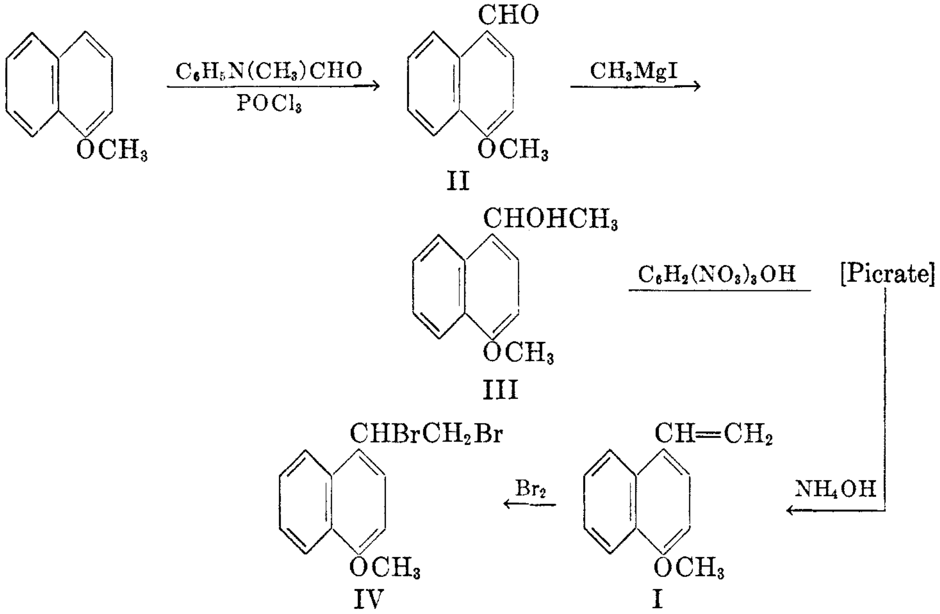
[Communication No. 1394 from the Kodak Research Laboratories]

4-METHOXY-1-VINYLNAPHTHALENE

J. A. VanALLAN

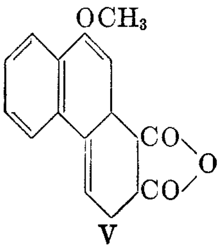
Received March 8, 1951

The hitherto unknown 4-methoxy-1-vinylnaphthalene (I), which was needed for another problem, has been synthesized by converting the methyl ether of α-naphthol to the aldehyde (II) by the N-methylformanilide-phosphorus oxychloride procedure (1), transforming the aldehyde to the carbinol (III) with methylmagnesium iodide, and dehydrating the carbinol with picric acid; the picrate of the unsaturated ether is an intermediate product.



The yields are good at each step. A synthesis of the ether (I) from the aldehyde (II) by condensation with malonic ester, saponification, and decarboxylation gave a low yield.

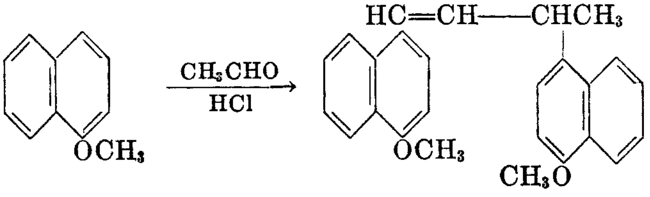
For reference compounds, the dibromide (IV) and the addition product (V) with maleic anhydride were prepared without difficulty; the position of the double bonds on the adduct (V) was inferred by analogy with similar substances.



V

The use of picric acid as a dehydrating agent appears to be a useful innovation; no similar instances have come to our attention.

The isomeric 6-methoxy-1-vinylnaphthalene has been prepared by a long procedure (2, 3) which is not necessary for the 4-isomer. The attempted preparation of 1-vinyl-4-methoxynaphthalene from 1-methoxynaphthalene, acetaldehyde, and hydrogen chloride was unsuccessful; the product appears to be the dimer (VI) comparable to anethole dimer (4). This type of reaction has been applied to anisole successfully, giving 4-vinylanisole (5).



VI

EXPERIMENTAL

4-Methoxynaphthaldehyde (II). This substance was made from 1-methoxynaphthalene essentially by the procedure for 2-ethoxy-1-naphthaldehyde (1). The yield of product, b.p. 168–170°/2 mm. (m.p. 34°), was 80%. The phenylhydrazone melted at 113°.

4-Methoxy-1-(1′-hydroxyethyl)naphthalene (III). A solution of methylmagnesium iodide was prepared from 22 ml. of methyl iodide and 8.75 g. of magnesium in 150 ml. of dry ether. The aldehyde (28.6 g.) in 50 ml. of ether was slowly added; at the completion of the addition it was stirred for 30 minutes longer. The magnesium complex was decomposed with a solution of 24 g. of ammonium chloride in 300 ml. of water. The ether layer was separated and allowed to evaporate spontaneously. There was thus obtained 29 g. of crude carbinol, m.p. 52–55°. After recrystallization from ligroin, it melted at 57°.

Anal. Calc'd for $C_{13}H_{14}O_2$: C, 77.2; H, 6.9.
Found: C, 77.5; H, 7.1.

Attempts to make the picrate of the above carbinol resulted in dehydration to give the picrate of 1-vinyl-4-methoxynaphthalene. The carbinol (19.2 g.) in 40 ml. of methanol was mixed with 12 g. of picric acid in 50 ml. of methanol and warmed until solution was complete. On chilling overnight, 17.9 g. of picrate separated; m.p. 101–102°. It formed reddish-orange crystals, m.p. 102°, upon recrystallization from methanol.

Anal. Calc'd for $C_{19}H_{15}N_3O_8$: C, 54.4; H, 3.6.
Found: C, 54.4; H, 3.5.

4-Methoxy-1-vinylnaphthalene (I). A mixture of 100 g. of the picrate, 1700 ml. of water, and 220 ml. of concentrated ammonium hydroxide was warmed on the steam-bath until all of the picric acid had entered into solution. The oil which was left was extracted with 100 ml. of chloroform and the chloroform extract was washed with water and dried over Drierite. After the chloroform was removed, under reduced pressure, the residue boiled sharply at 155–157°/7 mm.; the yield was 38 g. (94%). A picrate was made, and was found to be identical with the starting material.

4-Methoxy-1-(1′,2′-dibromoethyl)naphthalene (IV). The vinyl compound (0.5 g.) in 0.5 ml. of chloroform was treated with bromine in ligroin until a faint trace of bromine remained; the product crystallized out. It was recrystallized from chloroform-ligroin; m.p. 103°.

Anal. Calc'd for $C_{13}H_{12}Br_2O$: Br, 46.5. Found: Br, 46.0.

Maleic anhydride addition product of 4-methoxy-1-vinylnaphthalene (V). A mixture of 2.8 g. of the vinyl compound, 1.4 g. of maleic anhydride, and 10 ml. of toluene was allowed to stand at 45° for 60 hours; 1.7 g. of product separated. On recrystallization from acetic acid, it melted at 197°.

It decolorizes alkaline permanganate instantly.

Anal. Calc'd for $C_{17}H_{14}O_4$: C, 72.3; H, 5.0.
Found: C, 71.8; H, 4.9.

Dimer of 1-vinyl-4-methoxynaphthalene. A mixture of 39.5 g. (0.25 mole) of 1-methoxynaphthalene, 11 g. of paraldehyde, and 150 ml. of benzene was treated at 18° with a slow current of hydrogen chloride. After 1.5 hours, the reaction was complete; 5 ml. of water was separated, and the benzene was removed *in vacuo.* The residue was distilled and a forerun was collected up to 140°/5 mm.; 6 g., 140–210°/5 mm.; 14 g., 210–230°/5 mm. The last fraction was recrystallized from acetic acid; m.p. 113–114°.

Anal. Calc'd for $C_{26}H_{24}O_2$: C, 84.8; H, 6.5; M. W., 368; OCH_3, 16.8.
Found: C, 84.7; H, 6.3; M. W., 366 (in boiling benzene); OCH_3, 17.0.

4-Methoxynaphthylacrylic acid. The method described (6) for ethyl benzalmalonate was used to effect the condensation of 4-methoxynaphthaldehyde with ethyl malonate. A mixture of 100 g. of ethyl malonate, 133 g. of 4-methoxynaphthaldehyde, 1 ml. of acetic acid, 7 g. of piperidine, and 200 ml. of benzene was refluxed under the ester column until 13 ml. of water was collected; the benzene was then removed under reduced pressure. The residual product was dissolved in a solution made up from 200 g. of potassium hydroxide, and 200 ml. each of water and ethanol. After refluxing overnight, the alcohol was removed under a vacuum, 200 ml. of water was added, and the alkaline solution was filtered and acidified with hydrochloric acid. This crude yellow product, m.p. 187–190°, was mixed with 2 g. of copper carbonate and dry-distilled at 15 mm.; 41 g. of distillate, b.p. 185–200°/40 mm., was collected. Redistillation gave 23 g. of 4-methoxyvinylnaphthalene, b.p. 118–121°/2 mm. It was identified as the picrate.

SUMMARY

A procedure for the preparation of 4-methoxy-1-vinylnaphthalene in good yield is described.

The use of picric acid as a dehydrating agent for a secondary alcohol may be an innovation.

ROCHESTER, NEW YORK

REFERENCES

(1) *Org. Syntheses*, **20**, 11 (1940).
(2) COHEN, COOK, AND HEWETT, *J. Chem. Soc.*, 657 (1934); 451 (1935).
(3) COHEN AND WARNER, *J. Chem. Soc.*, 1319 (1937).
(4) GOODALL AND HAWORTH, *J. Chem. Soc.*, 2482 (1930).
(5) *Org. Reactions*, **1**, 73 (1942).
(6) *Org. Syntheses*, **25**, 42 (1945).