SODIUM PERSULFATE IN SOLID PHASE ORGANIC SYNTHESIS

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Alkali metal persulfates (AP) are well known as oxidizing agents for organic compounds. We have used AP in aqueous acetone for the oxidation of 2-hydroxy-3,5-di-tert-butylbenzyl alcohol to give 3,5-di-tert-butylsalicylaldehyde (I) in 65-68% yield.

However, our attempt to carry out this synthesis in the solid phase by the modified extrusion method [1] with a 1:2 alcohol/AP ratio at 20 \pm 5°C (the extrusion time was about 15 min) led to an unexpected result. 2,2'-Dihydroxy-3,3',5,5'-tetra-tert-butyl-dibenzyl ether (II), mp 136-137°C (from methanol-chloroform) was obtained in 86% yield instead of (I). Product (II) was isolated by preparative thin-layer chromatography. Found: C, 79.20; H, 10.22%. Calculated for $C_{30}H_{46}O_3$: C, 79.24; H, 10.19%. PMR spectrum in C_6D_6 at 80 MHz (δ , ppm): 1.28, 1.61 s (Me₃C), 4.23 s (CH₂), 6.72 and 7.50 d (Ph), 7.01 s (OH).



Such transformations of benzyl alcohols are usually carried out by the action of acidic reagents. Such a reagent is apparently generated under solid phase conditions in situ according to the following scheme:

$$\begin{array}{c} \operatorname{Na_2S_2O_8} \xrightarrow{- (\cdot)} \operatorname{Na_2SO_4} \cdot \operatorname{SO_3} \xrightarrow{\operatorname{RCH_2OH}} \\ \longrightarrow [\operatorname{RCH_2^{\circ 2}} \operatorname{HSO_4^{\circ }}] \xrightarrow{\operatorname{RCH_2OH}} (\operatorname{RCH_2)_2O} + \operatorname{H_2SO_4} \cdot \operatorname{Na_2SO_4}. \end{array}$$

A strongly acidic reaction of the products of solid phase extrusion is in accord with this scheme.

Thus, the range of application of AP may apparently be extended to its use in the solid phase as "preserved" SO_3 .

LITERATURE CITED

 E. L. Akopyan, A. Yu. Karmilov, V. G. Nikol'skii, et al., Dokl. Akad. Nauk SSSR, <u>291</u>, No. 1, 133 (1986).

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