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.

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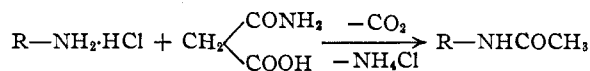
(1) Galat, THIS JOURNAL, **68**, 376 (1946).

could be accomplished by condensing an aldehyde with the mono-amide of malonic acid

$$R-CHO + CH_2\begin{subarray}{l} \diagup CONH_2 \\ \diagdown COOH \end{subarray} \xrightarrow[-CO_2]{-H_2O} R-CH=CH-CONH_2$$
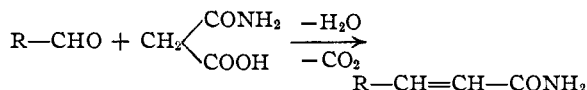
It was found that malon-monoamide did, in effect, readily condense with several representative aldehydes (benzaldehyde, p-dimethylaminobenzaldehyde, naphthaldehyde and furfural) to give satisfactory yields of the expected unsaturated amides.

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

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

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.   RECEIVED APRIL 30, 1948

Preparation of Aliphatic Fluorides

BY FRIEDRICH W. HOFFMANN

The exchange of halogen in aliphatic —CHX— and —CH₂X groups (X = Cl, Br) by means of an-

hydrous potassium fluoride has been described recently.[1,2,3] Since this reaction takes place only at higher temperatures, the use of pressure equipment is required and much trouble is due to coating of potassium fluoride with potassium chloride or potassium bromide, respectively. Only in the special case of the preparation of fluoroacetamide from chloroacetamide the use of xylene as reaction medium allows the reaction to be carried out at atmospheric pressure.[3]

By using suitable organic solvents for anhydrous potassium fluoride, it is possible to exchange the halogens in —CHX— and —CH₂X groups (X = Cl, Br, I) in a one-step reaction at atmospheric pressure in ordinary glass equipment. In order to obtain reasonably fast reaction rates, the method requires a temperature of about 140° and over, so that low-boiling solvents for potassium fluoride, such as methanol and ethanol cannot be used. Satisfactory solvents are aliphatic di- and poly-hydroxy compounds such as ethylene glycol, glycerol, diethylene glycol, polyethylene glycol, etc., either singly or mixed.

In this procedure the yields are fair and frequently considerably higher than those obtained by the pressure method. n-Hexyl fluoride can thus be obtained from n-hexyl chloride in 54% yield, whereas the halogen exchange under pressure without solvent for the potassium fluoride gives only a 20% yield.[2] 2-Fluoroethanol, which could not be obtained by heating of ethylene chlorohydrin with potassium fluoride under pressure by Gryszkiewicz-Trochimowski,[4] was, however, prepared by McCombie and Saunders[1] by the same method at 135–140° (no yield indicated). The subject method permits the preparation of this compound in 42.5% yield by using potassium fluoride in a glycol solvent at atmospheric pressure. Another advantage of the use of a solvent for the halogen exchange is the fact that the presence of small amounts of moisture in one of the reactants can lead to serious hazards by enormous pressure increase in the conventional method,[2] whereas in the described method only the yield of fluorinated product is correspondingly decreased.

Although the subject method is in some respects inferior to conventional methods using fluorides of mercury, etc., the ready availability of the inexpensive potassium fluoride makes it another convenient means for the preparation of aliphatic fluorides, especially since some fluorides such as 2-fluoroethanol, β-difluoroethyl ether, etc., which cannot be obtained by fluorination with silver or mercuric fluoride, are accessible from the corresponding chlorine compounds by fluorination with potassium fluoride.

A large number of new aliphatic fluorine compounds was synthesized by this method by the

writer in collaboration with R. Geier in the laboratories of W. Bockemüller in Würzburg, Germany.

The syntheses of 2-fluoroethanol and n-hexyl fluoride from the corresponding chlorine compounds by halogen exchange with anhydrous potassium fluoride in glycol solution are described in detail in the following.

Preparation of FCH₂CH₂OH.—A mixture of dry, powdered potassium fluoride (350 g., 6 moles), ethylene glycol (320 g.), and diethylene glycol (130 g.) was heated to 170° in a 3-neck, 1-liter, round-bottom flask fitted with a stirrer, dropping funnel, and a 30-cm., 3-step Vigreux column with attached condenser and receiver. Ethylene chlorohydrin (322 g., 4 moles) was added dropwise in the course of three hours to the reaction mixture maintained at 170–180° with constant stirring at such a rate that the distillate at the still head showed a temperature of 95–105°. After addition of ethylene chlorohydrin was complete, a slow stream of air was sucked through the apparatus for one hour in order to distil off the fluoroethanol completely. In the receiver, 152.5 g. of crude reaction product was obtained as a colorless liquid. After standing with 10 g. of sodium fluoride for two days to remove traces of hydrogen fluoride, distillation of the reaction product yielded 109 g. (42.5%) of fluoroethanol (b. p. 101°,[1] 100–102°[2]) between 97° and 104°.

Preparation of CH₃(CH₂)₄CH₂F.—A mixture of dry, powdered potassium fluoride (116 g., 2 moles), ethylene glycol (200 g.), and diethylene glycol (50 g.) was heated to 180° in a 3-neck, 1-liter, round-bottom flask fitted with a stirrer, dropping funnel and a 30-cm., 3-step Vigreux column with attached condenser and receiver. n-Hexyl chloride (120.6 g., 1 mole) was added dropwise in the course of eight hours to the reaction mixture maintained at 175–185° with constant stirring. Since the reaction product boils at 93.2°, it distils out of the reaction mixture at about the same rate at which the reagent is added. After addition of hexyl chloride was complete, the reaction mixture was allowed to cool to 110°. A slow stream of air was sucked through the apparatus in order to distil off the remaining reaction product from the mixture. In the receiver, 79.6 g. of distillate was collected. This consisted of n-hexyl fluoride with some hexene and some unreacted hexyl chloride. Fractionation yielded 56.3 g. (54.1%) of n-hexyl fluoride, boiling at 91–93.5°.

CHEMICAL CORPS TECHNICAL COMMAND
ARMY CHEMICAL CENTER, MARYLAND
                    RECEIVED FEBRUARY 24, 1948

(1) McCombie and Saunders, *Nature*, **155**, 382 (1946).
(2) Gryszkiewicz-Trochimowski, Sporzyński and Wnuk, *Rec. trav. chim.*, **66**, 413–418 (1947).
(3) Bradley, U. S. Patent 2,403,576 (July 9, 1946).
(4) Gryszkiewicz-Trochimowski, *Rec. trav. chim.*, **66**, 427 (1947).

The Terpenes of Oil Sweet Goldenrod

BY BRYANT R. HOLLAND

In a study of the production of essential oils, oil of Sweet Goldenrod (*Solidago odora*)[1] has been investigated. Miller and Moseley[2] examined this oil fairly extensively, but did not identify the terpenes. They identified methyl chavicol as the main constituent, and showed borneol to be present. To extend the findings of Miller and Moseley, the oil has been partially fractionated and the terpenes determined.

Experimental

A 600-ml. sample of fresh oil was fractionated using a Stedman column (24 inch packing, 1 inch diameter) at a pressure of 5 mm. with a reflux ratio of 0.5 (50% of the condensate returned to the column). The starch–glycerol

(1) The complete investigation is to be reported in a Texas Engineering Experiment Station Bulletin.
(2) Miller and Moseley, THIS JOURNAL, **37**, 1285 (1915).