IONIZATION CONSTANTS OF ALKYL-SUBSTITUTED CYCLOPROPANECARBOXYLIC ACIDS

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The information available in the literature [1-6] on the ionization constants of cyclopropanecarboxylic acids refers mainly to cyclopropanecarboxylic acid itself and also to phenyl derivatives because of the possibility provided for judging the transmission of electronic effects through the cyclopropane ring. Our synthesis of a number of alkyl-substituted cyclopropanecarboxylic acids [7-11] has made it possible in this present work to determine the relation of the strength of a cyclopropanecarboxylic acid to the number and structure of the alkyl substituents from the ionization constants of these acids. Roberts and Chambers [1], who determined the ionization constants of various cycloaliphatic carboxylic acids in 50% alcohol, showed that in its degree of ionization cyclopropanecarboxylic acid occupies an intermediate position between acrylic and cyclobutanecarboxylic acids, being weaker than the former and stronger than the latter. Later investigations [3] in which the Hammett and ionization constants of cinnamic, 2-phenylcyclopropanecarboxylic, and hydrocinnamic acids were determined showed a greater resemblance of the cyclopropane ring to the group $-CH_2-CH_2-$ than to $-CH=CH-$ with respect to its power of transmitting electron effects.

Fuchs and co-workers [4] measured the ionization constants of hydrocinnamic and 2-phenylcyclopropanecarboxylic acids in 50% alcohol and found that the second acid is much stronger than the first, i.e., that the cyclopropane ring transmits electronic effects much better than the group $-CH_2-CH_2-$ does. This is confirmed [5] by a comparison of the rates of alkaline hydrolysis of ethyl hydrocinnamate and ethyl 2-phenylcyclopropanecarboxylate. This discrepancy in the comparison of the powers of an aliphatic chain and a cyclopropane ring of transmitting electronic effects was explained [4] by the fact that Trachtenberg and Odian determined ionization constants in water, whereas Fuchs and co-workers determined them in aqueous alcohol, which increases the powers of the benzene and cyclopropane rings of transmitting electronic effects. This explanation is in accord with the still earlier observation [2] of the difference between the ionization constants of cycloaliphatic acids in water and in nonaqueous solvents.

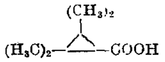
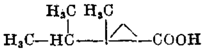
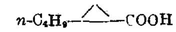
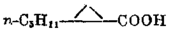
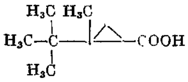
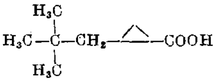
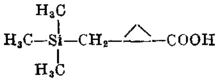
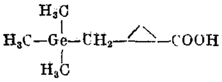
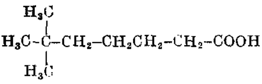
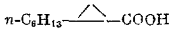
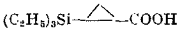
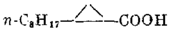
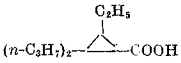
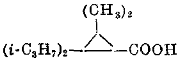
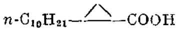
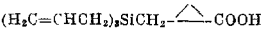
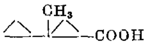
The comparison made in the present work (see Table 1) between the ionization constants of 2-[(trimethylsilyl)methyl]-, 2-[(trimethylgermyl)methyl]-, and 2-(triethylsilyl)-cyclopropanecarboxylic acids (VIII), (IX), and (XIII) respectively with those of the acid corresponding to these in structure and number of carbon atoms but not containing silicon or germanium, namely, 2-neopentylcyclopropanecarboxylic acid (VII) (respective values of $pK_A = 6.69$, 6.69, 6.58, and 6.54) leads to the conclusion that in the case of these acids electronic effects are not transmitted from the silicon or germanium atom to the carboxy group through the cyclopropane ring.

It is evident, however, from [12], which gives the ionization constants of some aliphatic silicon-containing carboxylic acids, that in these acids trialkylsilyl groups have a distinct electron-donor character and that this effect is transmitted from the silicon atom to the carboxy group through an unbranched aliphatic chain [$K_A \cdot 10^5$ is 0.60 for $(CH_3)_3SiCH_2COOH$, 1.00 for $(CH_3)_3CCH_2COOH$, 1.24 for $(CH_3)_3SiCH_2CH_2COOH$, and 1.34 for CH_3CH_2COOH].

The presence of silicon atoms in alkyl substituents in para-substituted benzoic acids also leads to change in the degree of ionization of these acids. Thus, Chernyshev and Tolstikova [13] found that p-(trialkylsilyl)-substituted benzoic acids are stronger than the corresponding p-alkylbenzoic acids [$K_A \cdot 10^6$ is 1.11 for $p-(CH_3)_3SiC_6H_4-COOH$ and 0.70 for $p-(CH_3)_3CC_6H_4COOH$]. This was explained by the authors by the ability of the silicon atom to form additional bonds by the filling of its vacant 3d-orbitals [14-17], which in the case of benzoic acids leads to a shift in the π-electron system of the aromatic ring toward the silicon atom and hence to increase in the strength of the acids.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11. pp. 2004-2009, November, 1966. Original article submitted June 4, 1964.

TABLE 1

No.	Acid	Composition	pK_A	B.p., °C (p, mm)	M.p. °C	d_4^{20}	n_D^{20}	Lit. ref.
I		$C_8H_{14}O_2$	6.81	—	121	—	—	[7]
II		$C_8H_{14}O_2$	6.83	119.5 (15)	—	0.9637	1.4470	[7]
III		$C_8H_{14}O_2$	6.48	119—120 (9)	—	0.9492	1.4430	[7]
IV	n-C_4H_9—$CH_2CH_2CH_2$—COOH	$C_8H_{16}O_2$	6.29	237 (760)	—	0.910	—	—
V		$C_9H_{16}O_2$	6.53	131 (6)	—	0.9506	1.4500	[8]
VI		$C_9H_{16}O_2$	6.82	120— 22 (5—6)	61	—	—	[9]
VII		$C_9H_{16}O_2$	6.54	120 (3)	—	0.9493	1.4487	—
VIII		$C_8H_{16}O_2Si$	6.69	119—121 (7)	—	0.9513	1.4553	—
IX		$C_8H_{16}O_2Ge$	6.69	130—131.5 (7)	—	1.1894	1.4705	—
X	 $H_3C-C(CH_3)_2-CH_2-CH_2CH_2-CH_2-COOH$	$C_9H_{18}O_2$	6.28	126 (8)	—	0.8975	1.4290	—
XI		$C_{10}H_{18}O_2$	6 68	131.5 (3.5)	—	0.9421	1.4526	[8]
XII	n-C_6H_{13}—$CH_2CH_2CH_2$—COOH	$C_{10}H_{20}O_2$	6.37	263—270 (760)	31	—	—	—
XIII		$C_{10}H_{20}O_2Si$	6.58	146—147.5 (6)	—	0.9619	1.4696	—
XIV		$C_{12}H_{22}O_2$	6.72	157 (4)	—	0.9282	1.4556	[8]
XV	n-C_8H_{17}—$CH_2CH_2CH_2$—COOH	$C_{12}H_{24}O_2$	6.35	176 (15)	44	—	—	—
XVI		$C_{12}H_{22}O_2$	7.26	142—143 (5)	—	0.9341	1.4580	[9]
XVII		$C_{12}H_{22}O_2$	7.43	—	154—155	—	—	[9]
XVIII		$C_{14}H_{26}O_2$	6.66	—	47	—	—	—
XIX		$C_{14}H_{22}O_2Si$	6.65	152—154 (0.7)	—	0.9791	1.5065	[10]
XX		$C_8H_{12}O_2$	6.65	129 (11)	—	1.0328	1.4710	[11]

It is known [18] that the nature of the substituent on the silicon atom scarcely alters the effect of the silyl group in aliphatic silicon-containing carboxylic acids. This also applies in the case of (trialkylsilyl)-substituted cyclopropanecarboxylic acids: the replacement of Si-methyl groups in the acid (VIII) (pK_A 6.69) by allyl groups does not alter the strength of the acid [the acid (XIX), pK_A 6.65]. There are data in the literature on the comparison of the effects of cyclopropyl and isopropyl on the strength of carboxylic acids. Thus, Levina and co-workers [6] studied the reactivity of aryl derivatives of cyclopropane with the aid of the Hammett equation, and on the basis of the ionization constants of p-cyclopropyl- and p-isopropyl-benzoic acids ($K_A \cdot 10^5 = 3.6$ and 4.4 respectively) concluded that the three-membered carbon ring has a higher electron-donating power than the isopropyl group. On the basis of this we supposed that the replacement of isopropyl by cyclopropyl in 2-isopropyl-2-methylcyclopropanecarboxylic acid (II) would lead to a diminution in the strength of the acid, but it proved that 2-cyclopropyl-2-methylcyclopropanecarboxylic acid (XX) is actually even somewhat stronger than (II) (pK_A = 6.65 and 6.83 respectively).

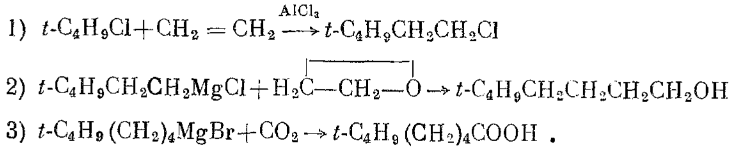
We considered that a comparison of the effects of the cyclopropane ring and the $-CH_2-CH_2-CH_2-$ group on the strength of carboxylic acids also merited attention. From a comparison of the ionization constants of octanoic and 2-butylcyclopropanecarboxylic acids (IV) and (III) (pK_A = 6.29 and 6.48), decanoic and

2-hexylcyclopropanecarboxylic acids (XII) and (XI) (pK_A = 6.37 and 6.68), lauric and 2-octylcyclopropanecarboxylic acids (XV) and (XIV) (pK_A = 6.35 and 6.72), and 6,6-dimethylheptanoic and 2-neopentylcyclopropanecarboxylic acids (X) and (VII) (pK_A = 6.28 and 6.54) it will be seen that replacement of $-CH_2-CH_2-CH_2-$ in the molecule of the acid by a cyclopropane ring leads to a diminution in the strength of the acid in all these cases.

Comparison of the ionization constants of the acids (I), (II), and (III), in which there are alkyl substituents on the carbon atoms of the three-membered ring which, taken together, have the same molecular weight, shows that increase in the number of substituents, even from one to two, leads to diminution in the strength of the acid (pK_A = 6.81, 6.83, and 6.48). On the other hand, increase in the branching of the alkyl substituents does not always affect the strength of the acid [the acids (V) and (VII)]. However, the displacement of only one methyl group from the alkyl substituent to the carbon atom forming the cyclopropane ring [the acids (VII) and (VI)] affects the strength of the acid (reduces it). From the ionization constants of the acids (I) and (VII) and (XVI) and (XVII) it is evident that the branching of the alkyl substituents affects the strength of cyclopropanecarboxylic acids when a secondary or tertiary carbon atom is in the α-position to the carbon atom forming the three-membered ring.

EXPERIMENTAL

6,6-Dimethylheptanoic acid was synthesized in accordance with the scheme



$$1)\ t\text{-}C_4H_9Cl + CH_2=CH_2 \xrightarrow{AlCl_3} t\text{-}C_4H_9CH_2CH_2Cl$$

$$2)\ t\text{-}C_4H_9CH_2CH_2MgCl + H_2\overline{C-CH_2-O} \rightarrow t\text{-}C_4H_9CH_2CH_2CH_2CH_2OH$$

$$3)\ t\text{-}C_4H_9(CH_2)_4MgBr + CO_2 \rightarrow t\text{-}C_4H_9(CH_2)_4COOH\ .$$

1-Chloro-3,3-dimethylbutane. A 1-liter autoclave was charged with a mixture of 370 g of t-butyl chloride and 35 g of aluminum chloride, and ethylene was passed in up to a pressure of 37 atm. The mixture was stirred for about 10 h at between − 9 and − 19°. We obtained 160 g of 1-chloro-3,3-dimethylbutane; b.p. 115-116° (753 mm); n_D^{20} 1.4152; d_4^{20} 0.8657. Found: MR 34.90. Calculated: MR 34.78. The literature [19] gives: b.p. 61-63° (17 mm); 117-119° (760 mm); n_D^{20} 1.4180.

5,5-Dimethyl-1-hexanol. 80 g of 1-chloro-3,3-dimethylbutane was added dropwise to 20 g of magnesium turnings in 500 ml of dry ether at 35°. When heat ceased to be liberated, the reaction mixture was cooled to − 10°, and ethylene oxide was passed in. The mixture was then heated for about 12 h in a water bath and treated with water. We obtained 45 g of the alcohol; b.p. 177-179° (753 mm); d_4^{20} 0.8348; n_D^{20} 1.4277. Found: MR 40.11. Calculated: MR 40.68.

1-Bromo-5,5-dimethylhexane. A mixture of 15 g of 5,5-dimethyl-1-hexanol and 11 g of PBr_3 was heated for 5-7 h and then treated with water. The organic layer was separated, washed with sodium carbonate solution, and dried with $CaCl_2$. We obtained 17 g of the bromide; b.p.183-184° (758 mm); n_D^{20} 1.4500; d_4^{20} 1.1033. Found: Br 39.47%; MR 47.04. $C_8H_{17}Br$. Calculated: Br 41.38%; MR 46.95.

6,6-Dimethylheptanoic Acid. 17 g of 1-bromo-5,5-dimethylhexane was added dropwise to a suspension of 3 g of magnesium in 100 ml of ether. Then, at between 0 and − 10°, carbon dioxide was passed through the reaction mixture. The mixture was treated with water, and we isolated 10 g of 6,6-dimethylheptanoic acid; b.p. 125-126° (8 mm); n_D^{20} 1.4300; d_4^{20} 0.8863. Found: C 68.18; 68.25; H 11.57; 11.60%. acid value 166.8; MR 45.45. $C_9H_{18}O_2$. Calculated: C 68.31; H 11.46%; acid value 158.2; MR 45.53.

2-Neopentylcyclopropanecarboxylic Acid. A mixture of 5 g of the ethyl ester of the acid and a solution of 1.8 g of KOH in 18 ml of alcohol was heated for about 20 h with stirring. We obtained 2.5 g of the acid; b.p. 120° (3 mm); n_D^{20} 1.4487; d_4^{20} 0.9493. Found: C 68.68; 68.67; H 10.20; 10.20%; MR 44.11. $C_9H_{16}O_2$. Calculated: C 69.19; H 10.94%; MR 44.04.

2-[(Trimethylsilyl)methyl]cyclopropanecarboxylic Acid. A mixture of 20 g of the ethyl ester of the acid and a solution of 7 g of KOH in 70 ml of alcohol was heated for about 20 h. We obtained 14 g of the acid; b.p. 119-121° (7 mm); n_D^{20} 1.4553; d_4^{20} 0.9513. Found: C 55.98; 55.92; H 9.53; 9.38; Si 16.29; 16.20%; MR 49.16. $C_8H_{16}O_2Si$. Calculated: C 55.77; H 9.36; Si 16.28%; MR 48.94.

2-[(Trimethylgermyl)methyl]cyclopropanecarboxylic Acid. A mixture of 19 g of the ethyl ester of the acid and a solution of 5 g of KOH in 50 ml of alcohol was heated for about 20 h. We obtained 11 g of the acid; b.p. 130-131.5° (7 mm); n_D^{20} 1.4705; d_4^{20} 1.1894. Found: C 44.59; 44.39; H 7.90; 7.62; Ge 33.37; 33.56%; MR 50.90. $C_8H_{16}O_2Ge$. Calculated: C 44.31; H 7.44; Ge 33.48%; MR 50.62.

2-(Trimethylsilyl)cyclopropanecarboxylic Acid. A mixture of 5 g of the ethyl ester of the acid and a solution of 1.5 g of KOH in 15 ml of alcohol was heated for 20 h. We obtained 4.2 g of the acid; b.p. 145.5-146.5° (3 mm); n_D^{20} 1.4696; d_4^{20} 0.9619. Found: C 60.16; 60.25; H 10.22; 10.03; Si 13.79%; MR 58.06. $C_{10}H_{20}O_2Si$. Calculated: C 59.95; H 10.06; Si 14.01%; MR 58.24.

Ethyl 2-Decylcyclopropanecarboxylate. A solution of 19 g of diazoacetic ester in 22 g of 1-dodecene was added dropwise with stirring to a suspension of 1 g of copper sulfate in 200 g of 1-dodecene at 100-110°. When reaction was complete, 198 g of 1-dodecene was vacuum-distilled off, and from the residue was isolated 25 g (59.5%) of ethyl-2-decylcyclopropanecarboxylate; b.p. 155.5-157° (7 mm); n_D^{20} 1.4440; d_4^{20} 0.8902. Found: MR 75.37. $C_{16}H_{20}O_2$. Calculated: MR 76.70.

2-Decylcyclopropanecarboxylic Acid. A mixture of 25 g of the ethyl ester of the acid and a solution of 7 g of KOH in 70 ml of alcohol was heated for about 20 h. We obtained 18 g of the acid; b.p. 180-181° (5 mm); b.p. 47° (decomp.). Found: C 74.55; 74.41; H 11.17; 11.40%. $C_{14}H_{26}O_2$. Calculated: C 74.28; H 11.57%.

Determination of Ionization Constants of Cyclopropanecarboxylic Acids. The ionization constants of the alkyl-substituted cyclopropanecarboxylic acids listed in Table 1 were determined from the half-neutralization points of solutions of the acids in 50% ethanol on a pH meter with glass and calomel electrodes.

We are extremely grateful to V. M. Belikov for providing the apparatus for the measurements.

CONCLUSIONS

1. From a comparison of the constants of cyclopropanecarboxylic acids containing trialkylsilyl and trialkylgermyl substituents it follows that the interaction between the silicon or germanium atom and the carboxy group is not transmitted through the cyclopropane ring irrespective of whether the silicon atom is in the α- or β-position relative to the carbon atom of the three-membered ring.

2. Replacement of an aliphatic chain by a cyclopropane ring in a carboxylic acid leads to diminution in the strength of the caid.

3. Increase in the number of alkyl substituents on the carbon atoms forming the cyclopropane ring leads to diminution in the strength of the cyclopropanecarboxylic acid.

4. Branching of the alkyl substituents leads to diminution of the strength of the cyclopropanecarboxylic acid when there is a secondary or tertiary carbon atom in the substituent in the α-position relative to the carbon atom of the three-membered ring.

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