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ADDITION OF BENZHYDROXAMIC ACID TO ALKOXYETHYLENES

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A method for the isolation of 1-alkoxyethyl esters of benzhydroxamic acid, based on the addition of this acid to alkoxyethylenes in the presence of the catalyst HBr, was developed. The possible structure of the adducts is discussed.

The interaction of hydroxamic acids with alkyl vinyl ethers has not been studied up to now. Taking the example of benzhydroxamic acid (I), we showed that the indicated acids undergo addition to the activated double bond of the alkoxyethylenes (II) according to the Markownikoff rule. The reaction proceeds at 20°C in the absence of traces of moisture. The catalyst for this was the solution of hydrogen bromide in acetone or benzene, prepared directly before application by means of the addition of the calculated amount of bromine to the acetone or the solution of the vinyl alkyl ether in benzene. The amount of the HBr introduced into the reaction comprised 5-10 mole % in relation to (I). The molar ratio (I):(II) is 1:10-20.

Since the anion (X^-) of hydroxamic acid may theoretically exist in four tautomeric forms $(X^- = PhCONHO^-, PhC(OH)=NO^-, PhC(O)N^-OH, PhC(O^-)=NOH)$, it is difficult to assign, a priori, one of the structures (III)-(VI) to the adducts which are formed.



However, it can be concluded from the data of mass spectrometry and IR spectroscopy, taking into consideration the ¹H, ¹³C, and ¹⁴N NMR spectra, that the isolated (1-alkoxy)ethylesters of hydroxamic acid occur mainly in the form of the hydroxamates (III).

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In the PMR spectra of the compounds obtained (cf. Experimental), the position and form of the signals of all the protons correspond to the structures (IIIa, b). However, the chemical shifts of the available proton are uncharacteristic, and do not permit a choice between the forms (IIIa, b) and (IVa, b). The presence of two multiplets of the OCH₂ is possibly a result of configurational differences in consequence of the chirality of the molecules.

Taken as a whole, the ¹³C NMR spectra confirm the structure (III) and (IV); however, it is also impossible to indicate the preference of one (i.e., to choose between C=O and C=N). The ¹⁴N NMR spectrum of the adducts obtained contains the signals at δ 172 ppm (IIIa) and 90 ppm (IIIb). These are values representing the mean of the values characteristic of the amides PhCONMe₂ (281.7 ppm) and oximes PhCH=NOH (26.3 ppm) [1]; this can be assessed as the occurrence of a tautomeric equilibrium between the structures (III) and (IV).

More definite conclusions can be made from the data of the IR spectroscopy. Thus, the IR spectra of the liquid 1-ethoxy- and 1-butoxyethylbenzhydroxamates (IIIa, b) and their concentrated solutions in CCl₄ (1·10⁻¹ M) contain bands with the maximums at 3475, 3410, 3200, and 1650 cm⁻¹. The last two are intense bands, disappearing on the dilution of the solution, which pertain to the stretching vibrations of the NH and C=O groups connected by intermolecular hydrogen bonds whereby the dimeric (VII) or oligomeric associates are possible (cf. [2]). On the dilution of these solutions (1·10⁻³ and 2·10⁻⁴ M), the appearance of the band at v C=0 1700 cm⁻¹ and the increase in the intensity of the band at v NH 3475 cm⁻¹ are observed; this allows the assignment of these bands to the vibrations of the free C=O and NH groups [the structure (III)] [3]. The band at the frequency 3410 cm⁻¹ is probably determined by the vibration of the NH group involved with the intramolecular hydrogen bond [the structure (VIII)].



Therefore, the esters of hydroxamic acids synthesized from alkoxyethylenes occur mainly in the form of hydroxamates in the dimeric form (VII). An equilibrium between the monomeric forms (III) and (VIII) evidently occurs in their solutions in CCl₄.

EXPERIMENTAL

The ¹H, ¹³C, and ¹⁴N NMR spectra were recorded on the Jeol FX-90Q instrument with the working frequency 89.95 (¹H) and 22.49 (¹³C) MHz in CDCl₃ using HMDS at the standard. The ¹⁴N NMR spectrum was recorded in the solution of CDCl₃; the working frequency was 6.43 MHz, and the standard was CH_3NO_2 . The IR spectra were taken on the Specord 75 IR instrument in a microlayer or in the solution of CCl₄ at the concentrations of $1 \cdot 10^{-1} - 1 \cdot 10^{-4}$ M. The mass spectra were obtained on the Varian MAT-212 instrument.

The thin layer chromatography of the reaction mixture was performed on plates of Silufol UV 254 using as the eluent the 3:2 mixture of benzene-ether. Development was performed by UV exposure, by spraying with the solution of 2,4-dinitrophenylhydrazine in 2 N HCl, and separately with an acidified solution of FeCl₃·6H₂O in methanol [4].

<u>(1-Ethoxyethyl)benzhydroxamate (IIIa)</u>. To the solution of 1.31 g (9.6·10⁻³ mole) of benzhydroxamic acid and 6.89 g (9.6·10⁻² mole) of dry ethyl vinyl ether in 100 ml of abs. diethyl ether was added the solution of the catalyst. The last was prepared by the sequential solution of 0.1 ml of ethyl vinyl ether and 0.05 ml of bromine in 10 ml of benzene. The reaction mixture was stirred until the solution of the hydroxamic acid was effected; the mixture was left at 20°C for 24 h in all. Triethylamine (1 ml) was added for the removal of unreacted initial acid and the catalyst. The residue was filtered off after 1 h. The filtrate was concentrated in vacuo: 50 mm (ether) and 1 mm (triethylamine). The residue (2.46 g) was dissolved in 30 ml of ether and applied to silica gel LL_{254} 5/40 (10 g); after vacuum evaporation, it was transferred to a column of length 60 cm and diameter 3 cm with dry silica gel of the same type. After the saturation with the 3:2 mixture of benzene—ether, the column of silica gel was forced out with compressed air. The substance was washed from the cut silica gel column with ether. Triethylamine (1 ml) was added to the ether solution of the substance for the removal of impurity appearing in the process of the partition on the column. The mixture was cooled to -78 °C, and the residue was filtered off. The filtrate was evaporated in vacuo for the removal of excess triethylamine. The substance remaining was dissolved in 5 ml of ether; hexane was added until turbidity was evident. The mixture was cooled to -78 °C, and the residue of (IIIa), melting at 20 °C, was filtered off. After the washing of the residue with ether and the evaporation of the latter, the yield of 1.29 g (64%) of (IIIa), in the form of a yellowish viscous liquid, was obtained. The substance decomposes on distillation in vacuo. The ¹H NMR spectrum (δ , ppm) is as follows: 1.37 d (CH₃, ³J = 5.9 Hz), 5.02 q (OCHO, ³J = 5.9 Hz), 1.12 t (CH₃ in OC₂H₅, ³J = 7.3 Hz), 3.89 m, 3.64 m (OCH₂), 7.34 m, 7.77 m (C₆H₅), and 9.94 s (NH). The ¹³C NMR spectrum (δ , ppm) is as follows: 15.3 (CH₃), 104.7 (OCHO), 18.8 (CH₃ in OC₂H₅), 64.0 (OCH₂), 133.8, 132.1, 128.6, 127.3 (C₆H₅), and 166.6 (C=O). Found: C 63.15, H 7.35, and N 6.42%. C₁₁H₁₅NO₃. Calculated: C 63.14, H 7.23, and N 6.69%. The mass spectrum, m/z (intensity, %) is as follows: [M]⁺ 209(1), [M - Et0]⁺ 164(7), [M - Et0H]⁺ 163-(49), 148(8), 122(8), [PhCONH₂]⁺ 121(8), [PhCONH₃]⁺ 120(35), 119(56), [PhCO]⁺ 105(48), 103(5), 91(22), Ph⁺ 77(55), and [EtOC₂H₄]⁺ 73(100), 64(14), 63(5).

 $\frac{(1-\text{Butoxyethyl})\text{benzhydroxamate (IIIb).}}{(II and 14.43 g (14.4 \cdot 10^{-2} mole) of dry butyl vinyl ether in 100 ml of abs. diethyl ether was added the solution of the catalyst prepared by the sequential solution of 0.02 ml of bromine in benzene and then of the butyl vinyl ether (until the disappearance of the coloration). The reaction mixture was treated analogously to (IIIa). The yield of 1.13 g (66%) of (IIIb) in the form of a yellowish viscous liquid was obtained. The ¹H NMR spectrum (<math>\delta$, ppm) is as follows: 1.41 d (CH₃, ³J = 5.9 Hz), 5.04 q (OCHO, ³J = 5.9 Hz), 0.85 t (CH₃ in C₄H₉, ³J = 7.0 Hz), 1.41 m (CH₂ in C₄H₉), 3.81 m, 3.48 m (OCH₂), 7.73 m, 7.38 m (C₆H₅), and 9.89 s (NH). The ¹³C NMR spectrum (δ , ppm) is as follows: 13.8 (CH₃), 104.9 (OCHO), 18.6 (CH₃ in C₄H₉), 19.1, 31.8 (CH₂ in C₄H₉), 68.3 (OCH₂), 132.1, 131.7, 128.4, 127.3 (C₆H₅), and 166.8 (C=O). Found: C 66.16, H 8.38, and N 5.64%. C₁₃H₁₉NO₃. Calculated: C 65.80, H 8.07, and N 5.90%. The mass spectrum, m/z (intensity, %) is as follows: [M]⁺ 237(3), [M - BuO]⁺ 164(6), [M - BuOH]⁺ 163(2), [PhCONH₂]⁺ 121(6), [PhCONH]⁺ 120(6), 119(10), [PhCO]⁺ 105(47), 103(15), [Bu- OC₂H₄]⁺ 101(100), 91(4), 83(6), [Ph]⁺ 77(23), and [Bu]⁺ 57(82).

The mass spectra of the esters obtained are in good agreement with the amide structure (IIIa, b) (cf. [5]).

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