151. Found: C, 63.60, 63.59; H, 6.04, 6.06; mol. wt.: (ebull.) 308 (ethanol).

The product was further characterized by a study of its infrared spectrum (Fig. 1), which showed clearly the absence of —NH, —SH, —OH, or C═O. Indications were strong that there was no C═S, C═C, or C═N.

A study of the nuclear magnetic resonance spectrum[2] showed hydrogen peaks indicative of only two types of C—H bonds. One occurred at +69 cycles per second (rel. to H_2O) quite characteristic of phenyl hydrogens. The second at +2 cycles was consistent with the shift to be expected for the eight equivalent hydrogen atoms on the 8-membered ring.

The above data indicate that the compound alleged to be 3-phenylthiazetidine is actually a dimer of this compound, probably with an 8-membered ring structure.

Acknowledgments. The author is indebted to Dr. Rudolf Zbinden, who measured and interpreted the infrared spectrum, and to Dr. Catherine Looney, who measured and interpreted the nuclear magnetic resonance spectrum.

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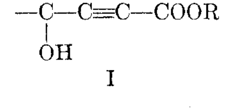
[2] L. H. Meyer, A. Saika, and H. S. Gutowsky, *J. Am. Chem. Soc.*, **75**, 4567 (1953).

Addition of Propargyl Acetal to Cyclohexanone in the Presence of Sodamide[1]

Elmer K. Raunio and Herbert A. Schroeder[2]

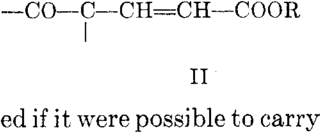
Received October 23, 1956

The addition of the sodio derivative of propiolic esters, NaC≡C—COOR, to the carbonyl group of certain ketones (cyclohexanone, 2-methyl-cyclohexanone, and 2-methyl-2-carbomethoxycyclohexanone) was reported several years ago.[3] In each case the reaction produced an acetylenic carbinol (I). A Michael type addition of certain aromatic ketones to the triple bond of propiolic ester in the presence of sodamide was also reported in the same series of papers.[4] In this case the products were β-substituted acrylic esters (II). The versatility of this reaction could be extended if it were possible to carry out a condensation of this type with aromatic ketones to produce acetylenic carbinols rather than the β-substituted acrylic esters. Since propargyl diethylacetal, $HC{\equiv}C{-}CH(OC_2H_5)_2$, does not have the conjugated structure necessary for a Michael type reaction, it should in all cases react with ketones to produce acetylenic carbinols.



$$\underset{\displaystyle OH}{\overset{|}{\underset{|}{-C}}}{-}C{\equiv}C{-}COOR$$

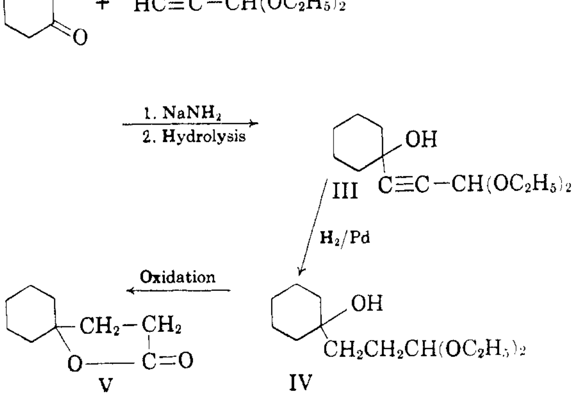
I



$$-CO-\overset{|}{\underset{|}{C}}-CH{=}CH-COOR$$

II

In the present paper we are reporting the successful addition of the sodio derivative of propargyl diethylacetal to cyclohexanone. The reaction with cyclohexanone was carried out by adding cyclohexanone to an ether suspension of the sodium derivative of propargyl diethylacetal. Acid hydrolysis liberated the acetylenic carbinol(III). Since attempted isolation of this acetylenic carbinol by distillation in a vacuum resulted in its polymerization, it was reduced catalytically and the reduction product, β-(1-hydroxycyclohexyl)propionaldehyde diethylacetal (IV) was isolated by vacuum distillation.



The structure of (IV) was established by oxidation to the known lactone of β-(1-hydroxycyclohexyl)-propionic acid (V).

The addition of the sodio derivative of propargyl acetal to the aromatic ketone 6-methoxy-1-tetralone was attempted using the conditions which were successful in the case of cyclohexanone as well as by a variety of other procedures. In no case was it possible to isolate anything other than unreacted 6-methoxy-1-tetralone from the reaction mixture.

EXPERIMENTAL

Reaction with cyclohexanone. A solution of 12.8 g. (0.1 mole) of propargyl acetal[5] in 10 ml. of absolute ether was added to a suspension of sodamide[6] [prepared from 2.3 g. (0.1 mole) of sodium] in approximately 150 ml. of liquid ammonia. A pale yellow precipitate of the sodio salt formed immediately. Cyclohexanone (9.8 g., 0.1 mole) in 10 ml. of absolute ether was added slowly and with continuous shaking. The ammonia was allowed to evaporate from the resulting red solution and the residue was shaken with 500 ml. of a cold saturated solution of ammonium sulfate containing 9.8 g. (0.1 mole) of concentrated sulfuric acid. The mixture was extracted with three 40-ml. portions of ether, the combined ether extract was washed twice with 15-ml. portions of water and the ether was removed by evaporation in a

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[1] This work was supported in part by a Frederick Gardner Cottrell grant from the Research Corporation.

[2] Taken from the Master's Degree thesis of Herbert A. Schroeder, June 1955.

[3] W. E. Bachmann and E. K. Raunio, *J. Am. Chem. Soc.*, **72**, 2530 (1950).

[4] W. E. Bachmann, G. I. Fujimoto, and E. K. Raunio, *J. Am. Chem. Soc.*, **72**, 2533 (1950).

[5] J. C. Sheehan and C. A. Robinson, *J. Am. Chem. Soc.*, **71**, 1436 (1949).

[6] J. A. Nieuwland, T. H. Vaughn, and R. R. Vogt, *J. Am. Chem. Soc.*, **56**, 2120 (1934).

vacuum. The remaining deep orange liquid (weight 18.8 g.) was dissolved in 40 ml. of absolute methanol, 0.1 g. of 5% palladium on activated carbon was added and the mixture was shaken under 45 lb. pressure of hydrogen. Sixteen hundredths mole of hydrogen was absorbed. The catalyst was removed by filtration and the methanol was removed by evaporation in a vacuum. The remaining liquid was distilled in a vacuum. The fraction boiling at 88–93° (0.1 mm.) was collected as β-(1-hydroxycyclohexyl)propionaldehyde diethylacetal. This fraction (17.2 g.) was redistilled and the fraction boiling at 90° (0.1 mm.) was collected as pure material, n_D^{21} 1.4560.

Anal. Calcd. for $C_{13}H_{26}O_3$: C, 67.83; H, 11.30. Found: C, 68.11; H, 11.65.

The 2,4-dinitrophenylhydrazone, after one recrystallization from aqueous ethanol, melted at 132.5°.

Anal. Calcd. for $C_{15}H_{20}N_4O_5$: C, 53.56; H, 5.99. Found: C, 53.29; H, 5.95.

The semicarbazone melted at 234°.

Lactone of β-(1-hydroxycyclohexyl)propionic acid. A solution containing 11.5 g. (0.05 mole) of β-(1-hydroxycyclohexyl)propionaldehyde diethylacetal in 60 ml. of ether was shaken periodically over a period of 1 hr. with 100 ml. of 3*N* sulfuric acid. Five g. (0.017 mole) of potassium dichromate in 200 ml. of water was added and the mixture was shaken vigorously and allowed to stand overnight. The ether layer was separated and the aqueous layer was extracted with three 50-ml. portions of ether. The combined ether extract was extracted with one 100-ml. and two 50-ml. portions of 15% potassium hydroxide. The potassium hydroxide extract was acidified and was extracted with three 25-ml. portions of ether. The combined ether extract was washed twice with 20-ml. portions of water and the ether extract was removed by evaporation in a vacuum. The lactone (4.4 g.) was obtained as a colorless liquid by distillation at 49° and 0.3 mm. pressure; sapon. equiv., 156 (calcd., 154); n_D^{30} 1.4772. The lactone crystallized upon standing in the refrigerator, m.p. 26°. A mixture of this material with an authentic specimen prepared by the procedure of Johnson and Hunt[7] melted at 26°.

The *amide* of β-(1-hydroxycyclohexyl) propionic acid was prepared by allowing 1.0 g. of the lactone to stand for 3 days in 10 ml. of water saturated with NH_3. After one crystallization from aqueous ethanol the amide melted at 144°. A mixture of this amide and an authentic specimen of the amide of β-(1-hydroxycyclohexyl)propionic acid melted at 144°.

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[7] W. S. Johnson and R. H. Hunt, *J. Am. Chem. Soc.*, **72**, 938 (1950).

Reduction and Benzylation by Means of Benzyl Alcohol. IV. 3-Benzylquinolines

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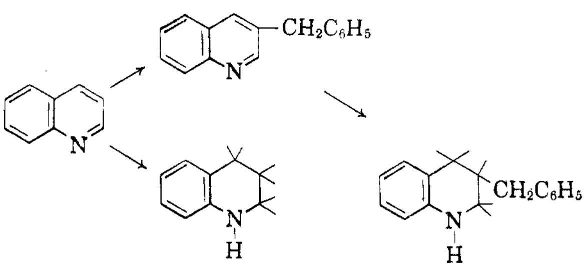
Received October 26, 1956

The preceding paper of this series[1] reported that quinoline is readily transformed into 3-benzyl-1,2,3,4-tetrahydroquinoline on heating with benzyl alcoholic potassium hydroxide, and that the reaction proceeds through the formation of 3-benzylquinoline, isolable from the reaction mixture after a short reaction time; at the same time, part of the quinoline is reduced to 1,2,3,4-tetrahydroquinoline.



It was further pointed out that substituents in the α- and γ-positions of the pyridine ring ordinarily inhibit reduction and ring benzylation.

We wish to report here the results of experiments with quinolines substituted in the benzene ring, *viz.*, 6-methyl-, 8-methyl-, 6-phenyl-, 8-phenyl-, and 6-methoxyquinoline, performed in order to test the scope of the reaction, in particular with regard to the β-benzylation of the pyridine ring. The structures of the various benzylated products obtained were established by independent (Skraup) synthesis.

6-Methyl-, 8-methyl-, and 8-phenylquinoline furnished, upon heating with the reagent, all three types of products obtainable from unsubstituted quinoline, namely, the corresponding 1,2,3,4-tetrahydroquinolines (I, II, and III), 3-benzylquinolines (V, VI, and VIII), and 3-benzyl-1,2,3,4-tetrahydroquinolines (X, XI, and XIII). With 6-phenylquinoline only the benzylated compounds (VII and XII) could be isolated; the absence of 6-phenyl-1,2,3,4-tetrahydroquinoline may be due to its reported instability.[2] A marked difference was observed between the reactivities of the 6- and the 8-substituted compounds, the reduction of the benzylquinolines formed initially being apparently slower for the 8-isomers (Table I). A 36% yield of XI could be obtained, however, when VI was used as the starting material and the time of reaction extended to 42 hr.; even under these conditions 15% of the starting material was recovered.

TABLE I

PER CENT YIELDS OF SUBSTITUTED QUINOLINES

Substituent	Reaction Time, Hr.	Tetrahydroquinoline	Benzylquinoline	Benzyltetrahydroquinoline
6-Methyl	3	10	19	26
8-Methyl	5	14	34	3
6-Phenyl	2	—	5	43
8-Phenyl	2	17	20	17

While the main reaction observed with 6-methoxyquinoline was hydrolysis to 6-quinolinol, 6-methoxy-1,2,3,4-tetrahydroquinoline (thalline, IV),

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[2] W. La Coste and C. Sorger, *Ann.*, **230**, 1 (1885).