

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF PENNSYLVANIA]

Aromatization Studies. IV. Palladium Dehydrogenation of Arylcyclohexenones to Phenols

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We have been interested for some time in the aromatization to phenols of alicyclic ketones which are isomers of aromatic compounds, and in dehydrogenations leading to phenols. A palladium-carbon catalyst is the most effective agent for bringing about alicyclic-aromatic isomerizations,^{1,2} and this catalyst is also an extremely effective dehydrogenation agent. In order to obtain additional information about catalytic dehydrogenation as applied to hydroaromatic ketones, a study has been made of the dehydrogenation of several arylcyclohexenones to the corresponding phenols in various solvents.

It has been known for some time that palladium dehydrogenations of hydroaromatic ketones can be carried out conveniently and in satisfactory yield by using boiling hydrocarbon solvents as a reaction medium. For example, Mosettig³ found that 1- and 4-ketotetrahydrophenanthrene could be dehydrogenated to the corresponding phenols in boiling xylene or naphthalene with palladium-black. 1-Phenanthrol was obtained in about 85% yield after twenty-four hours in boiling naphthalene; yields of 38, 53 and 70% were obtained in xylene after twenty-four, forty-eight and ninety-six hours, respectively. 4-Phenanthrol was obtained in 57% yield after heating the parent ketone for twenty-four hours in xylene with palladium-black. Linstead⁴ prepared 4-phenanthrol in 62% yield, using a palladium-carbon catalyst in boiling *p*-cymene (seven and one-half hours at 240°).

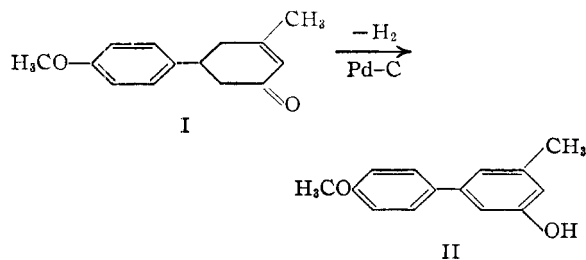
Most of the present experiments were carried out with 3-methyl-5-(*p*-methoxyphenyl)-2-cyclohexen-1-one (I). The hydrocarbon solvents used were ethylbenzene, isopropylbenzene, *p*-cymene and triethylbenzene. Although it has been customary not to employ non-hydrocarbon solvents in reactions of this kind, we have found that dehydrogenations can also be carried out in phenyl ether, ethylene glycol and diethylene glycol mono-

ethyl ether. The yields obtained in the latter two solvents, however, were considerably lower than those obtained in hydrocarbon solvents. Phenyl ether is a satisfactory solvent, although in this case its use offered no particular advantage since the yield of phenol (II) did not increase appreciably with increasing reaction temperature above about 175°. With a reaction time of two hours, the yields in *p*-cymene (b. p. 177°), triethylbenzene (b. p. 214°), and phenyl ether (b. p. 252°) were 82, 76 and 84% respectively (Table I).

It has generally been accepted that dehydrogenations, particularly of hydroaromatic ketones, carried out in solvents at temperatures up to about 200°, usually require long reaction times to obtain good yields. We have made a qualitative study of the rate of dehydrogenation of 3-methyl-5-(*p*-methoxyphenyl)-2-cyclohexen-1-one (I) in boiling *p*-cymene. With a 5% palladium-carbon catalyst (prepared according to Hartung⁵), a yield of over 60% of phenol (II) was obtained within fifteen minutes (Table I). No attempt was made to investigate a reaction period of less than fifteen minutes, but it is evident that in this case dehydrogenation takes place very rapidly.

TABLE I
DEHYDROGENATION OF 3-METHYL-5-(*p*-METHOXYPHENYL)-2-CYCLOHEXEN-1-ONE

Solvent	B. p., °C.	Time, hr.	Yield of phenol, %
Ethylbenzene	136	2	52
Isopropylbenzene	153	2	52
Cymene	177	0.25	63
Cymene	177	.50	70
Cymene	177	1	78
Cymene	177	2	82
Triethylbenzene	214	2	76
Phenyl ether	252	2	84
Ethylene glycol	197	2	55
Ethylene glycol monoethyl ether	202	2	56



At lower temperatures, in boiling ethylbenzene (b. p. 136°) and isopropylbenzene (b. p. 153°) the dehydrogenation of this ketone (I) also occurs readily, but at a slower rate, as would be expected. Both of these solvents gave about 52% yield of phenol for a two-hour reaction period.

3-Methyl-5-(3',4'-dimethoxyphenyl)-2-cyclohexen-1-one, 3-methyl-5-(2',3'-dimethoxyphenyl)-2-cyclohexen-1-one and 3-methyl-5-(*o*-methoxyphenyl)-2-cyclohexen-1-one were also dehydrogenated in boiling triethylbenzene. The yields of cor-

(1) Horning, *Chem. Rev.*, **33**, 89 (1943).(2) Horning, *J. Org. Chem.*, **10**, 263 (1945).(3) Mosettig and Duvall, *THIS JOURNAL*, **59**, 367 (1937).(4) Linstead and Michaelis, *J. Chem. Soc.*, 1134 (1940).(5) "Organic Syntheses," **26**, 77 (1946).

responding phenols were 86, 70 and 72% respectively, for a two-hour reaction period.

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Experimental

All melting points are corrected.

Palladium-Carbon Catalyst.—The catalyst was prepared according to the method of Hartung,⁶ but the amount of carbon (Norite) was increased to provide a 5% palladium catalyst.

Solvents.—Ethylbenzene, isopropylbenzene, *p*-cymene, phenyl ether and ethylene glycol were Eastman white label materials. Triethylbenzene and diethylene glycol monoethyl ether were Eastman technical and practical grades, respectively. No purification of the solvents was carried out beyond the precaution of redistillation.

3-Methyl-5-(*p*-methoxyphenyl)-phenol (Table I).—To 5.00 g. of 3-methyl-5-(*p*-methoxyphenyl)-2-cyclohexen-1-one in 15 ml. of solvent was added 1.50 g. of 5% palladium-carbon catalyst. The mixture was maintained under vigorous reflux for two hours (or for a shorter specified period). After cooling to about 50°, the catalyst was removed by filtration and washed with four 5-ml. portions of hot ethyl acetate. The solvent-ethyl acetate solution was extracted once with 40 ml. and then twice with 20-ml. portions of Claisen solution.⁶ The combined extracts were washed with 20 ml. of benzene, and the benzene was added to the original solution. The solvent-ethyl acetate-benzene solution was extracted with four 20-ml. portions of Claisen solution. The alkaline extracts were combined, washed with petroleum ether, and diluted with 160 ml. of water. Twenty milliliters of concentrated hydrochloric acid was added; the solution was then chilled in ice and neutralized with carbon dioxide. The phenol crystallized immediately; after chilling for several hours the product was removed by filtration, washed well with water and air-dried.

The crude phenol usually retained traces of solvents, and was purified by trituration with petroleum ether (35–60°). After filtration, washing, and drying, the crude product was weighed to determine the yield (Table I). The products obtained in this fashion were in the form of slightly discolored flakes. Melting points of all samples were above 113°.

Recrystallization was effected from ethyl acetate-petroleum ether. The colorless phenol melted at 115.5–117°.

Anal. Calcd. for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.35; H, 6.76.

The **benzoate** was prepared by the usual Schotten-Baumann procedure; m. p. 115–116°.

Anal. Calcd. for $C_{21}H_{18}O_3$: C, 79.22; H, 5.70. Found: C, 79.37; H, 5.72.

In preliminary experiments it was found that this phenol could not be extracted completely from organic solvents by means of aqueous alkali. Claisen alkali was satisfactory for extraction purposes.

The procedure was modified slightly when ethylene glycol or diethylene glycol monoethyl ether was used as a solvent. After filtration to remove the catalyst the solvent mixture was diluted with ether and washed several times with water. The phenol was then extracted and isolated as usual.

3-Methyl-5-(2',3'-dimethoxyphenyl)-phenol was obtained from 3-methyl-5-(2',3'-dimethoxyphenyl)-2-cyclo-

hexen-1-one by dehydrogenation in the same fashion in boiling triethylbenzene. The reaction period was two hours. The yield was 3.48 g. (70%) of slightly discolored flakes, m. p. 109–111°. Recrystallization from ethyl acetate-petroleum ether gave a colorless sample, m. p. 110–111.5°.

Anal. Calcd. for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.86; H, 6.76.

The **2,4-dinitrophenyl ether** was prepared in the usual fashion; m. p. 108–109° from ethyl acetate-petroleum ether.

Anal. Calcd. for $C_{21}H_{13}O_7N_2$: C, 61.46; H, 4.43. Found: C, 61.56; H, 4.63.

The **aryloxyacetic acid** was prepared as usual; m. p. 88–89° from ethyl acetate-petroleum ether.

Anal. Calcd. for $C_{17}H_{18}O_5$: C, 67.54; H, 6.00. Found: C, 67.63; H, 6.12.

3-Methyl-5-(*o*-methoxyphenyl)-phenol was prepared from 3-methyl-5-(*o*-methoxyphenyl)-2-cyclohexen-1-one; the reaction was carried out in boiling triethylbenzene for two hours. The reaction product was a viscous oil which did not crystallize on standing. It was separated by extraction with ether; the ether solution was dried over anhydrous magnesium sulfate, and the phenol purified by evaporative distillation at 140–160° (1–2 mm.). The yield was 3.6 g. (72%) of a pale yellow, extremely viscous oil.

Anal. Calcd. for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.57; H, 6.51.

The **aryloxyacetic acid** was prepared in the usual fashion; m. p. 118–119° from ethyl acetate-petroleum ether.

Anal. Calcd. for $C_{16}H_{16}O_4$: C, 70.57; H, 5.92. Found: C, 70.87; H, 6.18.

3-Methyl-5-(3',4'-dimethoxyphenyl)-phenol was obtained from the corresponding cyclohexenone in triethylbenzene, with a two-hour reaction period. The yield was 4.3 g. (86%) of slightly discolored material, m. p. 102–105°. Purification was effected by evaporative distillation at 200–220° (1–2 mm.) followed by recrystallization from ether-petroleum ether; m. p. 108–109°, shrinking at 105°.

Anal. Calcd. for $C_{16}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.73; H, 6.48.

The **aryloxyacetic acid** derivative was recrystallized from aqueous ethanol; m. p. 140–141.5°.

Anal. Calcd. for $C_{17}H_{18}O_5$: C, 67.54; H, 6.00. Found: C, 67.41; H, 5.91.

3-Methyl-5-(3',4'-dimethoxyphenyl)-2-cyclohexen-1-one was prepared from veratraldehyde by the procedure published previously.⁷ Condensation of veratraldehyde with ethyl acetoacetate under the usual Knoevenagel conditions yielded ethyl α,α' -diacetyl- β -(3,4-dimethoxyphenyl)-glutarate; a sample of the crude *bis*-ester was removed and crystallized from cyclohexane-ethyl acetate. The colorless ester melted at 136.5–138°.

Anal. Calcd. for $C_{27}H_{28}O_8$: C, 61.75; H, 6.91. Found: C, 61.78; H, 6.86.

Cyclization, saponification and decarboxylation yielded the aryl-2-cyclohexen-1-one; its isolation was accomplished by distillation under reduced pressure; b. p. 202–207° (2 mm.). The yield (on 0.5 mole scale) was 55%. The ketone solidified on standing. Recrystallization from cyclohexane-ethyl acetate yielded colorless blocks, m. p. 88–89°, with previous shrinking.

Anal. Calcd. for $C_{13}H_{12}O_3$: C, 73.15; H, 7.36. Found: C, 73.10; H, 7.51.

The scarlet **2,4-dinitrophenylhydrazone** was recrystallized from benzene-ethyl acetate; m. p. 196–197°.

Anal. Calcd. for $C_{21}H_{22}O_6N_4$: C, 59.15; H, 5.20. Found: C, 59.26; H, 4.99.

(6) A solution of 350 g. of potassium hydroxide in 250 ml. of water, made up to 1 liter with absolute methanol.

(7) Horning and Field, *THIS JOURNAL*, **68**, 384 (1946).

Summary

A study of the dehydrogenation of 3-methyl-5-(*p*-methoxyphenyl)-2-cyclohexen-1-one in boiling solvents with a palladium-carbon catalyst has shown that dehydrogenation to the corresponding phenol occurs readily at temperatures from 136 to 252°. Yields of 78–84% may be obtained in *p*-

cymene, triethylbenzene and phenyl ether, with a reaction time of two hours. The corresponding *o*-methoxyphenyl-, 2,3-dimethoxyphenyl- and 3,4-dimethoxyphenylphenols were also obtained by the same procedure, in yields of 72, 70 and 86%, respectively.

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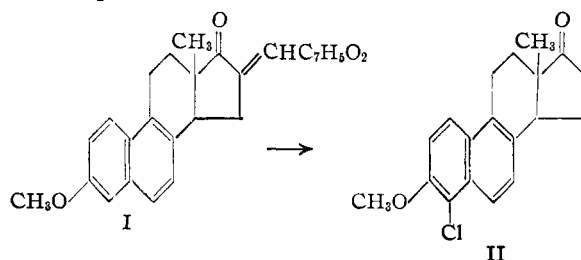
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[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Introduction of the Angular Methyl Group. III. The Alkoxyethylene Blocking Group¹

BY WILLIAM S. JOHNSON AND HARVEY POSVIC²

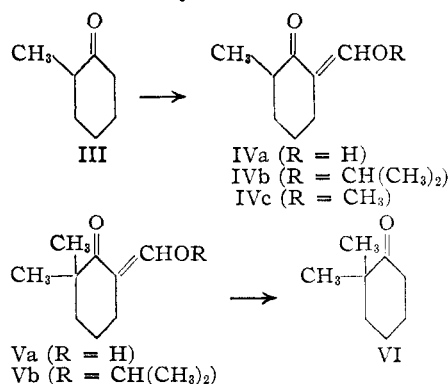
In order to introduce the methyl group into the angular position of a polycyclic ketone like decalone-1, VII, it has been found expedient to protect the methylene group (at C-2) with a substituent which can be removed after methylation. In the first paper of this series³ the use of the benzylidene residue as the blocking group was described. The removal was effected by chlorination of the double bond followed by a series of hydrolytic steps which finally involved the cleavage of an α -benzoyl ketone. Although the method proved to be very successful for the methylation of decalone-1, it promised to present some difficulties in further application because of the uncertainty involved in the direction of cleavage of the intermediate β -diketone. The hydrolysis of 2-benzoyl-6,6-dimethylcyclohexanone, for example, was particularly unfavorable for the preparation of 2,2-dimethylcyclohexanone, VI. Another difficulty was envisaged in the necessity of using a chlorination step. Indeed, Birch, Jaeger and Robinson⁴ applying our method to the removal of the piperonylidene group from the isoequilenin derivative I, found that nuclear chlorination occurred giving rise to a chloro ketone, probably II. Although the halogen could probably be removed by reductive methods, an additional operation would be involved.



In an effort to circumvent some of the aforementioned difficulties the use of the easily re-

movable alkoxyethylene residue ($=\text{CHOR}$) as a blocking group has been investigated. While our study was in progress Robinson and his collaborators^{4,5} reported on the successful use of the methyl-anilinomethylene ($=\text{CHNCH}_3\text{C}_6\text{H}_5$) blocking group. In the present work the methylation of four ketones, III, VII, XIIIa and XIIIb was investigated.

2-Methylcyclohexanone, III, was condensed with ethyl formate in the presence of alcohol-free sodium methoxide to give the hydroxymethylene derivative, IVa, in 72% yield. The best of various methods which were tried for effecting O-alkylation was that of Claisen which involved heating the hydroxymethylene derivative with an alkyl halide and potassium carbonate in acetone.⁶ When methyl iodide was used the product contained only about 20% of the O-methyl ether IVc, the remainder presumably being C-alkylation product. The proportion of O-alkylation could be greatly increased by using isopropyl iodide. The product thus obtained proved to contain at least 84% of the enol ether IVb, the amount being determined by submitting the mixture to the hydrolytic sequence described below for removing the alkoxyethylene group, and isolating the regenerated 2-methylcyclohexanone as the semicarbazone. Methylation of IVb was effected



(5) Birch and Robinson, *ibid.*, 501 (1944).

(6) The details of this method were published by v. Auwers, *Ber.*, 71B, 2082 (1938), eight years after the death of Claisen.

(1) For a preliminary announcement of this work see Johnson and Posvic, *THIS JOURNAL*, 67, 504 (1945).

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(3) Johnson, *THIS JOURNAL*, 65, 1317 (1943).

(4) Birch, Jaeger and Robinson, *J. Chem. Soc.*, 582 (1945).