583. *The Formation of Crystalline Complexes between Urea and Esters, and their Application to the Separation of Mixtures of Esters.*

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The remarkable difference between hydrocarbons containing normal and branched chains in their power of forming complexes with urea is also met among carboxylic esters. A number of branched-chain esters failed to form crystalline complexes under conditions which yielded stable adducts from normal esters with a total chain length of about ten atoms. Slightly shorter normal chains gave less stable complexes and very simple esters none at all. The difference in properties has been used to separate mixtures of esters.

There has recently been considerable interest in developments of the discovery made by Bengen (G.P. Appn. O.Z. 12,438, March 18, 1940; Bengen and Schlenk, *Experientia*, **1949**, **5**, 200), that urea formed crystalline adducts with normal, but not with branched-chain or cyclic compounds. Schlenk has made a detailed examination of the phenomenon (*Annalen*, **1949**, **565**, 204; cf. also Zimmerschied, Dinerstein, Weitkamp, and Marschner, *J. Amer. Chem. Soc.*, **1949**, **71**, 2947).

As there were under investigation in these laboratories a number of normal and branched-chain esters of suitable chain length, their reaction with urea was examined to see if there were differences in behaviour which might lead to methods of separation. When our experiments began, no details of the method were available. Accordingly a general technique (described in the Experimental portion) was first tested against pure hydrocarbons, crystalline and stable urea adducts being readily obtained from *n*-decane, *n*-undecane, *n*-tetradecane, and *n*-undecene. Unstable adducts were isolated from di-*n*-butyl ether and di-*n*-hexyl ether, but no adduct from anisole. " Stability " in this paper is used in the sense of resisting decomposition by treatment with cold ether or light petroleum.

The procedure was then applied to carboxylic esters. Stable crystalline adducts were isolated from the following esters of monocarboxylic acids : ethyl myristate, *n*-decanoate, octanoate, and crotonate (which reacted slowly). Ethyl acetate and diethyl oxalate failed to yield adducts. Among the esters of dicarboxylic acids, diethyl succinate, adipate, azelate, and sebacate gave urea complexes readily, diethyl malonate more slowly. As among hydrocarbons, branched-chain compounds of comparable molecular length failed to react. Thus, diethyl α-methylsuccinate, dimethyl β-methylglutarate, di*iso*propyl adipate, and dimethyl ββ'-dimethylsuberate all failed to give crystalline adducts. Methyl salicylate and ethyl benzoate also failed to react. Ethyl 3-methylundecanoate formed a urea complex very slowly.

At this stage the appearance of Schlenk's paper (*loc. cit.*) showed that he had already observed that certain normal esters resembled normal hydrocarbons in their behaviour with urea : he obtained complexes from nine esters, but does not describe any examination of branched-chain esters.

Taking all the results into consideration the known behaviour of carboxylic esters towards urea can be summarised as follows : (i) Esters containing a straight chain of from 9 to about 20 atoms form stable crystalline adducts with urea (for this purpose the $-CO_2-$ group is counted as 2 atoms). (ii) Cyclic and branched-chain esters fail to give stable complexes unless there is a long straight-chain sector in the molecule, as in 3-methylundecanoic ester.

In agreement with Schlenk the proportions of urea to ester in the adducts do not correspond with definite stoicheiometric ratios. Analyses of a number of our products showed them to contain urea : ester in molar ratios of the same order as those reported by Schlenk, *i.e.*, from 9—14 of urea to 1 of ester. However, the proportions were not reproducible and in the one case (diethyl sebacate), in which we had studied an ester examined by Schlenk, our ratios differed slightly from his. All our complexes were dissociated into their components by cold water. There is little doubt that they are of the general type established by Schlenk in which the normal hydrocarbon or ester lies in the central lumen of a modified urea lattice.

These differences have been applied to the separation of the mixtures of esters given in the following list. The component which yielded the urea complex is given first : (1) diethyl adipate and ethyl benzoate; (2) diethyl adipate and methyl salicylate; (3) diethyl adipate and ethyl crotonate; (4) dimethyl adipate and dimethyl β-methylglutarate; (5) diethyl sebacate and dimethyl ββ'-dimethylsuberate. All these separations were clear-cut. The third was possible because of the much lower stability of the urea complex of ethyl crotonate than that of ethyl adipate. A satisfactory separation of ethyl crotonate and ethyl benzoate could not be achieved. Separations involving ethyl succinate as the complex-former were also less satisfactory owing to the low stability of the complex.

EXPERIMENTAL.

General Procedure for Detecting Complex Formation.—Urea (300 mg.) was moistened with 4 drops of methanol, and the second component (100 mg.) added. Complex formation was indicated by a change in crystalline form and a disappearance of the liquid. After 30 minutes the solid was triturated with 50 ml. of light petroleum (b. p. 40—60°), or with dry ether if the second component was insoluble in light petroleum. The solid complex was dried and decomposed by the addition of a few drops of water (A). The light petroleum or ethereal washings were washed with water, dried, and evaporated to dryness (B). The appearance of oil at (A) but not at (B) showed the formation of a stable complex. The behaviour of the 29 compounds tested has already been summarised.

Separation of Esters.—General method. A mixture of substance A (a complex former) (5 g.) and substance B (5 g.), dissolved in light petroleum (b. p. 40—60°) (80 ml.), was added to urea (25 g.) which had previously been moistened with methanol. The mixture was set aside overnight, and the complex filtered off, and washed with light petroleum (200 ml.). The filtrate was washed with water (3 × 50 ml.), dried (Na_2SO_4), and evaporated, yielding substance B. The solid complex was decomposed with water, the oil was extracted with ether (5 × 50 ml.), and the ethereal extracts were washed thoroughly with water, dried (Na_2SO_4) and evaporated, giving substance A. The tests for purity described below were made on the undistilled products.

Results of Separations.—(1) *Diethyl adipate and ethyl benzoate.* Recovery of ethyl benzoate : 5·0 g. (100%). Equivalent on hydrolysis : 147 (Calc., 150). The recovery of diethyl adipate was 3·76 g. (75%) (Found : equiv., 102. Calc. : equiv., 101).

(2) *Diethyl adipate and methyl salicylate.* The methyl salicylate recovered (4·73 g., 94%) was completely soluble in alkali. The diethyl adipate fraction (3·92 g., 78% recovery) gave no colour with ferric chloride solution.

(3) *Diethyl adipate and ethyl crotonate.* Recovery of ethyl crotonate: 2·8 g. (56%). On hydrogenation over Raney nickel, 0·95 g. absorbed 179 ml. (Calc., 186 ml.). No hydrogen was absorbed when 1·0 g. of the diethyl adipate fraction (total wt., 4·3 g.; 86% recovery) was shaken with Raney nickel in an atmosphere of hydrogen.

(4) *Dimethyl adipate and dimethyl β-methylglutarate.* Dimethyl β-methylglutarate (3·93 g.; 78% recovery) was identified by the preparation (in 86% yield) of *β-methylglutarodihydrazide*, m. p. 158—161° (Found: C, 41·1; H, 8·2; N, 32·4. $C_6H_{14}O_2N_4$ requires C, 41·35; H, 8·1; N, 32·2%). Adipodihydrazide (97% yield), m. p. and mixed m. p. 170—171° (Curtius, *J. pr. Chem.*, 1915, [ii], **91**, 4, gives m. p. 171°), was prepared from the recovered dimethyl adipate (4·45 g.; 89% recovery).

(5) *Diethyl sebacate and dimethyl ββ'-dimethylsuberate.* Diethyl sebacate (4·40 g.; 89% recovery) was identified by preparation of sebacodihydrazide, m. p. and mixed m. p. 183—185° (Steller, *J. pr. Chem.*, 1900, [ii], **62**, 220, found m. p. 184—185°) (yield, 88%). Dimethyl ββ'-dimethylsuberate (2·56 g.; 64% recovery from 4 g.) gave an equivalent on hydrolysis of 113 (Calc., 115).

(6) *Diethyl succinate and diethyl methylsuccinate.* A small yield (1·91 g.; 38% recovery) of pure diethyl succinate, identified by preparation of the dihydrazide, m. p. and mixed m. p. 165—167° (Bulow and Weidlich, *Ber.*, 1906, **39**, 3376, give m. p. 167°) (73% yield), was obtained from the urea complex. The second fraction (5·82 g.) was a mixture of the two esters, the derivative obtained with hydrazine hydrate having an indistinct m. p.

(7) *Diethyl succinate and ethyl benzoate.* Determination of the equivalent by hydrolysis revealed that pure diethyl succinate (1·83 g.; 39%) was obtained (Found: 87·5. Calc.: 87·0). The fraction which did not form a complex (6·6 g.) was clearly a mixture (Found: equiv., 130).

(8) *Dihexyl ether and anisole.* Some dihexyl ether (1·81 g.; 36%) was extracted from the mixture. No anisole picrate could be obtained from a chloroform solution of this fraction.

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