of HBr, bromine and tetrahydronaphtaline are used.

CHCl₃ is of grade purum.

Preparation of samples

The stirred oscillating reaction solution is extracted by the same volume of diethylether. The ether is then dried by Na₂SO₄ and finally evaporated on a rotary evaporator. At room temperature 500 mg of the remaining oily slurry are added to 5 ml of methanol-HCl or methanol-HBr containing 5-7% by weight HCl, HBr resp. After a day the esters are extracted from this solution by addition of 8 ml CHCl₃ and 8 ml H₂O. The CHCl₃ solution is washed with 1 ml saturated NaHCO₃ and 1 ml H₂O successively, in order to remove remaining acids. Finally the solution is dried with Na₂SO₄.

Combined gas chromatography and mass spectrometry

Samples of 1 μl of these solutions are analysed by the combination of gas chromatography and mass spectrometry (Hewlett-Packard 5750/CH7 Varian MAT) under the following conditions: Column: Material siliconitril (2 m × 3 mm), temperature slope of: 20 °C/min from 50 to 200 °C; detector: total ion current (TIC); carrier gas flow: 10-15 ml/min.

The mass spectra are not corrected for total ion current. Therefore, the relative intensity might be used only as a qualitative measure. Furthermore, methylesters of samples of malonic acid, dibromoacetic acid and monobromomalonic acid are prepared for control experiments.

In order to estimate the areas below the chromatographic peaks, a gas chromatograph (Siemens L 400) without a mass spectrometer is used under following conditions: Column: 120 °C; 3 m × 2 mm glas packed with 10% LAC 2R 446 on chromosorb W. 80-100 mesh; carrier gas flow 13 ml/min of N₂; detector: FID at 250 °C, full scale of the recorder 64 pA. Temperature: 170 °C.

Results

A gas chromatogram of an extract prepared as given under methods is shown in Fig. 1. In this case the esters are produced by methanol-HCl. The peaks are analysed by mass spectrometry as shown in Figs. 2a–d. The esters can easily be identified by their M-peaks and their characteristic fragmentation pattern, increasing the peaks at mass units M-31 and M-59. Bromine or chlorine containing compounds show typical isotopic distributions which are clearly recognized in the spectra. Furthermore, it should be mentioned that always a M+1 peak is present in the methyl esters of the dicarboxylic acids.

The mass spectra of Fig. 2 identify dibromo-acetic acid methyl ester, monochloromalonic acid dimethylester, monobromomalonic acid dimethylester and malonic acid dimethylester as compounds of the gas chromatographic separation. If the esters are prepared in methanol-HBr, no peak of monochloromalonic acid dimethylester is observed, and the area below the monobromomalonic acid dimethylester peak increases by an appropriate amount. Therefore, it is concluded, that bromine atoms of the compound are exchanged by chlorine during esterification.

If the samples are drawn at different times after initialisation of the reaction by ceric ions, the gas chromatographic peaks of the products rise in time. The sample taken after 2 hours reaction time (given in Fig. 1) shows a ratio of the area in the peaks relative to the one of malonic acid dimethylester as follows: 0.185 for dibromoacetic acid methylester, 0.86 for monochloromalonic acid dimethylester and 0.13 for monobromomalonic acid dimethylester. Furthermore, a mass spectrum of the gas evolved during the oscillatory phase is recorded. It consists of the typical peaks of the CO₂ spectrum besides minor peaks of water and air from the reaction mixture and the atmosphere.

Discussion

The accumulated reaction products are identified as monobromomalonic acid and dibromoacetic acid.
Figs. 2a–d. Mass spectra of the peaks of the gas chromatogram shown in Fig. 1 (in parenthesis the relative area below the peak of Fig. 1 is given). The parent mass peaks calculated with the most abundant isotopes for the methylesters of the acids are as follows:

a. Monobromo malonic acid: $212 \text{ m/e (38.5)}$,

b. Monochloro malonic acid: $166 \text{ m/e (256)}$,

c. Dibromoacetic acid: $232 \text{ m/e (55)}$, 
acid in agreement with earlier results. An approximate ratio of the extent to which both compounds are produced after 2 hours of reaction time at room temperature can be obtained by accounting for the distribution ratio between a one to one mixture by volume of the aqueous and ether phase. The calculation yields a molar ratio of malonic-, monobromomalonic- and dibromoacetic acid of 1.0, 0.14 and 0.023 resp.. From this estimates it can be concluded that about 15% of malonic acid are converted into brominated products during the 2 hours reaction time and furthermore that the pool of bromomalonic acid is approx. 6 times higher than the pool of dibromoacetic acid.

Besides tribromoacetic acid and some other brominated compounds, dibromoacetic acid is also found as a product, when malic acid is used as reducing agent instead of malonic acid. In this case partial evaporation of the solvent CHCl₃ gives gas chromatograms with several additional minor peaks.

We wish to thank Mr. O. Paschold for his technical assistance in the analytical part of the paper and Dr. Johannes for recording the CO₂-spectra in an equipment of Prof. Dr. Budzikiewicz.