

Table 1

Triethyl-tin irradiated ( $\mu$ m. moles)	Diethyl-tin formed ( $\mu$ m. moles)	Diethyl-tin Triethyl-tin
15.8	18.6	1.18
31.6	33.3	1.05
47.3	48.6	1.03
63.0	65.5	1.04
78.8	78.5	1.00

0–20  $\mu$ gm. triethyl-tin sulphate in borate–versene buffer, *pH* 8.75 (ref. 1), were mixed with 6 ml. 0.0033 per cent (w/v) dithizone in chloroform. After allowing the layers to separate, the tubes were exposed to sunlight for 10 min., remixed with the aqueous layer, which was then removed and the absorption of the chloroform layer at 510  $m\mu$  read against a dithizone control. After reading, the chloroform layers were mixed with 3 ml. of a dilute aqueous solution of 2.3 dimercaptopropanol (this complexes very firmly with diethyl-tin (ref. 2)) and the absorption read again at 510  $m\mu$ . This allows a small correction to be made for the loss of dithizone due to the reaction.

These results are consistent with a reaction of triethyl-tin with dithizone to give diethyl-tin and eliminate a possible disproportionation of 2 mol. triethyl-tin to produce 1 mol. tetraethyl-tin and 1 mol. diethyl-tin. All the trialkyl-tin–dithizone complexes so far examined (trimethyl up to trihexyl) are similarly photochemically decomposed. Although there is a very slow production of diethyl-tin from triethyl-tin in chloroform without dithizone, we have no evidence that a neutralized solution of triethyl-tin sulphate in water produces any diethyl-tin upon storage. The liquid tetraethyl-tin slowly liberates triethyl-tin upon storage under laboratory conditions either neat or as a solution in chloroform.

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<sup>1</sup> Aldridge, W. N., and Cremer, J. E., *Analyst* (in the press).

<sup>2</sup> Aldridge, W. N., and Cremer, J. E., *Biochem. J.*, **61**, 406 (1955).

### A Method of promoting Water-forming Organic Reactions

THE great reactivity of the boric acid esters with water is well known; moreover, recently even the equilibrium constants of their hydrolysis have been measured<sup>1</sup>. So far as is known to us, hitherto the borates have not been used for promoting water-forming (condensation) reactions.

The basis of our investigations has been to add the esters of boric acid to reaction mixtures which form water during the reaction, in order to shift the equilibrium in the direction of the desired product.

Esterifications were studied first. In preparing the ethyl and methyl esters of benzoic acid we observed a marked increase of the reaction velocity with high yields. Then we extended our method to the secondary esters, which are more difficult to prepare. In the presence of 0.11 mol. secondary butyl borate, 0.10 mol. benzoic acid and 0.11 mol. secondary butanol was refluxed for eight hours with 0.2 ml. sulphuric acid. Secondary butylbenzoate was isolated with an 82 per cent yield. In a similar manner, but in the absence of the borate, no ester was formed, the benzoic acid remaining unchanged.

It seemed interesting to prepare the benzyl esters of amino-acids by the same method. It is well known that these esters are important in peptide synthesis,

and they are relatively difficult to prepare. In the presence of *p*-toluene-sulphonic acid<sup>2</sup>, in carbon tetrachloride solvent at about 95° the corresponding amino-acid, benzyl alcohol and the benzyl borate were stirred for 4 hr. The *p*-toluenesulphonic acid salt of the amino-acid benzyl ester is crystallized by further addition of carbon tetrachloride, generally with an 80 per cent yield. Thus glycine, L-glutamic acid and threo- $\beta$ -*p*-nitrophenylserine were esterified. Even in the case of glutamic acid the result was satisfactory.

The use of benzyl borates leads to almost quantitative yields in the case of peptides, for example, in the preparation of glycylglycine benzylester.

We have further used this method with another group of compounds in which we prepared acetals and ketals in the presence of borates. Benzaldehyde dimethyl acetal and diethyl acetal can be obtained with about 60 per cent yield. (Without adding the borates the yield is half this value.) The dimethyl ketal of cyclohexanone is prepared with a 65 per cent yield (without borate the yield is 30 per cent), and the diamyl ketal with a 40 per cent yield (without borate no ketal formed). The foregoing tests were carried out under reflux using 1 mol. of the carbonyl compound, 3 mol. alcohol and 1 mol. of borate with a small amount of hydrochloric acid.

This method may be considered useful for promoting other water-forming reactions. Details will be published elsewhere.

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<sup>1</sup> Bradley, J. A., and Cristopher, P. M., Abstracts of Papers 129th Meeting Amer. Chem. Soc., 39 N (1956).

<sup>2</sup> Cipera, J. D., and Nichols, R. V. V., *Chem. and Indust.*, **15** (1955).

### A Small Mercury Cut-off withstanding Large Pressure Differences

DURING the course of some work involving the handling of an easily adsorbed gas (ammonia) a number of taps and valves were tried and it was observed that all devices which incorporated greases, plastics or rubber were unsatisfactory owing to the large amount of gas adsorbed by these substances. It was a requirement that the valve for controlling the flow of gas should be vacuum-tight, withstanding a pressure difference between atmospheric pressure and  $10^{-3}$  mm. mercury, have a minimal hold-up of gas and be small and suitable for attachment to a portable piece of apparatus.

The miniature mercury cut-off shown in Fig. 1 was designed and found to be satisfactory. It consists of a 1-cm. No. 4 porosity sintered glass disk *A* which could be immersed in mercury by screwing down on the pressure tubing *B* with a screw clip *C*. This action was made more effective by soldering on the lugs *D* to the cross bars of the clip, giving a larger area of contact on the rubber. It should be possible to raise the mercury by incorporating bellows or a syringe, but the method described was found to be satisfactory and easy of construction.

On filling the valve with mercury, care had to be taken to leave a sufficient gap between the mercury surface and the sinter, since under vacuum this surface rises owing to slight collapse of the pressure tubing.