Reports of the Academy of Sciences of the USSR

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1957

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1957. Volume 114, No. 4

CHEMISTRY

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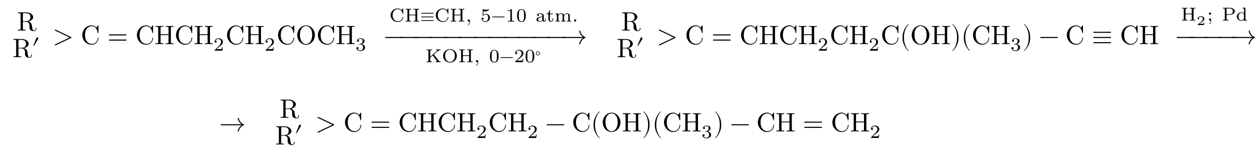
CONDENSATION OF ACETYLENE WITH METHYLHEPTENONE

AND ITS ANALOGS

SYNTHESIS OF LINALOOL AND ITS ANALOGS

Several years ago, in our laboratory, a simple method was developed for the synthesis of a variety of acetylenic alcohols by the condensation, under the influence of powdered caustic potash, of aldehydes and ketones with acetylene under slight pressure (5-10 atm.) (^{1}). It was of interest to apply this method to the condensation of acetylene with methylheptenone and similar ketones (^{2}), in order to obtain the corresponding acetylenic alcohols, from which linalool and its analogs can readily be obtained by partial hydrogenation with a Pd catalyst:



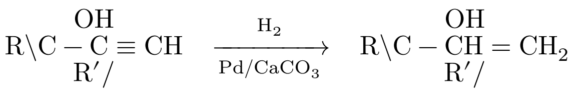
$$\begin{matrix}\mathrm{R}\\ \mathrm{R'}\end{matrix} > \mathrm{C} = \mathrm{CHCH_2CH_2COCH_3} \xrightarrow[\mathrm{KOH,\ 0-20^\circ}]{\mathrm{CH{\equiv}CH,\ 5-10\ atm.}} \begin{matrix}\mathrm{R}\\ \mathrm{R'}\end{matrix} > \mathrm{C} = \mathrm{CHCH_2CH_2C(OH)(CH_3)} - \mathrm{C} \equiv \mathrm{CH} \xrightarrow{\mathrm{H_2;\ Pd}}$$

$$\rightarrow \begin{matrix}\mathrm{R}\\ \mathrm{R'}\end{matrix} > \mathrm{C} = \mathrm{CHCH_2CH_2} - \mathrm{C(OH)(CH_3)} - \mathrm{CH} = \mathrm{CH_2}$$

Up to the present time such condensations have usually been carried out under the influence of metallic sodium in a solution of liquid ammonia, and the yield of dehydrolinalool, for example, was about 80% (^{3}).

It turned out that methylheptenone and its various analogs, under the influence of powdered caustic potash, condense extremely readily with acetylene under a pressure of 5-10 atm. at a temperature of 0-20° and give the corresponding tertiary acetylenic alcohols in almost quantitative yield (above 90%). The indicated condensation can also be carried out without acetylene pressure; however, in this case the reaction proceeds several times more slowly and with lower yields of acetylenic alcohols (60-80%).

Earlier it was shown in our laboratory (^{4}) that acetylenic alcohols containing an unsubstituted acetylenic hydrogen are hydrogenated, in the presence of palladium on calcium carbonate or coppered zinc dust, strictly selectively, and the corresponding vinyl alcohols are obtained in almost theoretical yield:

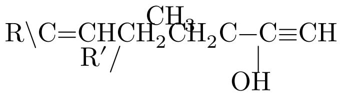


$$\mathrm{R\backslash C} - \underset{\mathrm{R'/}}{\overset{\mathrm{OH}}{\mathrm{C}}} \equiv \mathrm{CH} \xrightarrow[\mathrm{Pd/CaCO_3}]{\mathrm{H_2}} \mathrm{R\backslash C} - \underset{\mathrm{R'/}}{\overset{\mathrm{OH}}{\mathrm{CH}}} = \mathrm{CH_2}$$

With other catalysts (Ni, Pt), acetylenic alcohols are hydrogenated in a mixed manner (nonselectively), and therefore they are unsuitable for obtaining pure vinyl alcohols.

A similar picture is also observed in the hydrogenation of the acetylene alcohols described above, obtained by the condensation of acetylene with methylheptenone and its analogs. In the presence of a Pd catalyst these acetylene alcohols are likewise hydrogenated strictly selectively, forming linalool and its analogs in almost theoretical yield. The purity control of vinyl alcohols—

Table 1



$$\underset{\mathrm{R'/}}{\mathrm{R\backslash C}}\mathrm{=CHCH_2CH_2}\overset{\mathrm{CH_3}}{\underset{\mathrm{OH}}{\mathrm{C}}}\mathrm{-C{\equiv}CH}$$

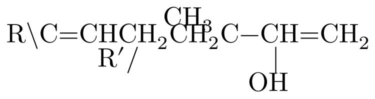
No.	R	R′	b.p., °C/mm	n_D^{20}	d_4^{20}	*MR* found	*MR* calc.	Analysis, % found C	Analysis, % found H	Analysis, % calc. C	Analysis, % calc. H	Yield, %
I	H	H	56–58/10	1.4530	0.8804	38.09	38.14	76.98	9.74	77.36	9.74	83
II	CH_3	H	66–67/8	1.4570	0.8774	42.87	42.76	78.20	10.21	78.17	10.20	83
III	CH_3	Cl	81–82/3	1.4800	1.0260	47.79	47.62	62.81	7.66	62.60	7.53	90
IV	CH_3	CH_3	81–82/10	1.4634	0.8788	47.63	47.44	78.90	10.45	78.94	10.52	92

No.	R	R′	b.p., °C/mm	n_D^{20}	d_4^{20}	*MR* found	*MR* calc.	Analysis, % found C	Analysis, % found H	Analysis, % calc. C	Analysis, % calc. H	Yield, %
V	CH_3	C_2H_5	81–83/2	1.4629	0.8826	51.87	51.99	79.52	11.17	79.52	10.84	91
VI	CH_3	iso-C_3H_7	84–85/2	1.4642	0.8738	56.84	56.67	79.81	11.10	80.00	11.11	90
VII	CH_3	tert.-C_4H_9	100–101/8	1.4680	0.8772	61.48	61.23	80.32	11.46	80.41	11.33	91
VIII	iso-C_3H_7	iso-C_3H_7	92/1.5	1.4610	0.8687	66.04	65.84	80.78	11.41	80.70	11.61	93
IX	$(CH_2)_5$		89–91/1	1.4925	0.9409	59.25	59.09	81.30	10.44	81.25	10.41	87
X	3-methyldehydrolinalool		104–106/13	1.4684	0.8886	52.01	51.99	79.53	11.12	79.45	10.90	88

* Repeated analyses are omitted throughout.

(linalool and its analogs) was carried out by means of the acetylene test (with an ammoniacal solution of silver or copper oxide), the sensitivity of which was determined by special experiments and amounted to 0.2–0.3%. In

Table 2



$$\begin{matrix}R\\R'\end{matrix}\!\!>C{=}CHCH_2CH_2\overset{CH_3}{\underset{OH}{C}}{-}CH{=}CH_2$$

No.	R	R′	b.p., °C/mm	n_D^{20}	d_4^{20}	*MR* found	*MR* calc.	Analysis, % found C	Analysis, % found H	Analysis, % calc. C	Analysis, % calc. H	Yield, %
XI	H	H	54–55/10	1.4500	0.8549	39.64	39.74	75.99	11.30	76.12	11.19	95
XII	CH_3	H	58–60/8	1.4492	0.8488	44.28	44.35	77.33	11.50	77.07	11.51	97

No.	R	R′	b.p., °C/mm	n_D^{20}	d_4^{20}	MR found	MR calc.	Analysis, % found C	Analysis, % found H	Analysis, % calc. C	Analysis, % calc. H	Yield, %
XIII	CH_3	Cl	65–66/3	1.4787	1.0060	49.03	49.22	61.69	8.63	61.89	8.59	93
XIV	CH_3	CH_3	80–81/10	1.4622	0.8664	48.95	48.97	77.64	11.86	77.80	11.68	96
XV	CH_3	C_2H_5	80–82/2	1.4622	0.8653	53.75	53.58	78.76	12.09	78.51	11.98	95
XVI	CH_3	iso-C_3H_7	87–88/3	1.4632	0.8575	58.48	58.27	78.97	12.00	79.12	12.09	95
XVII	CH_3	tert.-C_4H_9	103–104/9	1.4659	0.8632	62.88	62.82	79.85	12.20	79.64	12.24	96
XVIII	iso-C_3H_7	iso-C_3H_7	92/1.5	1.4610	0.8579	67.50	67.44	79.85	12.52	80.00	12.45	95
XIX	$(CH_2)_5$		88–89/1	1.4918	0.9227	60.97	60.63	80.15	11.28	80.47	11.32	92
XX	3-methyllinalool		86–88/7	1.4678	0.8746	53.43	53.59	78.40	12.00	78.57	11.98	91

hydrogenation of acetylene alcohols with a Pd catalyst, the acetylene test always disappears at the theoretical point, i.e., when exactly one molecule of hydrogen is added. The acetylene alcohols obtained in the present work are summarized in Table 1.

By partial hydrogenation of the above-mentioned acetylenic alcohols with a Pd catalyst, linalool and its analogs, presented in Table 2, were obtained.

Experimental Part

All condensations of methylheptenone and its analogs with acetylene under pressure were carried out in a steel reactor of 2 or 6 l capacity ([1]). The selective hydrogenation of the acetylenic alcohols thus obtained was carried out without solvent in the presence of small amounts of palladium on calcium carbonate in a steel reactor under a hydrogen pressure of 3–5 atm. (amounts greater than 200 g) or in an ordinary glass "duck" (amounts less than 200 g).

Dehydrolinalool (IV). A 6-liter steel reactor was charged with 3500 ml of dry ether, 360 g of powdered caustic potash, and 20 ml of ethyl alcohol. With vigorous stirring, the mixture was saturated with acetylene at 0° and a pressure of 6 atm., which was maintained throughout the experiment. Over 1.5 hours, 680 g of methylheptenone was introduced into the reactor, after which stirring of the reaction mixture was continued for another 3 hours. By the end of the experiment the temperature had slowly risen to 20°. The acetylene pressure was then released, and 720 ml of water was added to the mixture with stirring. The ether layer was separated, and the aqueous layer was extracted with ether. The combined ether extracts were neutralized with carbon dioxide and dried over magnesium sulfate. After distillation, 759 g (92%) of dehydrolinalool (IV) was obtained, b.p. 81-82°/10 mm; n_D^{20} 1.4634; d_4^{20} 0.8788.

Linalool (XIV). 740 g of dehydrolinalool was hydrogenated in the presence of 1.2 g of Pd/$CaCO_3$ catalyst (containing about 5% Pd) in a 2-liter autoclave at 20-35° and a hydrogen pressure of 1-3 atm. After 2 hr 20 min, 110 l of hydrogen had been absorbed (theoretical amount), the acetylene test became negative, and the hydrogenation was stopped; the catalyst was filtered off, and the product was distilled in vacuum. 713 g (95%) of linalool (XIV) was obtained, b.p. 81-82°/10 mm; n_D^{20} 1.4622.

3-Methyldehydrolinalool (X). A mixture of 160 g of powdered caustic potash, 2000 ml of dry ether, and 20 ml of ethanol was saturated with acetylene at 0° and a pressure of 7.5 atm.

Over 40 min, 204 g of 2,3-dimethyl-2-hepten-6-one was added, and stirring was then continued for another 5 hr. After the usual work-up and distillation, 206 g (88%) of 3-methyldehydrolinalool (X) was obtained, b.p. 104-106°/13 mm; n_D^{20} 1.4687 ([5]).

3-Methyllinalool (XX). 35 g of 3-methyldehydrolinalool was hydrogenated in a glass "duck" in the presence of 0.1 g of Pd/$CaCO_3$ catalyst. After absorption of 5300 ml of hydrogen (19°; 730 mm), the hydrogenation was stopped. The catalyst was filtered off and the product distilled. 32.1 g (91%) of 3-methyllinalool (XX) was obtained, b.p. 86-88°/7 mm; n_D^{20} 1.4678 ([5]).

2-Chloro-6-methyl-2-octen-7-yn-6-ol (III). A mixture of 350 g of powdered caustic potash, 2000 ml of dry ether, and 20 ml of ethanol was saturated with acetylene at 8° and a pressure of 6 atm. Over 2.5 hr, 355 g of 2-chloro-2-hepten-6-one was introduced into the reactor, and stirring was continued for another 2 hr. After the usual work-up, 377.5 g of 2-chloro-6-methyl-2-octen-7-yn-6-ol (III) was obtained, b.p. 81-82°/3 mm; n_D^{20} 1.4800.

On hydrogenation of 100 g of this alcohol in the presence of a Pd/$CaCO_3$ catalyst, 1450 ml of hydrogen was absorbed (19°; 746 mm), after which the hydrogenation was stopped. The catalyst was filtered off and the product distilled in vacuum. 93.6 g (93%) of 2-chloro-6-methyl-2,7-octadien-6-ol (XIII) was obtained, b.p. 65-66°/3 mm; n_D^{20} 1.4787.

2,2,3,7-Tetramethyl-3-nonen-8-yn-7-ol (VII). 120 g of powdered caustic potash, 1500 ml of dry ether, and 15 ml of ethanol were saturated with acetylene at −10° and a pressure of 6.5 atm. Over the course of 1 hour, 90 g of 2,2,3-trimethyl-3-octen-7-one was introduced into the reactor, and stirring was continued for another 4 hours. After the usual work-up, 95 g (91%) of 2,2,3,7-tetramethyl-3-nonen-8-yn-7-ol (VII) was isolated, b.p. 100–101°/8 mm; n_D^{20} 1.4680.

48.5 g of this alcohol (VII) was hydrogenated with hydrogen in the presence of a Pd/$CaCO_3$ catalyst. After absorption of 6300 ml of hydrogen (20°, 728 mm), the hydrogenation was stopped. 47.5 g (96%) of 2,2,3,7-tetramethyl-3,8-nonadien-7-ol (XVII) was obtained, b.p. 103–104°/9 mm; n_D^{20} 1.4659.

4-Methyl-1-cyclohexylidene-5-hexyn-4-ol (IX). 130 g of powdered caustic potash, 900 ml of dry ether, and 15 ml of ethanol were saturated with acetylene at 0° and a pressure of 9 atm. Over the course of 30 min, 100 g of 1-cyclohexylidenepentan-4-one was introduced into the reactor, and stirring was continued for another 3 hours. After the usual work-up, 100.3 g (87%) of 4-methyl-1-cyclohexylidene-5-hexyn-4-ol (IX) was isolated, b.p. 89–91°/1 mm; n_D^{20} 1.4925.

Upon selective hydrogenation of 23.1 g of the acetylenic alcohol (IX) in the presence of a Pd/$CaCO_3$ catalyst (the hydrogenation was stopped when 3050 ml of hydrogen had been absorbed at 19° and 725 mm), 21.5 g (92%) of 4-methyl-1-cyclohexylidene-5-hexen-4-ol (XIX) was obtained, b.p. 88–89°/1 mm; n_D^{20} 1.4918.

Other compounds listed in Tables 1 and 2 were obtained in an analogous manner.

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Received
12 III 1957

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