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Preparation of 300—500 mg Quantities of Isotopic Methyl Ketenes

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Methyl-[1-¹³C] ketene. 20 mmole ¹³C-enriched CO₂ (from 4 g 55 % enriched BaCO₃ (= Ba*CO₃)) was distilled into a cooled (−70°C) Grignard solution prepared from 30 mmole ethyl bromide (3.2 g), 0.85 g Mg and 0.4 g I₂ in 50 ml ether. Afterwards, over a period of 1 h, the temperature was raised to −20°C. In 10 min, 50 ml water was added, the temperature rising to 0°C. After filtering, CH₃CH₂*COOH was neutralized by 50 ml 2N NaOH in the combined water and ether phases and the ether phase discarded. 7 g Ag₂SO₄ with 100 ml water was added to the aqueous phase for precipitation of AgBr and AgI. 300 ml water was distilled-off at 100°C while an equal quantity of water was simultaneously added. 50 ml half-concentrated H₂SO₄ was added to the distillation flask, liberating CH₃CH₂*COOH, which was distilled-off at 100°C with 800 ml water, which was replaced during the

distillation as above. Titration of the aqueous distillate (I) showed that it contained 19.8 mmole acid. After neutralization, water was evaporated from one-half part of (I), and 15 ml phthaloylchloride was added. The flask was connected to a reflux condenser, heated to 175–180°C for 1 h and cooled. CH₃CH₂*COCl was separated from the reaction mixture by distillation in a high vacuum, the temperature of the bath surrounding the flask being gradually raised from 25°C to 60°C. By a following single-plate distillation *in vacuo*, 9.7 mmole of CH₃CH₂*COCl was obtained. The whole quantity was added to the residue of CH₃CH₂*COONa, resulting from evaporation of water from the other half of (I). After 24 h at room temperature, the mixture was heated *in vacuo* from 25° to 100°C over a period of 3–4 h under collection of a distillate of 9.6 mmole of (CH₃CH₂*CO)₂O (II). The pyrolysis of (II) was performed as already described.¹ Yield 400 mg or 7 mmole (70 % with respect to CO₂). The infrared gas-spectrum,² the PMR-spectrum,² and the microwave spectrum² showed that the product was pure. Kept at −190°C as crystals, it is stable over a period of at least one year. It contains 55 % methyl-[1-¹³C] ketene mixed with 45 % ordinary methyl ketene.

A mixture of methyl-[2-¹³C] ketene and [¹³C]-methyl ketene. Proceeding as in the previous case, but replacing ethyl bromide by 4.60 g methyl iodide (all other quantities being equal) we prepared an aqueous solution containing 19.9 mmole CH₃*COONa. After complete evaporation of water, 15 ml phthaloylchloride was added. Under a slight vacuum (650–680 mm Hg), the mixture was refluxed for 30 min at ca. 150°C. CH₃*COCl with a trace of HCl was separated by distillation *in vacuo*. After several single-plate distillations on the vacuum line, during which small quantities of HCl were discarded, 1.534 g or 19.4 mmole CH₃*COCl was obtained. The whole quantity was distilled into a 1.14 m LiAlH₄-solution in diethyleneglycol diethylether. After stirring for 1 h, the mixture was cooled (liquid N₂) and 15 ml diethyleneglycol monobutylether added. After the evolution of H₂ had stopped, the flask was heated to room temperature, and the vapors of the reaction mixture removed *in vacuo* over a period of 2 h and condensed in a trap, cooled in liquid N₂. By repeated distillations on the vacuum line, 0.907 g or 19.1 mmole CH₃*CH₂OH was obtained, contaminated only by insignificant

amounts of methanol (0.5 %) and diethylenglycol diethylether. The "marked" alcohol was distilled into a 1-liter evacuated glass ampulla containing 14 g P_2O_5 . The sealed-off ampulla was kept at 200°C for 2 h, cooled, and opened under vacuum. 18 mmole $^*CH_2=CH_2$ was obtained. This quantity with 19.9 mmole HBr and 0.02 mmole O_2 was placed in a 1-liter glass ampulla, afterwards sealed-off and irradiated by ultraviolet light for 2 h. After opening of the ampulla, excess HBr was removed by NaOH on celite, water by conc. H_2SO_4 on celite. By two single-plate distillations *in vacuo*, 1.897 g or 17.1 mmole of a mixture of equal parts of *CH_3CH_2Br and $CH_3^*CH_2Br$ was obtained. The conversion of ethyl bromide to methyl ketene has already been described. It resulted in ca. 6 mmole or 330 mg of a mixture of ca. 27.5 % methyl-[2- ^{13}C] ketene, 27.5 % [^{13}C]-methyl ketene, and 45 % ordinary methyl ketene of the same quality and stability as methyl-[1- ^{13}C] ketene.

Methyl- ^{18}O] ketene. 4.7 g ^{18}O -enriched water (25 %) was distilled *in vacuo* into an ampulla, containing 0.43 g Na (18.7 mmole). After evolution and removal of hydrogen, 1 g CH_3CH_2CN (18.1 mmole) was distilled into the same ampulla, which was sealed off and kept for 9 days at 60°C. Water and ammonia was removed *in vacuo* and the remaining $CH_3CH_2C^*O_2Na$ dried at 180°C for 1 h under pumping. Yield: 1.8 g, or 18.5 mmole. 0.944 g benzotrichloride was added, the ampulla sealed-off and kept for 15 h at 175°C. After cooling, a mixture of 67 % $(CH_3CH_2C^*O)_2^*O$ (b.p. 169°C) and excess benzotrichloride (b.p. 214°C) (33 %) was distilled off *in vacuo*. No further separation was carried out prior to the final pyrolysis, performed as already described. The yield of a mixture of 25 % methyl-[^{18}O] ketene and 75 % ordinary methyl ketene was ca. 5 mmole of high quality and stability.

Methyl-(2-D) ketene. By repeated exchange between $CH_3CH(COOH)_2$ and D_2O , 8 g (66 mmole) $CH_3CD(COOD)_2$ was prepared and afterwards decarboxylated at atmospheric pressure by refluxing for 1 h. Yield 5.12 g (66.5 mmole) CH_3CD_2COOD . By the procedure already described, this quantity was converted to ca. 32 mmole or 1.8 g methyl-[2-D] ketene of high quality and stability.

[D]-Methyl ketene. Gaseous DBr (220 mmoles) reacted with ethylene (240 mmole) and a trace of oxygen at 1 atm. and room temperature in a glass container, irradiated

by ultraviolet light. After 2 h, 23.6 g CH_3DCH_2Br of high purity was collected (215 mmole). By the method already indicated, this whole quantity was converted to 194 mmole of CH_3DCH_2COONa . 1.40 g (14.4 mmole) of this salt gave ca. 6 mmole [D]-methyl ketene of high purity and stability.

(D₃)-methyl ketene. By repeated exchange between $CH_3(COOH)_2$ and D_2O , 11 g $CD_3(COOD)_2$ (102 mmole) was prepared and afterwards decarboxylated at atmospheric pressure by refluxing for 1 h. Yield 6.2 g (96 mmole) CD_3COOD . By reaction with 12 g Ag_2O the acid was converted to CD_3COOAg (88 mmole). In an evacuated system, 2 g bromine was brought into contact with the silver salt. By slowly heating from room temperature to ca. 50°C an evolution of CD_3Br , CO_2 , CD_3COOCD_3 , and a small amount of O_2 or CO was observed, the products (with some bromine) being collected in a trap, cooled in liquid air, and occasionally freed from the non-condensing impurity by pumping. To make bromine react fully, the condensed gases were collectively distilled back to the silver salts a couple of times. Hereafter, NaOH on celite removed CO_2 , CD_3COOCD_3 , and Br_2 while conc. H_2SO_4 on celite removed water. Yield 59 mmole CD_3Br . 4 g (25 mmole) diethylmalonate was added to a solution of 0.6 g Na in 25 ml absolute ethanol. Under stirring, 25 mmole CD_3Br was added in the course of 20 min. After 40 min at room temperature, excess CD_3Br and part of the alcohol was removed by distillation, and 20 ml 5 N NaOH was added. After reflux for 1 h at atm. pressure, ethanol and water was distilled-off and 10 ml conc. HCl added. Hydrochloric acid was removed completely by distillation *in vacuo* at room temperature. The residue in the flask is dry $CD_3CH(COOH)_2$, which, after decarboxylation, gave 21.5 mmole CD_3CH_2COOH . In the usual way, this quantity was converted to 5 mmole of $CD_3CH=CO$, of the same high purity and stability as indicated for the remaining isotopic methyl ketenes.

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