With Water.—The reaction mixture was cooled to room temperature and diluted with benzene or low-boiling petroleum ether. An optimum quantity of 3 moles of water per mole of catalyst was stirred in as rapidly as foam control would allow. (Water was added either pure or as concentrated hydrochloric acid.) About 50 cc. more of solvent was then added. During the following brief period in which hydrogen chloride evolution ceased, the supernatant liquid was decanted. The solvent was then removed and the product vacuum-distilled.

Table I shows the effect of stirring different quantities of water, as concentrated hydrochloric acid, into 0.1:0.4:0.4-mole reaction mixtures of aluminum chloride, benzene and phosphorus trichloride.

TABLE I

YIELD OF PHENYLDICHLOROPHOSPHINE AFTER REMOVAL OF CATALYST WITH WATER

Moles water added	Yield $C_6H_5PCl_2$, g.
0.25	10.7
.275	15.3
.30	20.6
.325	20.9
.35	20.2
.40	16.8

The yield of phenyldichlorophosphine rose rapidly as the critical point of 3 moles water per mole aluminum chloride was approached, and as much as a 10% excess of water did no harm. When sufficient water was added, the hydrated catalyst separated as soft slightly coherent granules, free of product and easily filtered or decanted.

With Phosphorus Oxychloride.—One mole of phosphorus oxychloride per mole of aluminum chloride was added to the hot reaction mixture (with a temperature rise of about 5°), excess phosphorus trichloride and benzene were recovered by vacuum-stripping, the residue was cooled to 40° or below, the catalyst complex was completely precipitated by dilution with about three volumes of light petroleum, and the liquid layer was decanted and distilled. (Caution: In a few instances, involving large excess of phosphorus trichloride and benzene, the mixture separated into two layers when the oxychloride had been partly added, with consequent vigorous boiling of the more volatile layer. This can be prevented by stripping the excess of reactants before addition of phosphorus oxychloride.)

The utility of the latter procedure in Friedel–Crafts reactions in general seems limited only by the provision that the phosphorus oxychloride–aluminum chloride complex must be the most stable one possible in any given reaction mixture. The method has the advantage over the foregoing hydration process that there is no evolution of hydrogen chloride and consequently no tendency for the precipitate to float. Both of these methods appear suitable for isolating other Friedel–Crafts products decomposed by the conventional catalyst quenching process.

CHEMISTRY DIVISION
NAVAL RESEARCH LABORATORY
WASHINGTON, D. C.

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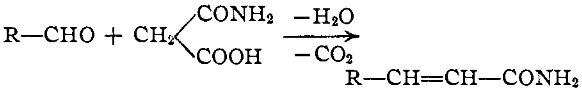
[5] Original manuscript received May 26, 1947.

A Synthesis of α,β-Unsaturated Amides

BY ALEXANDER GALAT

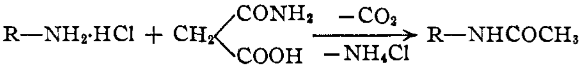
In a previous communication[1] we have reported a synthesis of α,β-unsaturated esters which involved the condensation of an aldehyde with a monoester of malonic acid. It appeared that a similar direct synthesis of α,β-unsaturated amides could be accomplished by condensing an aldehyde with the mono-amide of malonic acid



$$R{-}CHO + CH_2\begin{smallmatrix}\diagup CONH_2\\ \diagdown COOH\end{smallmatrix} \xrightarrow[-CO_2]{-H_2O} R{-}CH{=}CH{-}CONH_2$$

It was found that malon-monoamide did, in effect, readily condense with several representative aldehydes (benzaldehyde, *p*-dimethylaminobenzaldehyde, naphthaldehyde and furfural) to give satisfactory yields of the expected unsaturated amides.

The monoamide of malonic acid was prepared by treating diethyl malonate with one mole of potassium hydroxide in methanol, followed by ammonolysis of the monoester thus formed. The amide is a white, crystalline solid which melts at 110–115° with evolution of carbon dioxide and quantitative formation of acetamide. Its solution in water is strongly acid and can be accurately titrated. Heated with salts of primary amines, malon-monoamide reacts as an acetylating agent



$$R{-}NH_2{\cdot}HCl + CH_2\begin{smallmatrix}\diagup CONH_2\\ \diagdown COOH\end{smallmatrix} \xrightarrow[-NH_4Cl]{-CO_2} R{-}NHCOCH_3$$

Experimental

Malon-monoamide.—To a solution of 160 g. (1 mole) of diethyl malonate in 450 ml. of methanol was added slowly with stirring 280 ml. (1 mole) of 20% methanolic potassium hydroxide. After the addition was completed the mixture was stirred until the reaction became neutral. The crystalline precipitate was filtered off and the filtrate evaporated to dryness *in vacuo*. The combined solids weighed 132 g. (85%). The product is the potassium salt of mono-methyl malonate (ester interchange takes place when working in methanol).

The potassium salt was dissolved in 500 ml. of concentrated ammonium hydroxide and the solution kept at room temperature for one week. It was then evaporated to dryness *in vacuo*, treated with 76 ml. of concentrated hydrochloric acid and stirred until homogeneous. To the mixture was added 275 ml. of isopropanol, the precipitated potassium chloride filtered off, washed with isopropanol and the filtrate evaporated to dryness *in vacuo*. To the resulting sirup was added 150 ml. of hot isopropanol and an additional amount of potassium chloride removed by filtration. Malonmonoamide crystallized upon cooling and was filtered off, washed with isopropanol and dried at room temperature; yield, 52 g. (61%), m. p. 110–115° (dec.).

Anal. Calcd.: N, 13.59; neut. equiv., 103. Found: N, 13.4.; neut. equiv., 103.5.

Cinnamamide.—One gram of benzaldehyde (*ca.* 0.01 mole), 2 g. (*ca.* 0.02 mole) of malon-monoamide, 2 drops of piperidine and 5 ml. of pyridine were heated on a water-bath until the evolution of gas ceased. To the mixture was added 25 ml. of boiling water, the solution cooled and the precipitated amide recovered by filtration; yield, 0.8 g. (57%), m. p. 146–147° (cor.), lit. 142°.

61 SO. BROADWAY
YONKERS, N. Y.

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[1] Galat, THIS JOURNAL, **68**, 376 (1946).

Preparation of Aliphatic Fluorides

BY FRIEDRICH W. HOFFMANN

The exchange of halogen in aliphatic —CHX— and –CH_2X groups (X = Cl, Br) by means of an-