Crystal Structures of 2,2-Dibromo-1-methylcycloprop-anecarboxylic Acid, 2,2-Dichloro-1-methylcycloprop-anecarboxylic Acid and 2-(2,2-Dichloro-1-methyl-cyclopropyl)ethanoic Acid

Christian Rømming[a] and Leiv K. Sydnes[b]

[a]Department of Chemistry, University of Oslo, P.O.Box 1033, Blindern, N-0315 Oslo 3 and [b]Department of Chemistry, University of Tromsø, P.O.Box 953, N-9001 Tromsø, Norway

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The structures of the title compounds were determined from single-crystal X-ray diffraction data. $C_5H_6Br_2O_2$ crystallizes in the monoclinic space group $P2_1/c$ (No. 14) with $a = 7.237(1)$, $b = 8.586(1)$, $c = 12.810(2)$ Å, $\beta = 102.29(1)°$ and $Z = 4$. $C_5H_6Cl_2O_2$ is monoclinic, space group $P2_1/n$ (No. 14) with $a = 6.461(1)$, $b = 9.174(2)$, $c = 23.632(4)$ Å, $\beta = 90.73(1)°$ and $Z = 8$. $C_6H_8Cl_2O_2$ is monoclinic, space group $P2_1/n$ (No. 14) with $a = 7.061(1)$, $b = 11.609(2)$, $c = 9.890(1)$ Å, $\beta = 105.81(1)°$ and $Z = 4$. The molecules form hydrogen-bonded dimers in the crystals; in $C_5H_6Br_2O_2$ the dimers are disordered on centers of symmetry, in $C_5H_6Cl_2O_2$ the dimers are formed by molecules of the same chirality and they are thus not centrosymmetric, and in $C_6H_8Cl_2O_2$ the dimers are ordered and situated on centers of symmetry. The relationship between the structures of the title compounds and their reactivity towards alkyllithium is discussed.

When 1,1-dihalocyclopropanes containing a carboxyl group are treated with methyllithium (halo = bromo) and butyllithium (halo = chloro) the course of reaction depends on the structural relationship between the ring and the carboxyl group. MeLi attacks exclusively the *gem*-dibromo moiety if the COOH group is directly attached to the ring, as in acid **1** (see Scheme 1), whereas the reagent is completely consumed in an acid-base reaction with the carboxyl group when the latter is separated from the ring by a methylene group, as in **4**.[1] Acids **2** and **3** exhibit a similar, but much less pronounced pattern of reactivity towards BuLi (see Experimental). Such a difference in reactivity might be reflected in the structures of the acids and we therefore wanted to determine the crystal structures of 1–4. Unfortunately, irrespective of the solvent system employed, it was impossible to obtain crystals of acid **4** that were suitable for X-ray investigations.
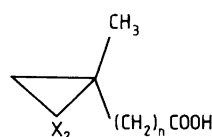
1   X=Br; $n=0$
2   X=Cl; $n=0$
3   X=Cl; $n=1$
4   X=Br; $n=1$

Scheme 1.

Experimental

The instruments used have been described elsewhere.[1]

Preparation of acids. Acids **1**, **2** and **4** were prepared as described in the literature[1,2] and purified by recrystallization from water.

2-(2,2-Dichloro-1-methylcyclopropyl)ethanoic acid (**3**) was prepared as follows. Dichlorocarbene, from chloroform (20.0 g, 0.17 mol) and 50 % aqueous NaOH (20 g, 0.25 mol), was added to 3-methyl-3-buten-1-ol (8.6 g, 0.10 mol) in the presence of triethylbenzylammonium chloride (0.30 g)[3] to give 2-(2,2-dichloro-1-methylcyclopropyl)ethanol (**5**) (10.4 g, 62 %) by distillation; b.p. 53–55 °C/0.45 mmHg. IR (film): 3310 (s), 1685 (m), 1460 (m), 760 cm^{-1}. ^{1}H NMR (60 MHz, CDCl$_3$): δ 1.0–1.5 (m, 5H), 1.6–2.1 (m, 2H), 2.65 (s, 1H), 3.65 (t, 2H, J 7 Hz); the spectrum also exhibits a triplet (J 7 Hz) at 4.27 ppm and a singlet at 7.91 ppm in a ratio of 2:1, probably due to the presence of approximately 10 % of 1-dichloromethoxy-2-(2,2-dichloro-1-methylcyclopropyl)ethane (**6**).[4] ^{13}C NMR (22.50 MHz, CDCl$_3$): **5**: δ 20.4 (CH$_3$), 28.6 (C), 32.7 (CH$_2$), 39.0 (CH$_2$), 60.2 (CH$_2$), 67.4 (C); **6**: δ 20.2 (CH$_2$), 28.3 (C), 32.6 (CH$_2$), 34.9 (CH$_2$), 61.3 (CH$_2$), 96.5 (C), 161.3 (CH). Jones oxidation[5] of alcohol **5** (8.4 g, 0.050 mol) afforded acid **3** (5.5 g, 60 %), purified by recrystallization from water;

m.p. 107–110 °C (uncorrected). Anal. C$_6$H$_8$Cl$_2$O$_2$: C, H. IR (CCl$_4$): 3400–2300 (m), 1702 (s), 1405 (m), 1265 (m), 1210 (m), 1030 (w); ^{1}H NMR (90 MHz, CDCl$_3$): δ 1.07 (d, 1H, J 6.5 Hz), 1.17 (d, 1H, J 6.5 Hz), 1.17 (s, 3H), 2.16 (d, 1H, J 13.5 Hz), 2.18 (d, 1 H, J 13.5 Hz), 8.68 (broad s, 1H); ^{13}C NMR (22.50 MHz, CDCl$_3$): 21.0 (CH$_3$), 27.7 (C), 32.4 (CH$_2$), 41.0 (CH$_2$), 66.2 (C), 177.2 (C).

Treatment of acids **2** *and* **3** *with alkyllithium.* The compounds were treated with methyllithium and butyllithium at 0 °C as previously described.[1] The acids were recovered unchanged when treated with MeLi, as was acid **3** after treatment with BuLi. When **2** was allowed to react with BuLi (1.1 equiv.), *trans*-2-chloro-1-methylcyclopropanecarboxylic acid was formed in 10 % and isolated in 4 % yield; b.p. 40 °C/16 mmHg. IR (film): 3520–2600, 1705, 1455, 1315, 750 cm^{-1}. ^{1}H NMR (60 MHz, CCl$_4$): δ 1.0–2.0 (m, 2H), 1.46 (s, 3H), 3.65 (m, 1H).

Table 1. Crystal and experimental data.

Compound	C$_5$H$_6$Br$_2$O$_2$	C$_5$H$_6$Cl$_2$O$_2$	C$_6$H$_8$Cl$_2$O$_2$
Diffractometer	SYNTEX $P\bar{1}$	NICOLET $P3/F$	NICOLET $P3/F$
Crystal dimensions/mm	0.35×0.3×0.2	0.43×0.22×0.10	0.3×0.3×0.2
Radiation	Graphite crystal monochromated MoKα(λ=0.71069Å)		
Crystal system	Monoclinic	Monoclinic	Monoclinic
a/Å	7.237(1)	6.461(1)	7.061(1)
b/Å	8.586(1)	9.174(2)	11.609(2)
c/Å	12.810(2)	23.632(4)	9.890(1)
β/°	102.29(1)	90.73(1)	105.81(1)
V/Å^3	777.7(2)	1400.6(4)	780.0(2)
Temp/°C	−130	−116	−135
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$
M	257.91	169.01	183.02
Z	4	8	4
$F(000)$	488	688	376
D_x/gcm^{-3}	2.203	1.603	1.558
Scan mode	θ/2θ	θ/2θ	θ/2θ
Scan speed (2θ)/°min^{-1}	4	2–4	2–4
Scan range (2θ)/°	2.0	2.0	2.6
Max. sinθ/λ /Å^{-1}	0.70	0.81	0.85
No. indep. meas.	2082	4418	3479
No. with $I>2.5\sigma(I)$	1987	4209	3182
$R=\Sigma(F_o-F_c)/\Sigma F_o$	0.042	0.046	0.041
$R_w=[\Sigma w(F_o-F_c)^2/\Sigma wF_0^2]^{1/2}$	0.042	0.051	0.050
$S=[\Sigma w(F_o-F_c)^2/(n-m)]^{1/2}$	1.83	1.76	2.66
Overdetermination ratio	17.2	19.9	25.9

pK$_a$ measurements for acids **2** and **3** were carried out as described in the literature.[1] The values are 3.24 for **2** and 4.36 for **3**.

X-ray experiments. Crystals of acids **1–3** suitable for X-ray experiments were grown from pentane. Suitable crystals of **4** ccould not be obtained from any of a number of pure solvents and solvent mixtures. Details of the collection of X-ray data are given in Table 1.

The standard deviations for the intensities were taken as $\sigma(I) = [C_T + (0.03C_N)^2]^{1/2}$, where C_T is the total number of counts and C_N is the net count. The intensities were corrected for Lorentz and polarization effects but not for absorption.

Descriptions of the computer programs used for the structure analysis are given in Refs. 6 and 7. Atomic scattering fractors were taken from Ref. 8. Crystal data are given in Table 1.

Table 2. Atomic fractional coordinates and U_{eq} (average value of U_{ii}).

| Atom	x	y	z	U_{eq}
C$_5$H$_6$Br$_2$O$_2$ (**1**)				
Br1	1.00340(6)	0.29449(5)	0.02387(3)	0.027
Br2	1.07968(6)	0.06031(5)	0.21893(3)	0.025
O1	0.5893(6)	0.4269(5)	0.1228(3)	0.029
O2	0.5317(5)	0.3072(5)	0.0353(2)	0.028
C1	0.8945(5)	0.1437(4)	0.1026(3)	0.018
C2	0.6940(5)	0.1676(5)	0.1175(3)	0.019
C3	0.7398(6)	0.0399(5)	0.0450(3)	0.023
C4	0.5991(5)	0.3108(5)	0.0645(3)	0.019
C5	0.6424(7)	0.1291(7)	0.2231(4)	0.029
(C$_5$H$_6$Cl$_2$O$_2$)$_2$ (**2**)				
Cl11	0.95663(8)	0.44949(5)	0.79628(2)	0.029
Cl12	1.31427(9)	0.28378(6)	0.76192(2)	0.035
O11	0.9985(2)	0.2533(2)	0.9389(1)	0.035
O12	0.7213(2)	0.2459(2)	0.8815(1)	0.030
C11	1.0728(3)	0.2763(2)	0.7952(1)	0.025
C12	1.0464(3)	0.1726(2)	0.8449(1)	0.023
C13	0.9404(3)	0.1457(2)	0.7879(1)	0.027
C14	0.9179(3)	0.2279(2)	0.8923(1)	0.024
C15	1.2255(4)	0.0779(2)	0.8644(1)	0.033
Cl21	0.27767(9)	0.07666(5)	1.04222(2)	0.034
Cl22	0.25763(10)	0.18685(7)	1.15698(2)	0.040
O21	0.5192(2)	0.3245(2)	0.9736(1)	0.030
O22	0.7849(2)	0.2785(2)	1.0324(1)	0.043
C21	0.3047(3)	0.2305(2)	0.1.0857(1)	0.026
C22	0.4702(3)	0.3436(2)	1.0736(1)	0.025
C23	0.2418(3)	0.3754(2)	1.0636(1)	0.027
C24	0.5934(3)	0.3142(2)	1.0215(1)	0.026
C25	0.5888(4)	0.4140(3)	1.1222(1)	0.034
C$_6$H$_8$Cl$_2$O$_2$ (**3**)				
Cl1	0.44633(4)	0.61207(3)	0.86103(3)	0.025
Cl2	0.33973(5)	0.81980(3)	0.69632(4)	0.031
O1	−0.1899(1)	0.9489(1)	0.8507(1)	0.024
O2	0.1136(2)	0.8844(1)	0.9556(1)	0.027
C1	0.2523(2)	0.6907(1)	0.7486(1)	0.019
C2	0.0500(2)	0.6859(1)	0.7720(1)	0.018
C3	0.0926(2)	0.6267(1)	0.6451(1)	0.020
C4	−0.0784(2)	0.7925(1)	0.7422(1)	0.021
C5	−0.0403(2)	0.8785(1)	0.8614(1)	0.020
C6	0.0228(2)	0.6097(1)	0.8926(1)	0.025
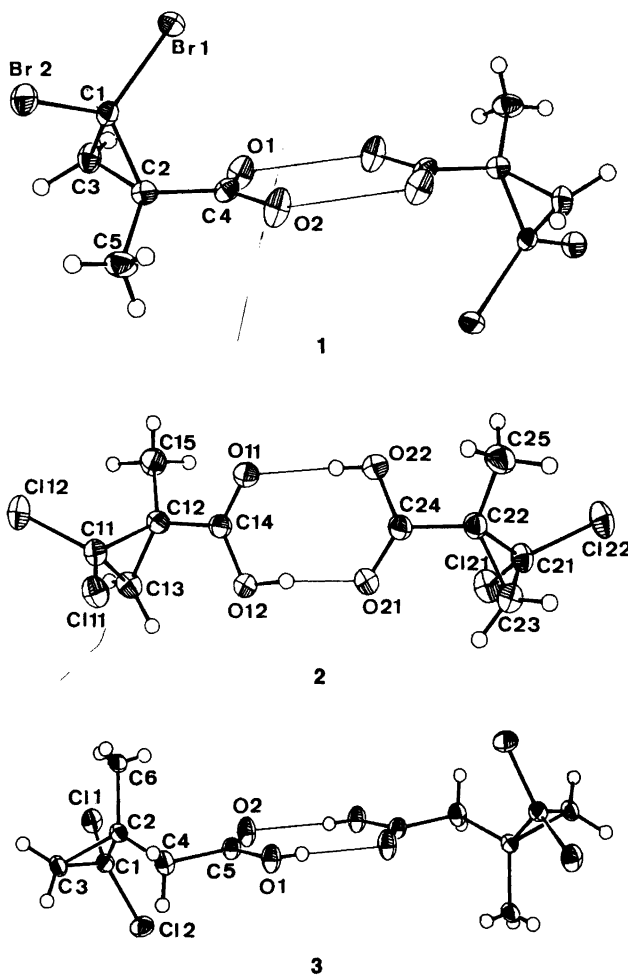
Fig. 1. ORTEP drawings of the molecules.

1

2

3

Structure determination and refinement. The three structures were solved by direct methods[7] and refined by Fourier and least-squares calculations. Positions for hydrogen atoms were calculated and (for the chlorine compounds **2** and **3**) refined with isotropic thermal parameters. The final figures of merit are given in Table 1. Final atomic coordinates are listed in Table 2. Tables of observed and calculated structure factors, hydrogen coordinates and thermal parameters are available from the authors on request. Drawings of the molecules are shown in Fig. 1, where the numbering of the atoms is also indicated. Bond lengths and angles are presented in Table 3; estimated standard deviations were calculated from the variance-covariance matrices.

Discussion

Hydrogen bonding. As usual for carboxylic acids, all three molecules crystallize as hydrogen-bonded dimers as shown in Fig. 1.

In the crystals of **1**, $C_5H_6Br_2O_2$, the dimers have a centre of symmetry with strong hydrogen bonds of length 2.61 Å. The hydrogen position was not located. The observed $C-O$ bonds being nearly of equal length, viz. 1.257 and 1.268 Å, respectively, the carboxylic acid groups are probably disordered with the $C=O$ and $C-OH$ groups statistically interchanged in the crystal.

The molecules of **2**, $C_5H_6Cl_2O_2$, form dimers in a somewhat unusual way. Two crystallographically non-equivalent molecules of the same chiral-

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Table 3. Bond distances (Å) and angles (°).

$C_5H_6Br_2O_2$ **(1)**

Distance		Distance	
Br1−C1	1.911(4)	Br2−C1	1.918(4)
O1−C4	1.257(6)	O2−C4	1.268(6)
C1−C2	1.518(6)	C1−C3	1.497(6)
C2−C3	1.518(6)	C2−C4	1.499(6)
C2−C5	1.515(6)	O1−O2′	2.611(6)

Angle		Angle	
Br1−C1−Br2	111.4(5)	Br1−C1−C2	119.2(6)
Br1−C1−C3	119.5(6)	Br2−C1−C2	118.8(3)
Br2−C1−C3	119.1(3)	C2−C1−C3	60.5(3)
C1−C2−C3	59.1(3)	C1−C2−C4	114.3(4)
C1−C2−C5	120.5(4)	C3−C2−C4	117.0(4)
C3−C2−C5	121.0(4)	C4−C2−C5	114.0(4)
C1−C3−C2	60.4(3)	O1−C4−O2	124.1(4)
O1−C4−C2	117.4(4)	O2−C4−C2	118.5(4)

$(C_5H_6Cl_2O_2)_2$ **(2)**

Distance		Distance	
Cl11−C11	1.757(2)	Cl12−C11	1.757(2)
O11−C14	1.233(2)	O12−C14	1.303(2)
C11−C12	1.525(2)	C11−C13	1.482(3)
C12−C13	1.523(3)	C12−C14	1.492(3)
C12−C15	1.514(3)	O11−O22′	2.631(2)
Cl21−C21	1.754(2)	Cl22−C21	1.761(2)
C21−C24	1.228(2)	O22−C24	1.303(2)
C21−C22	1.520(3)	C21−C23	1.483(3)
C22−C23	1.520(3)	C22−C24	1.498(3)
C22−C25	1.517(3)	O21−O12′	2.652(2)

Angle		Angle	
Cl11−C11−Cl12	110.7(1)	Cl11−C11−C12	120.1(1)
Cl11−C11−C13	119.2(2)	Cl12−C11−C12	118.5(1)
Cl12−C11−C13	119.6(1)	C12−C11−C13	60.8(1)
C11−C12−C13	58.2(1)	C11−C12−C14	115.8(2)
C11−C12−C15	120.0(2)	C13−C12−C14	118.2(2)
C13−C12−C15	120.6(2)	C14−C12−C15	113.4(2)
C11−C13−C12	61.0(1)	O11−C14−O12	123.4(2)
O11−C14−C12	120.1(2)	O12−C14−C12	116.5(2)
Cl21−C21−Cl22	111.1(1)	Cl21−C21−C22	120.3(1)
Cl21−C21−C23	119.4(1)	Cl22−C21−C22	117.8(1)
Cl22−C21−C23	119.4(1)	C22−C21−C23	60.8(1)
C21−C22−C23	58.4(1)	C21−C22−C24	114.5(2)
C21−C22−C25	119.8(2)	C23−C22−C24	115.6(2)
C23−C22−C25	121.0(2)	C24−C22−C25	115.4(2)
C21−C23−C22	60.8(1)	O21−C24−O22	124.1(2)
O21−C24−C22	122.6(2)	O22−C24−C22	113.4(2)

Table 3. (contd)

C$_6$H$_8$Cl$_2$O$_2$ (3)				
Distance			Distance	
Cl1−C1	1.765(1)		Cl2−C1	1.752(1)
O1−C5	1.318(1)		O2−C5	1.225(2)
C1−C2	1.509(2)		C1−C3	1.497(2)
C2−C3	1.531(2)		C2−C4	1.514(2)
C2−C6	1.539(2)		C4−C5	1.512(2)
O1−O2′	2.673(1)			
Angle			Angle	
Cl1−C1−Cl2	110.7(1)		Cl1−C1−C2	119.3(1)
Cl1−C1−C3	119.0(1)		Cl2−C1−C2	120.0(1)
Cl2−C1−C3	118.9(1)		C2−C1−C3	61.2(1)
C1−C2−C3	59.0(1)		C1−C2−C4	118.8(1)
C1−C2−C6	117.6(1)		C3−C2−C4	116.6(1)
C3−C2−C6	118.1(1)		C4−C2−C6	115.3(1)
C1−C3−C2	59.8(1)		C2−C4−C5	114.7(1)
O1−C5−O2	123.5(1)		O1−C5−C4	112.2(1)
O2−C5−C4	124.2(1)			

ity form a non-symmetric dimer through two strong nearly linear hydrogen bonds of lengths 2.631(2) and 2.652(2) Å, respectively. The O−H⋯O angles are both 173°. The carboxyl C−O bonds are normal for hydrogen-bonded dimers, the C=O bond lengths being 1.233(2) and 1.228(2) Å, respectively; both of the C−O (H) bond lengths are observed to be 1.303(2) Å.

The molecules of 3, C$_6$H$_8$Cl$_2$O$_2$, form normal centrosymmetric dimers through fairly strong hydrogen bond pairs of 2.673(1) Å; the O−H⋯O angle is 176°. The C−O bond lengths are 1.225(2) Å for the double bond and 1.318(1) Å for the single bond.

The substituents. The halogen-carbon bond lengths in all the compounds are as expected, with average values C−Br = 1.915 Å and C−Cl = 1.760 Å. The latter value compares well with the average of 1.758 Å reported in the survey on cyclopropane derivatives by Allen.[9] The C−CH$_3$ bond length in 1 and 2, viz. 1.515(2) Å, is significantly shorter than the corresponding bond in 3, viz. 1.539(2) Å.

The bond connecting the cyclopropane ring and the carboxyl group averages 1.496 Å in 1 and 2. The torsion angle τ as defined by Allen,[9] X−C−C=O, where X is the midpoint of the distal C−C bond, is different for the two molecules of 2, viz. −145.8 and 37.1°, respectively. These conformations, denoted *trans-gauche* and

cis-gauche by Allen, occur often, if not predominantly, for carbonyl-substituted cyclopropanes. The carbonyl group is thus close to being *trans* to the unsubstituted ring carbon atom in one molecule and *cis* in the other molecule. In the bromine compound 1, the two X−C−C−O torsion angles are −135.2 and 45.8°, respectively; the disordered carboxyl groups are thus distributed between the two conformations of compound 2.

The conformational angles of the carboxymethyl moiety of 3 are as follows: C1−C2−C4−C5 = 84.2°, C3−C2−C4−C5 = 151.7°, C2−C4−C5=O = −22.0° and C2−C4−C5−OH = 159.8°. This brings the carbonyl oxygen atom towards the chlorine atoms with Cl⋯O= separations of 4.19 and 3.45 Å to Cl1 and Cl2, respectively.

Cyclopropane ring geometry. The mean values of the cyclopropane C−C bond lengths are 1.511 Å in 1, 1.509 Å in 2 and 1.509 Å in 3, in good agreement with the value for unsubstituted cyclopropane[10] and the mean value of 1.509 Å for 115 cyclopropane derivatives found by Allen.[9]

The trigonal symmetry of the cyclopropane ring is expected to be influenced by chlorine and carbonyl substituents, whereas bromine substituents seem to have little effect. For Cl$_2$, a distal bond-lengthening of 0.025 Å and a vicinal bond-shortening of 0.012 Å relative to the mean C−C bond length is expected; for a carbonyl group, a

Table 4. Expected and found cyclopropane C−C bond lengths.

Compound	C1−C2		C2−C3		C1−C3	
	Predict.	Found	Predict.	Found	Predict.	Found
1	1.524	1.518(6)	1.524	1.518(6)	1.485	1.497(6)
2	1.510	1.523(3)	1.547	1.522(3)	1.471	1.483(3)
3	1.497	1.509(2)	1.534	1.531(1)	1.497	1.497(2)

distal bond-shortening of 0.026 Å and a vicinal bond-lengthening of 0.013 Å would be predicted.[9] Assuming the effects to be additive, the resulting calculated bond lengths are compared to those actually observed in Table 4. When the standard deviations of the correction term, 0.005 Å for C=O and 0.007 for Cl_2 are taken into account,[9] the predicted bond lengths agree very well with the observed values.

Chemical reactivity. The presence of conjugation between the cyclopropane ring and the carboxyl group in acids **1** and **2** is reflected in their crystal structures. Thus, their C1−C2 and C2−C3 bond lengths are equal and significantly greater than that of the C1−C3 bond, a pattern not observed in non-symmetric *gem*-dihalocyclopropanes without π-interacting substituents.[9] Surprisingly enough, however, the conjugation between the ring and the carboxyl group hardly influences the C−X bond lengths; thus, the C−Br bond lengths in **1** are not significantly different from those in a number of other compounds,[11–13] and the same is the case for the C−Cl bonds in **2** compared to those in **3** (Table 3), in 1-(2,2-dichloro-3,3-dimethylcyclopropyl)ethanol,[14] and in 6,6,12,12-tetrachloro-3,3,9,9-tetramethoxytricyclo-[9.1.0.0^{5,7}]-dodecane.[15] Consequently, the different reactivity exhibited by **1** and **4** towards methyllithium, and by **2** and **3** towards butyllithium is not reflected in the C−X bond lengths. We are therefore inclined to believe that RLi attacks a halogen atom more effectively than the

COOH group in **1** and **2** because the *gem*-dihalo moieties are more polarizable, owing to conjugation, in these compounds than in acids **3** and **4**.

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