SYNTHESIS OF TERTIARY ALKOXY- AND ALKYLTHIOENEDIYNIC ALCOHOLS

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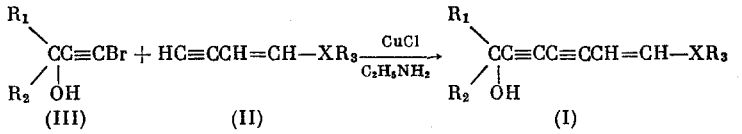
The discovery of new highly effective plant growth stimulators among the unsaturated cycloaliphatic ketols and ketones [1, 2] gives a basis for broad investigations of these compounds. The study of the relationship between their chemical structures and physiological action, and also the location of the active center of the molecule which is characteristic for this structure, is acquiring particular importance. In recent years a large number of polyacetylenic compounds has been isolated from various plants [3] from which it follows that the typical bond apparently takes part in physiological processes occurring in the plant organism. Since some of the alkoxy- and alkylthioenynic alcohols that we have synthesized previously exhibit growth-regulating activity, it appeared desirable to study the change in this activity in dependence on the number of conjugated triple bonds in the molecule. For this purpose we have undertaken the synthesis of alkoxy- and alkylthioenediynic alcohols (I) from ethynyl and vinyl ethers and sulfides (II) by their unsymmetrical condensation with bromo-substituted acetylenic alcohols (III) by Chodkiewiez' method



(III) (II) (I)

where $R_1 = R_2 = CH_3$, $XR_3 = OCH_3$ (a); $R_1 + R_2 = (CH_2)_5$, $XR_3 = OCH_3$ (b); $R_1 + R_2 = (CH_2)_5$, $XR_3 = OC_4H_9$ (c); $R_1 = R_2 = CH_3$, $XR_3 = SC_2H_5$ (d); $R_1 + R_2 = (CH_2)_5$, $XR_3 = SC_2H_5$ (e).

It was found that this reaction readily takes place in the presence of cuprous chloride, and the tertiary enediynic alcohols (I) formed were isolated with good yields. However, the analogous reaction with 1-diethylaminobut-1-ene-3-yne did not lead to the desired result, and only the corresponding acetylenic glycols, formed as the result of the oxidative condensation of the bromo-substituted acetylenic alcohols (III), were isolated from the reaction mixture.

The alkoxyenediynic alcohols (Ia-c) are viscous liquids which are unstable in the pure state but can be stored satisfactorily in solution. The alkylthioenediynic alcohols (Id, e) are crystalline and completely stable substances. To confirm their structure, the alkoxyenediynic alcohols (Ia-c) were subjected to exhaustive hydrogenation with 5% $Pd/CaCO_3$ to form the saturated alcohols (IVa-c) (Table 1). The structure of all the compounds isolated was also confirmed by their IR and UV spectra.

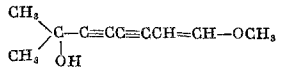
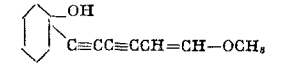
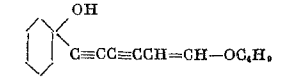
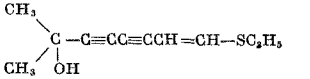
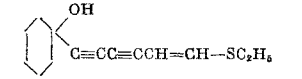
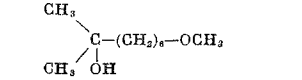
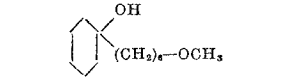
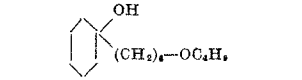
EXPERIMENTAL

The bromine-substituted acetylenic alcohols (III) were obtained by treating the alcohols with a solution of potassium hypobromite [7].

Synthesis of the Alkoxy- and Alkylthioenediynic Alcohols (I). With stirring, to 25 ml of a 40% aqueous solution of ethylamine containing 1 g of CuCl and 0.7 g of hydroxylamine hydrochloride was added a solution of 0.1 mole of the appropriate ethynyl vinyl ether or sulfide (II) in 20 ml of methanol and then, in drops, a solution of 0.1 mole of the bromine-substituted acetylenic alcohol (III) in 25 ml of methanol in such a way that the temperature of the reaction mixture did not exceed 35°. The mixture was stirred for 2 hr at 20° and was then treated with 10% HCl and extracted with ether; the extract was twice washed with dilute HCl (1 : 5) and with water and was dried over $MgSO_4$, and then the ether was driven

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 1, pp. 186-188, January, 1967. Original article submitted June 14, 1966.

TABLE 1. Characteristics of the Compounds Synthesized

Compound	Formula	B.p., °C (p, mm Hg)	n_D^{20}	Yield, % of theoretical	Found, % C	Found, % H	Empirical formula	Calculated, % C	Calculated, % H	IR spectrum, ν, cm^{-1}
Ia		117 (1)	1,5690	80	73,27 73,09	7,44 7,39	$C_{10}H_{12}O_2$	73,14	7,37	1280, 1628, 2136, 2220, 3330—3420
Ib		130 (0,05)	1,5680	80	76,63 76,65	7,93 8,12	$C_{13}H_{16}O_2$	76,44	7,89	1270, 1620, 2120, 2200, 3320—3380
Ic*		172 (1,5)	1,5652	82	78,10 78,02	8,86 9,02	$C_{16}H_{22}O_2$	78,01	9,00	1278, 1625, 2138, 2225, 3350—3430
Id†		M.p. 36—37 (n-Hexane)	—	87	68,08 68,08	7,57 7,31	$C_{11}H_{14}OS$	68,02	7,27	1270, 1550, 1615, 2140, 2225, 3360—3430
Ie‡		M.p. 70—72 (n-Hexane)	—	94	72,02 72,18	7,67 7,99	$C_{14}H_{18}OS$	71,77	7,74	1276, 1560, 1615, 2150, 2220, 3320—3360
IVa		84 (1,5)	1,4380	98	69,00 68,96	12,50 12,40	$C_{10}H_{22}O_2$	68,91	12,72	1125, 3380—3460
IVb		121,5 (2)	1,4688	98	73,02 73,27	12,30 12,10	$C_{13}H_{26}O_2$	72,84	12,23	1125, 3420—3480
IVc		130—132 (1,5)	1,4650	96	75,02 74,69	12,62 12,57	$C_{16}H_{32}O_2$	74,94	12,58	1125, 3400—3480

* UV spectrum: λ_{max} 223, 262, 276, 291 mμ (ε 16,600, 7000, 9600, 8000) (alcohol).

† Found %: S 16.51, 16.48. Calculated %: S 16.47. UV spectrum: λ_{max} 222, 233, 295, 307 mμ (ε 8200, 7000, 15,000, 18,000) (alcohol).

‡ Found %: S 13.48, 13.75. Calculated %: S 13.66. UV spectrum: λ_{max} 224, 234, 298, 307 mμ (ε 7800, 6800, 15,000, 17,400) (alcohol).

off and the enynic alcohols (I) were isolated by distillation or crystallization. The constants of the compounds synthesized and also the results of elementary analysis and the IR and UV spectra are given in Table 1.

CONCLUSIONS

A number of alkoxy- and alkylthioenediynic alcohols have been synthesized to study the growth-regulating activity of polyacetylenic compounds.

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