,88	8,78	7,0	5,2	7,0	7,0	—
(III)	7,19	7,69	5,43	6,41	8,86	2,82	8,4	6,2	7,0	—	—
(IV)	7,62	7,86	0,81	—	—	8,58	7,7	4,5	—	6,0	—
(V)	6,63	1,19	0,78	—	—	2,86	7,5	4,2	—	—	—

$$CHCl_3 + NaOH \xrightarrow{[C_6H_5CH_2N(C_2H_5)_3]Cl} :CCl_2 + NaCl + H_2O$$



(II), (III)

R = CH_3 (II), C_6H_5 (III)

R=CH_3 (IV), C_6H_5 (V)

(IV), (V)

carbene and chlorine anion. Apparently, the unconjugated aldehyde group in (IV) is more stable under pyrolysis conditions.

EXPERIMENTAL METHOD

The GLC analysis was run on a Tswett-2 instrument using columns with the following liquid phases (15% of the stationary phase deposited on Chromatone N: Carbowax-1500, Rheoplex-400, polymethylphenylsiloxane oil, Apiezon L). The NMR spectra were taken on a Tesla BS 487C instrument. As the internal standard we used TMS, and the values of the chemical shifts are given in ppm (τ scale) (Table 1). The IR spectra were taken on a UR-20 instrument as a thin layer.

1-Trichloromethyl-2-buten-1-ol (I). To a stirred mixture of 56 g (0.85 mole) of crotonaldehyde, 50 ml of diglyme, and 34.3 g (0.21 mole) of CCl_3COOH at 90-110°C was added in portions 77.9 g (0.42 mole) of CCl_3COONa in 2 h. The mixture was washed with water, dried, and distilled. We obtained 53 g (27%) of (I),bp 75° (3 mm); n_D^{20} 1.3946; d_4^{20} 1.5028. Found: C 31.94; H 3.91; Cl 56.76%; MR 25.97. $C_5H_7Cl_3O$. Calculated: C 31.69; H 3.72; Cl 56.13%; MR 26.30. Infrared spectrum (ν, cm^{-1}): 3450 m, 3040 m, 1450 m, 810 s.

1-Diethoxymethyl-2,2-dichloro-3-methylcyclopropane (II). To a stirred mixture of 72 g (0.5 mole of crotonaldehyde diethyl acetal, 100 ml of 50% NaOH solution, and 2 g of triethylbenzylammonium chloride at 30-35° was added in drops 60 g (0.5 mole) of $CHCl_3$ in 1.5 h. The mixture was stirred another 3 h at 35-40°, washed with water, dried, and vacuum distilled. We obtained 54.5 g (48%) of (II), bp 87-89° (7 mm); n_D^{20} 1,4522; d_4^{20} 1.1345. Found: C 47.84; H 7.38; Cl 31.03%; MR 53.99. $C_9H_{16}O_2Cl_2$. Calculated: C 47.58; H 7.10; Cl 31.24%; MR 53.57. Infrared spectra (ν, cm^{-1}): 2980 s, 2960 s, 1460 m, 1020-1200 s, 810 s.

1-Diethoxymethyl-2,2-dichloro-3-phenylcyclopropane (III). In a similar manner, from 23.7 g (0.115 mole) of cinnamaldehyde diethyl acetal, 0.46 g of triethyl benzylammonium chloride, 23 ml of 50% NaOH solution, and 13.9 g (0.115 mole) of $CHCl_3$ we obtained 19.11 g (57.5%) of (III), bp 160-164° (7 mm); n_D^{20} 1.5191; d_4^{20} 1.1979. Found: C 58.38; H 6.31; Cl 24.55%; MR 73.23. $C_{14}H_{18}Cl_2O_2$. Calculated: C 58.14; H 6.28; Cl 24.52%; MR 73.28. Infrared spectrum (ν, cm^{-1}): 2900 s, 1485 s, 1350 s, 1000-1200 s, 795 s.

2,2-Dichloro-3-methylcyclopropanecarboxaldehyde (IV). A stirred mixture of 36 g of acetal (II) and 60 ml of 12% H_2SO_4 solution was heated on the steam bath for 2 h. The reaction mass was washed with water, dried, and vacuum distilled. We obtained 21.5 g (87%)

of (IV), bp 60-65° (7 mm); n_D^{20} 1.5759; d_4^{20} 1.3277. Found: C 39.75; H 3.63; Cl 46.60%; MR 32.39. $C_5H_6Cl_2O$. Calculated: C 39.24; H 3.95; Cl 46.36%; MR 33.37. Infrared spectrum (ν, cm^{-1}): 2965 s, 1725 s, 1460 s, 1385 m, 815 s.

2,2-Dichloro-3-phenylcyclopropanecarboxaldehyde (V). In a similar manner, from 15.8 g of acetal (III) and 30 ml of 12% H_2SO_4 solution we obtained 9.4 g (80%) of (V), bp 145-147° (7 mm); n_D^{20} 1.5759; d_4^{20} 1.3277. Found: C 56.32; H 3.53; Cl 32.75%; MR 54.57. $C_{10}H_8Cl_2O$. Calculated: C 55.84; H 3.74; Cl 32.99%; MR 53.08. Infrared spectrum (ν, cm^{-1}): 2865 m, 1725 s, 1510 s, 1455 m, 750 s.

CONCLUSIONS

The thermolysis of sodium trichloroacetate in the presence of crotonaldehyde gives 1-trichloromethyl-2-buten-1-ol. Compounds that contain a cyclopropane ring are not formed under these conditions.

LITERATURE CITED

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3. V. S. Aksenov, L. A. Serkina, V. M. Shostakovskii, M. I. Kravchenko, and O. M. Nefedov, Reports of Fourth All-Union Conference on Acetylene Chemistry [in Russian], Vol. 1, Izd. AN KazSSR, Alma-Ata (1972), p. 223.