NEW REACTIONS OF ELECTROPHILIC ADDITION TO THE TRIPLE BOND

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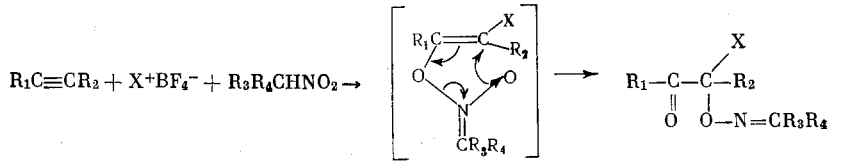
We were the first to discover that the reaction of mono- and dialkylacetylenes with strong protonic acids of the HBF_4 type, or with highly polarized cationoid complexes of the $X^+BF_4^-$ type (where X^+ = alkoxyalkyl or acyl), in a nitroparaffin medium, at −20 to −30°, results in the conjugated addition of a proton, the acyl or alkoxyalkyl radical, and the nitroalkane moiety to the triple bond, according to the scheme:



where X = H; $-CH_2OCH_3$; CH_3CO-.

The compounds obtained by these reactions are enumerated below:

(I) $R_1 = R_2 = C_4H_9$; $R_3 = R_4 = H$; X = H;
(II) $R_1 = R_2 = C_4H_9$; $R_3 = H$; $R_4 = CH_3$; X = H,
(III) $R_1 = R_2 = C_4H_9$; $R_3 = R_4 = CH_3$; X = H;
(IV) $R_1 = R_2 = C_4H_9$; $R_3 + R_4 = -(CH_2)_5$; X = H;
(V) $R_1 = C_4H_9$; $R_2 = H$; $R_3 = R_4 = H$; X = H,
(VI) $R_1 = R_2 = C_4H_9$; $R_3 = R_4 = H$; $X = -CH_2OCH_3$;
(VII) $R_1 = R_2 = C_4H_9$; $R_3 = H$; $R_4 = CH_3$; $X = -CH_2OCH_3$.
(VIII) $R_1 = R_2 = C_4H_9$; $R_3 = R_4 = H$; $X = -COCH_3$;
(IX) $R_1 = C_4H_9$; $R_2 = H$; $R_3 = R_4 = H$; $X = -CH_2OCH_3$.

The yield of products (I)-(V) is 70-80%, that of (VI), (VII) or (IX) is 50-60%, and that of (VIII) is 25-30%. Their composition follows from the elemental analysis data and mass spectra, while their structure was proved on the basis of the IR, NMR, and mass spectra. Thus, in the IR spectra of all of the compounds are present absorption bands at 1720 cm^{-1} (>C = O), 1630-1650 cm^{-1} (−C = N−) and 1050-1060 cm^{-1} (−O−N−). In the NMR spectra of (I)-(V) are present the signals of the proton of the group $-CO-CH-ON-CR_3R_4$ (δ, ppm relative to HMDS) at 4.15-4.30 (triplet), J = 6.7 Hz; in (I), (V), (VI), (VIII), (IX) are present the signals of the protons of the group $-N=CH_2$ at 7.0 and 6.4, AB spectrum, J_{AB} = 8 Hz; in (II) and (VII) are present the signals of the protons of the group $-N=CHCH_3$ at 6.7 and 1.86, AX_3 spectrum, J_{AX} = 6 Hz; and in (III) are present the corresponding signals for the group $-N=C(CH_3)_2$ at 1.80 and 1.75. In addition, in the NMR spectra of (VI), (VII), and (IX) are present the signals of the protons of the group $-CH_2OCH_3$ at 3.57 and 3.34, AB spectrum, J_{AB} = 10 Hz (2H), and 3.17 singlet (3H), while in (VIII) are present the signals of the protons of the group CH_3CO (2.01, singlet).

The chemical properties of the obtained products corroborate the presence of a keto group and the grouping $R_3R_4C=N-O-$ (acid hydrolysis leads to the formation of aldehydes or of ketones R_3R_4CO).

The obtained results show that the reaction discovered by us for the conjugated addition of an electrophile X and a nitroalkane moiety bears a general character for an X of variable nature, and could be of interest as a method for the synthesis of polyfunctional compounds based on acetylenes and nitroalkanes. Its mechanism and limits of application are being studied by us at the present time.

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