CYANOETHYLATION OF ACETYLENIC THIENYL ALCOHOLS

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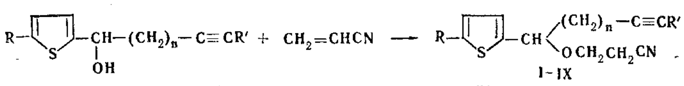
The reaction of 2-cyanoethyl ethers with phenylmagnesium bromide gives the corresponding 2-benzoylethyl ethers.

In a continuation of our investigation of the properties of acetylenic thienyl alcohols, we have studied the reaction of them with acrylonitrile in the presence of potassium hydroxide, as a result of which we obtained the previously unreported 2-cyanoethyl ethers (I-IX) (Table 1):



I-IX

I $R = R' = H$, $n = 0$; II $R = C_2H_5$, $R' = H$, $n = 0$; III $R = R' = H$, $n = 1$; IV $R = C_2H_5$, $R' = H$, $n = 1$; V $R = H$, $R' = CH_3$, $n = 0$; VI $R = C_2H_5$, $R' = CH_3$, $n = 0$; VII $R = H$, $R' = C_4H_9$, $n = 0$; VIII $R = H$, $R' = C_5H_{11}$, $n = 0$; IX $R = C_2H_5$, $R' = C_5H_{11}$, $n = 0$

The yields of the 2-cyanoethyl ethers depend to a considerable degree on the structure of the starting acetylenic thienyl alcohols (see Table 1).

An attempt to accomplish the alcoholysis of the cyanoethyl ethers by refluxing in methanol saturated with dry hydrogen chloride [1] was unsuccessful. The reaction products underwent pronounced resinification.

The corresponding 2-benzoylethyl ethers (X and XI) were obtained by the reaction of 2-cyanoethyl ethers I and V with phenylmagnesium bromide.

The structures of the compounds were confirmed by the IR spectral data. The stretching vibrations of the $C \equiv C$ bond give a narrow absorption band in the usual spectral range at 2118-2150 cm^{-1} and 2200-2250 cm^{-1} (for disubstituted acetylene derivatives). The absorption bands at 1066-1090 cm^{-1} correspond to the stretching vibrations of the $C-O-C$ grouping. An absorption band at 2252 cm^{-1} from the $C \equiv N$ group is observed in the IR spectra of ethers I-IV. The absorption band of the nitrile group for V-IX coincides with the absorption band of the $C \equiv C$ bond.

TABLE 1. 2-Cyanoethyl Ethers of Acetyleneic Thienyl Alcohols (I-IX)

Comp.	R	R'	n	bp, °C (mm)	n_D^{20}	d_4^{20}	MR_D found	MR_D calc.	Empirical formula	N, % found	N, % calc.	Yield, %
I	H	H	0	152—154 (3)	1,5335	1,1487	51,96	51,65	$C_{10}H_9NOS$	7,4	7,3	72
II	C_2H_5	H	0	153—154 (2)	1,5274	1,0958	61,47	61,20	$C_{12}H_{13}NOS$	6,5	6,4	85
III	H	H	1	155—157 (3)	1,5350	1,1220	56,87	56,27	$C_{11}H_{11}NOS$	6,9	6,8	36
IV	C_2H_5	H	1	158—160 (1)	1,5315	1,0821	66,40	65,82	$C_{13}H_{15}NOS$	6,0	6,0	31
V	H	CH_3	0	156—157 (2)	1,5340	1,1290	56,44	56,27	$C_{11}H_{11}NOS$	6,9	6,8	45
VI	C_2H_5	CH_3	0	198—200 (2)	1,5395	1,1072	65,98	65,82	$C_{13}H_{15}NOS$	6,5	6,0	32
VII	H	C_4H_9	0	175—177 (2)	1,5260	1,0741	70,03	70,43	$C_{14}H_{17}NOS$	5,7	5,7	45
VIII	H	C_5H_{11}	0	187—190 (2)	1,5420	1,0883	75,55	75,05	$C_{15}H_{19}NOS$	5,1	5,4	42
IX	C_2H_5	C_5H_{11}	0	200—203 (2)	1,5492	—	—	—	$C_{17}H_{23}NOS$	4,9	4,8	15

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The IR spectra of X and XI have an absorption band at 1690-1705 cm^{-1} that is related to the C=O stretching vibrations. The frequencies of the vibrations of the thiophene ring of I-XI are found at 690, 845-850, 1045-1052, 1530, and 3050-3090 cm^{-1}.

EXPERIMENTAL

1-(2-Cyanoethoxy)-1-(2-thienyl)-2-propyne (I). Acrylonitrile [0.58 g (0.011 mole)] was added with vigorous stirring to a mixture of 1.5 g (0.011 mole) of 1-(2-thienyl)-2-propyn-1-ol and 0.08 g of 40% aqueous potassium hydroxide at such a rate that the temperature of the mixture did not rise above 25°. The mixture was stirred at room temperature for 6 h and allowed to stand overnight. The alkali was neutralized with dilute (1 : 1) hydrochloric acid, the precipitated potassium chloride was removed by filtration, and the filtrate was vacuum distilled to give 1.5 g (72%) of compound I.

Ethers II and V-IX were similarly obtained. The cyanoethylation of 1-(2-thienyl)-3-butyn-1-ol and 1-(5-ethyl-2-thienyl)-3-butyn-1-ol was carried out at 60° for 4 h.

1-(2-Benzoylethoxy)-1-(2-thienyl)-2-propyne (X). A solution of 1.91 g (0.01 mole) of I in 10 ml of ether was added slowly to a Grignard reagent prepared from 3.45 g (0.022 mole) of bromobenzene and 0.53 g (0.022 g-atom) of magnesium in ether. The reaction mixture was heated on a water bath for 3 h, cooled to 0°, and decomposed with a saturated solution of ammonium chloride. The ether was evaporated, and the reaction mixture was heated at 80° for 1 h to complete the hydrolysis. The reaction product was extracted with ether, and the ether extract was washed with water and dried with Na_2SO_4. The ether was evaporated, and the residue was vacuum distilled to give 1.1 g (39%) of ketone X with bp 128-131° (2 mm), D_4^{20} 1.1407 and n_D^{20} 1.5645. Found %: C 71.2; H 5.2; S 11.9; MR_D 77.02. $C_{16}H_{14}O_2S$. Calculated %: C 71.1; H 5.2; S 11.8; MR_D 76.27.

1-(2-Benzoylethoxy)-1-(2-thienyl)-2-butyne (XI). This compound [0.6 g (36%)] was obtained like ketone X from 1.35 g (0.006 mole) of ether V, 1.27 g (0.08 mole) of bromobenzene, and 0.2 g (0.008 g-atom) of magnesium and had bp 158-160° (2 mm), D_4^{20} 1.1085 and n_D^{20} 1.5462. Found %: C 71.8; H 5.6; S 11.3; MR_D 81.15. $C_{17}H_{16}O_2S$. Calculated %: C 71.8; H 5.6; S 11.3; MR_D 80.89.

LITERATURE CITED

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