Synthesis of the *s*-Triazine System. V.[1] Cotrimerization of Imidates

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Extension of the acid-catalyzed imidate trimerization reaction[2] to the cotrimerization case has been examined as a method for the preparation of unsymmetrically substituted *s*-triazines. Although the formation of mixtures is unavoidable, the process is convenient and affords a number of hitherto unavailable compounds.

It was to be expected that two imidates having approximately the same trimerization rates would co-react to give an essentially statistical distribution of all possible *s*-triazines. It was, in fact, found that a 2:1 mixture of ethyl acetimidate and propionimidate gave 2-ethyl-4,6-dimethyl-*s*-triazine and 2,4-diethyl-6-methyl-*s*-triazine in a combined yield of 52%. These two products were obtained in a molar ratio of 1.6:1. When the reactants were used in inverse ratio, the product ratio was almost precisely reversed.

If the two imidates trimerize at substantially different rates, the more reactive one tends to trimerize independently until its concentration is reduced to a relatively small value. Some cotrimers are then formed, and finally the residual sluggish reactant trimerizes slowly. Examples of this behavior were found in the cotrimerization of ethyl acetimidate with ethyl 2-chloropropionimidate and ethyl propionimidate with methyl benzimidate. In such cases, some improvement can be achieved by slow addition of the more reactive imidate to a mixture of the sluggish reagent and the catalyst.

Experimental[3]

Cotrimerization of Ethyl Acetimidate with Ethyl Propionimidate.—A mixture of ethyl acetimidate[2] (0.50 mole), ethyl propionimidate[2] (0.25 mole), and acetic acid (0.053 mole) was held at 30–35° for 18 hr. The solution was distilled, and the fraction boiling above 150° was diluted with ether, washed with aqueous carbonate, dried, and redistilled. The product mixture was analyzed by mass spectrometry. The yields, based on the limiting reagent, were as follows: 2-ethyl-4,6-dimethyl-*s*-triazine, 32%; 2,4-diethyl-6-methyl-*s*-triazine, 38%; 2,4,6-trimethyl-*s*-triazine[2] > 28%; 2,4,6-triethyl-*s*-triazine[2] 17%.

Several similar products were combined and fractionated to obtain the pure cotrimers: 2-Ethyl-4,6-dimethyl-*s*-triazine: b.p. 87° (43 mm.), n^{25}_{D} 1.4687.

Anal. Calcd. for $C_7H_{11}N_3$: C, 61.29; H, 8.08; N, 30.63. Found: C, 61.34; H, 8.22; N, 30.57.

2,4-Diethyl-6-methyl-*s*-triazine: b.p. 94° (6 mm.), n^{25}_{D} 1.4680.

Anal. Calcd. for $C_8H_{13}N_3$: C, 63.54; H, 8.66; N, 27.79. Found: C, 63.67; H, 8.93; N, 27.59.

Cotrimerization of Ethyl Acetimidate and Ethyl 2-Chloropropionimidate.—Ethyl 2-chloropropionimidate[4] (0.14 mole) and acetic acid (0.017 mole) were heated at 70° while ethyl acetimidate (0.29 mole) was added dropwise during 135 min. The reaction temperature was maintained for 16 hr. longer, after which the concentration of the residual imidate was low as judged by infrared spectroscopy. The products were distilled directly from the reaction mixture. Fractions were analyzed by gas-liquid chromatography using a silicone stationary phase and yields were calculated as given below. Boiling points and analytical data were determined on material fractionated from combined lots:

2-(1-Chloroethyl)-4,6-dimethyl-*s*-triazine.—37% yield, b.p. 99–102° (24 mm.), $n^{28.5}_{D}$ 1.4901.

Anal. Calcd. for $C_7H_{10}N_3Cl$: C, 48.98; H, 5.87; N, 24.48; Cl, 20.66. Found: C, 49.23; H, 5.88; N, 24.64; Cl, 20.54.

2,4-Bis(1-chloroethyl)-6-methyl-*s*-triazine.—25% yield, b.p. 130–135° (24 mm.), $n^{27.5}_{D}$ 1.5046.

Anal. Calcd. for $C_8H_{11}N_3Cl_2$: C, 43.65; H, 5.04; N, 19.09. Found: C, 43.60; H, 5.13; N, 19.03.

Cotrimerization of Ethyl Propionimidate with Methyl Benzimidate.—A mixture of ethyl propionimidate (0.25 mole), methyl benzimidate[5] (0.50 mole), and acetic acid (0.15 mole) was held at room temperature for 2 days. 2,4,6-Triphenyl-*s*-triazine[2] was then filtered from the mixture (32% yield, m.p. 225–230°), and the filtrate was diluted with water and ether. After neutralization with carbonate, the ether phase was separated and dried. Distillation gave methyl benzimidate (37% recovery) and 2,4-diethyl-6-phenyl-*s*-triazine, b.p. 125–130° (3 mm.), n^{24}_{D} 1.5595, in 31% yield based on the propionimidate used.

Anal. Calcd. for $C_{13}H_{15}N_3$: C, 73.21; H, 7.09; N, 19.70. Found: C, 73.00; H, 7.34; N, 19.49.

Recrystallization of the distillation residue from ethanol gave a 3% yield of 2-ethyl-4,6-diphenyl-*s*-triazine, m.p. 68–69°.[6]

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[1] Paper IV, F. C. Schaefer and G. A. Peters, *J. Org. Chem.*, **26**, 2784 (1961).

[2] F. C. Schaefer and G. A. Peters, *ibid.*, **26**, 2778 (1961).

[3] Microanalysis were carried out in these laboratories under the direction of Dr. J. A. Kuck. Mass spectrometric analyses were obtained by Mr. A. H. Struck and Miss R. Herberich.

[4] F. C. Schaefer and G. A. Peters, *J. Org. Chem.*, **26**, 412 (1961).

[5] H. L. Wheeler, *Am. Chem. Soc. J.*, **17**, 398 (1895).

[6] H. Reinhardt and E. Schiefer, *Chem. Ber.*, **90**, 2643 (1957), give m.p. 66–67°.

Preparation of *ortho*-Alkyl- and *ortho*-Aralkylbenzoic Acids by Catalytic Hydrogenation of *ortho*-Acylbenzoic Acids

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Reports of unsuccessful attempts to reduce *ortho*-acyl substituted benzoic acids into the corresponding alkyl- or aralkylbenzoic acids[1,2] (trying to utilize the Clemmensen method and catalytic hydrogenation, respectively) prompt us to disclose our positive results.

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[1] R. Huisgen and E. Rauenbusch, *Ann.*, **641**, 51 (1961).

[2] Treibs and Klinkhammer, *Ber.*, **83**, 367 (1950); *ibid.*, **84**, 671 (1951).