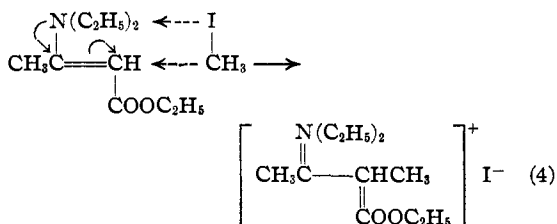
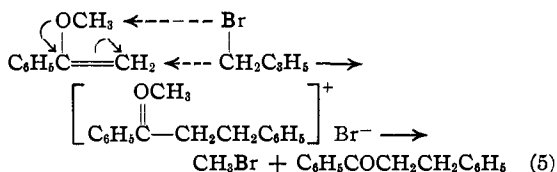


Ethyl chloroacetate yields 36% of ethyl β -benzoylpropionate and a trace of *sym*-triphenylbenzene. Benzoyl chloride heated with equimolecular amounts of α -methoxystyrene produces tribenzoylmethane in 9% yield; in large excess it gives 45% of the theoretical amount of *sym*-triphenylbenzene. The triphenylbenzene is the product of a side reaction and is not related to the condensation. It has its origin in the reaction of hydrogen chloride with α -methoxystyrene. Even at room temperature the ether gives triphenylbenzene in 54% yield simply on saturation with hydrogen chloride.

The condensation of α -methoxystyrene with alkyl halides has the appearance of a novel reaction, but in point of fact it has a close analogy in the addition of methyl iodide to ethyl β -diethylaminocrotonate (4).⁶ The reaction between α -



methoxystyrene and benzyl bromide may be similarly formulated (5); the only real difference



is that in the former addition the nitrogen atom is sufficiently basic to form a stable salt, whereas the onium compound formed from α -methoxystyrene decomposes instantaneously.

Experimental Part

All condensations were carried out in Pyrex tubes heated in an electrical bomb furnace.

Condensation with Benzyl Bromide.—Ten grams of α -methoxystyrene and 76 g. of benzyl bromide were heated for seventeen hours at 220°. When the cooled bomb was opened, a slight pressure was evident. The unreacted benzyl bromide and the propiophenone formed by normal rearrangement were removed by vacuum distillation. An 8.3-g. fraction was collected at 150° (1 mm.). It soon solidified, and after one crystallization from alcohol

(6) Robinson, *J. Chem. Soc.*, **109**, 1038 (1916); Lauer and Lones, *THIS JOURNAL*, **59**, 232 (1937).

yielded 8.0 g. of β -phenylpropiophenone; m. p. and mixed m. p. 72–73°. No dibenzyl could be detected in the residues.

In order to identify methyl bromide as a reaction product a mixture of α -methoxystyrene and benzyl bromide was heated under a reflux while the effluent gas was passed into a boiling solution of sodium saccharin in butyl carbitol and water. N-Methylsaccharin separated on dilution; m. p. 132°.

Condensation with *n*-Butyl Bromide.—A mixture of 4.6 g. of α -methoxystyrene and 105 g. of *n*-butyl bromide heated to 245° for thirty-six hours gave 1.7 g. of *n*-caprophenone boiling at 108–110° at 7 mm. It was characterized as the semicarbazone; m. p. and mixed m. p. 131–132°.

Condensation with Ethyl Chloroacetate.—Ninety-seven grams of ethyl chloroacetate and 7.7 g. of α -methoxystyrene were heated to 200° for twenty-five hours. Fractionation yielded 90 g. of ethyl chloroacetate, 1.7 g. of acetophenone and 4.3 g. of ethyl β -benzoylpropionate; b. p. 143–145° at 6 mm. The semicarbazone melted at 138–139° and a mixed melting point was not depressed.

Anal. Calcd. for $\text{C}_{13}\text{H}_{17}\text{O}_2\text{N}_2$: N, 16.0. Found: N, 16.1.

The non-volatile residue upon treatment with ether gave 0.3 g. of *sym*-triphenylbenzene; m. p. and mixed m. p. 173–174°.

Condensation with Benzoyl Chloride.—Equimolecular amounts of α -methoxystyrene and benzoyl chloride (4.5 g. and 4.7 g., respectively) heated to 180° for seven hours gave 0.5 g. of a white solid, sparingly soluble in organic solvents. It melted at 210° and gave a ferric chloride color test. The melting point was not depressed by a synthetic sample of tribenzoylmethane.

Similar heating of 5.2 g. of the ether with 134 g. of the acid chloride gave as the only identifiable substance 1.8 g. of *sym*-triphenylbenzene; m. p. and mixed m. p. 173–174°.

Reaction between Hydrogen Chloride and α -Methoxystyrene.—Dry hydrogen chloride was passed into 2 g. of α -methoxystyrene for two hours. The reaction mixture solidified to a brown mass. Crystallization from alcohol-acetone gave 0.8 g. of triphenylbenzene; m. p. and mixed m. p. 173–174°.

Summary

α -Methoxystyrene condenses with benzyl bromide, *n*-butyl bromide, ethyl chloroacetate and benzoyl chloride, but not with bromobenzene. A methyl halide is eliminated and a phenacyl derivative is formed. An interpretation of the course of the reaction is presented.

MADISON, WISCONSIN

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(7) Kohler, *Am. Chem. J.*, **42**, 391 (1909).

(8) Merritt, Levey and Cutter, *THIS JOURNAL*, **61**, 15 (1939).

(9) Schroeter, *Ber.*, **40**, 1603 (1907).

(10) Engler and Berthold, *ibid.*, **7**, 1123 (1874).

(11) Abell, *J. Chem. Soc.*, **101**, 998 (1912).