Brief Communications

(2*Z*)-2,3,4,5,5-Pentachloropenta-2,4-dienic acid as a minor product in the synthesis of 5,5-dimetoxytetrachlorocyclopentadiene from hexachlorocyclopentadiene

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Pentachloropentadienic acid was isolated, apart from the expected 5,5-dimetoxytetrachlorocyclopentadiene, in the reaction of hexachlorocyclopentadiene with potassium hydroxide in methanol. The structure of this minor product was established by X-ray crystallography. The plausible mechanism of its formation is discussed.

Key words: hexachlorocyclopentadiene, potassium methoxide, 5,5-dimetoxytetrachlorocyclopentadiene, pentachloropenta-2,4-dienic acid, X-ray diffraction.

5,5-Dimetoxytetrachlorocyclopentadiene (**1**) is used in organic synthesis as a diene in Diels—Alder reactions, thereby providing a convenient route to functionalized norbornene derivatives and original polycyclic structures that were previously difficult to access.[1—3] The synthesis of 5,5-dimetoxytetrachlorocyclopentadiene (**1**) from hexachlorocyclopentadiene (**2**) by the reaction with a KOH solution in methanol was described back in 1949 (Scheme 1).[4] According to this procedure, the mixture, which is obtained after the completion of the reaction, is diluted with water, the organic layer is separated, washed with water, and dried, and the target 5,5-dimetoxytetrachlorocyclopentadiene is isolated by distillation under reduced pressure. It should be noted that the aqueous layer was not previously analyzed. We performed this reaction under the same conditions, treated the reaction mixture as described earlier, and analyzed the aqueous layer. For this purpose, we acidified the aqueous phase to pH 2 and extracted it several times with chloroform, concentrated the combined extracts, and obtained a white powder. The crystallization of the latter from petroleum ether gave transparent plate-like crystals. Studies by ^{13}C NMR spectroscopy and mass spectrometry showed that this compound is (2*Z*)-2,3,4,5,5-pentachloropenta-2,4-dienic acid (**3**).

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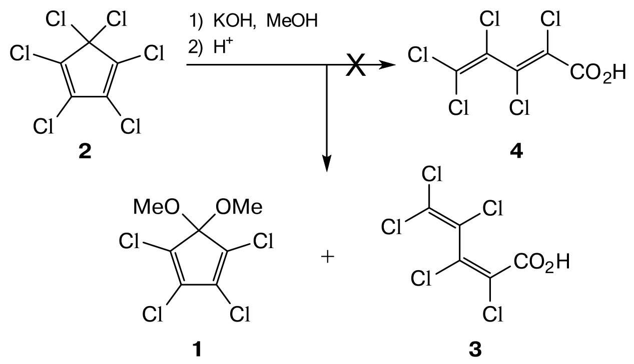
The formation of compound **3** in this reaction was not previously reported.

Scheme 1



Crystalline acid **3** melts in the range of 119.5—121 °C. Literature sources give different melting points for compound **3**: 124.5—125 °C,[4] 123 °C,[5] 121—123 °C,[6,7] and 120—121 °C.[8] Since the formation of both compounds **3** and **4** with Δ^2-*cis*- and Δ^2-*trans*-double bonds cannot be ruled out, the structure of **3** was additionally confirmed by X-ray diffraction. The structure of **3** is displayed in Fig. 1.

The X-ray diffraction study demonstrated that the planes of the dichlorobutene and trichloropropene moieties in pentachloropenta-2,4-dienic acid **3** (see Fig. 1) are perpendicular to each other, as evidenced by the dihedral angle of 92.2(5)°. The dichlorobutene moiety has a *Z* configuration.

Table 1. Bond lengths (*d*) in structure **3**

Bond	*d*/Å	Bond	*d*/Å
Cl(01)—C(007)	1.710(3)	C(007)—C(008)	1.487(4)
Cl(02)—C(010)	1.714(4)	C(007)—C(011)	1.327(5)
Cl(03)—C(011)	1.714(4)	C(008)—O(012)	1.231(4)
Cl(04)—C(009)	1.720(4)	C(009)—C(010)	1.275(5)
Cl(05)—C(010)	1.708(4)	C(009)—C(011)	1.499(5)
O(06)—C(008)	1.267(4)		

The O(06)—C(008)—C(007)—C(011) torsion angle is 171.3(4)°, which indicates that the carboxy group deviates from the plane of the dichlorobutene moiety. The C—Cl bond lengths (Table 1) are in agreement with the corresponding values in perchloroacrylic acid.[9] Compound **3** crystallizes in the centrosymmetric monoclinic space group $P2_1/c$. In the crystal structure, molecules **3** are linked to form cyclic dimers *via* O—H···O hydrogen bonds ($d_{\mathrm{H(06)...O(012)}}$ = 1.81(7) Å, the O(06)—H(06)···O(012) angle is 179.0(8)°) (see Fig. 1, *b*). In the crystal of **3**, there are also short intermolecular Cl···Cl contacts ($d_{\mathrm{Cl(02)...Cl(02)}}$ = 3.498(2) Å, $d_{\mathrm{Cl(02)...Cl(03)}}$ = 3.432(2) Å, and $d_{\mathrm{Cl(02)...Cl(05)}}$ = 3.498(2) Å).

Let us consider the plausible mechanism of the formation of acid **3**. The attack of the complex of MeOH with

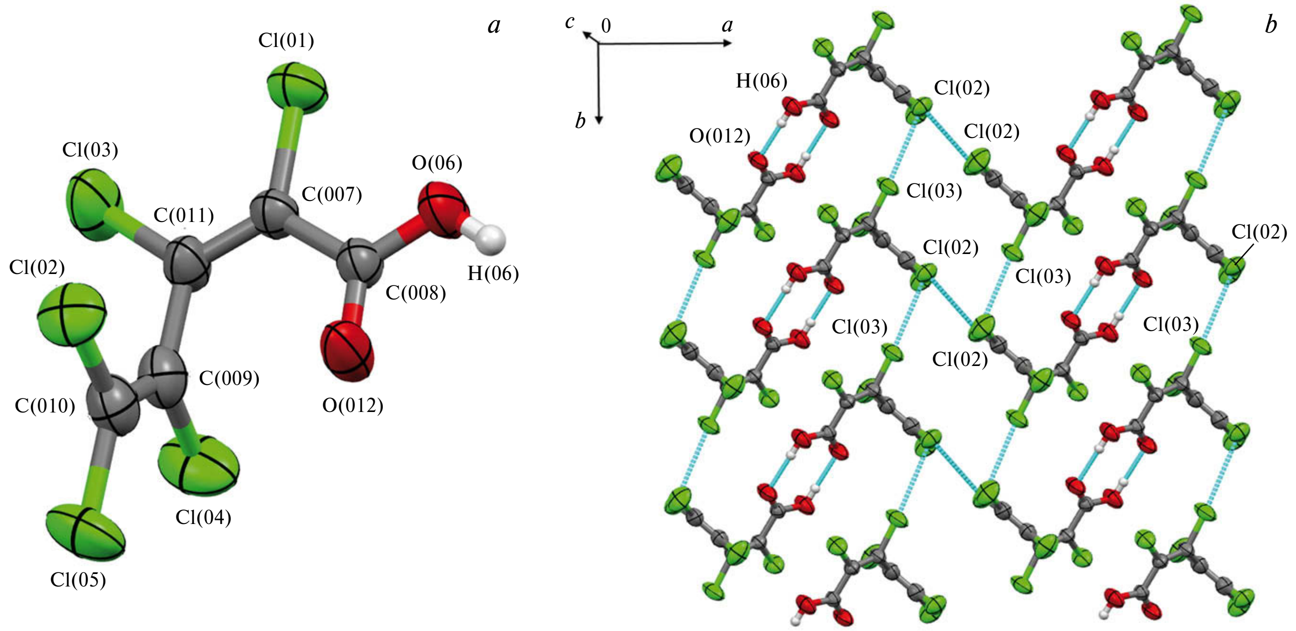
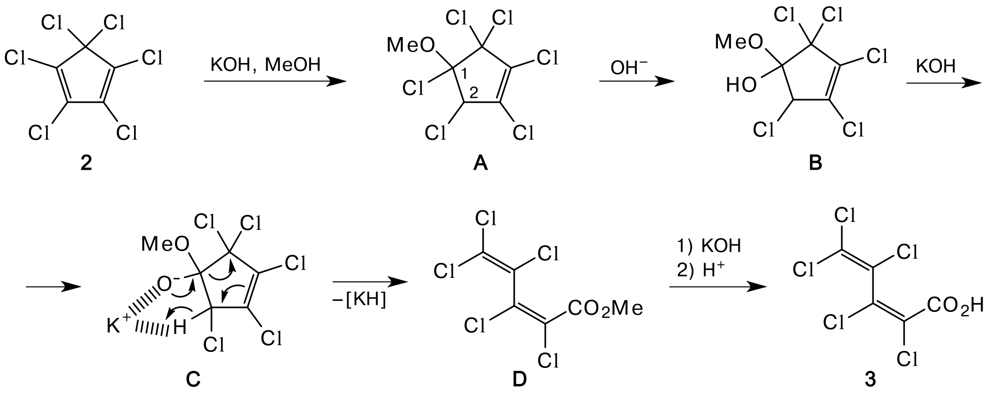


Fig. 1. (*a*) Molecular structure of compound **3** with displacement ellipsoids for nonhydrogen atoms at the 50% probability level. (*b*) The crystal structure projected along the *c* axis; O—H...O hydrogen bonds and short Cl...Cl contacts are indicated.
Note. Figure 1 is available in full color on the web page of the journal (https://link.springer.com/journal/volumesAndIssues/11172).

Scheme 2



KOH on the C(1)=C(2) double bond of diene **2** affords intermediate **A** (Scheme 2). The nucleophilic substitution of the Cl atom at C(1) with the OH group in the presence of KOH gives hemiketal **B**. The labile hydroxyl group in **B** is easily deprotonated under the reaction condition to generate tetrahedral intermediate **C**. The latter eliminates KH, which is then hydrolyzed, resulting in hydrogen release. The saponification of the ester affords potassium salt of acid **3**. The acidification of the latter gives acid **3**.

To conclude, we showed that the reaction of diene **2** with a KOH solution in methanol affords, apart from compound **1**, acid **3** with the *Z*-double bond as the minor product. The structure of acid **3** was confirmed by X-ray diffraction. The scatter in the melting point values reported in the literature is apparently attributed to the fact that, in some cases, the reaction produces 2*E*-acid **4** because the conditions of the synthesis of **3** by the chlorination (Cl_2, *h*ν) of the corresponding perchloropenta-3,4-dienic and perchloropenta-4-en-2-ynoic acids[6,7] are responsible for the formation of **4**.

Experimental

The IR spectrum was recorded on a Shimadzu IR Prestige-21 spectrophotometer using a film from a solution in $CHCl_3$. The ^1H and ^{13}C NMR spectra were measured on a Bruker AVANCE-500 spectrometer operating at 500.13 and 125.77 MHz, respectively, with $SiMe_4$ as the internal standard. The mass spectrum was obtained on a LCMS-2010EV mass spectrometer (Shimadzu). The melting point was determined on a Boetius hot-stage microscope (Germany). The course of the reaction was monitored by TLC on Sorbfil plates (Russia); the compounds were visualized by spraying with an alkaline solution of potassium permanganate. The reaction products were isolated by column chromatography on Macherey-Nagel silica gel (Germany, 70—230 mesh.; 30—60 g of the adsorbent per gram of the compound).

(2*Z*,4*E*)-2,3,4,5,5-Pentachloropenta-2,4-dienic acid (3). A solution of hexachlorocyclopentadiene (54.6 g, 0.2 mol) in methanol (200 mL) was added dropwise to a stirred solution of KOH (29.8 g, 0.2 mol) in anhydrous methanol (300 mL), the temperature being maintained below 50 °C. The reaction mixture was stirred at room temperature for 12 h. The KCl precipitate

Table 2. Crystallographic parameters and the X-ray data collection and refinement statistics for compound **3**

Parameter	Value
Molecular formula	$C_5HCl_5O_2$
Molecular weight	270.31
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell parameters	
a/Å	12.0274(5)
b/Å	6.6445(2)
c/Å	12.2796(6);
α/deg	90
β/deg	101.828(4)
γ/deg	90
V/Å^3	960.50(7)
Z	4
d_{calc}/g cm^{-3}	1.869
Absorption coefficient, μ/mm^{-1}	1.463
F(000)	528.0
2θ—Scanning range/deg	3.46—57.98
h, k, l ranges	$-15 \le h \le 16$, $-8 \le k \le 8$, $-16 \le l \le 16$
Number of reflections	
measured	11193
(R_{int})	(0.0248)
unique	2357
Number of reflections used in the refinement	2357
Number of refined parameters	113
GOOF	1.045
Final values of	
R_1	0.0528
wR_2	0.1123
Residual electron density (max/min)/e Å^{-3}	−0.50/0.94

was filtered off, the filtrate was diluted with water (150 mL), methanol was evaporated, and the residue was extracted with chloroform (4×70 mL). Then the residue was concentrated followed by vacuum distillation. The known 5,5-dimetoxytetrachlorocyclopentadiene[4] was isolated in a yield of 34.0 g (64%).

After the extraction, the aqueous layer was acidified with concentrated hydrochloric acid to pH 2 and extracted with chloroform (4½50 mL). The combined extracts were washed with a saturated NaCl solution and dried with $MgSO_4$. The solvent was evaporated under reduced pressure. The resulting white powder was recrystallized from petroleum ether (40—70 °C), and acid **3** was isolated as colorless plates in a yield of 12.0 g (22%). M.p. 119.5—121 °C. IR, ν/cm^{-1}: 3480, 2653, 2514, 1703, 1560, 1422, 1282, 1166, 1050, 1043, 961, 929, 881, 828, 717, 658. ^{1}H NMR ($CDCl_3$, 500 MHz), δ: 10.45 (br.s, 1 H, CO_2H). ^{13}C NMR ($CDCl_3$, 125 MHz), δ: 123.65 (C(2)), 124.85 (C(4)), 127.83 (C(3)), 139.54 (C(5)), 164.62 (C(1)). EI-MS, *m/z* (*I* (%)): 233 (235, 237, 239) $[M - Cl]^+$ (83).

X-ray diffraction study of acid 3 was performed on a XCalibur single-crystal X-ray four-circle diffractometer (λ(Mo-Kα) = = 0.71073 Å, graphite monochromator, ω-scanning technique, $2\theta_{max} = 62°$) equipped with a CCD detector at room temperature (T = 293—303 K). The X-ray data collection and processing were performed using the CrysAlis^{Pro} program.[10] The structure was solved and refined using the SHELXS and SHELXL program packages[11] with anisotropic displacement parameters for non-hydrogen atoms. The hydroxyl hydrogen atom was positioned geometrically. Crystallographic parameters and the X-ray data collection and refinement statistics are given in Table 2.

Atomic coordinates and displacement parameters were deposited at the Cambridge Crystallographic Data Centre (CCDC 1913021) and can be obtained, free of charge, on application to http://www.ccdc.cam.ac.uk.

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