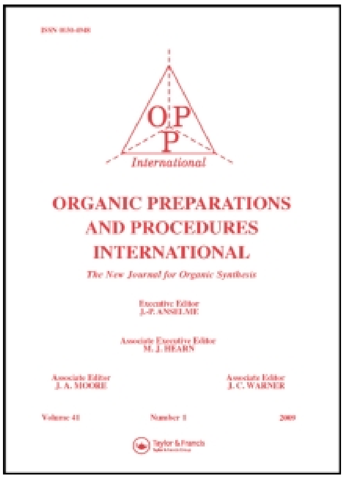

Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

2-METHOXY-1,3-BUTADIENE

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To cite this Article Dolby, L. J. and Marshall, K. S.(1969) '2-METHOXY-1,3-BUTADIENE', Organic Preparations and Procedures International, 1: 4, 229 — 233
To link to this Article: DOI: 10.1080/00304946909458388
URL: http://dx.doi.org/10.1080/00304946909458388

ORGANIC PREPARATIONS AND PROCEDURES 1(4), 229-233 (1969)

2-METHOXY-1,3-BUTADIENE[1a]

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$$CH_3OCH_2CH_2C(OCH_3)_2CH_3 \xrightarrow[\Delta]{H^+} CH_2{=}CHC(OCH_3){=}CH_2 + 2\ CH_3OH$$

2-Methoxy-1,3-butadiene has long been used in Diels-Alder reactions.[2] Recently, a novel condensation between 2-methoxy-1,3-butadiene and enols or phenols has been uncovered.[3] Owing to the difficulty we encountered in the preparation of 2-methoxy-1,3-butadiene, this procedure has been submitted.

The preparation of 2-methoxy-1,3-butadiene from the thermal decomposition of 1,3,3-trimethoxybutane has previously been reported.[4,5] Dykstra[4] used vinylacetylene as a source of 4-methoxy-2-butanone which was converted to 1,3,3-trimethoxybutane. Norris, et al.[5,6] prepared 1,3,3-trimethoxybutane by the direct catalytic addition of methanol to vinylacetylene. The present preparation[7] does not involve the use of vinylacetylene which is hard to obtain and handle in the laboratory, but uses methyl vinyl ketone, methyl orthoformate and anhydrous methanol for the direct preparation of 1,3,3-trimethoxybutane.

Experimental[8]

1,3,3-Trimethoxybutane.--Into a 4000 ml Erlenmeyer flask were placed methyl vinyl ketone (350 g, 5.00 moles), methylorthoformate (884 g, 8.34 moles), and anhydrous methanol (480 g, 15.00 moles). To this solution was added with stirring 206 mg of p-toluenesulfonic acid monohydrate (sometimes more acid was needed to initiate the reaction). After a five-minute induction period, the reaction became highly exothermic and the solution turned dark green in color. The stoppered flask was allowed to stand at room temperature for twelve days.

To the dark green solution was added 10 g of anhydrous sodium carbonate. The solution turned deep red in color, and the mixture was magnetically stirred for three days. The solids were filtered off, and the excess methanol and methyl formate were removed by simple distillation at atmospheric pressure; the head temperature was maintained below 70°. The dark residue was filtered a second time and then fractionated through a 20" helix-packed column using a nitrogen bleed. The yield of 1,3,3-trimethoxybutane boiling at 57-58° at 18 mm (lit:[4] bp 61-63° (20 mm)) was 576.7 g or 78% of the theoretical: n_D^{20} 1.4108 (lit:[4] n_D^{20} 1.4112); ir $\tilde{\nu}_{max}^{CCl_4}$ 2830 cm^{-1} (-OCH_3, sym. stretching), a group of five bands 1190-1050 cm^{-1};[9] nmr (CCl_4) δ1.31 (s, 3H), 1.98 (t, J=7.5 Hz, 2H), 3.22 (s, 6H), 3.38 (s, 3H) and 3.49 (t, J=7.5 Hz, 2H).

2-Methoxy-1,3-butadiene.-- Into a 250 ml 3-neck flask with a 500 ml pressure equalizing dropping funnel, a 25 cm asbestos wrapped vigreux column, and a condenser system were placed 47 mg of potassium acid sulfate (powdered reagent crystals) and approx. 40 g of 1,3,3-trimethoxybutane. The distillation apparatus was protected from moisture with a calcium chloride drying tube. The distillation of the decomposition products began when the pot flask was heated with a preheated (145-150°) wax bath. The distillate was collected in a 500 ml round bottom flask cooled in a dry ice-acetone bath. The remaining 1,3,3-trimethoxybutane (total amount 296 g, 2.00 moles) was added dropwise at such a rate as to keep approx. 40-50 g of material in the pot flask. The addition period of six hours can be shortened by the addition of additional potassium acid sulfate (approx. 20 mg added when the distillation slows down, usually four to six times). The bath was maintained at 150° during the addition period.

The clear distillate was allowed to warm to room temperature and washed very carefully with 100 ml water (mixture is poured back and forth in a separatory funnel, not shaken). If layers do not separate, additional water was added. This procedure was repeated until the volume of the organic layer remained constant, usually three or four times. The organic layer was filtered through a fluted filter paper to remove excess water and stored overnight in a coldroom over 4Å molecular sieves which dry and remove remaining methanol from the distillate.

A small amount of hydroquinone was added and the distillate was fractionated through a 36" spiral Podbielniak column at atmospheric pressure. The yield of 2-methoxy-1,3-butadiene boiling at 75-76° at 754 mm (lit:[4] bp 75° (760 mm)) is 74.9 g or 44.5% of theoretical: n_D^{20} 1.4434 (lit:[4] n_D^{20} 1.4442); ir $\tilde{\nu}_{max}^{CCl_4}$ 1845, 1650, 1580, 1418, 982, 920, and 895 cm^{-1}; nmr (CCl_4) δ3.55 (s,3H), 4.08 (s, 2H), and 4.83 to 6.38 (complex ABX pattern, 3H).

The fraction boiling at 80-96° (754 mm) contained 61.6 g of the decomposition intermediate 2,2-dimethoxy-1-butene, n_D^{20} 1.4104 (lit:[4] n_D^{20} 1.4038); nmr (CCl_4) δ1.28 (s, 3H), 3.11 (s, 6H), and 4.98 to 5.96 (complex ABX pattern, 3H, pattern different from that of 2-methoxy-1,3-butadiene), which can be re-pyrolyzed to increase the total yield of diene to 50-55% of theoretical.

1,3,3-Triethoxybutane and 2-ethoxy-1,3-butadiene have also been prepared by this procedure in comparable yields.

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1a The authors gratefully acknowledge financial support from the National Science Foundation (Grant 1266 GP3822) and a Public Health Service Career Program Award (1-K3-NB-28,105) from the National Institute of Neurological Diseases and Blindness.

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9 Characteristic of ketals, see K. Nakanishi, "Infrared Absorption Spectroscopy, Practical", p.36, Holden-Day, San Francisco, California, 1962.

(Received March 25, 1969)