Art. XXVI.—*Concerning the Purification of Esters;* by I. K. and M. A. Phelps and E. A. Eddy.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—clxxxii.]

Quantitative studies of the ester reaction were made under the direction of one of us and published earlier in this Journal.* In that work the exactness was shown with which in the preparation of the ethyl esters of succinic, malonic and benzoic acids, the crude product of esterification obtained in the special form of apparatus used, may be treated to isolate the pure ester. In brief this treatment consisted in shaking out the crude ester with ether, in the presence of an excess of sodium carbonate in solution, distilling off under diminished pressure the low boiling point products, and, finally, the ester which was collected and weighed. This method of purifying esters is a modified form of the procedure in common use for isolating a pure ester from the crude product obtained during esterification. Others† have separated by distillation under diminished pressure the water taken up by the ether during the shaking out of the crude ester from the sodium carbonate solution. This method of removing the water at as low a temperature as possible, so that hydrolysis may not take place, is particularly adapted for use in a quantitative study of the ester reaction. The organic acid unesterified and the mineral acid used as a catalyzer is commonly removed by treatment with sodium or potassium carbonate. Where the esters are soluble in water Fischer and Spier‡ varied the procedure by treating the crude product from esterification with an excess of pulverized potassium carbonate, and removed, after long shaking, the potassium salt by treatment with ether. The filtrate was freed from ether on a water bath and fractionated under diminished pressure.

A study is given here of the exactness with which dry potassium carbonate may be used in isolating succinic, malonic and benzoic ethyl esters impure with alcohol, water, unesterified organic acid and small amounts of mineral acid. For this purpose mixtures of the purified esters were made with the substances, as shown in the table, and the ester separated and weighed.

Definite portions, 75 grm. each, of carefully purified diethyl succinate, diethyl malonate, or ethyl benzoate were placed in a Claisen flask of 250^{cm^3} capacity, chilled in ice, together with 2 grm. of the corresponding acid, 2^{cm^3} of concentrated hydro-

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*This Journal, xxiii, 368; xxiv, 294; xxv, 39; xxvi, 143.

†J. Am. Chem. Soc., xxiii, 1105, 1896.

‡Berichte, xxviii, 3252.

chloric acid of commerce or 1$^{\text{cm}^3}$ of concentrated sulphuric acid of commerce, 10$^{\text{cm}^3}$ of alcohol nearly absolute and an excess—10 grm.—of either pure potassium carbonate of commerce or the same freshly fused and cooled before introducing into the ester mixed with impurities. These impurities are present here in larger proportion than would be expected if the ester were produced according to the procedure referred to earlier in this paper. The Claisen flask was connected for distillation under diminished pressure with a second Claisen flask of 100$^{\text{cm}^3}$ capacity used as a receiver. To secure a current of air through the apparatus during the entire operation an open glass tube was used in place of the usual capillary tube. The 100$^{\text{cm}^3}$ Claisen was connected either directly or with a glass tube held through a rubber stopper to the larger Claisen, the side neck of which was very short, in the same manner as has

						Ester	
No.	Alcohol cm^3.	HCl cm^3.	H_2SO_4 cm^3.	K_2CO_3 grm.	Organic acid 2 grm.	75 grm.	Recovered grm.
(1)	10	2		10	Succinic	Succinic	74·40
(2)	10	2		10	Succinic	Succinic	74·67
(3)	10		1	10	Succinic	Succinic	74·41
(4)	10		1	10	Succinic	Succinic	74·56
(5)	10	2		10	Malonic	Malonic	74·24
(6)	10	2		10	Malonic	Malonic	74·20
(7)	10		1	10	Malonic	Malonic	74·31
(8)	10		1	10	Malonic	Malonic	74·27
(9)	10	2		10	Benzoic	Benzoic	74·55
(10)	10	2		10	Benzoic	Benzoic	75·00
(11)	10		1	10	Benzoic	Benzoic	74·60
(12)	10		1	10	Benzoic	Benzoic	74·67

been described in a former paper* for the distillation of a substance where loss of some of it in the side neck of the flask might otherwise be expected. The 250$^{\text{cm}^3}$ flask was then heated under diminished pressure by means of an acid potassium sulphate bath at a temperature of 100°–110° for about an hour, or until no further evolution of carbon dioxide indicated that the acid was completely neutralized, while at the same time a current of water was allowed to strike the receiver constantly during neutralization to condense all products possible. The temperature of the acid bath was then raised and the ester carefully distilled into the receiver, taking care by raising the temperature of the bath and flaming to remove the final traces of the ester held on the side wall of the flask. The contents

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* This Journal, xxiv, 479.

—ester, alcohol and water—of the second 100^{cm^3} Claisen flask, connected in the manner just given for distilling under diminished pressure, were carefully fractionated by heating the Claisen flask in a water bath raised slowly to 60°, which temperature was maintained for 15 minutes after the manometer showed a pressure of 15^{mm}, and the ester distilled in the usual manner into the flask, weighed, in some instances, alone, in others, with the short tube held in place during distillation by the rubber stopper, and the weight of ester determined.

In all the experiments in the table except (3), (4), (8) and (10) the potassium carbonate was ignited before attempting to neutralize the esters mixed with organic and mineral acids. In experiments (3), (4), (7), (8), (9) and (10), both in distilling and redistilling the ester from the Claisen flasks the process was carried out in flasks where the shortened side-neck tube of the first flask was held with a glass tube through a rubber stopper. It seems evident that igniting freshly the potassium carbonate is unnecessary. Further, the jointed apparatus does not appear to diminish the small loss of ester.

The purity of the product obtained was shown by redistilling the recovered ester at atmospheric pressure, when it was found that the entire portion distilled within a fraction of a degree.

From an inspection of the results obtained it is clear that diethyl succinate, diethyl malonate and ethyl benzoate may be freed from small amounts of mineral and organic acids, when alcohol is present, by heating suitably with dry potassium carbonate under diminished pressure, and that the total product obtained in this way, fractionated under diminished pressure, gives a satisfactory indication that ester is not lost in considerable amounts. The losses in the treatment of the masses of 75 grm. each of pure ester as in the former work from this laboratory, referred to above, amounted to 0·6 grm. in the case of the recovery of succinic ester, to 1·25 grm. in the case of malonic ester, and to 0·25 grm. in the case of benzoic ester. While the loss in the recovery of ethyl benzoic ester by neutralizing as described with dry potassium carbonate is slightly greater than by shaking out with ether, the loss in recovering diethyl succinic ester is somewhat less, and the loss in recovering diethyl malonic ester is much less than by shaking out with ether. But, even in the case of ethyl benzoic ester, the treatment with dry potassium carbonate is to be preferred of the two procedures, both on account of the greater ease in manipulation and on account of the saving in expense, since dry potassium carbonate accomplishes the purpose of the aqueous sodium carbonate and shaking out with ether.

Obviously it is possible to neutralize the acid impurities present with these esters with dry potassium carbonate completely and advantageously. It is easy to see, however, that the smaller the amounts of free acid, the more completely can the total amount of ester present be recovered. With such amounts of unesterified acid as remain when organic acids are treated with alcohol containing mineral acid, on a return condenser, according to Fischer, the loss of ester might be considerable. But with such amounts of free acid as are left when esters are made in the special form of apparatus described in a former paper, neutralizing in the manner given here with dry potassium carbonate is easily done without loss of ester in considerable amount. This is obviously true, since in the mixtures shown in this paper the esters contain acid impurities far in excess of the amount that would be found when esterifying under proper conditions for ideal yields.