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Abstract

Full Text

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PREPARATION OF MALONIC ACID AND ITS ESTERS WITH THE AID OF CARBON SUBOXIDE

(Presented by Academician A. N. Nesmeyanov on 21 I 1960)

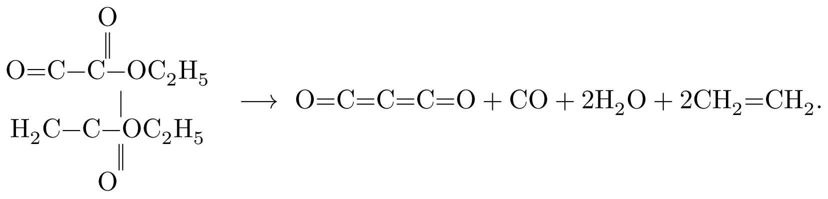
Carbon suboxide is an excellent malonylating agent. With its aid, under comparatively mild conditions, various substituted malonamides, pyrazolidines, dialkyl malonates, β-diketones, carbocyclic and heterocyclic compounds, etc., are obtained ($^{1-11}$). However, for a long time the only methods for obtaining carbon suboxide were syntheses of the suboxide from malonic-acid halide anhydrides and their dihalogen-substituted derivatives (^{12,13}), as well as pyrolysis of malonic acid (^{14}), malonic ester, and diacetylvinic acid anhydride (^{15,16}).

This was the main obstacle to the practical use of carbon suboxide as a malonylating reagent, since the above-listed methods of preparation either start from malonic acid and its derivatives, or give a very low yield and are associated with experimental difficulties.

We have developed a new method for preparing carbon suboxide, which consists in the high-temperature pyrolysis of diethyl oxaloacetate in a quartz tube. As the experiment showed, the use of catalysts (platinum, silver) promotes contamination of the carbon suboxide with carbomethylene, whereas noncatalytic pyrolysis gives a quite satisfactory yield of carbon suboxide and does not lead to formation of carbomethylene as a side product of the reaction.

It should also be noted that diethyl oxaloacetate is an accessible substance. It can readily be obtained by condensation of ethyl acetate and diethyl oxalate and is produced by our chemical industry.

The pyrolysis of diethyl oxaloacetate proceeds according to the following scheme:



$$\begin{array}{l} \mathrm{O{=}C{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OC_2H_5} \\ \qquad\quad | \\ \mathrm{H_2C{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}OC_2H_5} \end{array} \longrightarrow \mathrm{O{=}C{=}C{=}C{=}O + CO + 2H_2O + 2CH_2{=}CH_2}.$$

The preparation of malonic acid and dialkyl malonates does not require isolation of liquid carbon suboxide (b.p. 6–7°). High yields of these products are obtained by saturating water or the corresponding alcohols with gaseous carbon suboxide, entering directly from the furnace for pyrolysis. The authors who studied the interaction of carbon suboxide with alcohols propose carrying out the reaction with slight heating ([4]).

Experimental Part

Preparation of carbon suboxide by pyrolysis of diethyl oxaloacetate.

Pyrolysis of acetylenedicarboxylic and oxaloacetic acids, the anhydride of acetyloxymaleic acid, and the anhydride of diacetyltartaric acid showed that the yield of carbon suboxide can be increased if these substances are fed into the furnace in an acetic anhydride solution. This also proved to be true for diethyl oxaloacetate. Under the conditions of our experiments, acetic anhydride did not undergo pyrolysis and subsequently was regenerated practically completely. Pyrolysis was carried out in a tubular furnace 24 cm long. A quartz tube with an internal diameter of 16 mm was inserted into the furnace. On one side the tube was connected to a dropping funnel equipped with an ordinary pressure equalizer; on the other it communicated with two intermediate vessels connected in series, which were two-necked flasks with reflux coil condensers. Acetic anhydride was collected in the flasks. The flasks were then connected to two receivers arranged in series, filled with absolute ether and cooled in an ice bath. The acetic anhydride solution of diethyl oxaloacetate was fed to pyrolysis uniformly and at such a rate as to exclude the possibility of carbon suboxide passing through the ether. At 0°, 2.5 g of carbon suboxide dissolves in 100 ml of absolute ether. As is known, ethereal solutions of carbon suboxide are very stable. Even on prolonged boiling, the concentration continues to correspond to the state of saturation at the boiling temperature of ether, which, in all probability, is explained by the formation of an intermolecular compound of carbon suboxide with diethyl ether. The yield of carbon suboxide was determined by the anilide method.

Pyrolysis of diethyl oxaloacetate was carried out at various temperatures within the range from 650 to 900°. The best results were achieved at a temperature regime of 850–875°. 10 g of diethyl oxaloacetate in 70 ml of acetic anhydride were fed into the furnace for pyrolysis at 850° over 2 hours. The yield of carbon suboxide was 1.73 g (determined by the anilide method). On average, the yield of carbon suboxide obtained under the indicated conditions is 45% of the theoretical value calculated for diethyl oxaloacetate.

Preparation of malonic acid and some of its esters.

The reaction between malonic acid, alcohols, and phenol was carried out with heating in the range 60–70°. As catalyst, 2–3 drops of HCl were used. The calculated amount of gaseous carbon suboxide was passed through a capillary tube into water, alcohol, or phenol. After carbon suboxide had been passed through for 1.5–2 hours, the mixture was heated for another 1 hour, and the absence of carbon suboxide was checked by the anilide method. The aqueous solution of malonic acid, as is usually done, was evaporated under a slight vacuum at 60–

65°, and the malonic esters were isolated by ordinary or vacuum distillation.

For the reaction with carbon suboxide we used water, methyl, ethyl, propyl, *n*-butyl, cyclohexyl, and benzyl alcohols, as well as phenol, which were taken in amounts of 15-20 ml. As a result the following were obtained: dimethyl malonate with b.p. 179° and yield 96%, diethyl malonate with b.p. 198° and yield 97%, dipropyl malonate with b.p. 228°/764 mm and yield 94%, di-*n*-butyl malonate with b.p. 249-250°/761 mm and yield 90%, dicyclohexyl malonate with b.p. 193-

194°/15 mm and a yield of 61%, dibenzyl malonate with b.p. 234°/15 mm and a yield of 38%, diphenyl malonate with m.p. 48° (from petroleum ether), b.p. 209° and a yield of 69%, and malonic acid with m.p. 129-130° and a yield of 97%.

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Note: Figure translations are in progress. See original paper for figures.

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