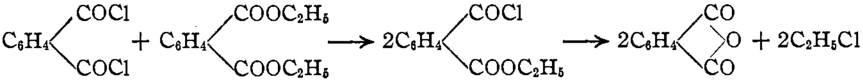
[Contribution from the Research Laboratories, Monsanto Chemical Company]

The Reaction between Some Acid Chlorides and Esters

By L. P. Kyrides and M. N. Dvornikoff

In a recent paper[1] it was stated that phthalyl chloride and diethyl ether react in presence of zinc chloride to give phthalic anhydride and ethyl chloride, and not diethyl phthalate, which had been expected. It was also intimated that the diethyl phthalate, if it had been formed, must have reacted with the excess of phthalyl chloride to give the products which were isolated.

Work carried out at the same time disclosed that phthalyl chloride and dialkyl phthalates also react in presence of traces of zinc chloride to give the anhydride and the corresponding alkyl chlorides. In these reactions it appears that the ester chloride of phthalic acid is first formed, which, being very unstable, is decomposed immediately into the anhydride and the alkyl chloride as follows



$$C_6H_4\begin{cases}COCl\\COCl\end{cases} + C_6H_4\begin{cases}COOC_2H_5\\COOC_2H_5\end{cases} \longrightarrow 2C_6H_4\begin{cases}COCl\\COOC_2H_5\end{cases} \longrightarrow 2C_6H_4\begin{cases}CO\\CO\end{cases}O + 2C_2H_5Cl$$

Zelinsky[2] attempted to prepare the ester chloride of phthalic acid and observed its great instability. He states that it is decomposed even on standing in a vacuum desiccator and gives ethyl chloride and phthalic anhydride on warming.

Succinyl chloride and succinic esters react similarly, indicating that the reaction may be general with alpha-beta and *o*-dicarboxylic acids.

Senff[3] by reaction of benzoyl chloride and ethyl benzoate in the presence of zinc chloride at the boiling temperature of the mixture observed only the formation of *m*-benzoylbenzoic acid. We have found that in this case the main reaction products are benzoic anhydride and ethyl chloride. We also isolated very small amounts of anthraquinone.

The reaction of a dialkyl phthalate with benzoyl chloride or of phthalyl chloride with an alkyl benzoate results in the formation of alkyl chloride and probably of a mixture of the anhydrides of the acids as the main reaction products.

Benzyl esters in similar reactions failed to give benzyl chloride and several attempts at reaction of diethyl phthalate with aliphatic monocarboxylic acid chlorides resulted in the formation of large amounts of hydrochloric acid and ethylene. No ethyl chloride was isolated in these cases, indicating that the course of the reaction was quite different.

Experimental

1. Reaction between Dialkyl Phthalates and Phthalyl Chloride.—The reaction was carried out in a 250-cc. three-necked flask carrying a thermometer, a dropping fun-

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(1) L. P. Kyrides, This Journal, **55**, 1209 (1933).

(2) Zelinsky, *Ber.*, **20**, 1010 (1887).

(3) Senff, *Ann.*, **220**, 250 (1883).

nel, and a reflux spiral condenser, which was kept at the proper temperature. In the case where ethyl chloride was a reaction product the condenser was cooled with running water at 14°. In the latter case the condenser was connected through a small flask containing water (for scrubbing the gases) to a spiral condenser which was cooled with ice and water, and the ethyl chloride was collected in a receiver cooled at about −5°.

Freshly distilled diethyl phthalate (166 g. (0.75 g. mole)) and 0.2 g. of technical zinc chloride were charged into the flask and heated over a gauze to 120°; 165 g. of 94% (0.764 g. mole) phthalyl chloride (containing 6% phthalic anhydride) was dropped in over a period of about three hours. Toward the end, the temperature was gradually raised to 180° and the reaction stopped when the evolution of gas ceased.

The condensate in the receiver was fractionated through a spiral condenser maintained at 14°. In this manner 88.3 g. (1.37 g. mole) of ethyl chloride was recovered. This amounts to 91% of the theoretical from diethyl phthalate. The residual phthalic anhydride, contaminated with traces of phthalyl chloride, weighed 236 g. (practically theoretical yield) and showed a crystallizing point of 128–129°. A very small amount of ethylene and some hydrochloric acid were also found to be evolved during the reaction. The reaction is, therefore, practically quantitative and follows the equation given above.

The reaction gives essentially the same yields if the components are mixed and heated very gradually to avoid too violent a reaction.

By heating di-*n*-butyl phthalate with a 10% excess of phthalyl chloride in presence of traces of zinc chloride, we obtained an 80% yield of butyl chloride. Some butylene and hydrochloric acid were also formed.

Di-*sec*-butyl phthalate and phthalyl chloride gave about 50% yield of *sec*-butyl chloride and a large amount of butylene.

Gram molecular equivalents of di-*sec*-butyl succinate and succinyl chloride were heated gradually with a trace of zinc chloride from 110–190°. The crude *sec*-butyl chloride amounted to 58% of the theoretical. At the same time 12 liters of gas (butylene) and 0.8 g. mole of hydrochloric acid were also formed.

2. **Ethyl Benzoate and Benzoyl Chloride,** $C_6H_5COOC_2H_5 + C_6H_5COCl = (C_6H_5CO)_2O + C_2H_5Cl$.—A mixture of equimolecular quantities of ethyl benzoate and benzoyl chloride containing about 1% by weight of technical zinc chloride was heated gradually. No appreciable reaction was apparent below 180°. The temperature was then raised slowly to 270° in the course of about two hours and maintained at 270–290° for two hours longer. The ethyl chloride obtained amounted to 77% of the theoretical. Some hydrochloric acid and ethylene were also formed. The reaction mixture was then subjected to vacuum distillation and benzoic anhydride was obtained in a 77% yield of the theoretical. The anhydride was contaminated with a very small amount of an impurity which was isolated and identified as anthraquinone.

3. **Diethyl Phthalate and Benzoyl Chloride.**—A mixture of 88.8 g. (0.4 g. mole) of diethyl phthalate, 112.4 g. (0.8 g. mole) of benzoyl chloride and 0.4 g. of zinc chloride was heated for one-half hour at 120–165°; 0.34 g. mole of ethyl chloride was obtained, which is equivalent to a yield of 42.5% of the theoretical. Hydrochloric acid was also formed corresponding to 0.08 mole per mole of benzoyl chloride. The reaction temperature was then raised and maintained at 180–200° for two hours longer. The yield of ethyl chloride was raised to 56%. A further heating for two hours longer increased the yield of ethyl chloride to 63%.

These results seem to indicate that the reaction proceeds in two stages. At first one mole of diethyl phthalate reacts with one of benzoyl chloride at the lower temperature giving phthalic anhydride (probably through the intermediate ester chloride of phthalic acid), ethyl benzoate and ethyl chloride. Then at the higher temperature and at a considerably slower rate, the ethyl benzoate formed reacts with another mole of benzoyl chloride as given under (2).

4. **Ethyl Benzoate and Phthalyl Chloride.**—This reaction was carried out as under (3) by heating 2 moles of ethyl benzoate with one of phthalyl chloride. The reaction started at about 180° and after heating at 180–200° for two hours gave a 65% yield of ethyl chloride.

Summary

Equimolecular amounts of phthalyl chloride and diethyl phthalate react in presence of traces of zinc chloride to give excellent yields of phthalic anhydride and ethyl chloride. Other alkyl esters of phthalic acid react similarly, except that the yields of the alkyl chlorides are lower due to the formation of larger amounts of alkylenes. Succinic esters and succinyl chloride react in the same manner.

Ethyl benzoate and benzoyl chloride react in the presence of zinc chloride at higher temperatures to give fair yields of benzoic anhydride and ethyl chloride.

Benzoyl chloride and phthalic esters react to give alkyl chlorides and presumably a mixture of the anhydrides of the acids as the main reaction products. The same is also true of the reaction of phthalyl chloride with ethyl benzoate.

ST. LOUIS, MISSOURI

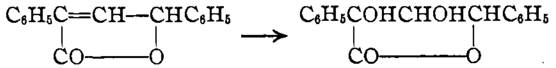
RECEIVED JULY 14, 1933
PUBLISHED NOVEMBER 7, 1933

Hydroxyl Derivatives of Alpha,Gamma-Diphenylbutyric Acid

BY E. P. KOHLER AND R. H. KIMBALL

The work herein described began many years ago with an attempt to add nitromethane to phenyl benzoyl ethylene oxide in the hope of finding an explanation for the peculiar behavior of certain aliphatic nitro compounds.[1] Addition appeared to occur readily enough but experiments carried out under the most diverse conditions invariably ended with an intractable oil from which no substance containing nitrogen could be isolated. By digestion with hydrochloric acid this oil was in part converted into a solid in which all that remained of the nitromethane was an atom of carbon and possibly one or two atoms of oxygen.

From a series of transformations which need not be discussed here we came to the conclusion that the nitrogen-free solid was a dihydroxy lactone. This conclusion has been confirmed by a synthesis of the substance that adequately establishes its structure



$$\begin{array}{l} C_6H_5C{=}CH{-}CHC_6H_5 \\ \quad\ | \qquad\qquad\ \ | \\ \quad CO{-\!-\!-\!-}O \end{array} \longrightarrow \begin{array}{l} C_6H_5COHCHOHCHC_6H_5 \\ \quad\ | \qquad\qquad\qquad\quad | \\ \quad CO{-\!-\!-\!-\!-\!-}O \end{array}$$

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[1] Kohler and Goodwin, THIS JOURNAL, **49**, 219 (1927).