green to colorless. To this solution was added with stirring a solution formed by adding 14.9 g. of sodium (0.65 mole) to 500 ml. of absolute ethanol. A greyish white precipitate was formed immediately, and to the slurry was added at once 13.2 g. (0.2 mole) of cyclopentadiene. The mixture was stirred at room temperature for 3 hr. and was then brought to reflux for 3 hr. The volume of the solution, filtered through asbestos, was reduced to 300 ml., and 1700 ml. of water was added. The ferrocene precipitated and after drying weighed 5.6 g. for 30% yield melting at 169–172°.

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Potassium Hydroxide as a Catalyst for the Condensation of Propiolic Acid or Propiolic Esters with Ketones

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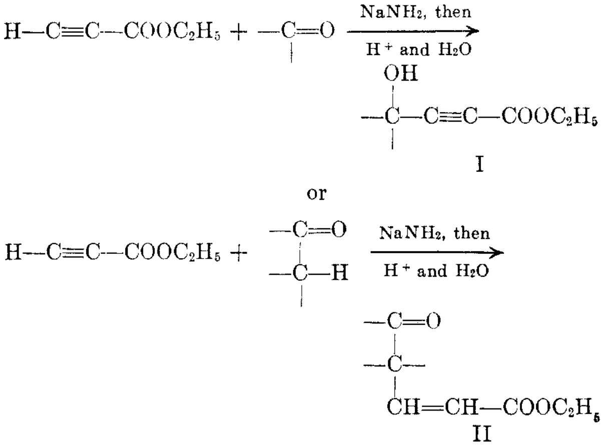
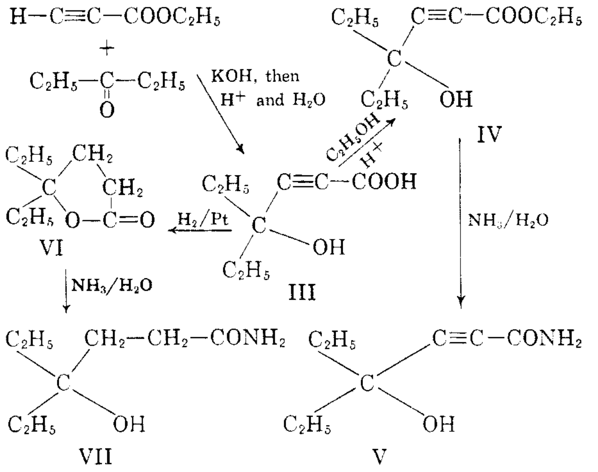
In previous communications[2,3] we have reported that sodamide in liquid ammonia will bring about the condensation of ethyl propiolate with various cyclic ketones to yield either acetylenic carbinols (I) or esters of substituted acrylic acids (II), depending upon the ketone used.



The ability of potassium hydroxide to bring about analogous condensations of acetylene with ketones is well known.[4] This fact prompted us to try potassium hydroxide as a condensing agent for the condensation of both propiolic acid and of ethyl propiolate with certain ketones. It was found that propiolic acid will add to cyclohexanone in the presence of a solution of potassium hydroxide in aqueous alcohol to yield the acetylenic carbinol.

Furthermore, a suspension of powdered potassium hydroxide in ether brought about the condensation of ethyl propiolate with cyclohexanone in as high yields as were obtained using sodamide in liquid ammonia as the condensing agent.[2] Likewise, a suspension of powdered potassium hydroxide in ether brought about the condensation of the acyclic ketone, diethyl ketone, with ethyl propiolate. In this case the product was isolated as the crystalline 4-ethyl-4-hydroxy-2-hexynoic acid (III).



This acid was further characterized through its crystalline amide (V) which was prepared through the ester (IV). The structure of the acid was established by conversion through the lactone (VI) to the amide (VII) of the known 4-hydroxy-4-ethylhexanoic acid. An authentic sample of this amide was obtained from the lactone which was prepared by the procedure of Hepworth.[5]

In the case of the diethyl ketone and ethyl propiolate, powdered potassium hydroxide in ether gave as good a yield of III, as did sodium hydride in ether. No identifiable condensation product was obtained when the condensation was attempted with sodamide in liquid ammonia as the condensing agent.

EXPERIMENTAL

Condensation of propiolic acid with cyclohexanone. A solution containing 25 g. (0.36 mole) of propiolic acid, 38 g. (0.39 mole) of cyclohexanone, 35 g. (0.52 mole, based on 85% purity) of potassium hydroxide, 5 ml. of water, and 100 ml. of ethanol was allowed to stand at room temperature for 2 days. The solution was refluxed for 10 min., cooled, diluted with 250 ml. of water, and was washed with three portions of ether (washings discarded). The aqueous layer was acidified with sulfuric acid and was extracted with three 35-ml. portions of ether. Removal of the ether under reduced pressure left 50 g. of acidic material from which 18 g. of β(1-hydroxycyclohexane)propiolic acid crystallized

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[1] Taken in part from the master's degree thesis of Louis P. Remsberg, Jr., June, 1956.

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

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

[4] Louis F. Fieser and Mary Fieser, *Organic Chemistry*, third edition, D. C. Heath and Co., Boston, 1956, p. 91.

[5] H. Hepworth, *J. Chem. Soc.*, **115**, 1207 (1919).

upon standing. A recrystallized sample melted at 122–124.5°; reported for β(1-hydroxycyclohexane)propiolic acid: 125°,[6] 123–126°.[2]

Condensation of ethyl propiolate with cyclohexanone and with diethyl ketone. The following procedure was used to condense both cyclohexanone and diethyl ketone with ethyl propiolate. A solution containing 5.0 g. (0.05 mole) of ethyl propiolate and 5.0 g. (0.05 mole) of cyclohexanone was added to a suspension of 4 g. of powdered potassium hydroxide in 50 ml. of ether. The mixture was shaken frequently over a period of 1 hr. and was then poured into cold water. Neutral material was removed by ether extraction; the solution was acidified and extracted with three small portions of ether. After removing the ether from the extract, the residue was kept under a current of air until it crystallized. A 2.77-g. sample of β(1-hydroxycyclohexane)propiolic acid (m.p. 123–126° after recrystallization from benzene-alcohol) was obtained.

The same procedure was used to condense ethyl propiolate (40 g.) with diethyl ketone (35 g.). 4-Hydroxy-4-ethyl-2-hexynoic acid (III) was obtained in 22% yield, m.p. (after repeated recrystallizations from carbon tetrachloride) 79.5–80°.

Anal. Calcd. for $C_8H_{12}O_3$: C, 61.52; H, 7.75. Found: C, 61.60; H, 7.57. The same product was obtained in a 19% yield when sodium hydride was substituted for the potassium hydroxide.

Amide of 4-hydroxy-4-ethyl-2-hexynoic acid. A sample of 4-hydroxy-4-ethyl-2-hexynoic acid was esterified by refluxing with absolute alcohol containing a little concd. sulfuric acid. The ester distilled at 136–139°, 14.5 mm. Upon standing for several days with a saturated ammonia solution, the ester was converted into the crystalline amide; m.p. 107.8–108.3° after recrystallization from chloroform.

Anal. Calcd. for $C_8H_{13}O_2N$: C, 61.93; H, 8.44. Found: C, 61.79; H, 8.64.

Amide of 4-hydroxy-4-ethylhexanoic acid. 4-Hydroxy-4-ethylhexynoic acid (1.35 g.) in 40 ml. of ethanol was shaken with 0.05 g. of platinum oxide under hydrogen (35 p.s.i.) until absorption of hydrogen ceased. After removal of the alcohol from the filtered solution, the lactone of 4-hydroxy-4-ethylhexanoic acid was purified by distillation, b.p., 105–110°, 12 mm. This lactone was allowed to stand with frequent shaking with a saturated solution of ammonia in water. The amide of 4-hydroxy-4-ethylhexanoic acid gradually crystallized from the solution, m.p., 120–121°, after recrystallization from chloroform.

Anal. Calcd. for $C_8H_{17}O_2N$: C, 60.36; H, 10.76. Found: C, 60.57; H, 10.71.

There was no depression in melting point when this amide was mixed with an authentic sample of the amide (prepared from the lactone of 4-hydroxy-4-ethylhexanoic acid which in turn was prepared by the method of Hepworth.[5]

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(6) L. J. Haynes and E. R. H. Jones, *J. Chem. Soc.*, 503 (1946).

Ketal *versus* Hemiketal Formation for Cyclohexanone and Methanol

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We have found, in agreement with Lorette, Howard, and Brown,[3] that ketal formation occurs to a significant extent for cyclohexanone and methanol. Lorette *et al.* have shown also that, in general, ketal formation from ketones and alcohols occurs to a significant extent under the proper conditions. Our investigation was started because of the obvious discrepancy between the work of McCoy *et al.*,[4] who also observed ketal formation for these reactants, and of Wheeler,[5] who concluded that hemiketal formation is the predominant reaction even at mole ratios as high as 100:1 of methanol to cyclohexanone.

The approximate equilibrium constant has been determined for ketal formation from cyclohexanone and methanol at three mole ratio levels. The values of K_x were calculated from mole fractions, with the concentrations of all of the constituents having been determined by chemical analysis. The results are shown in Section I of Table I. It is thus seen that K_x is reasonably constant over a rather large mole ratio range.

The yields of ketal, based on chemical analysis are 28, 59, and 71% for the 2:1, 8:1, and 15:1 mole ratio mixtures, respectively. These yields are considerably less than those previously reported by McCoy *et al.*[4] but are in line with the yield (46%) obtained by Lorette *et al.*[3] for a 4:1 mole ratio.

The reaction mixtures, which had been analyzed chemically were then diluted in 1,4-dioxane and the concentrations of cyclohexanone were determined by means of the ultraviolet spectrum (carbonyl absorption). In a similar manner, the analyzed mixtures were diluted in *t*-butyl alcohol and these solutions were analyzed for cyclohexanone by means of the ultraviolet and the infrared spectra. The concentrations of the other constituents of the equilibrium were calculated on the basis of the concentrations of cyclohexanone and the stoichiometry for ketal formation. The values of K_x (mole fraction) are shown in Table I-B (ultraviolet dioxane), Table I-C (ultraviolet *t*-butyl alcohol) and Table I-D (infrared - *t* - butyl alcohol). The values of K_m (molarities) are also shown and are seen to vary by a factor of 10 to 20 as the mole ratio was changed from 15:1 to 2:1.

On the basis of these results we conclude that ketal formation is the predominant reaction whether the reaction is conducted neat or in an inert solvent and K_x is approximately 0.15 at 27° ±5. The results by spectral analysis appear to be somewhat less reliable than the results by chemical analysis

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(5) O. H. Wheeler, *J. Am. Chem. Soc.*, **79**, 4191 (1957).