silver nitrate. After 12 hours the precipitate was removed, the filtrate was treated with hydrogen sulfide, charcoal was added and the mixture was filtered. The water was removed by distillation under reduced pressure and the red, gummy residue was refluxed for 30 minutes with 200 cc. of reagent acetone. The white solid, obtained when the mixture was cooled, was dissolved in a hot mixture of 85 cc. of acetone and 20 cc. of absolute methanol. After several days the precipitate weighed 11.0 g. (20%), m.p. 163–165° dec. after an additional recrystallization.

Anal. Calcd. for $C_{16}H_{25}O_3N$: C, 68.78; H, 9.02; N, 5.02. Found: C, 68.80; H, 9.05; N, 5.01.

α-Phenyl-α-(1-methyl-4-hydroxy-4-piperidyl)-acetic Acid.—After isopropylmagnesium chloride had been prepared from 29.2 g. of magnesium, 130 cc. of isopropyl chloride and 300 cc. of ether, an additional 300 cc. of ether was added. Phenylacetic acid (81.6 g.), dissolved in 500 cc. of benzene, was added and the material was refluxed for 24 hours. Then 45.2 g. of 1-methyl-4-piperidone,[2] dissolved in 500 cc. of benzene, was added and the mixture was refluxed for 4 hours. It was poured into an ice-cold solution of 120 cc. of concentrated hydrochloric acid in 500 cc. of water. The layers were separated and the organic layer was extracted with 10% hydrochloric acid. The combined aqueous layers were washed with ether and evaporated to dryness under reduced pressure. The residue was refluxed with 250 cc. of nitromethane for 30 minutes and the hot mixture was filtered through a sintered glass funnel. After this extraction process had been repeated four times, the combined nitromethane solutions were concentrated under reduced pressure. The hydrochloride of the product, which separated, was recrystallized from nitromethane as solvent, yield 70.9 g. Treatment of this salt with silver oxide, prepared from 62 g. of silver nitrate, yielded an aqueous solution of the free basic acid. The solution was concentrated under reduced pressure and the precipitate was removed at intervals. A gummy residue of unknown nature remained in the distillation flask; yield 50.9 g. (51% based on the piperidone); when heated, the product started to decompose at 231°.

Anal. Calcd. for $C_{14}H_{19}O_3N$: C, 67.44; H, 7.68; N, 5.62. Found: C, 67.14; H, 7.56; N, 5.63.

α-Phenyl-α-(1-ethyl-4-hydroxy-4-piperidyl)-acetic Acid.—This compound was prepared in the manner described above except that 51.5 g. of 1-ethyl-4-piperidone[3] was employed. The hydrochloride, which separated from the nitromethane solution, was recrystallized from isopropyl alcohol; yield 87.0 g. (72%); after further recrystallization it melted at 201–207° dec.

Anal. Calcd. for $C_{15}H_{22}O_3NCl$: C, 60.08; H, 7.40; N, 4.67; Cl, 11.83. Found: C, 59.60; H, 7.27; N, 4.68; Cl, 11.77.

The hydrochloride (60.0 g.) was dissolved in 250 cc. of water and treated with silver oxide which had been prepared from 38.0 g. of silver nitrate. The acid, isolated as described above, weighed 40.0 g. (75%). After recrystallization from absolute methanol, it began to decompose at 229° and melted at 234° dec.

Anal. Calcd. for $C_{15}H_{21}O_3N$: C, 68.40; H, 8.04; N, 5.33. Found: C, 67.94; H, 8.30; N, 5.39.

Methyl α-Phenyl-α-(1-methyl-4-hydroxy-4-piperidyl)-acetate.—(A) The required acid (20.0 g.) was dissolved in 100 cc. of absolute methanol and treated with ethereal diazomethane until the yellow color became permanent. The mixture was filtered immediately and the solvent and excess diazomethane were removed by distillation. The residue was extracted with three 200-cc. portions of boiling petroleum ether (60–75°). A considerable amount of residue remained. Upon concentration of the extract, 5.5 g. (21%) of the ester was obtained; m.p. 82–83° after recrystallization from petroleum ether (60–75°).

Anal. Calcd. for $C_{15}H_{21}O_3N$: C, 68.40; H, 8.05. Found: C, 68.57; H, 8.24.

The hydrochloride melted at 133–135° after recrystallization from absolute methanol–ether.

Anal. Calcd. for $C_{15}H_{22}O_3NCl$: N, 4.68; Cl, 11.82. Found: N, 4.66; Cl, 11.64.

(B) Ten grams of the acid chloride, 70 cc. of absolute methanol and 5 cc. of concentrated sulfuric acid were refluxed for 18 hours and most of the methanol was removed by distillation under reduced pressure. The residue was dissolved in water and the solution, after it had been washed with ether, was cooled in an ice-bath, made alkaline and extracted with ether. The solvent was removed from the dried extract and the oily residue was extracted with three 50-cc. portions of boiling petroleum ether (60–75°). After the extract had been concentrated to a volume of 50 cc. the solution was placed in a refrigerator; yield 7.5 g. (82%), m.p. and mixed m.p. 82–83° after recrystallization from petroleum ether (60–75°).

Methyl α-Phenyl-α-(1-ethyl-4-hydroxy-4-piperidyl)-acetate.—By the use of procedure A, 11.2 g. (71%) of ester was obtained from 15.0 g. of the required acid; m.p. 70.5–71.5° after recrystallization from petroleum ether (40–60°).

Anal. Calcd. for $C_{15}H_{21}O_3N$: C, 69.40; H, 8.04; N, 5.33. Found: C, 67.94; H, 8.30; N, 5.39.

The hydrochloride melted at 162–164° after recrystallization from absolute methanol–ether.

Anal. Calcd. for $C_{16}H_{24}O_3NCl$: N, 4.46; Cl, 11.30. Found: N, 4.44; Cl, 11.35.

The methobromide melted at 204–205° dec. after recrystallization from absolute methanol–ether.

Anal. Calcd. for $C_{17}H_{26}O_3NBr$: N, 3.76; Br, 21.47. Found: N, 3.77; Br, 21.35.

COLLEGE OF PHARMACY
UNIVERSITY OF MICHIGAN
ANN ARBOR, MICHIGAN

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Endocyclic α,β-Unsaturated Ketones. IV. Reaction of 4,4-Dimethyl-1-keto-1,4-dihydronaphthalene with Cyclohexylmagnesium Bromide

BY RICHARD D. CAMPBELL[1a] AND NORMAN H. CROMWELL[1b]

RECEIVED MAY 13, 1955

The previous papers of this series[2] point out the importance of steric restrictions in the reactions of endocyclic α,β-unsaturated carbonyl systems. The present note extends the study of 4,4-dimethyl-1-keto-1,4-dihydronaphthalene (VI).

A new synthesis of 4,4-dimethyltetralone-1 (IV) is presented, employing a route used by Barnes[3] for a similar compound. Each step gives excellent yields. The procedure of Arnold[4] for converting IV to the desired unsaturated ketone VI was modified and simplified with some increase in yield.

In paper I of this series[2a] the action of organometallic reagents with the endocyclic α,β-unsaturated ketone VI was described. In the instances cited, the reaction of Grignard reagent with VI was nearly quantitative. Addition was mainly, if not exclusively, to the carbonyl group. The resulting carbinols dehydrated and rearranged in the presence of acid. A mechanism of the retropinacol type was proposed.

In the present study the ketone VI was treated with a four-mole excess of cyclohexylmagnesium bromide. The reaction was not quantitative. Instead, a 30% yield of the starting material VI

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[1] (a) du Pont Teaching Fellow 1954–1955. (b) To whom correspondence regarding this article should be addressed.

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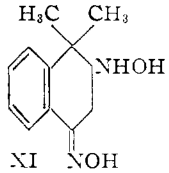
was recovered. Exhaustive attempts to obtain evidence for 1,4-conjugate addition resulted in no such indications. The expected carbinol, 1-cyclohexyl-4,4-dimethyl-1,4-dihydronaphthalenol-1, resulting from addition to the carbonyl group was not isolated. It spontaneously dehydrated and rearranged to give the expected 1,2-dimethyl-4-cyclohexylnaphthalene (VIII) in 51–53% yield. Polymer obtained from the reaction indicated that some exocyclic dehydration of the carbinol may have occurred.[2a] However, this semi-naphthalene 1,1-dimethyl-4-cyclohexylidene-1,4-dihydronaphthalene so produced apparently did not undergo rearrangement to 1-methyl-4-(1′-methylcyclohexyl)-naphthalene). Fuson and Miller[5] describe such a rearrangement in which the migrating group is the more electronegative dichloromethyl group.

The structure of VIII was indicated by analogy of reaction, and confirmed by conversion of VIII to 1,2-dimethyl-4-(1′-cyclohexenyl)-naphthalene (IX).[2a] Additional evidence for the structure of VIII is furnished by the ultraviolet spectra studies of VIII, IX and 1,2-dimethyl-4-phenylnaphthalene (X).[6]

An abnormal reaction of VI occurred in an attempt to form the oxime. The product isolated analyzed for 4,4-dimethyl-3-hydroxylamino-1-oximino-1,2,3,4-tetrahydronaphthalene (XI). One molecule of hydroxylamine must have added 1,4 across the dienone system, and a second molecule of hydroxylamine reacted normally with the carbonyl group. Harries,[7] in an excellent study, obtained β-hydroxylamino oximes from phorone, dibenzalacetone and cyclohexenone.



XI

Thus, VI will undergo 1,4-conjugate addition with hydroxylamine, but apparently no 1,4-addition occurs with the organometallic reagents which have been tried. Alexander and Coroar[8] indicate that a secondary alkylmagnesium halide shows the greatest tendency for 1,4-conjugate addition to α,β-unsaturated ketones.

The product XI obtained from hydroxylamine and the unsaturated ketone VI displayed infrared absorption maxima at 3240 and 3310 cm.$^{-1}$ (in Nujol). These were attributed to N–H and O–H stretching vibrations. No absorption maximum was observed in the carbonyl region (1600–1800 cm.$^{-1}$).

Experimental

4-Methyl-4-phenylpentanone-2 (I).—Compound I was synthesized by the procedure of Hoffman.[9] Quantities to 5.6 moles were used with no decrease in yield.

4-Methyl-4-phenylpentanothiomorpholide (II).—A mixture of 477 g. (2.7 moles) of I, 130 g. (4.1 moles) of sulfur and 375 ml. (4.3 moles) of morpholine was refluxed for 20 hours. While the mixture was still hot, 540 ml. of ethyl alcohol was added. The mixture was cooled to 15° and transferred to a beaker. A few drops of water initiated crystallization. The mixture was warmed to permit formation of large crystals. This crop was filtered and weighed 395 g. Three additional crops brought the total yield to 465 g. (62%). The crude product melted at 93–95°. Two recrystallizations from 95% ethanol gave white plates, m.p. 101.5–102°.

Anal. Calcd. for $C_{16}H_{23}NOS$: C, 69.27; H, 8.36; N, 5.05. Found: C, 69.12; H, 8.42; N, 5.12, 5.01.

4-Methyl-4-phenylpentanoic Acid (III).—Hydrolysis of II was accomplished by refluxing 464.8 g. of II with 1390 ml. of 65% sulfuric acid for 36 hours. The mixture was cooled and diluted with water to 1.8 l. This aqueous solution was extracted with benzene in a continuous liquid–liquid extractor for 48 hours. The benzene solution was extracted with twice the theoretical amount of 25% sodium hydroxide solution. The alkaline solution was acidified with sulfuric acid. The aqueous mixture was extracted in the continuous extractor with benzene for 45 hours. The benzene extract was washed once with water and distilled. The acid III was collected at 185–190° (17 mm.), yield 216 g. (67%); neutral equivalent: calcd. 192.2, found 192.4; anilide, m.p. 116.5–117.5° ($n^{25}D$ 1.518). Späth and Kainrath[10] report (III): b.p. 130–140° (1 mm.); anilide, m.p. 115–117°.

4,4-Dimethyltetralone-1 (IV).—The acyl chloride of III was formed by adding 151 g. of III to 125 g. of refluxing thionyl chloride over 25 minutes. Reflux was maintained an additional 30 minutes. The cooled mixture was dissolved in 450 ml. of CS_2. This solution was stirred rapidly as 210 g. of $AlCl_3$ was added over 2.5 hours. The reaction mixture was refluxed for one hour and allowed to stand overnight. The complex was decomposed by pouring the mixture over crushed ice and concd. hydrochloric acid. The decomposition mixture was extracted with benzene. The extract was washed and distilled. The ketone IV collected at 145–152° (12 mm.) and weighed 109 g. (80%).

2-Bromo-4,4-dimethyltetralone-1 (V).—The procedure of Arnold[4] was modified. A solution of 127.4 g. of bromine in 300 ml. of CCl_4 was added over one hour to a stirred solution of 137.6 g. of IV in 900 ml. of CCl_4. The solvent was removed under reduced pressure and the crystalline residue was charcoaled and recrystallized from methanol. The product V obtained in two crops weighed 170 g. (85%) and melted at 87–88°.

4,4-Dimethyl-1-keto-1,4-dihydronaphthalene (VI).—The procedure of Arnold was used. The distillation of VI was omitted. Crystalline VI was obtained from methanol solution with no change in yield; m.p. 65°; infrared carbonyl band in Nujol, 1657 cm.$^{-1}$, in CCl_4 solution at 1665 cm.$^{-1}$.

Grignard Reagent Addition to (VI).—The Grignard reagent was made from 12 g. of fresh magnesium turnings and 80 g. of cyclohexyl bromide, according to Gilman's procedure.[11]

A solution of 18 g. of VI in 150 ml. of anhydrous ether was added dropwise to the Grignard reagent mixture with rapid stirring. After the addition was complete the mixture was allowed to stand one hour and poured over ammonium chloride. The ether layer was separated and washed with dilute ammonia chloride, then dried over anhydrous magnesium sulfate. The ether was removed under vacuum, finally at 0.3 mm., at 25°. The residual oil A weighed 24.4 g.

Distillation of Oil A.—A 7.2-g. sample of oil A was vacuum distilled at 1 mm. The first fraction was 1.7 g. of bicyclohexyl, $n^{25}D$ 1.492, b.p. 78° (1 mm.). Heilbron[12] reports for bicyclohexyl, $n^{25}D$ 1.484, b.p. 233°. The yield of bicyclohexyl was 15% based on cyclohexyl bromide. The second fraction distilled at 150–164°, and weighed 2.6 g., oil B. The pot residue, 1.1 g., was only slightly soluble in methanol, and rapidly decolorized bromine in CCl_4.

When 0.29 g. of oil B was dissolved in 10 ml. of saturated ethanolic picric acid, 0.3 g. of orange needles, m.p. 137.5–

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(5) R. C. Fuson and T. G. Miller, *J. Org. Chem.*, **17**, 316 (1952).

(6) For comparison with related compounds see R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951, Plates 197–199, 290, 297.

(7) C. Harries, *Ann.*, **330**, 200 (1904). See also A. H. Blatt, THIS JOURNAL, **61**, 3494 (1939); E. Nageli, *Ber.*, **16**, 496 (1883); N. H. Cromwell, *Chem. Revs.*, **38**, 83 (1946).

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138.5°, formed. This is the picrate VII of 1,2-dimethyl-4-cyclohexylnaphthalene.

Anal. Calcd. for VII, $C_{24}H_{23}N_3O_7$: C, 61.66; H, 5.36; N, 9.12. Found: C, 61.94; H, 5.14; N, 8.94.

Rearrangement, Acid Conditions.[4]—A 4-g. sample of the oil A was dissolved in glacial acetic acid with a drop of concd. sulfuric acid. After standing four hours at room temperature, the mixture was poured into water, and extracted with low boiling petroleum ether. The organic extract was washed with Claisen alkali and then distilled. The oil collected at 170–178° (0.2 mm.) and was treated again with Claisen alkali and redistilled. The product collected at 190° (0.12 mm.) and weighed 0.45 g. It solidified on standing. Two recrystallizations from methanol gave white plates of VIII melting at 77.5–78°.

Anal. Calcd. for VIII, $C_{18}H_{22}$: C, 90.69; H, 9.31. Found: C, 90.63; H, 9.05.

A solution of A in petroleum ether was washed with several portions of concd. sulfuric acid until the acid layer was colorless. The ether layer was washed with water, and dried over anhyd. magnesium sulfate. The solvent was replaced with methanol. Fine white plates of VIII were obtained, m.p. 76–77°, alone or mixed with the sample of VIII described above.

Chromatogram of Oil A.—A sample of oil A equivalent to 6.67 g. of ketone VI was dissolved in benzene, and passed into the column. The column previously was slurry-packed with 400 g. of alumina. Eluent fractions were 50 ml. each. The column was developed with 1.2 l. of benzene and eluted with one liter of 4% ethanol in benzene. The solvent was removed from each fraction at 80–100° (12 mm.). The first few fractions had the odor of bicyclohexyl. A 2.1 g. (15%) yield of bicyclohexyl was to be expected; total weight of fractions 1–20, 7.0 g.; weight of VIII, 4.9 g. (53% based on VI).

Fractions 25 and 29 gave 2,4-dinitrophenylhydrazones, m.p. 240° dec. (Arnold[4] 237°). No depression of melting point occurred when these samples were mixed with the authentic derivative of VI. Attempts to form a ketone derivative from fractions 18, 21 and 22 resulted only in recovered 2,4-dinitrophenylhydrazine. Fractions 23–35 weighed 2 g. This represents 30% recovered VI.

Ketone Reagents with Oil B.—Treatment of samples of oil B with sodium bisulfite, hydroxylamine or semicarbazide in the usual manner gave no ketone derivatives. The only crystalline product isolated in each instance was a 51–53% yield of the hydrocarbon VIII.

1,2-Dimethyl-4-(1′-cyclohexenyl)-naphthalene (IX).—A 3.3-g. sample of VIII was refluxed in 40 ml. of CCl_4 with 2.6 g. of N-bromosuccinimide and a trace of benzoyl peroxide for one hour. The succinimide was removed by filtration. The solvent was removed under vacuum. The residue was dissolved in 12 ml. of glacial acetic acid along with 13 g. of potassium acetate and refluxed for 30 minutes. The mixture was poured into water and worked up for the neutral portion. The resulting oil was distilled to give 1.5 g. of yellow oil at 150–170° (0.4 mm.). A 0.1-g. portion of this oil in 2 ml. of saturated ethanolic picric acid solution gave IX as the picrate. The orange needles melted at 112–113°.

Picrate of Authentic (IX).—Two milliliters of saturated ethanolic picric acid solution was warmed with 0.1 g. of authentic IX.[2a] The golden-orange needles melted at 113–114°; mixed with the picrate obtained above, m.p. 112–113°. Attempts to obtain an analytical sample by recrystallization resulted in the decomposition of this picrate.

Hydroxylamino Oxime (XI) of Ketone VI.—A solution of 1 g. of VI, 1 ml. of pyridine, and 1 g. of hydroxylamine bisulfate in 10 ml. of ethanol was refluxed for two hours, and then water was added. The resulting semi-solid was recrystallized from ethanol. The hard, white crystals of XI melted at 168.5–170° and weighed 0.6 g.

Anal. Calcd. for XI, $C_{12}H_{17}N_2O_2$: C, 65.43; H, 7.32; N, 12.72. Found: C, 65.51; H, 7.35; N, 12.57.

Ultraviolet Absorption Spectra.—The spectra were determined with the Beckman model DU instrument. Concentrations were from 10^{-6} to 10^{-4} molar in isoöctane. The general shapes of the curves are similar to the corresponding unmethylated compounds,[6] except for further degradation of fine structure, and broader general absorption. For 1,2-dimethyl-4-cyclohexylnaphthalene (VIII): $\lambda_{\text{max.}}$ 2320, 2840, 2920 Å.; $\lambda_{\text{min.}}$ 2480 Å.; with log ϵ 4.83, 3.79, 3.85, 2.95, respectively. For 1,2-dimethyl-4-(1′-cyclohexenyl)-naphthalene (IX): $\lambda_{\text{max.}}$ 2290, 2910, 3250 Å.; $\lambda_{\text{min.}}$ 2550, 3230 Å.; with log ϵ 4.77, 3.90, 3.04, 3.30, 3.01, respectively. For 1,2-dimethyl-4-phenylnaphthalene (X): $\lambda_{\text{max.}}$ 2330, 2950 Å.; $\lambda_{\text{min.}}$ 2600 Å.; with log ϵ 4.72, 3.98, 3.53, respectively.

Infrared Absorption Spectra.—The infrared absorption spectra were taken from 700 to 4000 cm.$^{-1}$ on the Perkin and Elmer model 21 double-beam instrument. The solution of VI in CCl_4 was 2.5% by weight. The solution was used in a 0.1-mm. cell with a matched cell of solvent in the compensating beam.

LINCOLN, NEBRASKA

The Reaction of 2,4-Dinitrobenzenesulfenyl Chloride with *p*-Tolyl Isocyanide

BY ANTON J. HAVLIK AND MILTON M. WALD

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By analogy to the reaction of ethyl hypochlorite,[1] acid halides[2] and hydrogen sulfide[3] with the isocyanides, a sulfenyl halide could lead to the formation of an imido derivative of a chlorothioformate I.

$$\begin{aligned} &RNC + R'OCl \longrightarrow RN{=}CCl{-}OR' \\ &RNC + R'COCl \longrightarrow RN{=}CCl{-}COR' \\ &RNC + H_2S \longrightarrow RNH{-}CSH \\ &RNC + R'SCl \longrightarrow RN{=}CCl{-}SR' \qquad (I) \end{aligned}$$

The reaction of a sulfenyl halide with an isocyanide, however, was not reported previously. The present purpose was to determine whether *p*-tolyl isocyanide would undergo addition of a sulfenyl halide[4] at the position of unsaturation.

The reaction between 2,4-dinitrobenzenesulfenyl chloride and *p*-tolyl isocyanide in anhydrous ethylene chloride gave a good yield of a yellow crystalline product which contained chloride halogen but no positive chlorine. Structure I for this compound ($R = p\text{-}CH_3C_6H_4$, $R' = 2,4\text{-}(O_2N)_2C_6H_3$) is supported by a strong absorption[5] at 6.0 μ in the infrared spectrum (Nujol mull).

Ackowledgment.—We wish to express our gratitude to Dr. N. Kharasch for making this work possible.

Experimental[6, 7]

2,4-Dinitrophenyl N-*p*-Tolylchloroformothiolimidate.—To 7.0 g. of *p*-tolyl isocyanide[8] (b.p. 89–90°, 24 mm.) dissolved in 100 ml. of ethylene chloride (dry) was added a solution of 13.3 g. of 2,4-dinitrobenzenesulfenyl chloride[9] (m.p. 95–96°) in 100 ml. of dry ethylene chloride. The solution was allowed to stand at room temperature for 12 hours, after which time a negative test for sulfenyl halide (aq. sodium iodide–starch test) was obtained. The solvent was then removed at room temperature at a water-pump and the yellow, crystalline solid separated from a small amount of oil by filtration. This product weighed 15.2 g. (75% yield) and melted at 114–115°. About 1 g. of this

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[1] J. U. Nef, *Ann.*, **287**, 301 (1895).

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[6] We are indebted to W. J. Schenck of this Laboratory and M. Robinson of the Riker Laboratories, respectively, for assistance with the microanalyses and infrared spectra.

[7] Melting points were taken on a Fisher–Johns block.

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[9] N. Kharasch, G. I. Gleason and C. M. Buess, THIS JOURNAL, **72**, 1796 (1950).