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Abstract

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SYNTHESIS AND TRANSFORMATIONS OF MONOCYCLIC SECONDARY ACETYLENIC ALCOHOLS

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The subject of the present investigation is secondary acetylenic alcohols of types I-VII, synthesized from acetylene and Δ^3-cyclohexene aldehydes VIII-XV, which are readily obtained by condensation of available dienes and dienophiles. We use such alcohols for constructing cycloaliphatic polyene systems closely related in their structure to natural ones. This can be accomplished either by hydration of the acetylenic bond in the alcohols under study, with conversion into ketols and then into tertiary acetylenic glycols, or by isomerization of secondary acetylenic alcohols into α,β-unsaturated aldehydes and ketones, followed by extension of the side polyene chain:

$$\text{(cyclohexenyl)}-\text{CH}=\text{CH}-\text{CHO} \leftarrow \text{(cyclohexenyl)}-\text{CHOH}-\text{C}\equiv\text{CH} \xrightarrow{\text{H}_2\text{O}}$$

$$\longrightarrow \text{(cyclohexenyl)}-\text{CHOH}-\text{C}(=\text{O})-\text{CH}_3 \xrightarrow{\text{CH}\equiv\text{CH}} \text{(cyclohexenyl)}-\text{CHOH}-\text{C(OH)(CH}_3)-\text{C}\equiv\text{CH}.$$

The scant information on secondary acetylenic alcohols ([1–6]) and the absence of any data on the properties of acetylenic alcohols of the series selected by us made necessary a detailed and systematic study of their reactivity. The availability to us of such alcohols with different numbers, characters, and positions of substituents in the Δ^3-cyclohexene ring made it possible to trace the influence of structural factors on the properties of the alcohols themselves, as well as of intermediate compounds obtained at later stages in the construction of complex cyclopolyene systems.

We synthesized the alcohols I-VII under study from acetylene and the corresponding Δ^3-cyclohexene aldehydes VIII-XIV in the presence of sodium in liquid ammonia at temperatures from -40 to -70°.* The starting aldehydes VIII-XV were obtained by diene condensation of acrolein, crotonaldehyde, and cinnamaldehyde with butadiene, piperylene, 2-methylbutadiene, or 1-phenylbutadiene; the condensation was carried out at 160-200° in the presence of hydroquinone in a metal ampoule. The yields of monocyclic secondary

acetylenic alcohols are 30-60% and depend to a large extent on the structure of the aldehyde taken. Thus, the para-substituted Δ^3-cyclohexenal XII readily reacts with acetylene, whereas the ortho-substituted cyclohexenals IX, X, XI enter into this reaction with difficulty, and the phenyl-substituted aldehyde XV, under comparable conditions, does not react with acetylene at all. However, the influence of the character and position of the substituents is not observed for the hydrogenated analogs of the Δ^3-cyclohexane aldehydes,—all of them ob-

* The reaction must be carried out in dimethoxymethane (and not in ether), using an excess of liquid ammonia, which makes it possible to considerably reduce the formation of a nitrogen-containing by-product.

form secondary acetylenic alcohols with great ease and in good yield.

$$\text{VIII–XV} + HC{\equiv}CH \longrightarrow \text{I–VII}$$

$$\text{I–VII} \xrightarrow[\text{HgSO}_4,\ \text{H}_2\text{SO}_4]{+H_2O} \text{XXX–XXXVI}$$

$$\text{I–VII} \xrightarrow[\text{Pd/CaCO}_3]{H_2} \text{XVI–XXII}$$

$$\text{I–VII} \xrightarrow[\text{Pd/CaCO}_3 \text{ or } \text{PtO}_2]{+3H_2} \text{XXIII–XXIX}$$

$$\text{XVI–XXII} \xrightarrow[\text{Pd/SrCO}_3 \text{ and } \text{PtO}_2]{+2H_2} \text{XXIII–XXIX}$$

$$\text{XXIII–XXIX} \xrightarrow{\text{KHSO}_4} \text{XXXVII–XLII}$$

$$\text{I–VII} \xrightarrow{+\text{POCl}_3} \text{XLVII, XLVIII}$$

$$\text{XLVII, XLVIII} \xrightarrow[\text{Pd/CaCO}_3]{H_2} \text{XLIX, L}$$

$$\text{XVI–XXII} \xrightarrow{+\text{POCl}_3} \text{XLIX, L}$$

$$\text{XVI–XXII} \xrightarrow{\text{KHSO}_4} \text{XLIII–XLVI}$$

I, VIII, XVI, XXIII, XXX, XXXVII, XLIII, XLVII, XLIX: $R_1 = R_2 = R_3 = H$
II, IX, XVII, XXIV, XXXI, XXXVIII, XLIV: $R_1 = CH_3;\ R_2 = R_3 = H$
III, X, XVIII, XXV, XXXII, XXXIX: $R_1 = C_6H_5;\ R_2 = R_3 = H$
IV, XI, XIX, XXVI, XXXIII, XL: $R_1 = R_3 = CH_3;\ R_2 = H$
V, XII, XX, XXXVII, XXXIV, XLI, XLV: $R_1 = R_3 = H;\ R_2 = CH_3$
VI, XIII, XXI, XXVIII, XXXV: $R_1 = H;\ R_2 = R_3 = CH_3$
VII, XIV, XXII, XXIX, XXXVI, XLII, XLVI, XLVIII, L: $R_1 = R_2 = H;\ R_3 = CH_3$
XV: $R_1 = CH_3;\ R_2 = H;\ R_3 = C_6H_5$

Acetylenic alcohols I–VII are selectively hydrogenated over the Lindlar catalyst, or with 1 mole of hydrogen over a palladium catalyst, to the corresponding ethylenic alcohols XVI–XXII. Exhaustive hydrogenation of the acetylenic I–VII and ethylenic XVI–XXII alcohols is readily accomplished on $Pd/CaCO_3$ or PtO_2 and leads to their saturated analogs XXIII–XXIX.

Secondary acetylenic alcohols I–VII are hydrated in the presence of mercuric sulfate and sulfuric acid to the corresponding oxy ketones XXX–XXXVI. It should be noted here that hydration of acetylenic alcohols II and III does not proceed, and the alcohols are recovered unchanged; however, repeating the experiment with the alcohols recovered from the reaction leads to the corresponding ketols XXXI and XXXII.

Saturated alcohols XXIII, XXIV, XXV, XXVI, XXVII, XXIX are dehydrated rather easily and in quantitative yield to ethylenic hydrocarbons XXXVII–XLII on heating with potassium bisulfate at 160–190°. Dehydration of secondary ethylenic alcohols under the same conditions takes a different course –the alcohols XVI, XVII, XX, XXII form simple ethers XLIII–XLVI in good yield. Secondary acetylenic alcohols I–VII do not change under the indicated dehydration conditions with potassium bisulfate. If, however, their dehydration is carried out in the presence of phosphorus oxychloride, in pyridine under a nitrogen atmosphere, the corresponding hydrocarbons are obtained. Of the latter, hydrocarbons XLVII and XLVIII were isolated in analytically pure form; according to IR-spectral data, they are vinylacetylenic hydrocarbons with conjugated multiple bonds.* Dehydration of secondary ethylenic alcohols XVI

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* The frequency of the acetylenic bond (2137 cm^{-1}) is more intense and is shifted downward by approximately 20 cm^{-1} in comparison with that of the initial alcohol, and in the region of absorption frequencies of double bonds there are two frequencies: 1654 cm^{-1}, characteristic of the double bond in the ring, and 1635 cm^{-1}, more intense than the first. From the shift of the frequency characteristic of an acetylenic bond, and from the intensity of the 1635 cm^{-1} frequency, one may infer conjugation of the acetylenic and ethylenic bonds in the molecules of hydrocarbons XLVII and XLVIII.

and XXII under the action of phosphorus oxychloride leads to the formation of hydrocarbons XLIX and L with conjugated ethylenic bonds; in the IR spectrum of these hydrocarbons there is an intense band (1602 cm^{-1}), which indicates conjugation of the multiple bonds in the molecule. The diethylenic hydrocarbons XLIX and L were obtained as a result of the selective hydrogenation of hydrocarbons XLVII and XLVIII. It should be noted that, in a number of cases, isolation of the products from the reaction mixture after dehydration with $POCl_3$ is greatly hindered owing to resinification and the presence of chlorine-containing products. Therefore, from the ethylenic alcohols XVII–XXI and the acetylenic alcohols II–VI it was not possible to obtain analytically pure dehydration products (dehydration of such alcohols in the vapor phase with P_2O_5

or with $Al_2(SO_4)_3$ led to resinification).

Table 1

	Yield, %	B.p., °C/mm	n_D^{20}	d_4^{20}	Calculated, % C	Calculated, % H	Found, % C	Found, % H
I	54	83–85/3	1,5032	0,9818	79,11	8,82	79,53	9,12
II	40	84/2,5	1,4990	–	80,00	9,33	80,00	9,44
III	26	139–140/1	1,5657	–	84,82	7,60	84,73	7,85
IV	50	89/3	1,4970	0,9869	80,48	9,73	79,88	9,98
V	53	88–90/2	1,5005	1,9804	80,00	9,33	79,76	9,22
VI	45	99–101/4	1,4980	0,9805	80,48	9,75	80,30	9,95
VII	60	77–78/1	1,4988	0,9827	80,00	9,33	80,20	9,29
XVI		89–91/6	1,4940	0,9591	78,26	10,14	78,19	10,40
XVII	80	78/4	1,4905	0,9826	78,95	10,52	78,62	10,30
XVIII	83	151/4	1,5804	1,0502	84,03	8,46	83,8	8,46
XIX	83	92/4	1,4968	0,9590	79,51	10,84	79,35	11,09
XX		88–89/5	1,4845	0,9480	78,95	10,52	78,86	10,52
XXI		98/5	1,4787	0,9475	79,51	10,84	79,51	10,96
XXII	80	71–72/1	1,4920	0,9555	78,94	10,52	79,09	10,50
XXIII		82–84/5	1,4625	0,9140	76,05	12,67	75,89	12,60
XXIV	80	55/0,4	1,4655	0,9177	76,92	12,82	76,33	12,6
XXV	86	134/0,5	1,5320	1,0102	82,54	10,16	82,58	9,99
XXVI	85	68,5/2	1,4681	0,9130	77,64	12,94	77,39	12,89
XXVII		87–89/6	1,4575	0,8990	76,92	12,82	76,87	12,51
XXX	24	95–96/3	1,4965	1,0644	70,13	9,09	70,04	9,00
XXXI		95–97/2,5	1,4898	1,0234	71,42	9,52	70,03	9,70
XXXII	50	141–142/0,4	1,4490	1,1058	78,25	7,87	78,04	7,90
XXXIII	66	90/1,5	1,4915	1,0105	72,52	9,89	72,62	10,09
XXXIV	25	100–101/2,5	1,4990	1,0470	71,43	9,52	71,32	9,52
XXXV	35	120–122/10	1,4951	1,0233	72,52	9,89	72,48	10,34

	Yield, %	B.p., °C/mm	n_D^{20}	d_4^{20}	Calculated, % C	Calculated, % H	Found, % C	Found, % H
XXXVI		89/1	1,4870	–	71,43	9,52	71,35	9,68
XXXVII	70	65–66/15	1,4552	–	87,10	12,90	87,24	12,82
XXXIX	67	93,5–94/1	1,5990	0,9418	89,99	10,10	90,00	10,00
XLI		79–82/26	1,4715	–	86,90	13,04	86,70	13,20
XLII		63–64/13	1,4560	–	86,90	13,04	86,67	12,90
XLIII	80	156–157/1,5	1,5094	0,9568	83,72	10,07	83,67	10,24
XLIV		138/0,3	1,5057	–	83,91	10,49	83,51	10,70
XLV		165–166/3	1,5190	–	83,91	10,49	84,13	10,01
XLVI	80	160–161/1	1,5017	0,9495	83,91	10,49	83,88	10,66
XLVII	20	75–76/14	1,5184	0,9332	91,52	8,47	91,20	8,32
XLVIII	26	84/17	1,5170	0,9251	90,91	9,09	90,74	9,11
XLIX	18	65–67/15	1,5075	0,8920	90,00	10,00	89,74	10,23
L	25	75/17	1,5055	0,8820	89,55	10,45	89,32	10,44

The characteristics of the synthesized compounds are given in Table 1. All the saturated, ethylenic, and acetylenic alcohols obtained were additionally characterized in the form of acetates.

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Note: Figure translations are in progress. See original paper for figures.