

mol.wt 286. Calc. for C_8H_7ISe : C 25.29; H 2.48; mol.wt 286).

4-Methyl-3-selena-4-octene-6-yne. To 20 ml 1.13 N ethereal ethyllithium cooled to $-70^\circ C$ 5.00 g (0.0175 mole) of 2,5-dimethyl-3-iodoselenophene was added with stirring and under nitrogen. After 10 min, the temperature was allowed to rise to room temperature and the mixture poured into 1 N potassium hydroxide solution. The ethereal layer was washed with potassium hydroxide solution and water. The combined aqueous washings were extracted with ether and the combined ether phases were dried and the ether evaporated *in vacuo* yielding 2.13 g of an oil, which according to NMR analysis contained about 25 % of 2,5-dimethylselenophene and 75 % of the title compound. Fractional distillation yielded pale yellow, evil-smelling 4-methyl-3-selena-4-octene-6-yne, b.p. $110^\circ C/18$ mm Hg. NMR: (see text); mass spectrum: (*m/e*, %) 77, 15.3; 78, 20.2; 79, 22.2; 91, 5.0; 103, 1.3; 104, 1.2; 105, 2.7; 106, 1.0; 107, 4.6; 108, 1.0; 109, 1.2; 115, 0.66; 116, 0.83; 117, 1.5; 118, 0.83; 119, 3.0; 120, 1.5; 121, 0.66; 122, 0.66; 127, 0.33; 128, 0.33; 129, 0.66; 130, 0.5; 131, 1.3; 132, 0.66; 133, 1.2; 134, 0.5; 135, 0.5; 136, 0.5; 141, 2.3; 142, 2.3; 143, 6.0; 144, 0.66; 145, 12.0; 146, 0.83; 147, 2.7; 155, 4.0; 156, 4.3; 157, 10; 158, 3.0; 159, 18.3; 160, 4.3; 161, 3.8; 162, 1.0; 169, 2.2; 170, 2.0; 171, 5.3; 172, 1.0; 173, 10.0; 174, 1.3; 175, 2.0; 176, 0.33; 184, 20.2; 185, 18.9; 186, 50.9; 187, 8.7; 188, 100; 189, 10.0; 190, 20.0. (Found: C 51.00; H 6.52. Calc. for $C_8H_{12}Se$ (187.15): C 51.34; H 6.46).

NMR spectra were recorded with a Varian A60 NMR spectrometer. Mass spectra were obtained with an LKB A 9000 combined gas chromatograph-mass spectrometer. Separation of 4-methyl-3-selena-4-octene-6-yne from 2,5-dimethylselenophene was obtained using an NPGS (5 %) column. IR spectra were recorded on a Perkin-Elmer 257 grating infra-red spectrophotometer.

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The Acid Strengths of Propionic, 2-Bromopropionic and 3-Bromopropionic Acids in Aqueous Potassium Chloride Solutions

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In connection with studies on the magnetic and spectral properties of copper(II) complexes of propionic, 2-bromopropionic, and 3-bromopropionic acids,¹ the values of the dissociation constants of these acids were required. The earlier investigations of the dissociation of bromopropionic acids are few in number and were carried out under differ-

ent experimental conditions. Therefore a reinvestigation was necessary. Propionic acid was included for comparison.

Experimental. Propionic acid (a *puriss. p.a.* reagent from Fluka AG.) and DL-2-bromopropionic acid (Fluka AG., *puriss.*) were purified by distillation at reduced pressure. 3-Bromopropionic acid (Fluka AG., *purum*) was purified by recrystallization from hexane.

A Radiometer PHM 4d potentiometer connected to a Beckman glass electrode and an open liquid junction reference calomel electrode filled with saturated potassium chloride was used. The titrations with sodium hydroxide solution were carried out in a nitrogen atmosphere at 25°C.

Table 1. pK_a values of propionic and bromopropionic acids in aqueous solutions of different ionic strength adjusted with potassium chloride (25°C).

	\sqrt{I}	pK_a	
		Observed	Calculated (eqn. 3)
Propionic acid	0.052	4.850	4.849
$pK_a^\circ = 4.89$	0.228	4.731	4.736
$\alpha = 1.45$	0.309	4.708	4.704
$B = 0.24$	0.574	4.664	4.658
	0.939	4.699	4.705
	1.330	4.862	4.861
2-Bromopropionic acid	0.055	2.969	2.959
	0.228	2.844	2.852
$pK_a^\circ = 3.01$	0.387	2.792	2.798
$\alpha = 1.72$	0.628	2.770	2.769
$B = 0.17$	0.940	2.796	2.792
	1.211	2.861	2.856
	1.533	2.973	2.975
3-Bromopropionic acid	0.053	4.013	4.016
	0.221	3.908	3.905
$pK_a^\circ = 4.07$	0.316	3.869	3.865
$\alpha = 1.46$	0.601	3.805	3.808
$B = 0.19$	0.939	3.826	3.828
	1.211	3.899	3.896
	1.531	4.023	4.024

The customary method for the determination of the equilibrium constant

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad (1)$$

in which potentiometric titration data are substituted in the equation

$$K_a = \frac{[H^+](c_B + [H^+])}{(c - c_B - [H^+])} \quad (2)$$

where c_B is the stoichiometric concentration of sodium hydroxide added and c the initial concentration of the acid, was used. The hydrogen ion concentrations of the solutions containing potassium chloride were calculated with the aid of the apparent hydrogen ion activity coefficient values reported by Näsänen *et al.*¹

The Debye-Hückel equation

$$pK_a^\circ = pK_a + 1.018\sqrt{I}(1 + \alpha\sqrt{I}) - B \cdot I \quad (3)$$

was fitted by the method of least squares to the data from titrations carried out at different ionic strengths for the calculation of the values of the parameters α and B .

Table 1 contains the results obtained. Each value for a dissociation constant is based on the mean value of 10–12 potential measurements in each buffer range. Larsson³ has reported the value $pK_a^\circ = 2.971$ for 2-bromopropionic acid and the value $pK_a^\circ = 3.991$ for 3-bromopropionic acid at 18°C. Both of these values are somewhat lower than our values at 25°C, $pK_a^\circ = 3.01$ and 4.07, respectively. No other values seem to be available in the literature. The dissociation of propionic acid has, on the other hand, been studied previously by several workers. Our values $pK_a^\circ = 4.89$ at 25°C and $pK_a = 4.69$ at $I = 0.1$ (KCl) and 25°C for this acid are in good accordance with values reported earlier.⁴

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