[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF NOTRE DAME]

The Pinacol Rearrangement of Some α,β-Acetylenic Glycols[1]

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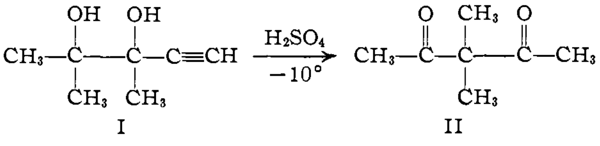
An improved method is offered for the preparation of α,β-acetylenic glycols. The pinacol rearrangement of 3,4-dimethyl-3,4-dihydroxypentyne-1 and 3-methyl-4-ethyl-3,4-dihydroxyhexyne-1 was accomplished, yielding 3,3-dimethylpentyne-1-one-4 and 3-methyl-3-ethylhexyne-1-one-4, respectively. A complete proof of structure of the products is offered.

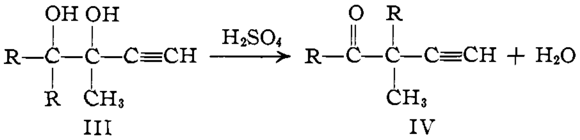
Favorskii and Onishchenko[3] reported that the α,β-acetylenic glycol, 3,4-dimethyl-3,4-dihydroxypentyne-1 (I), on treatment with cold concentrated sulfuric acid underwent a pinacol rearrangement accompanied by a simultaneous hydration of the triple bond to produce dimethylacetylacetone (II).



$$CH_3-\underset{CH_3}{\overset{OH}{C}}-\underset{CH_3}{\overset{OH}{C}}-C\equiv CH \xrightarrow[-10^\circ]{H_2SO_4} CH_3-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-CH_3$$

I II

We have accomplished the pinacol rearrangement of this same glycol I and also of 3-methyl-4-ethyl-3,4-dihydroxyhexyne-1 without hydration of the triple bond, using dilute sulfuric acid and employing variations of the Hill and Flosdorf method.[4]



$$R-\underset{R}{\overset{OH}{C}}-\underset{CH_3}{\overset{OH}{C}}-C\equiv CH \xrightarrow{H_2SO_4} R-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\overset{R}{C}}-C\equiv CH + H_2O$$

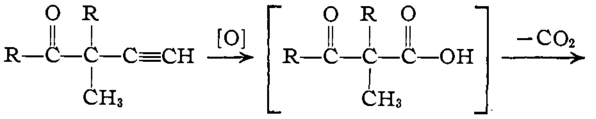
III IV

R = CH_3 and CH_3-CH_2

Following this procedure, using 25% sulfuric acid, 3,4-dimethyl-3,4-dihydroxypentyne-1 (I) was converted to 3,3-dimethylpentyne-1-one-4 in 11% yield, a large mass of tarry material also being produced. Best results were obtained by allowing a water solution of the glycol I to drop into a reaction mixture of 40% sulfuric acid, and simultaneously distilling the mixture at the rate of addition of the glycol–water solution. By this method, 3,3-dimethylpentyne-1-one-4 was obtained in 28% yield.

The pinacol rearrangement of 3-methyl-4-ethyl-3,4-dihydroxyhexyne-1 proceeded more smoothly and in better yield. Following the method previously cited,[4] using 25% sulfuric acid, 3-methyl-3-ethylhexyne-1-one-4 was obtained in 54% yield. Employing an alternate method,[4] using 42% phosphoric acid, the same ketone was obtained in 32% yield.

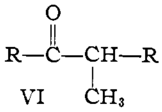
The structure of the products IV was conclusively established, the most salient facts being: characteristic infrared absorption bands were found in the region of 4.73 μ, indicating the presence of the terminal triple bond, and in the region of 5.85 μ, indicating the presence of the carbonyl group.[5] Ultraviolet absorption spectra showed maximum peaks at 284 mμ for 3,3-dimethylpentyne-1-one-4 and at 281 mμ for 3-methyl-3-ethylhexyne-1-one-4, which were in favorable agreement with values reported for similar non-conjugated ketones.[6] Had the triple bond been conjugated with the carbonyl group in these ketones, the maximum peaks would have been expected at 214 mμ.[7] The final products IV were oxidized with potassium permanganate to the corresponding β-ketoacids (V) and characteristic of β-ketoacids,[8] these were readily decarboxylated to corresponding known ketones.



$$R-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\overset{R}{C}}-C\equiv CH \xrightarrow{[O]} \left[R-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\overset{R}{C}}-\overset{O}{\overset{\|}{C}}-OH\right] \xrightarrow{-CO_2}$$

IV V

R = CH_3 and CH_3-CH_2

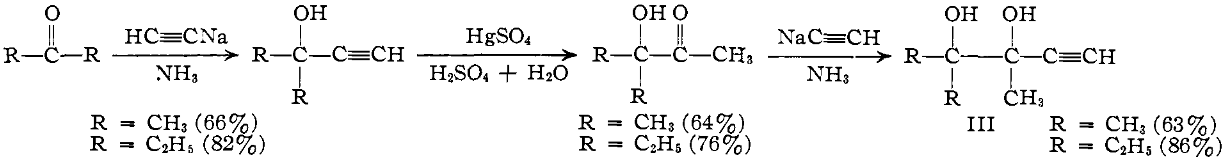


$$R-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{CH}-R$$

VI

In this manner, 3,3-dimethylpentyne-1-one-4 gave 3-methyl-2-butanone, and 3-methyl-3-ethylhexyne-1-one-4 gave 4-methyl-3-hexanone.

The α,β-acetylenic glycols III were prepared by the reaction of sodium acetylide in liquid ammonia with acetone and diethyl ketone,[9] respectively, followed by hydration of the triple bond.[10] The hydroxyketones thus formed, reacted with an excess of sodium acetylide in liquid ammonia to give the corresponding acetylenic glycols III in excellent yield.



$$R-\overset{O}{\overset{\|}{C}}-R \xrightarrow[NH_3]{HC\equiv CNa} R-\underset{R}{\overset{OH}{C}}-C\equiv CH \xrightarrow[H_2SO_4\,+\,H_2O]{HgSO_4} R-\underset{R}{\overset{OH}{C}}-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[NH_3]{NaC\equiv CH} R-\underset{R}{\overset{OH}{C}}-\underset{CH_3}{\overset{OH}{C}}-C\equiv CH$$

R = CH_3 (66%) R = CH_3 (64%) III R = CH_3 (63%)
R = C_2H_5 (82%) R = C_2H_5 (76%) R = C_2H_5 (86%)

The reaction of α-hydroxyketones with sodium acetylide in liquid ammonia to produce α,β-acetyl-

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[1] Further work is in progress.

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enic glycols gave much improved yields over former methods, the best yields having been reported by Cologne and Bernard[11] who obtained 3,4-dimethyl-3,4-dihydroxypentyne-1 in 11% yield and 3-methyl-4-ethyl-3,4-dihydroxyhexyne-1 in 61% yield by treatment of the sodium derivatives of the corresponding hydroxyketones with acetylene under pressure.

Experimental[12]

α,β-Acetylenic Glycols.—Acetone and diethyl ketone were treated with sodium acetylide in liquid ammonia according to the method of Campbell, Campbell and Eby[9] to give dimethylethynylcarbinol in 66.4% yield and diethylethynylcarbinol in 81.6% yield. The ethynylcarbinols were hydrated according to the procedure of Hennion, Davis and Maloney[10] to give 3-methyl-3-hydroxy-2-butanone, b.p. 79° at 90 mm. (64% yield); semicarbazone m.p. 162.5–163.5° (lit. val.[3] 163°), and 3-ethyl-3-hydroxy-2-pentanone, b.p. 85–85.5° at 54 mm. (75.5% yield); semicarbazone m.p. 158–160° (lit. val.[13] 155–156°).

The hydroxyketones were treated with sodium acetylide in liquid ammonia following substantially the procedure of Campbell, Campbell and Eby,[9] with the exception that two moles plus a slight excess of sodium acetylide was used for each mole of hydroxyketone. 3,4-Dimethyl-3,4-dihydroxypentyne-1 was obtained in 62.5% yield; b.p. 90–91° at 19 mm., m.p. 17–18°, n^{25}_D 1.4600, and 3-methyl-4-ethyl-3,4-dihydroxyhexyne-1 was obtained in 85.7% yield; b.p. 99–100° at 13 mm., m.p. 36–37°, n^{25}_D 1.4691.

Pinacol Rearrangement of 3,4-Dimethyl-3,4-dihydroxypentyne-1 (I).—A solution of 138 g. of I and 400 g. of water was added dropwise to a boiling solution of 280 g. of concentrated sulfuric acid and 420 g. of water, distilling the reaction mixture at the rate of addition of the glycol mixture. After the addition was complete, distillation was continued until no oil appeared in the distillate. The distillate was extracted with ether, washed with dilute potassium carbonate and dried over calcium chloride. Fractional distillation gave 33.5 g. of 3,3-dimethylpentyne-1-one-4 (28.1% yield); b.p. 117.5°, n^{25}_D 1.4180, d^{25} 0.8514, MR_D calcd. 32.54, obsd. 32.58.

Anal. Calcd. for $C_7H_{10}O$: C, 76.37; H, 9.16. Found: C, 76.45; H, 9.33.

The 3,3-dimethylpentyne-1-one-4 gave a yellow-orange 2,4-dinitrophenylhydrazone, m.p. 139°. The ketone gave a positive test for terminal acetylene with alcoholic ammoniacal silver nitrate. The ultraviolet absorption spectrum showed a maximum peak at 284 mμ. Characteristic infrared absorption bands appeared at 4.73 and at 5.85 μ.

Following the method of Hill and Flosdorf,[4] using 25% sulfuric acid, 50 g. of I gave 5.3 g. of 3,3-dimethylpentyne-1-one-4 (10.6% yield).

Pinacol Rearrangement of 3-Methyl-4-ethyl-3,4-dihydroxyhexyne-1.—Following substantially the method of Hill and Flosdorf,[4] 150 g. of 3-methyl-4-ethyl-3,4-dihydroxyhexyne-1 was treated with 25% sulfuric acid to give 71.1 g. (53.6% yield) of 3-methyl-3-ethylhexyne-1-one-4; b.p. 79.5–81° at 56 mm., n^{25}_D 1.4328, d^{25} 0.8594, MR_D calcd. 41.77, obsd. 41.78.

Anal. Calcd. for $C_9H_{14}O$: C, 78.26; H, 10.15. Found: C, 78.40; H, 10.54.

The 3-methyl-3-ethylhexyne-1-one-4 gave an orange 2,4-dinitrophenylhydrazone, m.p. 108–109°. The ketone gave a positive test for terminal acetylene with alcoholic ammoniacal silver nitrate. The ultraviolet absorption spectrum showed a maximum peak at 281 mμ, and characteristic infrared absorption bands appeared at 4.73 and 5.85 mμ.

When 77 g. of the acetylenic glycol was refluxed with 400 g. of 42% phosphoric acid for four hours,[4] 22 g. of 3-methyl-3-ethylhexyne-1-one-4 was obtained (32.1% yield).

Potassium Permanganate Oxidation of the Acetylenic Ketones and Subsequent Decarboxylation.[8] 3,3-Dimethylpentyne-1-one-4.—To a mixture of 20 g. of the ketone, 200 g. of water and 1 g. of sodium hydroxide was added portionwise with stirring over a period of three hours 60 g. of potassium permanganate. The mixture was then filtered and the precipitate washed twice with 25 cc. of water. The filtrate was extracted twice with 50 cc. of ether. The water layer was then acidified with dilute sulfuric acid and extracted three times with 100 cc. of ether. After adding 2 g. of 50% sulfuric acid and 3 g. of glacial acetic acid, the ethereal solution was refluxed until carbon dioxide ceased to be evolved—approximately four hours. After all acids were neutralized, the ether was removed and the product was distilled, giving 4 g. of 3-methyl-2-butanone (25.3% over-all yield); b.p. 92–93° (lit. val.[14] 92–94°); 2,4-dinitrophenylhydrazone, m.p. 122–123° (lit. val.[15] 117°); *p*-nitrophenylhydrazone, m.p. 102–103° (lit. val.[16] 103.5°). The ketone gave a positive iodoform test.

3-Methyl-3-ethylhexyne-1-one-4.—In similar manner, 20 g. of this acetylenic ketone was oxidized and the ketoacid produced was decarboxylated to give 6 g. of 4-methyl-3-hexanone (36.4% over-all yield), b.p. 134–136° (lit. val.[17] 134–136°); 2,4-dinitrophenylhydrazone, m.p. 76–77° (lit. val.[18] 78°). The ketone failed to give an iodoform test.

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