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Brief Communications

Alkylation of acetylene by *tert*-butyl alcohol

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A reaction of acetylene with *tert*-butyl alcohol in the presence of sulfuric acid leads to *tert*-butylacetylene.

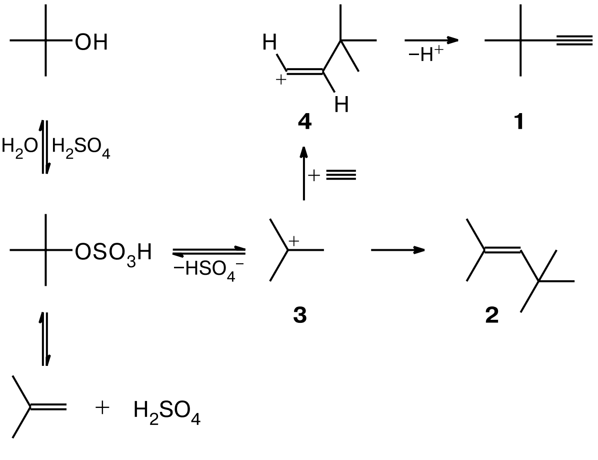
Key words: *tert*-butyl alcohol, *tert*-butyl hydrogen sulfate, acetylene, *tert*-butylacetylene, nickel sulfate, 2,2,4-trimethylpent-2-ene.

tert-Butylacetylene (**1**) is widely used in the preparative organic synthesis, for example for the introduction of *tert*-butylethynyl group and a synthesis of diverse compounds (propargyl alcohols, ketones, *etc.*[1]). However, the practical use of *tert*-butylacetylene is limited due to the absence of a convenient method for its preparation.

By now essentially the only way of preparation of this compound is the laborious and expensive synthesis from pinacolin and phosphorus pentachloride followed by dehydrochlorination[2] of formed dichloride.

The condensation of acetylene with lower alkenes in sulfuric acid in the presence of mercury salts was previously reported,[3] but the nature of products was not defined.

We investigated a reaction of acetylene with *tert*-butyl alcohol in the presence of 70% sulfuric acid. It was found that at low temperature (0—5 °C) the reaction gives *tert*-butylacetylene (**1**) in ~0.8% yield (based on starting *tert*-butyl alcohol), while diisobutylene (**2**) is practically absent. Increasing the temperature to 25—30 °C leads to a slight decreasing in the yield of *tert*-butylacetylene (~0.5%) and rising in the content of diisobutylene in the reaction products. The main product of the reaction at 40—45 °C is diisobutylene (**2**).



The formation of *tert*-butylacetylene (**1**) can be explained by the addition of *tert*-butyl cation (**3**) to acety-

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lene, which leads to the *tert*-butylvinyl carbocation (**4**), followed by the rejection of the proton from the latter.

Since the use of mercury salts as a catalysts has no prospects for industrial application we investigated the influence of zinc and nickel sulfates on this process. It was shown that $ZnSO_4$ practically does not affect the reaction at 25—30 °C (the yield of *tert*-butylacetylene is ~0.6%). Meanwhile the presence of $NiSO_4$ rises the yield of *tert*-butylacetylene up to ~2% based on the starting *tert*-butyl alcohol. The increase in the yield can be explained by the increase in the solubility of acetylene in the reaction mixture which is due to the formation of π-complex of acetylene with the catalyst.

Thus, we have shown for the first time the fundamental possibility of the formation of *tert*-butylacetylene by the reaction of *tert*-butyl alcohol with acetylene. In spite of the low yield of *tert*-butylacetylene, this previously unknown reaction may become a base of technological method for the preparation of *tert*-butylacetylene, since the reaction provides easy isolation of the target product, does not need implementation of complicated devices, and furthermore it does not give nonutilizable waste.

Experimental

The ^{1}H NMR spectra were recorded on a Bruker AM-370 spectrometer (360.13 MHz) with Me_4Si as the internal standard. *tert*-Butylacetylene was identified in the distillate by GLC on a LKhM-80M chromatograph (katharometer as detector, helium as the carrier gas, 20 L min^{-1}, 2 m columns packed with 10% SKTF-100 on Chromaton, evaporator temperature 240 °C, detector temperature 190 °C). A specimen of *tert*-butylacetylene obtained by the known method[2] was used as a standard. The retention time was 1.3 min (isothermal mode, column temperature 120 °C).

***tert*-Butylacetylene (1).** Acetylene (3 L) was bubbled through a mixture of 70% H_2SO_4 (30 mL, 47.8 g, 0.34 mol), Bu^{t}OH (30 mL, 23.57 g, 0.32 mol), and $NiSO_4$ (1 g) at 25—30 °C during 2 h. Gases from the reactor were condensed in a trap, cooled to −5 °C (totally 0.8 g of liquid was collected in the trap). Then the reaction mixture was poured onto ice (40 g) and distilled. The fraction *1* collected (0.84 g, b.p. 37—40 °C) was combined with the condensate from the trap to give 1.64 g of a liquid (according to the GLC data the united fraction *1* contains *tert*-butylacetylene (28%), *tert*-butyl alcohol (21%), diisobutylene (51%)). The fraction *2* (26.8 g, b.p. 85 °C) contains 81% of *tert*-butyl alcohol. The united fractions *1* (14.5 g) from the several experiments (obtained from 141.42 g (1.909 mol) of Bu^{t}OH) were combined and distilled to give *tert*-butylacetylene (3.3 g, 5.0 mL, 0.04 mol), b.p. 37—38 °C, n_D^{20} 1.3750 (*cf.* Ref. 2: b.p. 39—40 °C, n_D^{20} 1.3738). ^{1}H NMR (CCl_4), δ: 1.23 (s, 9 H, Bu^t); 1.91 (s, 1 H, C≡CH). Similarly, fractions *2* gave 134.2 g (1.813 mol) of unreacted Bu^{t}OH. *tert*-Butylacetylene was obtained in ~2.1% yield based on initial Bu^{t}OH and 42% based on reacted Bu^{t}OH.

References

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