Studies on the Occurrence of Hydrogen Transfer. 65.* The Significance of Solvents and Solvent Mixtures in the Reductive Cleavage of Compounds of the Type ArSO_2Y ($\text{Y}=\text{OR}$, Ar' , Cl) with Alkali Amalgams

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The dependence of the yields of the reductive fission of hexyl benzenesulfonate and mesitylphenyl sulfone with alkali-metal amalgams (primarily lithium amalgam) was studied under standard conditions in toluene using a series of eight aprotic and six protic solvents as co-solvents. Yields about 5 % were measured in toluene, but addition of equimolar amounts (w.r.t. ester or sulfone) of the alcohols methanol, ethanol, isopropyl alcohol or tert-butyl alcohol as co-solvent raised the yields to 80–100 % (Fig. 1).

In toluene, portion-wise addition of sub-stoichiometric amounts (w.r.t. ester) of the co-solvents DMF, THF, dioxane and isopropyl alcohol resulted in the values recorded in Fig. 2. The observed effects are attributed to the different solubilities of Li^+ -solutions (of unknown composition) in toluene.

A reaction mechanism for the reductive fission of ArSO_2Y ($\text{Y}=\text{OR}$, Ar' , Cl) with alkali-metal amalgams is proposed.

In the 64th communication of this series we described a surprisingly high influence of the

reaction medium on the cleavage of some arylsulfonfyl chlorides and -hexyl esters and diarylsulfones (ArSO_2Y ; $\text{Y}=\text{Cl}$, OC_6H_{13} , Ar') with alkali amalgams (M/Hg ; $\text{M}=\text{Li}$, Na , K), yielding arylsulfonates ArSO_2M and MY . In toluene the reaction (1) is nearly totally suppressed using lithium amalgam. However, the addition of an amount of isopropyl alcohol equimolar to ArSO_2Y leads to a yield of more than 90 %.

In this context the influence of the following solvents on the yield of ArSO_2M and YH was investigated with and without admixture of isopropyl alcohol in amounts equivalent to ArSO_2Y : diethyl ether, tetrahydrofuran (THF), acetonitrile (ACN), dioxane and *N,N*-dimethylformamide (DMF). The behaviour of diethylether, THF and ACN was similar to toluene. Higher yields were observed using dioxane. Nevertheless DMF is the best solvent overall; the “normal” reductive cleavage (1) and also the “anomalous” reductive cleavage (2) of sterically hindered ArSO_2Y proceed with yields greater than 90 %.

The aim of this paper was to obtain a better understanding of the factors influencing the behaviour of good and bad solvents and co-

Scheme 1. $\text{Y}=\text{Cl}$, OR , Ar' .

* Part 64, see Ref. 1.

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Scheme 2. Y=OR, Ar¹.

solvents in the reductive cleavage of ArSO₂Y by alkali amalgams.

The influence of the reaction media and the co-solvents on the reductive cleavage of arylsulfonfyl hexyl ester and diarylsulfones with alkali amalgams. Hexyl benzenesulfonate is cleaved to benzenesulfinate and hexanol according to Scheme 1 under standard conditions¹ using the following solvents without (and with) isopropyl alcohol as a co-solvent (the yields of hexanol and sulfinate are, in general, equal). Toluene 5(90); diethyl ether 7(91); THF 86(98); dioxane 97(98); ACN 65(89); ACN 65(89); DMF 95(98). The following yields were obtained in the following solvents without (and with) isopropyl alcohol starting with hexyl-4-methoxybenzenesulfonate which possesses a more negative reduction potential:⁴ Toluene 5(6); diethyl ether 5(5); THF 9(67); dioxane 41(88); ACN 5(7); DMF 90(98).

With the sterically hindered hexyl mesityl sulfonate and hexyl 2,4,6-tri-isopropylbenzene sulfonate, the reaction media influence the yields of the products obtained with lithium amalgam according to Scheme 1; on occasion the partition of the reactions (1) and (2) can be altered in favour of reaction (2).

Hexylmesitylsulfonate gave (in %): (Hex~hexanol; Sulf~sulfinate; Mes~mesitylene; TiPB~1,3,5-triisopropylbenzene).

Toluene. (~5 (Hex), trace (Sulf), 5 (Mes);

Diethyl ether. 6 (Hex)~5 (Mes); *THF* 65 (Hex), 11 (Sulf), 26 (Mes);

Dioxane. 85 (Hex), 69 (Sulf), 10 (Mes); *ACN:* 7 (Hex), ~5 (Mes);

DMF. 99 (Hex), trace(Sulf), 85 (Mes).

Only in the case of dioxane was a shift favoring reaction (2) observed on addition of an equimolar amount of isopropyl alcohol 88 (Hex), 21 (Sulf), 61 (Mes).

For 2,4,6-tri-isopropylbenzenesulfonylhexyl ester the yields of the cleavage (2) are zero in toluene, diethyl ether and THF, and low in dioxane (7 % Hex; with the equimolar amount of isopropyl alcohol: 59 (Hex), 54 (TiPB)); in DMF however, the yield is practically quantitative!

Starting from sodium or potassium amalgam and hexyl benzyl sulfonate, the yields of the cleavage products are somewhat lower, following the more positive reduction potentials¹ of the sodium and potassium amalgams. The same strong influence of solvent and co-solvent exists for the reductive cleavage of benzene mesityl sulfone and dimesityl sulfone.

The influence of the pK_a-values of the co-solvents on the reductive cleavage of benzenesulfonyl hexyl ester and benzene mesityl sulfone with lithium amalgam according to (1). The reductive cleavage with lithium amalgam under standard conditions was investigated for a series in toluene, using hexyl benzenesulfonate and 14 solvents of different pK_a-values in the molar relation 1:1. The results are compiled in Fig. 1. (A similar dependence is found for the electroreductive cleavage of phenyl mesityl sulfone.

Co-solvents containing alcoholic functions and a pK_a-value of 14–18 (but not diethylmalonate or cyclopentadiene) strongly favour the reductive cleavage; it would be incorrect, however, to assume that the pK_a-value alone is responsible for this effect; thus also in the aprotic solvents THF, dioxane and especially DMF, practically quantitative yields are obtained. In our opinion the increase in yield is caused by undefined processes at the interface of the amalgams. The

Fig. 1. Dependence of the reductive cleavage of C₆H₅SO₂OC₆H₁₃(n) with Li/Hg in toluene from the pK_a-values of the added proton donors. Plot of the pK_a-values vs. the yield of hexanol in %. MDE=malonicacid diethylester.

Fig. 2. Dependence of the reductive cleavage of $C_6H_5SO_2OC_6H_{13}(n)$ (2.5 mmol) with Li/Hg (0.67 % w.w. Li=7.5 g = 6 mmol Li) in toluene (5 ml) on the added amount of DMF, THF, dioxane and isopropyl alcohol; temperature $23^\circ C \pm 1$; reaction time: 2 h. Co-solvents: added amount of DMF, THF, dioxane and isopropyl alcohol in mol % in relation to the mol number of the ester (2.5 mmol=100 %).

transfer of electrons from the amalgam to substrate will be favoured (a) by solvation of the substrate and (b) by increasing the solubility of the reaction products, which have to be removed from the surface of the amalgam. We assume that the effect (b) is more important than (a).

The influence of other co-solvents on the standardized reductive cleavage of benzenesulfonyl hexyl ester with lithium amalgam. Fig. 2 shows the results obtained for the reductive cleavage of n-hexyl-benzenesulfonate in the standardized experiment in toluene after stepwise addition of increasing amounts of co-solvents such as THF, DMF, dioxane and isopropyl alcohol (max. substrate co-solvent 1:1).

For the co-solvents THF and DMF a roughly linear relationship is observed between the formation of hexanol and the amount of added co-solvents. (20 mol percent co-solvent leads to the formation of 15–20 % hexanol; the yields of hexanol are 60–80 % if the relation substrate–co-solvent is 1:1. However the yield continues to increase on super stoichiometric addition of the co-solvent.)

Bearing in mind that the yields of the reductive cleavage of both arylsulfonylestes and diaryl sulfones depend in a parallel fashion on the

nature and amount of the added co-solvent, we conclude that the solubility (in toluene) of the lithium salts ($ArSO_2Li$ and LiY) formed at the surface of the amalgam is the predominant factor and not the solvation of the starting material. On this basis we assume that the aryl-sulfinate $ArSO_2Li$ and the co-solvent form a 1:1 adduct, which is soluble in toluene. In the case of dioxane as co-solvent, linearity ($ArSO_2Li$ –dioxane 1:1) was observed only to the limit of 30 % dioxane; thereafter, increasing amounts of dioxane hindered the reductive cleavage corresponding to a solvation complex of a hypothetical composition: $ArSO_2Li$ –dioxane $(1:2)_n$ which presumably has a low solubility in toluene and therefore will be accumulated at the surface of the amalgam.

There are likewise two linear areas for isopropyl alcohol as a co-solvent. Addition of 10 mol percent of isopropyl alcohol leads to the formation of 40 mol percent of lithiumhexanolate (and $ArSO_2Li$). We assume that $ArSO_2Li$, lithiumhexanolate and isopropyl alcohol form a solvation complex with a high solubility in toluene. The steeper part of the curve seems to correspond to a second solvation complex of a different composition but also with a sufficient solubility in toluene.

For the interpretation of the solvation complex formation, we refer to the solvation concept development by Gutmann.³ In this view the lithium ion is the electrophile, the oxygen function in the co-solvents, the nucleophile.

If the assumption is correct that the surface of the amalgam has to be freed by solution of the lithium salts formed, then isopropyl alcohol is the most efficient co-solvent. It is, however, too early to speculate on the composition of the solvation complex which seems to be a dynamic species.

Mechanistic considerations on the reductive cleavage at the interface of amalgams. The reductive processes at the surface of alkali amalgams on the one hand, and the normal electroreduction using a mercury cathode with supporting electrolytes and an electric field on the other, show many common features but also differences.

Common features. It is characteristic for both procedures that the electrons leave the mercury surface under over-voltage conditions and are transferred to the depolarizer (double bonds,⁴ sulfonyl derivatives⁴ and onium salts⁴). The potential of the mercury surface is constant,

Scheme 4. Solv=Solvents; Y=OC₆H₁₃, Ar'.

alcohol and DMF remove the cleavage products from the mercury surface by solvation. With DMF as solvent or co-solvent the reduction of *p*-toluenesulfonylchloride consumes more than 2 mols of lithium (available as Li/Hg) and simultaneously DMF is partially destroyed.

In summary. (a) The course of the reduction will be determined by the potentials of the amalgams and the substrates.

(b) Both the potential of the amalgam ⁶ and the reactivity of the substrate can be influenced by the solvent, which removes the chemisorbed cleavage products from the mercury surface by solvation.

(c) Using aprotic solvents in the amalgam reduction, a sequence of decreasing reductive power is observed following the rule of Gutmann ³ for the decreasing donor quality of the solvents: DMF>THF≥dioxane>ACN>diethylether>toluene.

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