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SYNTHESIS AND SOME PROPERTIES OF GEM-DICHLOROCYCLOPROPANE CARBOXALDEHYDE ACETALS AND CYCLOPROPANE CARBOXALDEHYDE ACETALS

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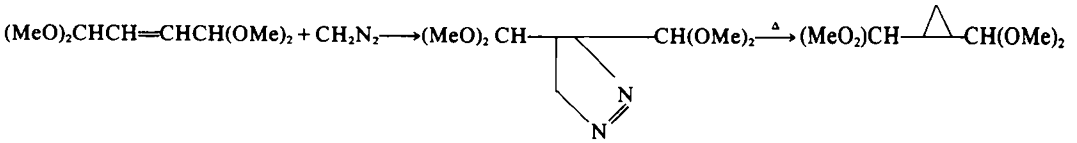
Abstract—α,β-Unsaturated aldehyde acetals add $:CCl_2$ (obtained in accordance with Makosza procedure) to form gem-dichlorocyclopropanecarboxaldehyde acetals (1) in high yields when the ratio of reactants is no less than 1:4. The addition of $:CCl_2$ to polyunsaturated aldehyde acetals in the above conditions proceeds regioselectively at double bonds enriched by electrons. Compounds 1 are reduced by sodium in liquid ammonia to give cyclopropanecarboxaldehyde acetals (2). Both 1 and 2 are hydrolized by dilute H_3PO_4 to the corresponding aldehydes and are added to vinyl ethers in the presence of $BF_3 \cdot Et_2O$ to produce only 1:1 adducts which are hydrolyzed by a mixture of AcOH–AcONa–H_2O to give β-formylcyclopropanes which were previously unknown.

Cyclopropane aldehydes and especially their acetals are little known though they are promising intermediates for the preparation of many cyclopropanes occuring in nature such as chrysantemic acids, hypoglicin, etc. Therefore in this work we investigated general routes for the synthesis of cyclopropane aldehydes and their acetals with the intention to explore the synthetic potential of such compounds. A variety of efficient synthetic methods for the cyclopropanes have been developed,[1] however most of them gave poor results when applied to the preparation of cyclopropanecarboxaldehydes or their acetals.

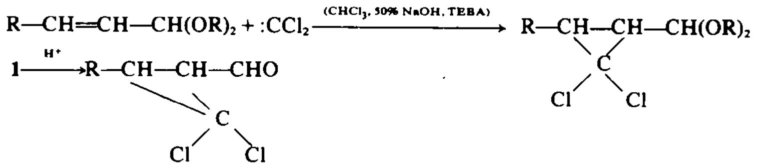
A stereospecific path of the cyclopropane synthesis through the pyrolysis of Δ^1-pyrazolines formed by the addition of diazomethane to olefins gave satisfactory result when applied to the preparation of formylcyclopropane acetals from acrolein acetals.[2] Satisfactory results were also obtained with bis-dimethylacetal of fumaraldehyde which reacted with an ether solution of diazomethane to form bis-dimethylacetal of cyclopropane-1,2-bis-carboxaldehyde.[3]



Diethylacetals of β,β-dichloroacrolein, vinyl acetic aldehyde and β,β-dimethylacrolein as well as dimethylacetal of crotonaldehyde would not react with diazomethane under ordinary conditions, and the diethylacetal of crotonaldehyde or the bis-dimethylacetal of glutaconaldehyde formed mixtures of isomeric pyrazolines in small yields (22–27%) by the action of diazomethane. The flash pyrolysis of these mixtures gave rise to reaction products (60–80% yield), which contained no more[3] than 65% of cyclopropane derivatives.[4]

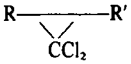
The well known Simmons and Smith stereospecific synthesis of cyclopropanes, which involves treatment of olefins with methylene iodide and zinc–copper couple to acrolein diethylacetal gave only a poor yield of cyclopropanecarboxaldehyde diethylacetal. (about 12%)[5] α,β-Unsaturated aldehydes polymerized under these conditions.[6] However $:CCl_2$ generated[8] by the action of 50% aqueous NaOH on $CHCl_3$, in the presence of triethylbenzylammonium chloride (TEBA) reacted with acrolein-diethylacetal.[7] We decided to take advantage of this simple and accessible Makosza method.[8] However some acetals (glutaconaldehyde bis-dimethylacetal or 1,1,3-triethoxyhex-1-en) did not react when treated with equimolar (or even with twofold excess) quantities of $:CCl_2$, and other acetals (crotonaldehyde diethylacetal or vinylacetic aldehyde acetal) gave low yields (21–23%) of the expected gem-dichlorocyclopropanecarboxaldehyde acetals (1).[9] These data coincide with the results of Billups *et al*,[10] who added $:CCl_2$ to *cis*-2-pentenal dimethylacetal under the Makosza conditions[8] and obtained *cis* - 2,2 - dichloro - 3 - ethylcyclopropanecarboxaldehyde dimethylacetal with 19.3% yield.

Intending to raise the yields of the desired **1** compound, we investigated the influence of the reactant ratio on the yield and found that increasing the $CHCl_3$ to a fourfold excess raised substantially the yield of **1** (two–three times)



1′   1

Table 1. Yields and some properties of acetals of the type I and corresponding aldehydes I'

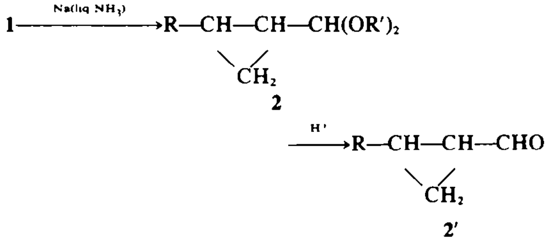


Compounds					Found/Required %			
R	R'	Yield %(1)	B.p. °C/mm	n_D^{18}	C	H	Cl	PMR-spectra(2), δ, ppm, J, Hz
H	$CH(OEt)_2$	38(47)	81–82/8	1.4485				1.05–1.20 m (7H, $2CH_3$, H_c); 1.75 d (2H, $2H_c$, $J_{H_c-H_c} = 6$); 3.35–3.85 m (4H, $2CH_2O$); 4.35 d (1H, $CH(OEt)_2$, J = 6)
Me(3)	$CH(OEt)_2$	82(93)	87–90/8	1.4495	47.58 47.60	7.05 7.01	31.25 31.23	1.05–1.45 m (10H, $3CH_3$, H_c); 1.65 m (1H, H_c); 3.3–3.7 m (4H, $2CH_2O$); 4.20 d (1H, $CH(OEt)_2$, J = 6)
Ph	$CH(OEt)_2$	45	131–132/0.8	1.5220	58.07 58.14	6.18 6.27	24.16 24.52	1.11 t (3H, CH_3, J = 6.5); 1.13 t (3H, CH_3, J = 6); 2.14 dd (1H, H_c, $J_{H_c-H_c} = 8.5$, $J_{H_c-CH(OEt)_2} = 6$); 2.32 d (1H, H_c, $J_{H_c-H_c} = 8.5$); 3.2–3.8 m (4H, $2CH_2O$); 4.47 d (1H, $CH(OEt)_2$, J = 6); 7.13 s (5H, Ph)
H	$CH_2CH(OEt)_2$	63(70)	90–91/8	1.4485	48.16 47.60	7.35 7.01	31.15 31.23	1.17 t (7H, $2CH_3$, H_c, $J_{CH_3-CH_2} = 7$); 1.80 m (4H, CH_2, $2H_c$); 3.2–3.8 m (4H, $2CH_2O$); 4.50 t (1H, $CH(OEt)_2$, J = 5.5)
$(MeO)_2CHCH_2$(4)	$CH(OMe)_2$	24(48)	115–118/0.8	1.4625	44.14 43.97	6.71 6.64	24.88 25.96	1.45–1.90 m (4H, CH_2, $2H_c$); 3.3 s, 3.35 s (12H, $4CH_3O$); 4.17 d (1H, $CH(OMe)_2$, $J_{H_c-CH(OMe)_2} = 6$); 4.45 t (1H, $CH(OMe)_2$, $J_{CH(OMe)_2-CH_2} = 6$)
Me(4)	$CH(OEt)CH_2CH(OEt)_2$	67	130–132/10	1.4525	52.48 52.18	8.08 8.08	23.20 23.70	1.05 t (9H, $3CH_3$, $J_{CH_3-CH_2} = 7$); 1.33 d (3H, CH_3, $J_{CH_3-H_c} = 5$); 1.6–2.0 m (3H, CH_2, H_c); 3.2–3.8 m (7H, $3CH_2O$, CH–O–); 4.7 t (1H, $CH(OEt)_2$, J = 5)
H(5)	CH_2CHO	60	104–108/40	1.4905	39.43 39.25	4.24 3.95	45.44 46.34	0.81–1.05 m (1H, H_c); 1.5–1.75 m (2H, CH_2); 2.3–2.6 m (2H, CH_2); 9.75 s (1H, CHO)
Me(6)	CHO	60	66–67/13	1.4822	39.12 39.25	4.40 3.95	45.18 46.34	1.43 d (3H, CH_3, J = 6); 1.90–2.25 m (2H, $2H_c$); 9.95 d (1H, CHO, J = 4)
Diethylacetal of 1-formyl-2,2-dichloro-3,3-dimethylcyclopropane		75	98–99/9	1.4515	49.38 49.59	7.61 7.91	29.45 29.29	1–1.50 m (13H, $4CH_3$, H_c); 3.50 m (4H, $2CH_2O$); 4.33 d (1H, $CH(OEt)_2$, $J_{CH_c-CH(OEt)_2} = 7.5$)

(1)Yield on the consumed is olefin is shown in parentheses. (2) $H_c = H_{cyclopropane}$; s, singlet; t, triplet; d, doublet; q, quartet; m, multiplet. (3)21–23% yield in conditions.[5,6] (4)In conditions[5,6] the product did not formed. (5)ν_{CO} 1736 cm^{-1}. (6)ν_{CO} 1720 cm^{-1}.

and introduced into the reaction those acetals which did not react under ordinary conditions. Thus we obtained a number of **1** compounds (Table 1) which were easily hydrolyzed to the corresponding aldehydes (**1′**) in satisfactory yields (Table 1).

Compounds **1** were reduced by sodium in liquid ammonia to form the corresponding acetals, in good yields (55–80%).[11]

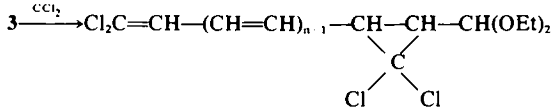


2

2′

These cyclopropanecarboxaldehyde acetals (**2**) were also easily hydrolyzed (heating with a dilute solution of H_3PO_4) to the corresponding aldehydes (**2**) in satisfactory yields (see Table 2). The structures of acetals **1** and **2** were confirmed by the elemental analyses and NMR spectra.

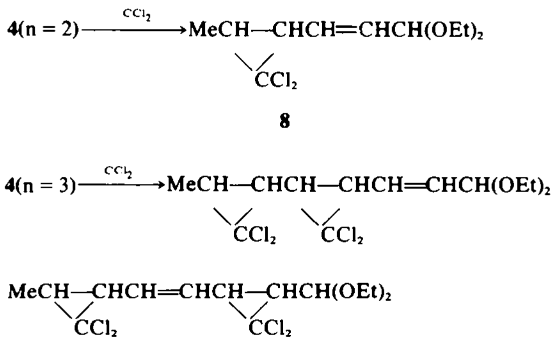
A typical electrophylic reaction with $:CCl_2$ was applied to determine the order of the addition to double bonds of some polyunsaturated acetals[12] such as $Cl_2C{=}CH(CH{=}CH)_n$ $CH(OEt)_2$ (**3**), $Me(CH{=}CH)_n$ $CH(OEt)_2$ (**4**) or diacetals of the general formula $(RO)_2$-$CH(CH{=}CH)_n$ $CH(OR)_2$ (**5**). Using a fourfold excess of $CHCl_3$ β,β-dichloroacrolein diethylacetal (**3**, n = 0) did not react with $:CCl_2$, however acetals **3** (n = 1, 2) reacted with $:CCl_2$ to form adducts (**6** and **7**) with one mole of $:CCl_2$ to the double bond adjacent to the acetal group



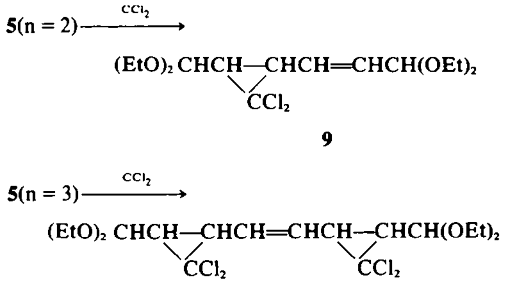
6, n = 1; **7**, n = 2

The yield of the acetal **7** (33%) was substantially higher than that of **6** (8.5%). Thus the extension of the unsaturated chain in **3** decreased the influence of strong electronegative Cl atoms which prevent the addition of electrophylic reagents to the double bond.

As was anticipated that the addition of $:CCl_2$ to **4** (n = 2) using an equimolar ratio of reactants, proceeded at the double bond adjacent to the Me group and produced 2,2 - dichloro - 3 - methylcyclopropane - 1 - carboxaldehyde diethylacetal (**8**). In the case of **4** (n = 3) a mixture of two 1:2-adducts in the ratio 2:3 was obtained:

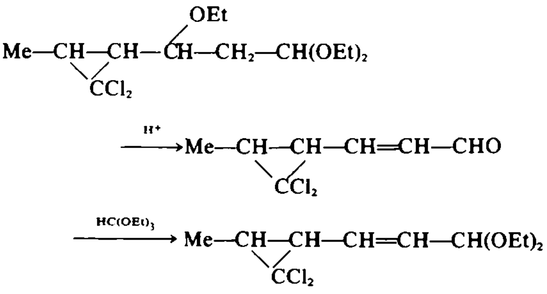


5 (n = 1) did not react with $:CCl_2$ and **5** (n = 2) with $:CCl_2$ produced only a single product: bis-diethylacetal of 2,2 - dichloro - 1 - formyl - 3 - (β - formylvinyl) cyclopropane (**9**) in a yield of 24%. The addition of $:CCl_2$ to **5** (n = 3) took place at two double bonds adjacent to the acetal groups and resulted in bis-diethylacetal of 1,2 - di - (1 - formyl - 2,2 - dichloro - 3 - cyclopropyl) ethylene (**10**) in 85% yield.



10

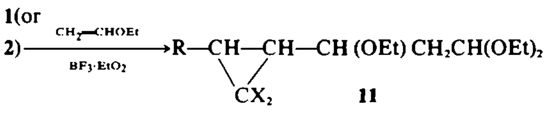
The structure of compounds **6**–**10** was confirmed by elemental analyses and nmr spectra (Table 3) and in the case of **8** by an unambiguous synthesis according the following scheme:



8

The data for compounds **6**–**10** are given in Table 3.

The reaction of acetals with vinyl ethers in the presence of Lewis acids is of great importance.[13] We found that **1** (R = Me) as well as **2** (R = H, Me) added to vinyl ethyl ether in the presence of $BF_3{\cdot}Et_2O$ and formed only 1:1 adducts (**11**):

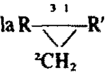


R—H, Me; X=H, Cl

The yields of the final triethoxy derivatives were good (Table 4) for the acetals **2**. Acetal **1** (R = Me) formed a triethoxy compound in 15% yield when the ratio of reactants was 1:1 and 30% yield when the ratio of reactants was increased to 4:1.

The absence of telomers shows that cyclopropane acetals behave like acetals of aromatic or α,β-unsaturated aldehydes.[14] The reaction between **1** (or **2**) and vinyl ether is evidence that the carbonium ion (**12**) which formed during the first stage was stabilized by the cyclopropane ring to a greater extent than by the $-CH_2$-link in the carbonium ion (**13**) which formed at the second stage of the reaction.

Table 2. Yields and some properties of acetals and aldehydes of the general formula



Compound					$\frac{\text{Found}}{\text{Required}}$%		
R	R′	Yield %	B.p. °C/mm	n_D^{18}	C	H	PMR-spectra, δ, ppm, J, Hz⁽¹⁾
H	$CH(OEt)_2$	64	65–68/35	1.4090	$\frac{66.60}{66.63}$	$\frac{11.42}{11.18}$	0.37 d (4H, $2H_{c\text{-}2}$, $2H_{c\text{-}3}$, J = 7); 0.7 m (1H, $H_{c\text{-}1}$); 1.12 t (6H, $2CH_3$, J = 6.5); 3.5 m (4H, $2CH_2O$); 4.1 d (1H, $CH(OEt)_2$, J = 5)
Me	$CH(OMe)_2$	60	51–52/35	1.4120	$\frac{64.80}{64.58}$	$\frac{10.94}{10.84}$	0.22–0.66 m (3H, $3H_c$); 1.05 m (4H, CH_3, $H_{c\text{-}1}$); 3.21 s (6H, $2CH_3O$); 4.10 d (1H, $CH(OMe)_2$, J = 5)
Me	$CH(OEt)_2$	68	85/50	1.4140	$\frac{68.09}{68.31}$	$\frac{11.60}{11.47}$	0.58 m (3H, $3H_c$); 1.12 t (10H, $3CH_3$, $H_{c\ 1}$, J = 7); 3.58 m (4H, $2CH_2O$); 4.10 d (1H, $CH(OEt)_2$, J = 5)
Ph	$CH(OEt)_2$	55	90–91/0.3	1.4978	$\frac{76.55}{76.32}$	$\frac{9.42}{9.14}$	0.8–1.5 m (3H, $2H_c$, $H_{c\text{-}1}$); 1.3 t (6H, $2CH_3$, J = 7); 2.12 m (1H, $H_{c\text{-}3}$); 3.75 m (4H, $2CH_2O$); 4.50 d (1H, $CH(OEt)_2$, J = 5); 7.25 m (5H, Ph)
H	$CH_2CH(OEt)_2$	80	84–85/40	1.4189	$\frac{68.05}{68.31}$	$\frac{11.46}{11.47}$	0.20–0.70 m (5H, $5H_c$); 1.16 t (6H, $2CH_3$, J = 7); 1.37 t (2H, CH_2, $J_{CH_2\text{-}H_c, CH_2\text{–}CH(OEt)_2} = 6$); 3.54 m (4H, $2CH_2O$); 4.47 t (1H, $CH(OEt)_2$, J = 6)
$(MeO)_2CHCH_2$	$CH(OMe)_2$	60	95–96/8	1.4250	$\frac{58.62}{58.80}$	$\frac{10.07}{9.87}$	0.20–1.00 m (4H, $4H_c$); 1.5 t (2H, CH_2, J = 6); 3.33 s (12H, $4CH_3O$); 4.20 d (1H, $CH(OMe)_2$, $J_{H_c\text{–}CH(OMe)_2} = 5$); 4.39 t (1H, $CH(OMe)_2$, $J_{CH_2\text{–}CH(OMe)_2} = 6$)⁽²⁾
CH_3	$CH(OEt)CH_2CH(OEt)_2$	85	98–102/6	1.4350	$\frac{66.65}{67.78}$	$\frac{11.36}{11.38}$	0.20–0.80 m (3H, $3H_c$); 1.16 t (13H, $4CH_3$, H_c, $J_{CH_3\text{–}CH_2, CH_3\text{–}H_{c\text{-}3}} = 7$); 1.72 t (2H, CH_2, $J_{CH_2\text{–}CH(OEt)_2} = 6$); 3.50 m (7H, $2CH_2O$, CH–OCH_2); 4.55 t (1H, $CH(OEt)_2$, J = 6)
H	CH_2CHO⁽³⁾	65	112⁽⁴⁾	1.4250			0.16–0.55 m (5H, $5H_c$); 2.17 q (2H, CH_2, $J_{CH_2\text{–}CHO} = 2$, $J_{CH_2\text{-}H_{c\text{-}1}} = 8$); 9.64 t (1H, CHO, J = 2)
H	CHO	60	97–100⁽⁵⁾	1.4240			1.1 d (4H, $4H_c$, $J_{H_c\text{–}H_{c\text{-}1}, H_{c\text{-}1}\text{–}CHO} = 6.5$); 1.85 d quintet (1H, $H_{c\text{-}1}$, $J_{H_{c\text{-}1}\text{–}H_{c\text{-}2}, H_{c\text{-}1}\text{–}CHO} = 6.5$); 8.95 d (1H, CHO, J = 6.5)

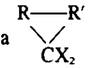
(1) $H_c = H_{cyclopropane}$, s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. (2) The assignment of H_c and CH_2 in this compound was made by double NMR (acetal proton at 252 Hz and 272 Hz). (3) ν_{CO} 1710 cm⁻¹. (4) 2,4-Dinitrophenylhydrazone, m.p. 136–137°, found %: C, 49.57; H, 4.55; N, 21.76, required %: C, 50.00; H, 4.50; N, 21.20. (5) 2,4-Dinitrophenylhydrazone, m.p. 168–170°, found %: C, 47.56; H, 4.05; N, 22.61, required %: C, 48.00; H, 4.06; N, 22.39.

Table 3. Yields and properties of some cyclopropane compounds

Compound	Yield %	B.p. °C/mm	n_D^{18}	$\frac{\text{Found}}{\text{Required}}$ % C	H	Cl	PMR-spectra(1), δ, ppm, J, Hz
6	8.5(18)(2)	117–120/0.6	1.4985	$\frac{40.34}{39.48}$	$\frac{4.88}{4.64}$	$\frac{43.16}{45.36}$	1.05–1.33 m (6H, $2CH_3$); 1.8 dd (1H, H_c, J = 6, J = 8); 2.40 t (1H, H_c, J = 8); 3.35–3.75 m (4H, $2CH_2O$); 4.41 d (1H, $CH(OEt)_2$, J = 6); 5.65 d (1H, $CCl_2 = CH$, J = 8)
7	33(40)(2)	135–140/0.2	1.5686	$\frac{42.60}{43.13}$	$\frac{4.62}{4.82}$	$\frac{42.46}{44.77}$	1.15–1.27 m (6H, $2CH_3$); 1.74 dd (1H, H_c, J = 6, J = 8); 2.16 t (1H, H_c, J = 8); 3.25–3.70 m (4H, $2CH_2O$); 4.35 d (1H, $CH(OEt)_2$, J = 6); 5.25–5.75 m (1H, $CCl_2 = CH$); 6.30–6.50 m (2H, CH=CH)
8	44(61)(2)	81–83/0.35	1.4730	$\frac{52.21}{52.18}$	$\frac{7.16}{7.25}$	$\frac{28.26}{27.91}$	1.18 t (6H, $2CH_3$, J = 5); 1.33 d (3H, CH_3, J = 6); 1.48–1.97 m (2H, $2H_c$); 3.23–3.72 m (4H, $2CH_2O$); 4.8 d (1H, $CH(OEt)_2$, J = 3); 5.5 m (2H, CH=CH)
9(3)	24(33)(2)	106–108/0.1	1.4750				1.00–1.35 m (12H, $4CH_3$); 1.47–1.85 m (2H, $2H_c$); 3.25–3.90 m (8H, $4CH_2O$); 4.35 d (1H, $CH(OEt)_2$, J = 6); 4.8 d (1H, $CH(OEt)_2$, J = 3); 5.55 m (2H, CH = CH)
10	85	200–210/0.3	1.4958	$\frac{46.75}{48.01}$	$\frac{5.98}{6.27}$	$\frac{32.70}{31.50}$	1.03–1.35 m (12H, $4CH_3$); 1.65–1.90 dd (1H, H_c, J = 6, J = 8); 2.05–2.30 m (1H, H_c); 3.33–3.75 m (8H, $4CH_2O$); 4.40 d (2H, $2CH(OEt)_2$, J = 6); 5.4–5.6 m (2H, CH=CH)

(1) $H_c = H_{cyclopropane}$. (2) Yields on consumed olefin are given in parentheses. (3) At conservation 9 transforms into 1-(2-formylvinyl)-2-(2,2-diethoxymethyl) - 3,3-dichlorocyclopropane (9′), found %: C, 49.11; H, 6.80; Cl, 26.80. required %: C, 49.25; H, 6.04; Cl, 26.52. ν_{CO} (CCl_4) 1690 cm^{-1}, λ_{max} (alcohol) 242 nm.

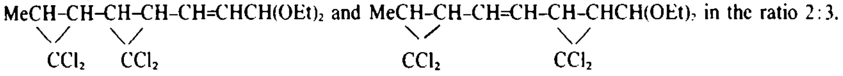
Table 4. Yields and some properties of aldehydes and acetals of the general formula



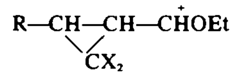
$$\underset{CX_2}{R\!-\!\!-\!\!-R'}$$

Compound	R	R′	X	Yield %	B.p. °C/mm	n_D^{20}	Found/Required % C	Found/Required % H	PMR-spectra[1], δ, ppm, J, Hz
11	H	$CH(OEt)CH_2CH(OEt)_2$	H	45	108–109/16	1.4250	66.57/66.63	11.40/11.18	0.1–0.8 m (5H, $5H_c$); 1.15 t (9H, $3CH_3$, J = 6.5); 1.76 t (2H, CH_2, J = 6.5); 3.50 m (7H, $2CH_2O$, CH_2–O–CH); 4.60 t (1H, $CH(OEt)_2$, J = 6)
14	$CH_2CH(OMe)_2$	$CH(OMe)CH_2CH(OMe)_2$	H	70	114–116/0.6	1.4390			0.20–1.0 m (4H, $4H_c$); 1.67 t (4H, $2CH_2$, J = 6); 3.25 s (16H, $4CH_3O$ MeO–CH–); 4.40 t (1H, $CH(OMe)_2$, J = 6); 4.45 t (1H, $CH(OMe)_2$, J = 6)
15[2]	H	CH=CHCHO	H	81	73–75/15	1.5015			0.3–1.0 m (4H, $2H_{2c}$); 1.25–1.67 m (1H, H_c); 6.0 m (2H, CH=CH); 9.3 m (1H, CHO)[3]
15[4]	CH_3	CH=CHCHO	H	86	76–77/16	1.5012			0.78–1.4 m (7H, CH_3, $4H_c$); 6.05 m (2H, CH=CH); 9.3 d (1H, CHO, J = 7)
15[5]	CH_3	CH=CHCHO	Cl	68	105–110/10	1.5242	46.86/46.95	4.65/4.50	1.42 d (3H, CH_3, J = 6); 1.97 m (2H, $2H_c$); 6.4 m (2H, CH=CH): 8.45 d (1H, CHO, J = 7.5)
16	CH_3	$CH{=}CHCH(OEt)_2$	H	60	94–95/15	1.4465			0.2–1.02 m (7H, CH_3, $4H_c$); 1.12 t (6H, $2CH_3$, J = 6); 3.42 m (4H, $2CH_2O$); 4.5 m (1H, $CH(OEt)_2$); 5.05 m (2H, CH=CH)
	CH_3	$CH{=}CHCH(OEt)_2$[6]	Cl	60	81–83/0.35	1.4725			
	CH_3	$CH(OEt)CH_2CH(OEt)_2$[7]	H	70					
see[8]				43	115–120/0.1	1.5070	46.62/46.34	5.59/5.56	1.22 m (9H, $3CH_3$); 1.75–2.17 m (4H, $4H_c$); 3.5 m (4H, $2CH_2O$); 4.4 d, 4.8 d (1H, $CH(OEt)_2$, J = 6, J = 3); 5.5 m (2H, CH=CH)

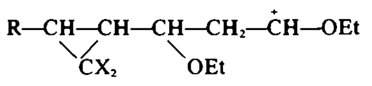
[1] $H_c = H_{cyclopropane}$. [2] ν_{CO} 1695 cm^{-1}, λ_{max} 246 (ε 16200), 2,4-dinitrophenylhydrazone m.p. 174–175°, found %: C, 51.96; H, 4.41; N, 20.06. required %: C, 52.17; H, 4.48; N, 20.23. [3] The assignment of H_C in this compound was made by double NMR at 350 Hz (aldehyde proton multiplet was transformed into singlet, and multiplet at 1.25–1.67 ppm was simplified). [4] ν_{CO} 1690 cm^{-1}, λ_{max} 251 (ε 16900), 2,4-dinitrophenylhydrazone m.p. 161–162°, found %: C, 53.46; H, 4.87; N, 18.98, required %: C, 53.79; H, 4.86; N, 19.50. [5] ν_{CO} 1690 cm^{-1}, λ_{max} 243 (ε 34700). [6] See Table 3. [7] See Table 2. [8] A mixture of



$\underset{CCl_2}{MeCH\text{–}CH}\text{–}\underset{CCl_2}{CH\text{–}CH}\text{–}CH{=}CHCH(OEt)_2$ and $\underset{CCl_2}{MeCH\text{–}CH}\text{–}CH{=}\underset{CCl_2}{CH\text{–}CH\text{–}}CHCH(OEt)_2$ in the ratio 2:3.

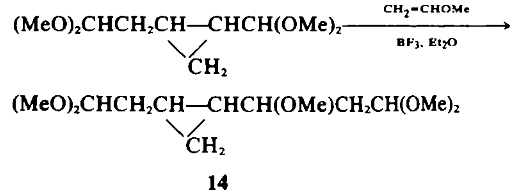


12



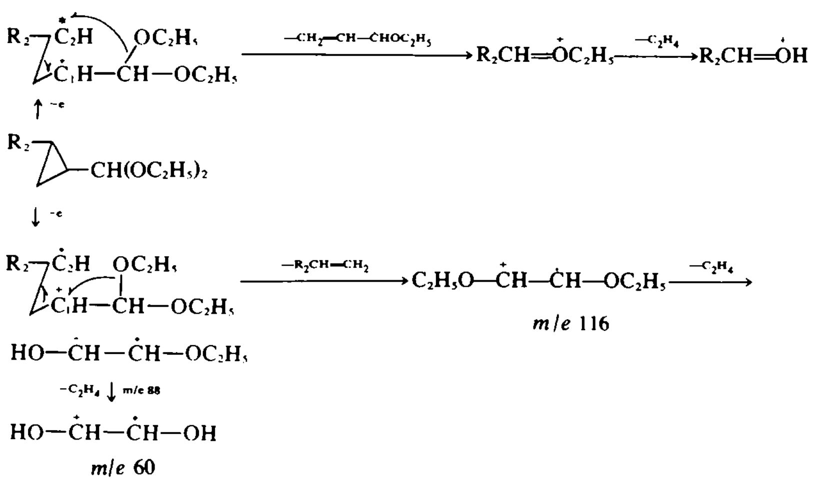
13

The enhanced ability of cyclopropane ring to stabilize carbonium ions of the type **12** was clearly evident in the case of **2** (R = $(MeO)_2CHCH_2$, R′ = Me) which added to vinyl methyl ether exclusively on the site of the acetal group joined to cyclopropane ring:

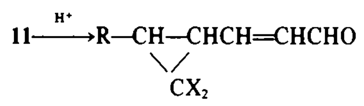


14

We have studied the fragmentation of **1** and **2** under electron impact.[15] The fragmentation of these compounds led to the formation of three groups of ions. The first group included ions the appearence of which is connected with the localization of the charge on the acetal group. These ions were observed before in the mass spectra of aliphatic acetals. The second group of ions consisted of cyclopropenyl ions, their analogs and also degradation products of these ions. The ions of the third group were formed as a result of cyclopropane ring opening which created favorable conditions for the migration of the acetal alkoxyl groups to the place of the bond break. In the substituted cyclopropanes the opening of the ring usually took place on the site of the C–C bond next to the substituent and as a result ions with a "normal" propane chain were formed. This process was also observed for **1** and **2**. The charge localization on the cyclopropane ring may lead to the break of 1–2 bond and as a result the ethoxyl radical migrates either to C_1 or to C_2 atoms depending on the place of the charge localization as shown on the following scheme:



Alkoxylacetals **11** and **14** were easily hydrolyzed by a mixture of $AcOH$-$AcONa$-H_2O to form β-formylvinylcyclopropanes (**15**) unknown before:



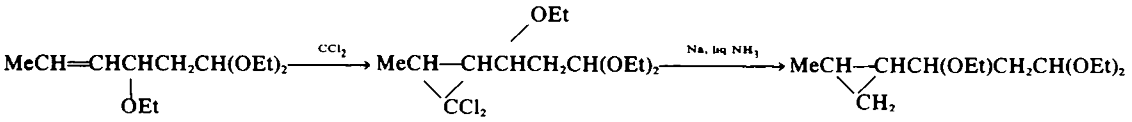
15

The structures of compounds **11** and **15** were confirmed by elemental analyses, NMR spectra and in the case of **15** by IR and UV spectra (see Table 4). Aldehyde **15** (R = Me, X = H) was transformed by the action of $HC(OEt)_3$ in alcohol solution in the presence of NH_4NO_3 into the corresponding acetal (**16**). Ethoxyacetal **11** (R = Me, X = H) was also obtained by an independent method:

Acetals **1** revealed some peculiarities in their behavior under electron impact. At first the presence of Cl atoms in the cyclopropane ring served as a natural isotope mark and therefore with its help it was possible to confirm the mechanism of the formation of a number of the observed ions. The chlorine presence did not have much effect on the intensities of peaks of the first group, but supressed peaks of the second group and very strongly influenced the rearrangement processes which led to the formation of the ions belonging to the third group (see the above scheme). Thus this direction of fragmentation becomes the principal one for many compounds **1**.

EXPERIMENTAL

GLC analyses were performed with LHM-8 MD-5 gas chromatograph; gas-carrier-N_2; glass columns: (1). 1.4 × 0.003 M; 5% SE-30 on chromaton N-AW-DMCS (0.16–0.20 mm); (2). 2.4 × 0.003 m, 5% XE-60 on chromaton N-AW-DMCS (0.16–0.20 mm).



NMR-spectra were taken in CCl_4 with DA-60-IL (60 MHz) spectrometer (hexamethyldisiloxane, tetramethylsilane, CH_2Cl_2, or benzene as internal standards). IR spectra were run in CCl_4 with UR-20 spectrophotometer. UV-spectra were measured in alcohol with Specord instrument.

Preparation of 1,2-*diformylcyclopropane.* An ether soln of CH_2N_2 (0.13 M) was added dropwise to a stirred ether soln of bis-dimethylacetal of fumaraldehyde (0.065 M) cooled in an ice bath. The resulting mixture was stirred for 1.5 hr. and then poured into thick-walled vessel cooled in an ice bath. The vessel was closed and left at room temp. for 10–15 days. Distillation after concentration *in vacuo* gave the bis-dimethylacetal of 3,4 - diformyl - Δ^1 - pyrazoline with 80% yield, b.p. 102–104°/2 mm; n_D^{20} 1.4505. (Found: C, 49.53; H, 8.37; N, 12.95. $C_9H_{18}O_4$ Requires: C, 49.53; H, 8.31; N, 12.84%). IR spectrum (CCl_4) 1560 cm^{-1} (–N=N–). The flash pyrolysis of the Δ^1-pyrazoline was performed at 450° and 2–3 mm following the known method.[2] A mixture of pyrolysis products was collected in a trap cooled by dry ice and then distilled, bis-dimethylacetal of 1,2-diformylcyclopropane was obtained with 93% yield, b.p. 75–7°/7 mm, n_D^{19} 1,4320. (Found: C, 56.60; H, 9.49; $C_9H_{18}O_4$ Requires: C, 56.82; H, 9.54%).

Bis-dimethylacetal of 1,2-diformylcyclopropane was stirred and heated with excess of 6% H_3PO_4 in a boiling water bath with simultaneous distillation of MeOH formed. After the destillation, the mixture was stirred 30 min; then diluted with CH_2Cl_2 and stirred 40 min with pulverized $CaCO_3$. After filtration the mixture was dried ($MgSO_4$). Distillation gave 1,2-diformycyclopropane in 60% yield, b.p. 71–73/7 mm, n_D^{16} I, 4728. (Found: C, 61.21; H, 6.17, $C_5H_6O_2$ Requires: C, 61.50, H, 6.40%).

Synthesis of 1,1-*dichlorocyclopropanecarboxaldehyde acetals* (**1**). TEBA (0.5 g) was added to a soln of the appropriate unsaturated aldehyde acetal (0.04 M) in 0.16 M $CHCl_3$. The mixture was warmed until 40° and 24 ml of 50% NaOH aq was added dropwise during 10 min under vigorous stirring. The mixture was extracted three times with ether or CH_2Cl_2. The combined extracts were washed with water, dried (Na_2SO_4) and evaporated. Distillation gave acetals **1** or **6–10**. Yields and some physical data for the compounds are given in Tables 1 and 3.

1,1-*Dichlorocyclopropane aldehydes.* A 6% solution of H_3PO_4 (4 ml) was added to acetal **1** (0.044 M) during vigorous stirring and heating (100° in a bath), the heating was continued during 1 hr. with distillation of alcohol. After cooling the mixture was stirred 15 min with $CaCO_3$ then diluted with 100 ml ether. The organic layer was separated, dried (Na_2SO_4), ether was distilled off, and the residue was distillated *in vacuo.* Yields and some characteristics of aldehydes are given in Table 1.

Preparation of acetals (**2**). Compound **1** (0.025 M) in 20 ml abs ether was added dropwise to a soln of 0.1 g-atom of Na in 20 ml liquid ammonia at $-70 \sim -75°$. After 20 min stirring the mixture was worked up with water and extracted with 50 ml stirring the mixture was worked up with water and extracted with 50 ml ether, the organic layer was separated and after drying ($MgSO_4$) distilled. Yields and some data of obtained acetals **2** are given in Table 2.

Cyclopropane aldehydes. These compounds were obtained as above, their yields and physical data are given in Table 2.

Synthesis of 1,1,3 *triethoxypropylcyclopropanes and -gem-dichlorocyclopropanes.* (Vinyl ether (0.02 M) was added dropwise to a mixture of **1** or **2** (0.02 M) and one drop of $BF_3 \cdot Et_2O$ at 4°. The ppt for the mixture was stirred 1.5 hr cooled in a water bath and 0.5 hr at room temp. After neutralization with an alcohol solution of NaOEt or MeOH soln of NaOMe the mixture was destilled *in vacuo.* Yields and some physical data for compounds **11**, **14** and **16** are given in Table 4.

Preparation of formylvinylcyclopropanes. 1,1,3-Triethoxycyclopropane (15.0.025 M) and 24 ml of a mixture of 100 ml AcOH, 10 g AcONa and 6.5 ml water were stirred and boiled under N_2 (100–110° in bath) during 2 hr, the mixture was poured on 100 g of ice, extracted with ether, dried ($MgSO_4$) and distilled. Yields and some physical data for compound **15** are given in Table 4.

Diethylacetals of 1 - *methyl* - 2 - (3 - *formylvinyl cyclopropane and* 1,1 - *dichloro* - 2 - *methyl* - 3 - (3 - *formylvinyl*) - *cyclopropane* (**16**). Orthoformic ester (0.018 M) and aldehyde **15** (0.015 M) were added in one portion to a hot soln of NH_4NO_3 (0.1 g) in 1 ml alcohol and the mixture was boiled 3 hr. After cooling the mixture was diluted with ether, washed with $NaHCO_3$ aq, dried ($MgSO_4$) and distilled. Physical data for **16** are given in Table 4.

REFERENCES

[1] L. A. Yanovskaya and V. A. Dombrovsky, *Uspekhi Khimii* **44**, 335 (1975).

[2] I. M. Stewart, C. Carlisle, K. Kem and G. Lee, *J. Org. Chem.* **35**, 2040 (1970).

[3] V. A. Dombrovsky, L. A. Yanovskaya and V. F. Kucherov, *Izv. Akad. Nauk SSSr, Ser. Khim.* 898 (1974).

[4] A. Kh. Khusid, V. I. Kadentsev, G. V. Kryshtal, O. S. Chizhov and L. A. Yanovskaya, *Ibid.* in press. N3 (1977).

[5] H. E. Simmoth and R. D. Smith, *J. Am. Chem. Soc.* **81**, No. 16, 4256 (1959).

[6] V. I. M. Conia, *Angew. Chem.* **80**, No. 15, 578 (1968).

[7] V. S. Axenov, V. M. Shostakovsky, M. I. Kravchenko, L. A. Serkina and O. M. Nefedov, *Dokl* IV *Vsesoyuznoi conferencii po khimii acetilena*, v. 1, p. 222, Alma-Ata (1972).

[8] M. Makosza and M. Wawrzyniewiez, *Tetrahedron Letters*, 4659 (1969).

[9] A. Kh. Khusid, G. V. Kryshtal, V. F. Kucherov and L. A. Yanovskaya, *Izv. Akad. Nauk SSSR*, 2787 (1975); preliminary communication.

[10] W. E. Billups, I. H. Cross and A. I. Blakeney, *J. Org. Chem.* **40**, 1848 (1975).

[11] A. Kh. Khusid, G. V. Kryshtal, V. F. Kucherov and L. A. Yanovskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.* 415 (1976); preliminary communication.

[12] G. V. Kryshtal, A. Kh. Khusid, V. F. Kucherov and L. A. Yanovskaya, *Ibid.* 424 (1976), preliminary communication.

[13] L. A. Yanovskaya, C. C. Yufit and V. F. Kucherov, *Khimia acetalei Nauka* Moscow (1975).

[14] A. Kh. Khusid, G. V. Kryshtal, V. F. Kucherov and L. A. Yanovskaya, *Izv. Akad. Nauk, Ser. Khim.* 444 (1976), preliminary communication.

[15] V. I. Kadentsev, O. S. Chizhov, A. Kh. Khusid, V. F. Kucherov and L. A. Yanovskaya, *Ibid.* 1519 (1976).