Preparation of 2-Iodothiazole and 2-Iodobenzothiazole

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In connection with a current polarographic investigation in this laboratory, a sample of 2-iodobenzothiazole was needed as a standard. The preparation of this compound has hitherto only been reported by Todesco and Vivarelli [1] who obtained a low yield from a Sandmeyer-type of reaction with 2-aminobenzothiazole. We decided to try the reaction sketched in eqn. (1) with 2-benzothiazolyllithium

$$\mathrm{ArLi} \xrightarrow{\mathrm{I_2}} \mathrm{ArI+LiI} \qquad (1)$$

which is easily available through metalation [3] of the parent base; the experiment was done on one tenth mole scale resulting in a rather high conversion to the desired 2-iodo derivative which was purified and isolated in about 75 % yield. Reaction (1) has not been very widely used for the introduction of iodine in aromatic systems and, if so, mostly with moderate yields, the more general methods *via* mercury-organic compounds [2] being preferable. Besides the literature cited in Ref. 2, only 3-iodothiophene [4] (60 %), 1-iodo-3-bromo-2-naphthol [5] (yield not stated), and 1-iodopyrene [6] (56 %) seem to have been prepared by this method. The coupling reaction (2) which becomes the main reaction, *e.g.* with 2-picolyllithium [7] can ob-

$$2\mathrm{RLi}+\mathrm{I_2} \rightarrow \mathrm{R-R}+2\mathrm{LiI} \qquad (2)$$

viously occur only to a minor extent in the present case, and the possible presence of a small amount of dimer was not investigated.

It is peculiar that high conversions to the iodo compounds have only been obtained with equimolar amounts of iodine and lithium-reagent.

The surprisingly high yield in the benzothiazole series encouraged us to try the reaction with thiazole itself; 2-iodothiazole has only been prepared from 2-aminothiazole in a Sandmeyer-type of reaction (30 %) [8] or *via* the 2-chloromercuri derivative.[9] The results of our experiments show that 2-iodothiazole can be isolated in about 90 % yield from 2-bromothiazole [10] by double halogen-metal exchange. Reaction (1) thus seems to be the method of choice for the preparation of 2-iodothiazoles which hitherto have been prepared only in low yields by the methods cited above, because the lithium-reagents are easily obtained from available materials.

Experimental. Melting and boiling points are uncorrected. The 2-aminothiazole and benzothiazole were obtained from EGA-Chemie, Steinheim, and Schuchardt, Munich, respectively.

2-Iodothiazole. An ethereal solution of 0.2 mole of 2-thiazolyllithium is prepared as described previously [11] and stirred at temperatures below −75° for an additional ½−1 h. 53.4 g (0.21 mole) of finely powdered iodine are quickly introduced, the cooling bath is removed, the reaction mixture is stirred for 1 h, and then washed with 100 ml of aqueous sodium thiosulphate solution to remove a possible excess of iodine. The organic layer is separated, washed with 100 ml of water, and dried over sodium sulphate. The solvent is stripped off and the dark oily residue fractionated *in vacuo;* after a small forerun consisting largely of butyl bromide, 36.7−39.8 g (87−89 %) of the fraction with $\mathrm{b.p._{10}}$ 84−86°, n_D^{25} 1.6665−1.6680 is collected. Pure 2-iodothiazole is a heavy, yellowish oil $\mathrm{b.p._{10}}$ 85.5°, n_D^{25} 1.6670 ($\mathrm{b.p._{40}}$ 118°) [8] which must be stored cold and in the dark as it rapidly deteriorates at room temperature.

2-Iodobenzothiazole. An ethereal solution of 0.1 mole of the lithium-reagent is made according to Gilman and Beel [3] (5 % excess of butyllithium) and treated as above for 2-iodothiazole. Evaporation of the ethereal solution leaves, in practically quantitative yield, the crude 2-iodobenzothiazole (m.p. 66−68°) which is extracted with 50−75 ml of hot ligroin (b.p. 60−80°); the hot solution is decanted from some insoluble material, cooled, and filtered to give 19.3−19.8 g (74−76 %) of product, m.p. 77−78°. Another recrystallisation gives pure, yellowish 2-iodobenzothiazole m.p. 79° (79−80°).[1]

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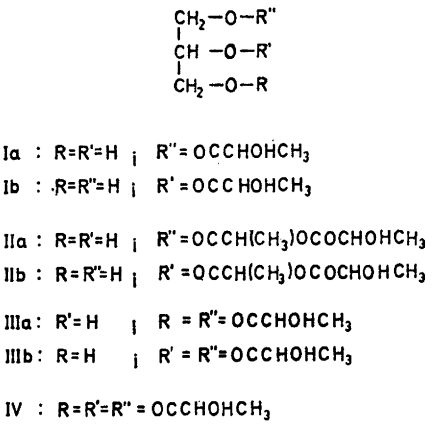

Mass Spectrometry of Glycero-lacto Esters

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In connection with an investigation of glyceryl-lactyl esters of fatty acids, a type of commercial emulsifying agents, the isomeric glyceryl monolactates (I a, I b), glyceryl-monolactyl lactates (II a, II b), glyceryl dilactates (III a, III b), and glyceryl trilactate (IV) have been prepared in order to study their mass spectroscopic fragmentation.

Prior to mass spectrometry the compounds (I)—(IV) were converted into their volatile *O*-trimethylsilyl (TMS) derivatives, essentially as described by Wood *et al.*,[1] yet without isolation of the individual derivatives. These were merely separated by vapour phase chromatography and introduced directly into a combined mass spectrometer (see Experimental). Fig. 1 portrays the separation of (I a) and (I b), representative of the degree of separation achieved for all TMS-derivatives of (I)—(IV). Table 1 presents the retention times of the derivatives.

The mass numbers (*m/e*) of the most characteristic ions observed as a result of electron impact are presented in Table 2, together with a tentative assignment to the respective ions.

Table 1. Retention times of TMS-derivatives of glyceryl lactates.

Starting material	Physical constants of the starting material	Compound formed	R.t. of the TMS derivative, min
2,3-Isopropylidene glycerol [3]	b.p. 83.0—83.5°/12 mm	1-Glyceryl lactate (I a) [3]	10.7
1,3-Benzylidene glycerol [5]	m.p. 66.0°	2-Glyceryl lactate (I b)	10.3
1-Lactoyl-2,3-isopropylidene glycerol [3]	b.p. 68.5—70°/0.05 mm	1-Glyceryl lactyllactate (II a)	15.3
—	—	2-Glyceryl lactyllactate (II b)	15.7
2-*O*-Benzyl glycerol [6]	m.p. 38—39°	1,3-Glyceryl dilactate (III a)	15.6
1-*O*-Benzyl glycerol [7]	b.p. 152°/1.5 mm	1,2-Glyceryl dilactate (III b)	15.3
Glycerol [3]	synthetic (98 % purity)	1,2,3-Glyceryl trilactate IV [3]	19.4