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The Synthesis of Methyl α-Methoxyacrylate

Norio Ogata, Shun-ichi Nozakura and Shunsuke Murahashi
Faculty of Science, Osaka University, Toyonaka, Japan

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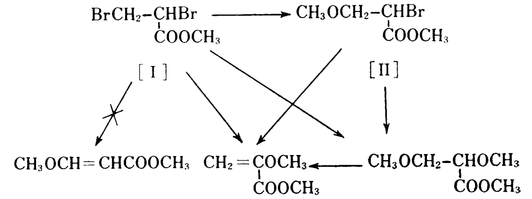
In the course of our study of the polymerization of internal olefins, we attempted to prepare methyl β-methoxyacrylate (β-MMOA) and undertook the reaction of sodium methoxide ($NaOCH_3$) with methyl α,β-dibromopropionate (I). It was found, however, that methyl α-methoxyacrylate (α-MMOA) is unexpectedly formed. This is in contrast with the case of α,β-dibromopropionic acid,[1] where it has been shown that α,β-dibromopropionic acid, on treatment with boiling methanolic $NaOCH_3$, yields β-methoxyacrylic acid.

α-MMOA has been prepared either by the reaction of phosphorous pentoxide with methyl α,α-dimethoxypropionate[2] or by the reaction of piperidine with methyl β-bromo-α-methoxypropionate.[3]

In the present study, the reaction of $NaOCH_3$ with compound I at various molar ratios at room temperature was examined, and the course of the reaction leading to the formation of α-MMOA was elucidated.



[β-MMOA]　[α-MMOA]　[III]

Fig. 1

The reaction paths are summarized in Fig. 1. The reaction of more than 2 mol equivalents of $NaOCH_3$ with compound I gives α-MMOA in good yields. The structure of α-MMOA was established by the study of its NMR spectra and that of its hydrogenated product, methyl α-methoxypropionate, and by derivation to a known compound, α-methoxypropionamide. When the reactions were carried out in boiling methanol, similar results were obtained, but in somewhat lower yields.

When an equimolar amount of $NaOCH_3$ is used in the reaction, the main product is compound II, as has been reported in the literature.[4] The structure of compound II was confirmed by a comparison of its NMR and IR spectra with those of authentic methyl α-bromo-β-methoxypropionate prepared by the procedure of Carter.[5]

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[1] L. N. Owen and H. M. B. Somade, *J. Chem. Soc.*, **1947**, 1030.

[2] K. Auwers, *Ber.*, **44**, 3514 (1911).

[3] J. W. Baker, *J. Chem. Soc.*, **1942**, 520.

[4] J. L. Wood and V. du Vigneaud, *J. Biol. Chem.*, **134**, 413 (1940).

[5] a) L. R. Schilz and H. E. Carter, *ibid.*, **116**, 793 (1936). b) H. E. Carter and H. D. West, "Organic Syntheses," Coll. Vol. III, p. 774 (1955).

Table 1. Dependence of product distribution on the molar ratio of $NaOCH_3$ to compound I[a)]

$NaOCH_3$/I (molar ratio)	Addition[b)] procedure	Yield (%)[c)] II	III	α-MMOA
1.15	B	77	19	0
1.20	A	75	24	0
1.48	A	45	52	3
1.82	A	9	62	21
1.85	B	4	53	36
2.05	A	0	8	67
2.31	A	0	7	75
2.38	B	0	6	79
2.99	A	0	5	79

a) After 5 days, at room temperature. Amounts of compound I and methanolic $NaOCH_3$ were 8 m*l* (6.35—6.50 mol) and 50 m*l*, respectively.

b) A: A methanolic $NaOCH_3$ was added to compound I at −4°C.
B: Compound I was added to $NaOCH_3$-methanol solution at −4°C.

c) Determined by gas chromatography using calibration curves.

When the reaction is carried out with 1.50—1.85 mol equivalents of $NaOCH_3$, the main product is methyl α,β-dimethoxypropionate (III). Its structural assignment was based on elementary analysis and its NMR spectrum.

The distribution of the product is remarkably affected by the molar ratio of $NaOCH_3$/I, but only slightly by the addition procedure, as is shown in Table 1. From these data, it seems reasonable to assume that the reaction of $NaOCH_3$ with compound I results in the formation of compound II in the first stage, followed by the formation of compound III and/or α-MMOA. In order to clarify these points, the behavior of compounds II and III in a high concentration of $NaOCH_3$ was examined. The reaction of compound II with methanolic $NaOCH_3$ (the molar ratio of $NaOCH_3$/II=0.98) resulted in the formation of α-MMOA (85%), together with a small amount of compound III (9%). By the reaction of compound III with methanolic $NaOCH_3$ (the molar ratio of $NaOCH_3$/III=1.64), α-MMOA was also obtained (80%). These results suggest that the reaction route is in the order:

$$\text{I} \rightarrow \text{II} \rightarrow \text{III} \rightarrow \alpha\text{-MMOA}.$$

Experimental

Equimolar Reaction of $NaOCH_3$ with Compound I. A solution of 7.7 g (0.34 mol) of sodium in 100 m*l* of dry methanol was added dropwise with mechanical stirring into 80.3 g (0.33 mol) of compound I (bp 97—98°C/24 mmHg) at −2—−4°C. At the end of addition, the ice-salt bath was removed and the mixture was stirred at room temperature for 1.5 hr. After dry ice had then been added to neutralize remaining alkali, the precipitate was removed by filtration. Water was added to the filtrate, and it was extracted with chloroform. The chloroform solution was washed with water and dried over anhydrous magnesium sulfate. Distillation gave a product, II; bp 68—70°C/11 mmHg; yield, 48.5 g (76%). Found: C, 30.54; H, 4.69; Br, 40.0%. Calcd for $C_5H_9O_3Br$: C, 30.48; H, 4.60; Br, 40.6%. NMR (CCl_4, 60 MHz): τ= 6.22 (s, $COOCH_3$), 6.63 (s, OCH_3), 5.67—6.42 (m, α and β C*H*).

Methyl α-Bromo-β-methoxypropionate. Methyl α-bromo-β-methoxypropionate was prepared by the procedure of Carter[5b)] from 54 g of methyl acrylate, 120 g of mercuric acetate, 72 g of potassium bromide, and 90 g of bromine. Yield, 54 g. The dibromoester was removed from the reaction mixture by gas chromatography (Apiezon M—Celite 545, 2 m; 130°C). (Found: C, 30.83; H, 4.69; Br, 41.0%).

Reaction of 2 Mol Equivalents of $NaOCH_3$ with Compound I. Compound I (110 g, 0.45 mol) was added to a solution of 21.6 g (0.94 mol) of sodium in 310 m*l* of dry methanol. The mixture was allowed to stand at room temperature overnight and then treated as has been described above. The product (47 g), which boiled at 43.5—54.0°C/7 mmHg, was found by gas chromatography to contain compounds II, III, and α-MMOA in 10, 43, and 47 mol% respectively. Compound III was purified by gas chromatography. Found: C, 48.29; H, 8.08%. Calcd for $C_6H_{12}O_4$: C, 48.62; H, 8.16%. NMR (CCl_4, 60 MHz) : τ= 6.29 (s, $COOCH_3$), 6.63 and 6.68 (s, α and β OCH_3, respectively), 6.08—6.67 (m, α and β C*H*).

Reaction of 2.5 Mol Equivalents of $NaOCH_3$ with Compound I. Compound I (106 g, 0.43 mol) was similarly added to a solution of 25.3 g (1.1 mol) of sodium in 400 m*l* of dry methanol. The mixture was kept at room temperature for 10 days, until there were no peaks of compounds II and III in a gas chromatogram, and then worked up as before. Fractional distillation in the presence of 0.5 g of hydroquinone under a reduced pressure of nitrogen gave α-MMOA. Bp 50.5—51.0°C/10 mmHg (lit, 51.5—52.0°C/11 mmHg[3)]). Yield, 38.9 g (78%). Found: C, 51.76; H, 6.94%. Calcd for $C_5H_8O_3$: C, 51.72; H, 6.94%. NMR (CCl_4, 60 MHz): τ=6.23 (s, $COOCH_3$), 6.39 (s, OCH_3), 4.78 and 5.47 d, *J*=2.4 Hz, $=CH_2$). IR (liq.): 3130 (w, $\nu_{=CH_2}$), 1625) cm^{-1} (vs, $\nu_{C=C}$). The hydrogenationof the ester was performed by Raney nickel to give methyl α-methoxypropionate. Bp 130.5—131.0°C. NMR (CCl_4, 60 MHz): τ=8.67 (d, *J*=6.8 Hz, CH_3), 6.01—6.37 (q, C*H*), 6.27 (s, $COOCH_3$), 6.67 (s, OCH_3). α-MMOA was converted by aqueous ammonia into α-methoxyacrylamide. Mp 108—110°C(lit, 109°C[3)]), after recrystallization from benzene. The hydrogenation of α-methoxyacrylamide catalyzed by palladium chloride gave α-methoxypropionamide. Mp 83—84°C, after recrystallization from ligroin. NMR ($CHCl_3$, 60 MHz) : τ=8.53 (d, *J*=6.9 Hz, CH_3), 6.00—6.35 (q, C*H*), 6.51 (s, OCH_3).

Reactions of $NaOCH_3$ with Compounds II and III. Compounds II and III were added to methanolic $NaOCH_3$. The reactions were followed by taking gas chromatograms of the reaction mixtures using calibration curves.