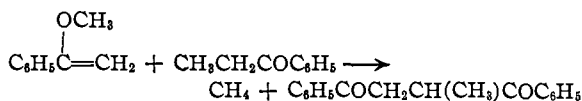


[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Condensation of α -Methoxystyrene with Hydrocarbons

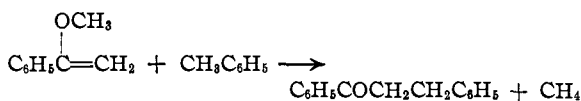
BY M. A. SPIELMAN AND C. W. MORTENSON

This paper is concerned with a novel type of condensation reaction in which α -methoxystyrene takes part. Methane is eliminated and the product is a phenacyl derivative of the other reactant. An example is the condensation of α -methoxystyrene with propiophenone to form 1,2-dibenzoylpropane.¹



This is a side reaction in the molecular rearrangement of α -methoxystyrene to propiophenone.²

In the present work it was found that α -methoxystyrene condenses not only with ketones but also with hydrocarbons. When the unsaturated ether is heated with toluene, methane appears as a gaseous product, and β -phenylpropiophenone results. Increase in the proportion of



hydrocarbon greatly favors the condensation reaction over the rearrangement as might be predicted on the basis of kinetic studies.³ For example, when equimolecular amounts of toluene and the unsaturated ether are heated, the condensation proceeds only to the extent of 8% of the theoretical, but an eighty-fold increase in the amount of toluene raises the yield of condensate to 35%.

Mesitylene, ethylbenzene and diphenylmethane also undergo the condensation. With diphenylmethane a small amount of *sym*-tetraphenylethane appears as a by-product, but no hydrogen, ethane or ethylene could be detected in the methane.

Incidental to determining the type of grouping in the hydrocarbon necessary for condensation, negative results were obtained with triphenylmethane, benzene and diphenyl. *p*-Nitrotoluene which, in the ordinary sense, has an "active" methyl group also failed to react. 4-Methoxytoluene behaved much like toluene. Cyclohexane

was tested as an example of a saturated hydrocarbon, and the experiment led to ω -cyclohexylacetophenone in 42.7% of the theoretical yield. This unexpected result with cyclohexane is probably to be attributed as much to the large number of groups available for condensation as it is to the ability of the individual methylene groups to condense.

Experimental Part⁴

The α -methoxystyrene was synthesized by a method previously reported.⁵ All heating was done in steel bombs, electrically heated and controlled by a Micromax regulator.

Condensation with Toluene.—A mixture of 10.7 g. of α -methoxystyrene and 845 g. of toluene was heated to 250° for twenty-four hours. Toluene and propiophenone were removed by distillation, after which crystallization of the residue yielded 6.0 g. (35%) of β -phenylpropiophenone; m. p. and mixed m. p. 72–73°. The oxime melted at 87–88°.⁶

A second run, using 10.8 g.⁷ of α -methoxystyrene and 62 g. of toluene, yielded 5.5 g. of propiophenone, 4.2 g. or 24.8% of β -phenylpropiophenone and 0.15 g. of 1,2-dibenzoylpropane.¹

Condensation with 4-Methoxytoluene.—A mixture of 168 g. of 4-methoxytoluene and 9.6 g. of α -methoxystyrene was heated to 200° for fifteen hours and then to 300° for three hours. From a non-volatile residue of 7.4 g. was isolated 4.5 g. (26%) of β -(*p*-anisyl)-propiophenone by crystallization from alcohol and from petroleum ether. It melted at 67–68°, and the mixed melting point was not depressed by a sample prepared by the catalytic hydrogenation of *p*-anisalacetophenone.⁷ The semicarbazone melted at 135–136°, which is 17° higher than reported by Bargellini and Bini.⁸

Condensation with Diphenylmethane.—Ninety-eight grams of the hydrocarbon and 10.8 g. of the ether were heated to 250° for ten hours. After distillation of the volatile part there remained 11.5 g. of residue which yielded 0.5 g. of *sym*-tetraphenylethane by washing with cold ether; m. p. and mixed m. p., 211–212°. Concentration of the mother liquor gave 6.4 g. (27.3%) of β,β -diphenylpropiophenone; m. p. and mixed m. p., 91–92°. The distillable fraction gave 1.6 g. of acetophenone, 2.2 g. of propiophenone and 90.3 g. of diphenylmethane. The gas was collected and analyzed in the conventional Orsat apparatus. There was no unsaturated hydrocarbon and the ratio of contraction on burning to volume of carbon dioxide formed was 2.00, the theoretical figure for methane.

(4) Some of the preliminary experiments were carried out by Miss Margaret Chittenden.

(5) Lauer and Spielman, *THIS JOURNAL*, **53**, 1533 (1931).

(6) Kohler, *Am. Chem. J.*, **42**, 391 (1909).

(7) Pfeiffer and Negreanu, *Ber.*, **50**, 1473 (1917).

(8) Bargellini and Bini, *Gazz. chim. ital.*, [2] **41**, 444 (1911).

(1) Lauer and Spielman, *THIS JOURNAL*, **55**, 4923 (1933).

(2) Claisen, *Ber.*, **29**, 2931 (1896); Claisen and Haase, *ibid.*, **33**, 3778 (1900).

(3) MacDougall, Lauer and Spielman, *ibid.*, **55**, 4089 (1933).

Condensation with Mesitylene.—A mixture of 130 g. of mesitylene and 9.5 g. of α -methoxystyrene was heated to 250° for ten hours. The non-volatile fraction weighed 9.5 g. and manipulation with methanol yielded 20.8% of the theoretical amount of ω -(α -mesityl)-acetophenone; m. p. 54–55°.

Anal. Calcd. for $C_{17}H_{18}O$: C, 85.7; H, 7.6. Found: C, 85.7; H, 7.8.

The oxime gave considerable trouble in that a sharp melting point was difficult to attain. The highest value was 118°.

Anal. Calcd. for $C_{17}H_{18}NO$: C, 80.6; H, 7.6. Found: C, 80.4; H, 7.9.

Condensation with Ethylbenzene.—Sixty-five grams of hydrocarbon and 8.6 g. of the ether at 250° for ten hours yielded 3.4 g. (23.6%) of β -phenylbutyrophenone; m. p. 74°; m. p. of the oxime 93.5–94°.⁹

Condensation with Cyclohexane.—A mixture of 8.5 g. of α -methoxystyrene and 263 g. of cyclohexane was heated to 250° for twenty-four hours. Fractionation yielded

(9) Kohler, *Am. Chem. J.*, **31**, 642 (1904).

5.4 g. or 42.7% of ω -cyclohexylacetophenone as a colorless liquid; b. p. 117–118° at 1 mm.; n_D^{25} 1.5330. After freezing it melted at 17–18°.

Anal. Calcd. for $C_{14}H_{18}O$: C, 83.1; H, 9.0. Found: C, 82.9; H, 9.2.

The oxime formed needles melting at 104.5–105.5°.

Anal. Calcd. for $C_{14}H_{18}NO$: C, 77.4; H, 8.8. Found: C, 77.6; H, 9.1.

For comparison, a sample of the ketone was synthesized by condensing cyclohexylacetyl chloride with phenylzinc chloride. The product, isolated in 64% yield, was identical with the above compound.

Summary

α -Methoxystyrene undergoes a condensation reaction with toluene, mesitylene, ethylbenzene, diphenylmethane, 4-methoxytoluene and cyclohexane. Methane is eliminated and a phenacyl derivative is formed.

MADISON, WISCONSIN

RECEIVED JANUARY 23, 1939

[CONTRIBUTION NO. 410 FROM THE FOOD RESEARCH DIVISION, BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

Volatile Flavor and Fixed Acids of Montmorency Cherry Juice¹

BY E. K. NELSON AND A. L. CURL

The juice of Montmorency cherries was obtained by pressing the carefully pitted fruit in Geneva, New York.¹ The juice was pasteurized and shipped to Washington by express, arriving in good condition, with no evidence of fermentation.

ANALYSIS OF THE JUICE

	G. per 100 cc.
Total acidity, as malic	1.4
Total solids	14.7
Total sugars as invert, after inversion	9.91
Alcohol precipitate	0.037
Volatile acids (as acetic)	.0012
Ash	.432

The juice (94 liters) was distilled *in vacuo* at 54°, with a trap surrounded by solid carbon dioxide and alcohol to recover any volatile material which might pass through the condenser. Nineteen liters of distillate was collected. The residual liquor in the still was then devoid of odor. The distillate was cohobated in the same manner until a distillate of 500 cc. was obtained. This final distillate, which had a strong flavor suggestive of benzaldehyde, was treated with 1 g. of semicarbazide hydrochloride and 1.5 g. of sodium acetate and distilled to small volume. The distillate was reserved for further examination. The residual liquor in the distilling flask was extracted with ether. On evaporation of the ether, 0.4098 g. of semicarbazone

was obtained. This, recrystallized once from alcohol, melted at 214°, and a mixture with benzaldehyde semicarbazone showed no depression in melting point. The weight of semicarbazone corresponded to 0.27 g. of benzaldehyde, or 2.8 mg. per liter of cherry juice.

Since the appearance of the flow of the first runnings through the condenser indicated the presence of some alcohol, the distillate from the semicarbazone was carefully distilled through a twenty-inch (51-cm.) Widmer column. A fraction boiling at 75–80° was thus obtained. This was redistilled from a small flask through a Vigreux column and 10 cc. of liquid boiling at 73–76° was recovered. By the colorimetric method² this was found to consist of a mixture of 35% methyl alcohol with 65% of ethyl alcohol.

After distillation of the alcohol (the tails being returned to the aqueous solution), the solution was extracted with ether. On careful evaporation of the ether at room temperature, a very small residue remained which had a strong rose-like odor. This was shaken up with 10% sodium hydroxide solution and the insoluble portion extracted with ether. The ether, on evaporation, left a residue of 0.0067 g. It had a rose-like odor and when oxidized with potassium bichromate and sulfuric acid gave a very faint lemon-like odor, indicating that a very small amount of geraniol might be present.

The sodium hydroxide solution, acidified and extracted with ether, afforded 0.0016 g. of material which did not give a phenol reaction with ferric chloride.

(1) Cherry juice was prepared by E. A. Beavens in the fruit juice laboratory of the Food Research Division in Geneva, New York.

(2) "Official and Tentative Methods of Analysis," A. O. A. C., 4th ed., p. 578.