

SHORT
COMMUNICATIONS**1-*tert*-Butoxypropan-2-one as Direct Reaction Product of Acetone with *tert*-Butyl Hydroperoxide**

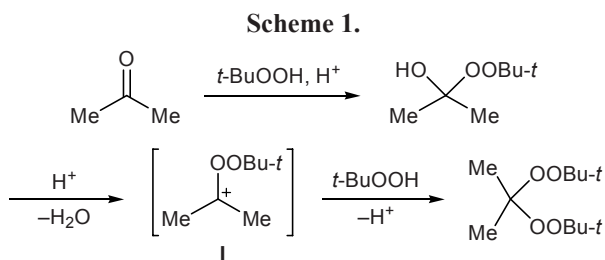
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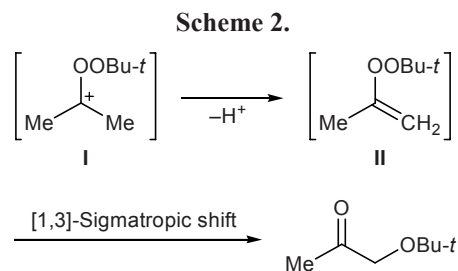
Hydroxyacetone is the main by-product impairing the quality of phenol obtained from cumene. It is now believed to be well established [1, 2] that this compound is formed mainly at the stage of acid decomposition of 1-methyl-1-phenylethyl hydroperoxide. Zakoshanskii et al. [2] presumed that hydroxyacetone arises from the reaction of acetone with 1-methyl-1-phenylethyl hydroperoxide; however, no experimental proofs for the proposed scheme were given in [2]. We used as a model *tert*-butyl hydroperoxide instead of 1-methyl-1-phenylethyl hydroperoxide, taking into account higher stability of the former under acidic conditions. It is well known [3] that reactions of carbonyl compounds with hydroperoxides derived from alkanes lead to the formation of peroxy ketals (Scheme 1).



We have found that the reaction of *tert*-butyl hydroperoxide with acetone under certain conditions gives 1-*tert*-butoxypropan-2-one in a good yield. This compound is formed via rearrangement of 2-*tert*-butyldioxyprop-1-ene (II) resulting from elimination of proton from intermediate cation I (Scheme 2). The process competes with the substitution reaction leading to the formation of peroxy ketal.

Alkyl alkenyl peroxides were not isolated as individual substances, but their formation as intermediates

was reported [4]. 1-*tert*-Butoxypropan-2-one may be regarded as an ether derived from hydroxyacetone and *tert*-butyl alcohol. Such ethers are known to undergo decomposition to give the corresponding olefin (2-methylpropene) and primary alcohol (hydroxyacetone). In fact, we observed formation of hydroxyacetone upon decomposition of 1-*tert*-butoxypropan-2-one in acetone in the presence of sulfuric acid at 100°C (in a sealed ampule).



1-*tert*-Butoxypropan-2-one. A solution of 45 g (0.5 mol) of *tert*-butyl hydroperoxide in 50 ml of dioxane was added under stirring to a mixture of 58 g (1 mol) of acetone, 35 g (0.5 mol) of finely ground B₂O₃, 0.3 g (0.003 mol) of H₂SO₄, and 200 ml of dioxane, maintaining the temperature below 40°C. When the addition was complete, the mixture was stirred for 4 h at 55°C. Excess acetone and most part of the solvent were distilled off, the precipitate was filtered off, and the filtrate was diluted with water and extracted with chloroform (3 × 100 ml). The extracts were combined, washed with water until neutral reaction, and dried over CaCl₂, the solvent was distilled off, and the residue was distilled under reduced pressure, a fraction with bp 55–60°C (30 mm) being collected. Published data [5]: bp 54°C (25 mm). Yield 39 g (60%). ¹H NMR

spectrum (CDCl₃), δ , ppm: 3.8 s (2H, CH₂), 2.0 s (3H, CH₃), 1.0 s [9H, C(CH₃)₃]. ¹³C NMR spectrum (CDCl₃), δ_C , ppm: 208.7 (C=O), 74.4 [C(CH₃)₃], 68.9 (CH₂), 27.6 (CH₃), 26.8 (COCH₃).

1-Hydroxypropan-2-one. A heat-resistant glass ampule was charged with 1 g (0.008 mol) of 1-*tert*-butoxypropan-2-one and 25 g of a 0.025% solution of sulfuric acid in acetone. The ampule was sealed and placed in a thermostat heated to 100°C. After 60 min, the ampule was cooled and opened, and the mixture was diluted with water and extracted with diethyl ether (3 × 20 ml). The extracts were combined, dried over Na₂SO₄, and evaporated. Hydroxyacetone was identified as the corresponding 2,4-dinitrophenylhydrazone, mp 136°C; published data [6]: mp 137°C. ¹H NMR spectrum (DMF-*d*₇), δ , ppm: 11.5 s (1H, NH), 9.2 s (1H, H_{arom}), 8.6 d (1H, H_{arom}), 8.1 d (1H, H_{arom}), 5.6 t (1H, OH), 4.5 d (2H, CH₂), 2.3 s (3H, CH₃).

The ¹H and ¹³C NMR spectra were recorded on a Bruker DPX-300 spectrometer at 300 and 75 MHz, respectively.

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