Chemistry

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1964

SovietRxiv

Abstract

Full Text

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Vinylation of Cyclanes and Cyclic Ethers

The vinylation by acetylene of organic compounds containing active hydrogen bound to a heteroatom (oxygen, sulfur, nitrogen) is well known, whereas the vinylation by acetylene of saturated cyclic compounds with formation of a C—C bond has not been investigated.

We have previously shown that, in the presence of di-tert-butyl peroxide, addition of saturated cyclic compounds to an unsaturated bond is observed ([1]). Taking into account the free-radical character of this reaction, we assumed that in the presence of the peroxide it would be possible to effect addition of cyclic compounds to the unsaturated bond of acetylene.

Table 1

Vinylation of cyclic compounds

Cyclic compound	Amount of cyclic compound (g-mol)	Amount of peroxide (g-mol)	Degree of conversion of cyclic compounds, %	Yield of vinyl-substituted products, %
tetrahydrofuran	3.66	0.11	15.0	40.0
tetrahydropyran	3.66	0.11	13.0	21.0
dioxane	3.66	0.11	12.1	17.0
cyclohexane	1.71	0.055	12.8	27.4

The experiments were carried out in a rotating autoclave at 150° under an acetylene pressure of 15 atm for 3 hr, using di-tert-butyl peroxide as initiator.

The vinylation products were analyzed by gas-liquid chromatography, combinational light scattering, and infrared spectroscopy*.

The results of the experiments are given in Table 1.

In the vinylation of cyclohexane, vinylcyclohexane was obtained with b.p. 123°/740 mm, n_D^{20}1.4458, d_4^{20}0.8065. MR_D found 36.42; calculated 36.48. Yield

27%, calculated on the cyclohexane that reacted. Literature data: b.p. 125°, n_D^{20}1.4470, d_4^{20}0.8091 ([2]):

$$C_6H_{12} + CH{\equiv}CH \longrightarrow C_6H_{11}{-}CH{=}CH_2$$

The structure of the isolated vinylcyclohexane is confirmed by its Raman spectrum:

$\Delta\nu$, cm^{-1} : 233 (0sh), 281 (1sh), 360 (3sh), 407 (1), 443 (2), 491 (3r), 643 (2sh), 782 (10r), 834 (5r), 881 (1), 917 (2), 938 (1sh), 997 (2), 1032 (5), 1047 (5), 1085 (2sh), 1111 (1sh), 1153 (1), 1175 (1), 1238 (3), 1263 (5), 1284 (2), 1300 (3), 1312 (0), 1349 (10sh), 1414 (3), 1440 (0sh), 1642 (10), 2851 (10sh), 2892 (2), 2917 (8), 2936 (10), 2992 (7sh), 3076 (5).

In the Raman spectrum of this compound, the intense band at 1642 cm^{-1} corresponds to stretching vibrations of the terminal C=C bond.

In the reaction of decalin with acetylene, vinyldecalin was obtained with b.p. 99—100°/6 mm, n_D^{20}1.4975, d_4^{20}0.9089.

* We express our gratitude to G. K. Gaivoronskaya for recording the Raman spectra.

The intense band at 1637 cm^{-1} in the Raman spectrum of the isolated vinyl decalin corresponds to stretching vibrations of the C=C bond.

Vinylation of cyclic ethers was studied using the interaction of acetylene with tetrahydrofuran, dioxane, and tetrahydropyran as examples.

In the vinylation of tetrahydrofuran, 2-vinyltetrahydrofuran was obtained with b.p. 109°/753 mm, n_D^{20} 1.4358; d_4^{20} 0.8859:

$$\text{tetrahydrofuran} + CH \equiv CH \longrightarrow \text{2-vinyltetrahydrofuran}$$

According to the literature: b.p. 109°, n_D^{20} 1.4358; d_4^{20} 0.8831 (3). Yield 40%, calculated on the reacted tetrahydrofuran.

Below is the Raman spectrum of the isolated 2-vinyltetrahydrofuran:

$\Delta\nu$, cm^{-1} : 147 (2), 351 (1sh), 447 (3), 923 (8sh), 986 (0sh), 1023 (0sh), 1110 (10sh), 1238 (1sh), 1290 (4sh), 1405 (1), 1423 (1), 1446 (2), 1482 (1), 1640 (10), 2870 (10sh), 2907 (2), 2933 (3), 2982 (7), 3010 (8), 3080 (4sh).

The intense line with frequency 923 cm^{-1} corresponds to the symmetric vibration of the tetrahydrofuran ring, and the line 1640 cm^{-1} indicates the presence of a terminal double bond C=C.

In the interaction of dioxane with acetylene, vinyldioxane was obtained with b.p. 131-132°/760 mm, n_D^{20} 1.4437, d_4^{20} 0.9955. The degree of conversion of dioxane was 12.1%. The yield of vinyldioxane was 17.0%.

The structure of vinyldioxane was confirmed by the Raman spectrum:

$\Delta\nu$, cm^{-1} : 145 (2), 395 (3), 443 (1), 460 (1), 516 (1), 651 (1), 832 (8), 876 (2), 902 (2), 970 (0), 1082 (1sh), 1115 (1), 1165 (0), 1231 (2), 1258 (1), 1295 (3), 1320 (1), 1347 (1), 1385 (2), 1410 (1), 1443 (3), 1650 (6), 2854 (5sh), 2910 (3), 2968 (6), 2988 (2), 3000 (6).

The values of a number of frequencies in the Raman spectrum of the vinyldioxane obtained coincide with the frequency values in the spectrum of 1,4-dioxane (4):

440 (1), 845 (8), 1082 (1sh), 1115 (1), 1162 (6), 1230 (2), 1258 (1), 1295 (3), 1347 (1), 1385 (2), 1443 (3), 2854 (5sh).

In particular, the band 835 cm^{-1} may be assigned to symmetric vibrations of the dioxane ring, while the frequency 1650 cm^{-1} indicates the presence of a double bond C=C in the compound.

In the vinylation of tetrahydropyran, a narrow fraction was isolated, in whose IR spectrum there are bands characteristic of the C=C bond and of the tetrahydropyran ring. According to chromatographic analysis, the yield of vinyltetrahydropyran is 21%.

The radical mechanism of vinylation and the initiating action of peroxide are confirmed by the presence of tert-butyl alcohol in the reaction products:

$$(CH_3)_3COOC(CH_3)_3 \rightarrow 2(CH_3)_3CO\cdot$$

$$(CH_3)_3CO\cdot + \text{cyclohexane} \rightarrow (CH_3)_3COH + \text{cyclohexyl radical}$$

$$\text{cyclohexyl radical} + CH \equiv CH \rightarrow \text{cyclohexyl-}CH = CH\cdot$$

$$\text{cyclohexyl-}CH = CH\cdot + \text{cyclohexane} \rightarrow \text{cyclohexyl-}CH = CH_2 + \text{cyclohexyl radical}$$

Institute of Organic Chemistry named after N. D. Zelinsky
Academy of Sciences of the USSR

Received
28 V 1964

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