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Solvolysis of 3,5-Di-*tert*-butyl-4-hydroxybenzyl Acetate in Alcohol Solutions

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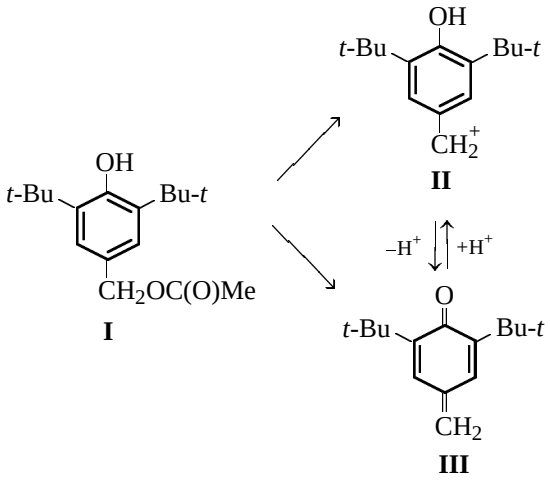
Abstract — Solvolysis of 3,5-di-*tert*-butyl-4-hydroxybenzyl acetate in alcohol solutions involves intermediate formation of 2,6-di-*tert*-butyl-4-methylene-1-benzoquinone that further takes up a molecule of the alcohol.

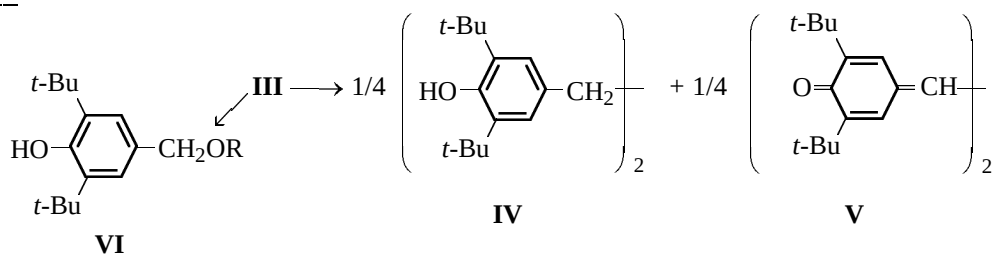
It is known that 3,5-di-*tert*-butyl-4-hydroxybenzyl-benzyl acetate (**I**) is a highly reactive precursor of 3,5-di-*tert*-butyl-4-hydroxybenzyl cation (**II**) and 2,6-di-*tert*-butyl-4-methylene-1-benzoquinone (**III**). For this reason, compound **I** is active in reactions with aromatic hydrocarbons and certain nucleophiles, which allow synthesis of compounds with sterically congested benzyl fragments under mild conditions and in high yields [1–5].



Reactions of benzyl acetate **I** with alcohols, because of the low nucleophilicity of the latter, are not so smooth. Alcohols are insufficiently active with benzyl cation **II** and methylenequinone **III**, which results in formation of appreciable amounts of by-products **IV** and **V** [6].

The formation of compounds **IV** and **V** can be suppressed by using an excess of alcohols. Under these conditions, 3,5-di-*tert*-butyl-4-hydroxybenzyl-substituted alcohols **VI** (for instance, 3,5-di-*tert*-butyl-4-hydroxybenzylmethanol) are formed in high yields [7].

We studied conversions of benzyl acetate **I** in methanol-d_4 and ethanol-d_6 by ^{1}H NMR spectroscopy. As seen from Fig. 1, the spectra of freshly prepared solutions of compound **I** in methanol-d_4 show two groups of signals (subspectra A and B), between which there is a rapidly established reversible concentration and temperature equilibrium. Increasing concentration of benzyl acetate **I** and lowering temperature render subspectrum A stronger and subspectrum B weaker. The same pattern is characteristic of the spectra of benzyl acetate **I** in ethanol-d_6. The concentration and temperature variations of the spectra of compound **I** in deuterated alcohols can be explained in terms of equilibrium (1).



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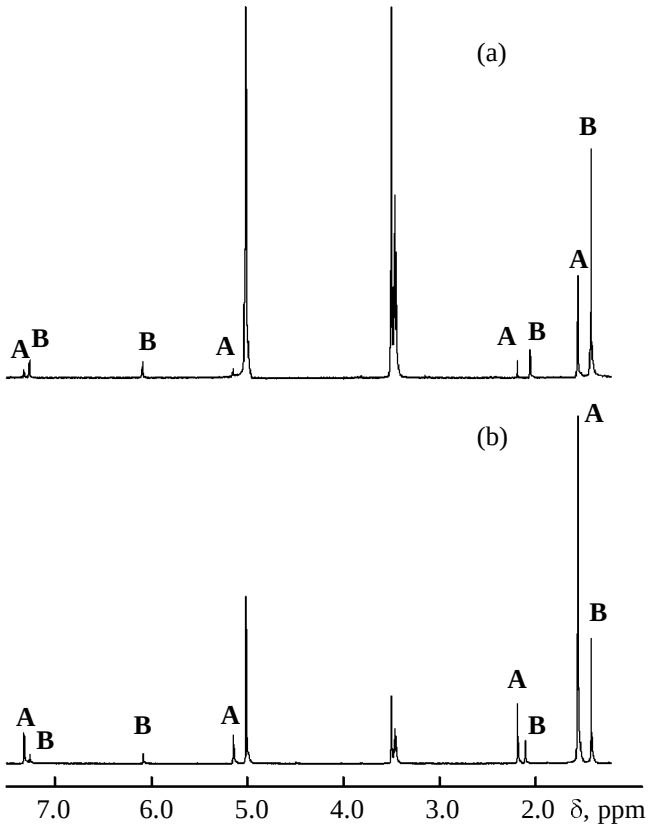


Fig. 1. ^{1}H NMR spectra of solutions of benzyl acetate **I** in methanol-d_4. $c_{\mathbf{I}}$, M: (a) 3.50×10^{-3} and (b) 4.72×10^{-2}.

$$\mathbf{I} \rightleftarrows \mathbf{III} + \mathrm{MeCOOH} + Q. \quad (1)$$

VII

In this case, subspectrum A contains signals of *tert*-butyl, acetyl, methylene, and aryl protons of benzyl acetate **I**, and subspectrum B, signals of *tert*-butyl, vinyl, and cyclohexadienyl protons of methylenequinone **III** and methyl protons of acetic acid. The lack of signal of the hydroxy group of benzyl acetate **I** is explained by fast proton exchange with the solvent. According to [8], the ^{1}H NMR spectrum of methylenequinone **III** in tetrachloromethane contains four signals (δ, ppm, 80 MHz): 1.27 s (CMe_3), 5.62 s (CH_2), 6.82 s (CH), and the UV absorption maximum of this compound in hexane is at 286 nm. The same absorption maximum we observe in the UV spectrum of benzyl acetate **I** in methanol (Fig. 2).

From the temperature dependences of the concentrations of compounds **I** and **III** in the temperature ranges 20–50 (methanol-d_3) and 20–60°C (ethanol-d_6) by Eqs. (2)–(4) we calculated thermodynamic parameters of equilibrium (1) in alcohol solutions of benzyl acetate **I**.

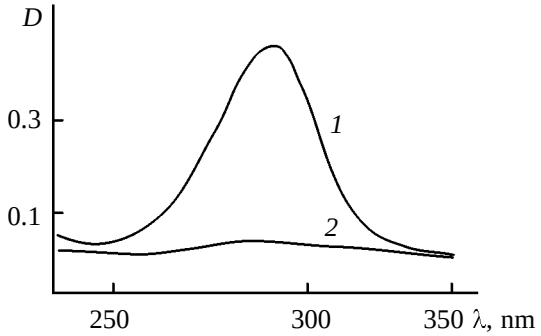


Fig. 2. Fragments of the UV spectra of solutions of benzyl acetate **I** in (*1*) methanol and (*2*) carbon tetrachloride ($c_{\mathbf{I}}$ 2×10^{-5} M).

$$K_e = [c_{\mathbf{III}}][c_{\mathbf{VII}}]/[c_{\mathbf{I}}], \quad (2)$$

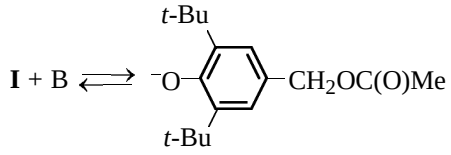
$$\Delta G^0 = -RT\ln K_e, \quad (3)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0. \quad (4)$$

In methanol-d_4, K_e 6.6×10^{-3} (20°C), ΔH^0 22.2 ± 1.3 kJ/mol, ΔS^0 34.9 ± 4.3 J deg^{-1} mol^{-1}. In ethanol-d_6, K_r 2.1×10^{-3} (20°C), ΔH^0 28.8 ± 1.9 kJ/mol, ΔS^0 72.1 ± 6.2 kJ/mol.

The endothermicity of a direct reaction (1) is not surprising, since in its course the six-membered ring loses aromaticity, while the heat release associated with formation of new bonds is scarcely sufficient to compensate for the energy consumption for cleavage of old bonds.

It is known that methylenequinone **III** is readily generated from benzyl acetate **I** under the action of bases [5].



However, the formation of methylenequinone **III** is alcohol solutions of benzyl acetate **I** cannot be explained by basic properties of these solvents. Methylenequinone **III** is not detected by ^{1}H NMR spectroscopy in solutions of benzylacetate **I** in acetone and dimethyl sulfoxide. The latter is much more basic than alcohols. Moreover, the formation of methylenequinone **III** in chloroform from compound **I** under the action of a strong base, triethylamine, is much slower than in alcohol solutions of benzyl acetate **I**. In this connection we suggest that in the latter solutions methylenequinone **III** is formed by acid dis-

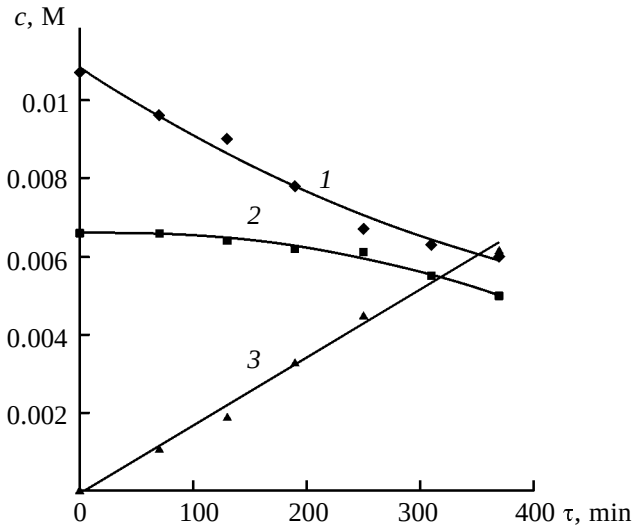
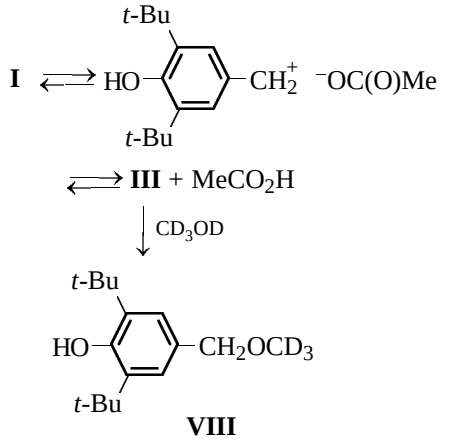


Fig. 3. Concentrations of (*1*) benzyl acetate **I**, (*2*) methylenequinone **III**, and (*3*) ether **III** vs. time of methanolysis of benzyl acetate **I** ($c_{\mathbf{I}}^0$ 0.0173 M).

sociation of benzyl cation **II** which, in its turn, is formed as an ion pair by alcoholysis of benzyl acetate **I** [scheme (5)].



(5)

VIII

In the ^{1}H NMR spectrum of a solution of benzyl acetate **I** in methanol-d_4, 10–15 min after its preparation, the signal of methyl protons of acetic acid begins to grow (compared with equilibrium) and signals of 3,5-di-*tert*-butyl-4-hydroxybenzyl methyl ether (**VIII**) appear at 7.28 (Ar–H) and 4.49 ppm (CH_2–O); the chemical shifts of *tert*-butyl protons of compounds **I** and **VIII** are coincident. Figure 3 shows the plots the concentrations of benzyl acetate **I**, methylenequinone **III**, and compound **VIII** vs. time of methanolysis of benzyl acetate **I**. After 1 day, the ^{1}H NMR spectrum of the solution contained no other signals than those of benzyl ether **VIII**.

Parameters of solvolysis of benzyl acetate **I** in methanol-d_4

$c_{\mathbf{I}}$, M	c_{D_2O}, M	$c_{\mathbf{III}}/c_{\mathbf{I}}$	Yield of ether **VIII**, %[a]	k_{app}^{20}, s^{-1}
0.0730	–	0.22	12	1.6×10^{-5}
0.0173	–	0.62	26	3.1×10^{-5}
0.0180	0.5	0.75	33	4.1×10^{-5}

[a] Reaction time 4 h.

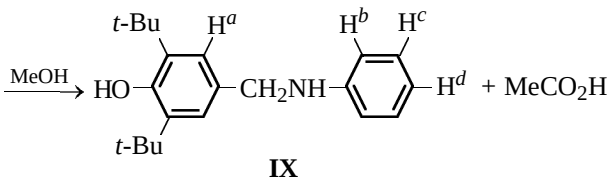
According to scheme (5), solvolysis of benzyl acetate **I** with a fast reversible stage is a pseudo-first-order reaction. At the same time, the kinetics of this process exert effect on the position of the benzyl acetate **I**–methylenequinone **III** equilibrium, which depends on the initial concentration of benzyl acetate **I** (Fig. 1) and changes as the concentration varies in the course of reaction because of the different number of molecules in the left- and right-hand parts of scheme (1). For this reason, the dependence of the negative logarithm of the current concentration of benzyl acetate **I** on time is a straight line only at conversions no higher than 40–50%. Therewith, the slopes of these dependences for different initial concentrations of benzyl acetate **I** are different (see table).

The table lists the yields of ether **VIII** for different reaction times, and the apparent first-order rate constants for solvolysis of benzyl acetate **I** in solutions with different **I**:**III** ratios, depending on the concentration of the initial reagent and the composition of the solvent. The rate constants were determined from the semilog anamophoses of the initial parts of the kinetic curves of variation of the concentration of benzyl acetate **I**. As seen from the table, the solvolysis rate increases with increasing concentration of methylenequinone **III** in the solution, which is consistent with scheme (5).

Since the benzyl acetate **I**–methylenequinone **III** equilibrium is established almost immediately after dissolution of benzyl acetate **I** and methylenequinone **III** slowly reacts with alcohols, the latter can be involved in generation of methylenequinone **III** from benzyl acetate **I** in reactions with weak nucleophiles. Thus, for instance, aromatic amines in the absence of stronger bases fail to react with benzyl acetate **I**, because they are incapable of generating methylenequinone **III** from the latter. We found that in methanol, unlike carbon tetrachloride, chloroform, and benzene, benzyl acetate **I** rapidly reacts with aniline already at room temperature. In the ^{1}H NMR spectrum of a solution of benzyl acetate **I** in methanol-d_4 (c 5×10^{-3} M) 20 min after addition of excess aniline we observed disappearance of the signals of *tert*-butyl protons of methylenequinone **III** at 1.43 ppm and of

acetyl protons of benzyl acetate **I** at 2.19 ppm and appearance of a signal at 4.19 ppm due to methylene protons of benzylaniline **IX**.

I + $PhNH_2$



IX

At a higher concentration of compound **I**, the reaction with aniline, like methanolysis, slows down because of decreasing concentration of methylenequinone **III** in the reaction mixture.

Thus, the reactions of benzyl acetate **I** with alcohols in the absence of acidic and basic catalysis involve ionic dissociation of compound **I** with intermediate formation of methylenequinone **III** which then slowly takes up a molecule of the alcohol.

The use of alcohols as solvents is an effective way of generation of methylenequinone **III** from benzyl acetate **I**, which allows one to avoid application of stong bases in reactions of the latter with weak nucleophiles.

EXPERIMENTAL

The ^1H NMR spectra were obtained on a Varian Gemini-200 spectrometer (200 MHz) using signals of residual protons of deuterated solvents as internal references. The electronic spectra were measured on a Specord UV-Vis spectrophotometer. Solvents were preliminarily dried over Zeolite NaX.

3,5-Di-*tert*-butyl-4-hydroxybenzylaniline (IX). A solution of 2.78 g of benzyl acetate **I** and 23.25 g of aniline in 55 ml of methanol was allowed to stand at room temperature for 1 day and then poured into 400 ml of water. The precipitate was filtered off, washed with water, and dried in air. Recrystallization from ethanol gave colorless crystals, mp 104 × 105°C, yield 79%. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.44 s (18H, CMe_3), 4.19 s (2H, CH_2N), 5.21 s (1H, OH), 6.65–6.85 m (3H, H^b, H^d), 7.18 (2H, H^a), 7.21 t (2H, H^c).

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