MECHANICAL ACTIVATION OF THE KOH-DMSO SUPERBASE SYSTEM AND ITS USE IN THE REACTION WITH CYCLOHEXANONE

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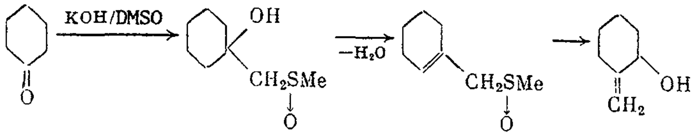
Mechanical activation, which is commonly employed in the treatment of mineral raw materials, coal [1], and high-molecular-weight compounds [2], was virtually not used in fine organic synthesis, in contrast, for example, to ultrasound [3].

We may propose that the heterophase alkali-DMSO superbase system is activated by mechanical activation since a high degree of pulverization of the alkali, which has low solubility in DMSO, is required at 20-80°C [4].

In order to check this hypothesis, we selected the following reaction of cyclohexanone in the KOH-DMSO system [5]



(I) (II) (III) (IV)

In our previous work [5], hydroxysulfoxide (II) was isolated in only 4% yield. Prior mechanical activation of the KOH-DMSO system with the subsequent addition of cyclohexanone at 20°C enhanced the yield of (II) to 33%, which is higher than in the dimsylsodium-DMSO system (17%) [6]. The simultaneous mechanical treatment of all the reagents does not lead to such an increased yield (24%). This behavior is related to autooxidation reactions of (I) and the dehydration of hydroxysulfide (II) to give allylsulfoxide (III). The use of previously pulverized alkali under the conditions studied (20°C) leads to a complex mixture of products, containing traces of sulfoxides (II) and (III).

The observed enhanced reactivity of the KOH-DMSO system as a result of mechanochemical activation is apparently a result of the generation of a highly active KOH surface and significant facilitation of the ionization processes, which permit us to surpass the activity of a homogeneous system.

The mechanical activation was carried out in a Pulverisette-6 centrifugal agate mill with angular velocity of $\omega = 60^{-1}$ and amplitude A = 24 mm. A sample of 25 agate balls (Ø 10 mm), six agate balls (Ø 20 mm), 80 ml pure-grade DMSO, and 16 g analytical-grade KOH (with -15% water content) were placed into a 250-ml vessel. The mechanical activation time was 15 min. Then, 8 g cyclohexanone was added to the suspension obtained. The mixture was agitated for 5 min, left for 1 h, neutralized with 15.6 g ammonium chloride, and filtered. DMSO was distilled off. The residue was extracted with CH_2Cl_2 and the solvent was removed. Fractionation and recrystallization from ethyl acetate-2-propanol gave 4.6 g (33%) methyl-(1-hydroxycyclohexyl)methylsulfoxide (II), mp 56-57°C. Found: C, 54.35; H, 9.16; S, 18.16%. Calculated for $C_8H_{16}O_2S$: C, 54.51; H, 9.15; S, 18.19%. IR spectrum (ν, cm^{-1}): 610, 690, 850, 900, 950, 980, 1000, 1030, 1080, 1120, 1170, 1380, 1410, 1430, 2830, 2900, 2905, 3205. PMR spectrum (δ, ppm): 1.35-1.90 m [10H, $(CH_2)_4$], 2.65 s (3H, CH_3), 2.83 two d (2H, AB system, CH_2), 3.58 br. s (1H, OH).

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LITERATURE CITED

1. E. G. Avvakumov, Mechanical Methods for the Activation of Liquid-Phase Reactions [in Russian], Khimiya, Novosibirsk (1986).
2. N. K. Baramboim, The Mechanochemistry of High-Molecular-Weight Compounds [in Russian], Khimiya, Moscow (1978).
3. T. J. Mason, Lab. Practice, 33, 13 (1984).
4. B. A. Trofimov, A. M. Vasil'tsov, and S. V. Amosova, Izv. Akad. Nauk SSSR, Ser. Khim., No. 4, 751 (1986).
5. B. A. Trofimov, A. M. Vasil'tsov, O. V. Petrova, and A. I. Mikhaleva, Zh. Org. Khim., 24, 2002 (1988).
6. E. J. Corey and M. Chaykovsky, J. Am. Chem. Soc., 87, 1345 (1965).