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Unprecedented Reaction of 1,1'-Bicyclopropylidene with Tetrachlorocyclopropene[1)]

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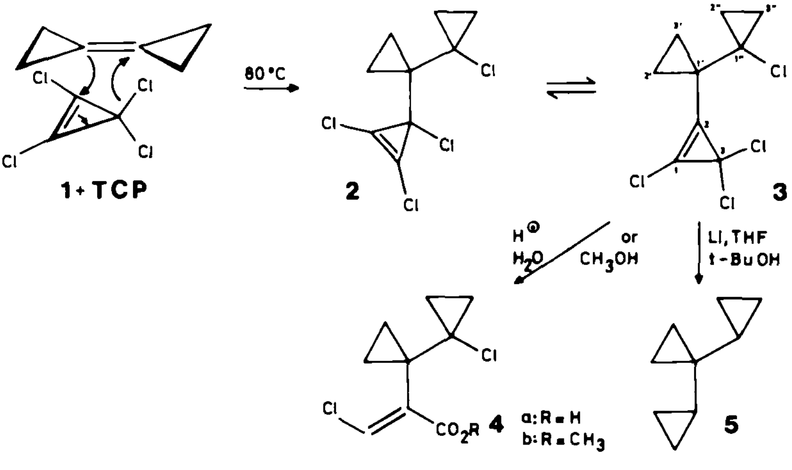
Ungewöhnliche Reaktion von 1,1'-Bicyclopropyliden mit Tetrachlorcyclopropen[1)]

1,1'-Bicyclopropyliden (**1**) reagiert als Nucleophil mit Tetrachlorcyclopropen zu dem chlorbicyclopropyl-substituierten Trichlorcyclopropen **2**. Das Addukt hydrolysiert rasch und in guter Ausbeute zu der Carbonsäure **4a**.

Methylenecyclopropanes are known to be more reactive olefins than ordinary alkenes and hence can undergo facile cycloaddition reactions[2,3)]. 1,1'-Bicyclopropylidene (**1**)[4)] is a unique methylenecyclopropane derivative in which two of the essential structural units share a common double bond. The HOMO energy of **1** ($\varepsilon(\pi) = -8.93$ eV[5)]) is about 0.59 eV higher than that of the parent methylenecyclopropane[6)]. Accordingly, **1** surpasses the latter in its reactivity towards electron deficient double bond systems and in the multitude of products formed in such reactions[7,8)]. The outstanding chemical properties of **1** are once again exemplified by its unprecedented addition to tetrachlorocyclopropene (TCP).



Reaction between **1** and TCP occurred at 80 °C and led to a moisture sensitive product (73% yield), which was clearly different from the type of adduct of TCP to ordinary alkenes[9)]. It readily hydrolyzed, facilitated by hydrochloric acid, to a crystalline material (87% yield), identi-

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fied by an X-ray structure analysis as (*E*)-3-chloro-2-[1-(1-chlorocyclopropyl)cyclopropyl]acrylic acid (**4a**). Methanolysis gave the corresponding methyl ester (**4b**), reductive dechlorination yielded the known hydrocarbon 1,1-dicyclopropylcyclopropane (**5**)[10].

Accordingly, the primary adduct of **1** and TCP was 1,2,3-trichloro-3-[1-(1-chlorocyclopropyl)-cyclopropyl]cyclopropene (**2**), apparently arising from a nucleophilic attack of **1** on TCP most probably in a S_N2' fashion. The ^{13}C NMR spectroscopic data of the isolated material, however, are best interpreted in terms of structure **3**. Under the reaction conditions the primary adduct **2** apparently isomerizes to the thermodynamically more stable isomer **3**. It is remarkable, that **1** is nucleophilic enough to attack TCP with a reasonable rate at 80 °C.

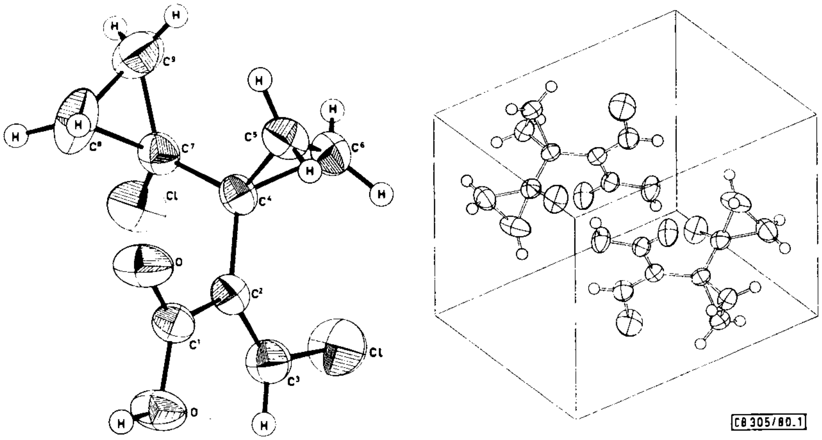

Fig. 1. ORTEP plot of the molecule of 3-chloro-2-[1-(1-chlorocyclopropyl)cyclopropyl]acrylic acid (**4a**) and its unit cell

Table 1. Structural parameters of **4a**

Distance	[pm]	Bond angle	[°]	Torsional angle	[°][a]
C^3-Cl	171.7 (3)	C^2-C^3-Cl	125.3 (2)	$O=C^1-C^2-C^3$	−7.2
C^7-Cl	177.5 (3)	C^4-C^7-Cl	112.2 (2)	$C^1-C^2-C^3-Cl$	180.0
$C^1=O$	122.9 (3)	C^8-C^7-Cl	115.0 (2)	$C^2-C^4-C^7-Cl$	−58.1
C^1-O	129.5 (3)	C^9-C^7-Cl	114.0 (2)	$H-O-C^1-C^2$	180.0
C^1-C^2	148.7 (3)	$O=C^1-O$	122.4 (2)	$C^1-C^2-C^4-C^7$	−79.4
$C^2=C^3$	132.2 (4)	$O-C^1-C^2$	117.0 (2)	$C^5-C^4-C^7-C^8$	−58.1
C^2-C^4	149.5 (3)	$C^1-C^2-C^3$	116.0 (2)	$C^6-C^4-C^7-C^8$	−125.5
C^4-C^5	150.8 (4)	$C^1-C^2-C^4$	117.3 (2)	$C^6-C^4-C^7-C^9$	−51.9
C^4-C^6	150.8 (3)	$C^2-C^4-C^5$	116.9 (2)		
C^4-C^7	149.1 (3)	$C^2-C^4-C^6$	119.5 (2)		
C^5-C^6	148.4 (4)	$C^5-C^4-C^6$	59.0 (2)		
C^7-C^8	148.6 (4)	$C^2-C^4-C^7$	115.0 (2)		
C^7-C^9	149.2 (4)	$C^5-C^4-C^7$	117.5 (2)		
C^8-C^9	149.5 (5)	$C^6-C^4-C^7$	117.6 (2)		
C − H (av.)	96.6 (4)	$C^4-C^5-C^6$	60.5 (2)		
O − H	95.3 (5)	$C^4-C^7-C^9$	123.5 (2)		
		$C^8-C^7-C^9$	60.3 (2)		
		$C^7-C^8-C^9$	60.1 (2)		

[a] The torsional angles A − B − C − D are defined as zero, when looking down the B − C bond, A − B and C − D are synplanar and are counted positive, when C − D is rotated clockwise relative to A − B.

With regard to the structural parameters of **4a** (see fig. 1 and table 1) it is noteworthy that the C^4-C^7 bond appears to be slightly shorter than the average of the cyclopropyl bonds. Although this difference is close to the insignificance level, it is in the same direction as that found for the corresponding bonds in the parent hydrocarbon 1,1'-bicyclopropyl[11,12].

The bicyclopropyl group in **4a** adopts a *gauche*-conformation characterized by a dihedral angle of 55°, which differs completely from the *s-trans*-conformation of crystalline 1,1'-bicyclopropyl[12], but corresponds to that of the predominant conformation of 1,1'-dimethyl-1,1'-bicyclopropyl[13]. In **4a** the dihedral angle between the plane of the chlorovinyl group and the plane bisecting the neighboring cyclopropyl group is 81°, this is again due to non-bonded interactions.

Experimental Part

Reaction of **1** *with tetrachlorocyclopropene:* 2.64 g (15 mmol) of tetrachlorocyclopropene and 1.20 g (15 mmol) of **1** were sealed under nitrogen in a 20 ml glas ampoule and heated to 80°C for 50 h. The reaction mixture was distilled in a Kugelrohr yielding 2.66 g (73%) of *1,3,3-trichloro-2-[1-(1-chlorocyclopropyl)cyclopropyl]cyclopropene* (**3**), b.p. 80°C/0.05 torr. – ^{13}C-NMR (67.88 MHz, $CDCl_3$): δ_{TMS} = 133.5 (C-1), 121.5 (C-2), 60.5 (C-3), 44.6 (C-1"), 25.5 (C-1'), 15.6 (C-2" (3")), 15.2 (C-2' (3')).

(E)-3-Chloro-2-[1-(1-chlorocyclopropyl)cyclopropyl]acrylic acid (**4a**): 2.61 g (10 mmol) of **3** were stirred with 10 ml of 5 N HCl for 18 h at room temperature. The reaction mixture was extracted with five 20 ml portions of chloroform and the organic phase concentrated on a rotatory evaporator. The residue upon sublimation at 60°C/0.05 torr gave 1.94 g (87%) of **4a**, m.p. 114°C. – ^{1}H-NMR (270 MHz, $CDCl_3$): δ_{TMS} = 0.96 (m, 4H), 0.98 (s, 4H), 7.70 (s, 1H), 9.90 (broad s, 1H). – ^{13}C-NMR (15.08 MHz, $CDCl_3$): δ_{TMS} = 171.2, 140.3, 134.2, 48.5, 23.9, 15.3, 14.5. – IR (KBr): significant bands at 3080 (C=C–H), 3010 (cyclopropyl C–H), 1684 (νC=O), 1590 (νC=C).

$C_9H_{10}Cl_2O_2$ (221.1) Ber. C 48.90 H 4.56 Cl 32.08 O 14.47
Gef. C 48.91 H 4.53 Cl 31.87 O 14.71

X-ray structure analysis of **4a**: The triclinic crystals have the space group $P\bar{1}$ with a = 619.6 (9), b = 697.4 (11), c = 1221.2 (18) pm, α = 92.83 (8)°, β = 91.11 (7)°, γ = 108.96 (7)°, D_x = 1.474 g/cm^3. Employing an automated four circle diffractometer, 1416 reflections were recorded (monochromatized Mo-K_α) out to Θ_{max} = 30°. The structure was solved by direct methods using the program system SHEL-X. Refinement of the atomic coordinates and anisotropic temperature factors by the full matrix technique gave a convergence factor of R = 0.036 after inclusion of the hydrogen atoms.

Methylester **4b**: To a solution of 300 mg (1.16 mmol) of **3** in 2 ml of dry ether 1 ml of dry methanol was added dropwise with stirring at –5 to 0°C. The mixture was stirred for an additional 12 h at room temperature. After evaporation of the solvents the residue was purified by preparative g.c. (0.4 m 10% SE, 100°C) to yield 147 mg (54%) of **4b** as the main product. – ^{1}H-NMR (270 MHz, $CDCl_3$): δ_{TMS} = 0.96 (m, 4H), 1.22 (m, 4H), 3.78 (s, 3H), 6.45 (s, 1H). – IR (film): 3090 (C=C–H), 3020 (cyclopropyl C–H), 2950 (νC–H), 1731 (νC=O), 1635 (νC=C), 1625 cm^{-1} (νC=C).

$C_{10}H_{12}Cl_2O_2$ (235.1) Ber. C 51.08 H 5.14 Cl 30.15 Gef. C 50.42 H 5.18 Cl 31.87

Reductive dechlorination of **3**: A mixture of 1.72 g (0.25 mol) of lithium, cut into small pieces, 9.00 g (0.12 mol) of *tert*-butyl alcohol, 1.38 g (80 mmol) of water, and 1.29 g (5.0 mmol) of **3** in 50 ml of dry tetrahydrofuran was refluxed for 4 h under a nitrogen atmosphere. After it had cooled down to room temperature, the mixture was poured into 100 ml of water and extracted with 3 50 ml portions of pentane. The pentane extract was washed with 5 50 ml portions of saturated NaCl solution, dried over sodium sulfate, and the pentane distilled over a 40 cm column packed with glass helices. The residue (4 – 5 ml), containing a single product, was purified by preparative g.c. (2 m 10% SE30, 80 °C). Yield 296 mg (49%) of *1,1-dicyclopropylcyclopropane* (**5**), identified by its ^{1}H-NMR spectrum$^{10)}$.

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