THE BENZOATE AND THE METHYL ETHER OF 4-HYDROXYCYCLOHEXENE¹

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Abstract

Satisfactory preparations, from hydroquinone and its monomethyl ether respectively, were devised for the above compounds which were thought to be new. The methyl ether of 4-hydroxycyclohexene was an oil, n_D^{20} 1.4566, boiling at 136°C.; the uncrystallized benzoate had n_D , 1.5360 and b.p. 149°C. at 12 mm. pressure.

Introduction

The original objective of the work was to study the *cis-trans* isomerism of the four cyclohexane-1,2,4-triols, members of which have been prepared in crude form by Senderens and Aboulenc (7) and by Zelinsky and Titowa (9). Circumstances, however, made it necessary to discontinue the research after preparing 4-hydroxycyclohexene, its methyl ether, and its benzoate (structures III), any of which would yield one pair or another of the desired triols by a directed *cis* or *trans* hydroxylation of the double bond.

The high pressure hydrogenation of hydroquinone (I, R = H) over a Raney nickel catalyst gave up to 96% yields of crude, crystalline cyclohexane-1, 4-diol (II, R = H, quinitol), the *cis-trans* isomers of which have been studied on several occasions (1, 2, 4, 5). Distillation of the quinitol over a little concentrated sulphuric acid (6) yielded the known substance 4-hydroxycyclohexene (III, R = H), the new monobenzoate of which was then readily prepared



Helfer's (3) methylation of hydroquinone gave a 40 to 44% yield of the crystalline monoether (I, $R = CH_3$), which on hydrogenation (3, 8) gave 66 to 83% yields of the methoxycyclohexanols (II). Dehydration of the latter resulted in the new compound (III, $R = CH_3$) in 58% yield.

Manuscript received June 21, 1951.

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Experimental

here reported may be slightly higher than the correct values.

Benzoate of 4-Hydroxycyclohexene

A solution, 1100 cc., of pure hydroquinone, 525 gm., in ethanol was hydrogenated over 80 gm. of Raney nickel catalyst at 170°C. and 3000 p.s.i., or substantially as recommended by Coops, Dienske, and Aten (2). The product, boiling correctly at 140° to 143°C. at 8 mm., crystallized at once to 527.5 gm. (96%) of the mixed *cis* and *trans*-cyclohexane-1,4-diols. A 527.5 gm. sample of the diols, heated with 2 cc. of 65% sulphuric acid in a bath at 190° to 200°C. (6) yielded a distillate containing water, cyclohexadiene, and 168 gm. (38%) of crude 4-hydroxycyclohexene boiling at 154° to 157°C. Redistillation gave the pure substance with the correct boiling point of 164° to 165°C.

A cold solution of 87.2 gm. (0.89 mole) of the 4-hydroxycyclohexene in 200 cc. of pyridine was mixed with 128 gm. (0.91 mole) of benzoyl chloride diluted with 350 cc. of chloroform. The product, recovered after the mixture had remained for 16 hr. at room temperature, was twice distilled at 12 mm. pressure through a Vigreux column. Cyclohexene-4-ol benzoate was a colorless oil boiling at 149° to 150°C. (12 mm.); d_4^{20} , 1.083 and n_D^{20} , 1.5360. Found: C, 77.3%, H, 6.9%; mol. refraction, 58.23. Calcd. for C₁₃H₁₄O₂: C, 77.2%; H, 7.0%; mol. refraction, 57.64.

The benzoate was insoluble in water but soluble in benzene, alcohol, acetone, and chloroform. It decolorized dilute solutions of bromine in carbon tetrachloride, and of aqueous potassium permanganate, instantly.

4-Methoxycyclohexene

Hydroquinone, 660 gm., was methylated in two batches at room temperature with 574 cc. of technical dimethyl sulphate in presence of 600 gm. of sodium hydroxide and 3600 cc. of water (3). *p*-Dimethoxybenzene, 130.8 gm., was separated by filtration, and, after recovery, the *p*-methoxyphenol remained as a light brown oil boiling at 118° to 130°C. at 8 mm. pressure. The distillate rapidly solidified to crystals melting at 55° to 57°C.; yield, 330.6 gm. or 44%. Helfer (3) obtained a 55% yield of material melting at 53°C. The high pressure hydrogenation of the *p*-methoxyphenol, 771.8 gm., with 100 gm. of Raney nickel catalyst was as described by Van Duzee and Adkins (8) and proceeded rapidly at 180° to 190°C. An 83% yield (665.7 gm.) of crude 4-methoxycyclohexanol boiling in the range 85° to 120° (7 mm. pressure) was obtained.

A total of 603.6 gm. of this crude product was distilled at 205°C. in three batches, each containing about 2 cc. of 50% sulphuric acid (6). Redistillation yielded first a mixture (91 gm.) of water with cyclohexadienes and then 257 gm.

of pure 4-methoxycyclohexene boiling at 135.5° to 136.5°C. (760 mm.). Redistillation of the still residue with an additional 2 cc. of 50% sulphuric acid produced an additional 42.0 gm. of pure material and increased the yield to 58%.

4-Methoxycyclohexene was a colorless oil with d_4^{20} , 0.9009 and n_D^{20} , 1.4566. Found: C, 74.7%; H, 10.4%; mol. refraction, 33.89. Calcd. for C7H12O: C, 74.9%. H, 10.8%; mol. refraction, 33.54. The compound was soluble in organic liquids but not in water, and instantly decolorized bromine in carbon tetrachloride, or dilute aqueous potassium permanganate.

Acknowledgment

The authors thank the National Research Council of Canada not only for grants-in-aid but also for the Studentships and Fellowship awarded to two of them (C. J. G. and R. Y. M.).

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