

Sulfolane: A Versatile Dipolar Aprotic Solvent

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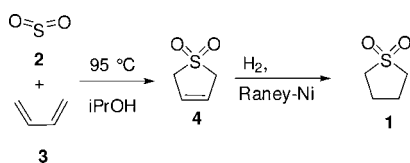
ABSTRACT: Sulfolane is a highly stable and attractive alternative to other more common dipolar aprotic solvents such as DMSO, DMF, DMAC, and NMP. Sulfolane is more toxic than the other solvents but has a very low skin penetration in comparison to that of the others. A high skin penetration is not beneficial for organic solvents as dissolved toxic compounds might be transferred through the skin. Sulfolane has a high dipole moment ($\mu = 4.7$ debye), elevated relative permittivity ($\epsilon_v = 43.4$), and a high Hildebrand solubility parameter ($\delta = 27.2$ [MPa]^{1/2}). This means a high solvency power for reactions containing polarizable intermediates. Sulfolane is capable of strong solvation of cations by the oxygens in the sulfone group which increases the nucleophilicity of the corresponding less solvated anions. With its high stability against strong acids and bases as well as its thermal stability sulfolane is a solvent that can be operated within a wide range of reaction conditions. This makes it the solvent of choice for different acid-catalyzed reactions at elevated temperatures. Sulfolane has also found use in halo exchange reactions for the formation of various fluoroaromatic compounds. It has also been used as solvent for oxidations, nitrations, rearrangements, phosphorylations, and condensation reactions.

INTRODUCTION

Sulfolane (tetrahydrothiophene sulfone or tetrahydrothiophene-1,1-dioxide)¹ (**1**) is a dipolar aprotic industrial solvent, commonly used in gas production and oil refining. It is a medium polar, very stable, water-soluble compound. It is also very stable at elevated temperatures in air; e.g. at 200 °C the rate of decomposition is only 0.009%/h. In the combination with water and carbon steel there is no corrosion at 200 °C, indicating no or very little release of sulfur dioxide. Due to the high boiling point and its stability sulfolane is easily recovered, especially if it ends up in waste streams because there is an extraction process available for the recovery of the solvent.¹

Sulfolane was first produced by Shell in the 1940s. The original method developed by the Shell Oil Company who was first to allow sulfur dioxide (**2**) to react with butadiene (**3**) in a chelotropic reaction. This yields first sulfolene (**4**) that is subsequently hydrogenated using Raney nickel as a catalyst to give sulfolane (**1**) (Scheme 1).

Scheme 1. Industrial process for the synthesis of sulfolane



Shortly thereafter, it was discovered that both the product yield and the lifetime of the catalyst could be improved by adding hydrogen peroxide and then neutralizing the reaction mixture to a pH of roughly 5–8 before hydrogenation.²

The main applications are (i) the Shell Sulfolane Extraction Process where sulfolane is used in extraction processes to recover high-purity aromatic components from hydrocarbon mixtures¹ and (ii) the Sulfinol Process for purifying gas streams, where sulfolane is used to purify acidic or sour gas streams by

removing sulfur compounds and carbon dioxide to provide gas that meets commercial specifications.¹

In this article we have compared sulfolane with the most commonly used dipolar aprotic solvents dimethylsulfoxide (DMSO), *N*-methyl pyrrolidin-2-one (NMP), *N,N*-dimethyl formamide (DMF), and *N,N*-dimethyl acetamide (DMAC). Sulfolane is completely miscible with water and all polar organic solvents. It is also completely miscible with aromatic solvents. It behaves the same as all other dipolar aprotic solvents: it does not dissolve in alkanes. Sulfolane is miscible with ester, ketone, and ether solvents in the same way as are all other solvents from the group dipolar aprotic solvents. In the case of sulfolane there is one exception: sulfolane is not miscible with *tert*-butyl methyl ether (MTBE). This simplifies the workup of reactions where the product is soluble in MTBE, as sulfolane will remain as a separate phase when MTBE is added. In some cases where the product acts as a detergent, it is necessary to add a small amount of water to obtain complete separation.

COMPARATIVE SOLVENT DATA FOR DIPOLAR APROTIC SOLVENTS

Sulfolane is a dipolar aprotic sulfone solvent and has physicochemical properties comparable to those of DMSO, NMP, DMF, and DMAC, and other solvents in the category dipolar aprotic solvents.

From the solvents in Table 1 sulfolane (anhydrous) has the highest boiling point and the highest freezing point at 28.4 °C. The viscosity at 30 °C is also much higher than that for the other dipolar aprotic solvents. The melting point can be lowered by addition of small amounts of water. Sulfolane with 3 vol % water has a melting point of 10 °C. This mixture is also commercially available. In cases where a small amount of water

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Table 1. Physical properties of sulfolane and four related, commonly used dipolar aprotic solvents

property	sulfolane	DMSO	NMP	DMF	DMAC
relative molecular mass	120.17	78.13	99.13	73.09	87.12
density (g·cm ³)	1.26	1.10	1.03	0.94	0.94
boiling point (°C)	287.3	189.1	201.9	153.1	166.2
freezing point (°C)	28.4	18.6	-24.4	-60.4	-20.1
relative permittivity (ε _r)	43.4 @ 30 °C	46.7 @ 25 °C	32.2 @ 25 °C	36.7 @ 25 °C	37.8 @ 25 °C
dipole moment (debye)	4.69	3.96	4.09	3.8	3.72
Hildebrand solubility parameter	27.2	26.6	23.6	24.1	23.3
normalized empirical solvent polarity parameter (E _T)	0.410	0.444	0.355	0.386	0.377
viscosity (cP)	10.35 @ 30 °C	2.0 @ 25 °C	1.67 @ 25 °C	0.9 @ 20 °C	2.14 @ 20 °C
flash point (°C)	177	89	86	58	63
autoignition point (°C)	528	302	270	445	445
vapour pressure (kPa)	0.0091 @ 30 °C	0.060 @ 25 °C	0.050 @ 25 °C	0.37 @ 25 °C	0.13 @ 25 °C

does not harm the reaction, it is beneficial to use this mixture. With 10 vol % of water the melting point is as low as 0 °C.

For further information concerning solvents and solvent effects see refs 3a and 3b.

The acute toxicity of sulfolane is higher than that of the other solvents if swallowed (Table 2). For sulfolane the level is 1.9 g/kg for rat, and for DMSO it is 14 g/kg. The skin permeability is highest for DMSO. Sulfolane has a skin permeability of only 0.2 mg/(m²/h) which is much lower than that of the other solvents. Although DMSO is not toxic as a pure compound, it can carry dissolved toxic compounds through the skin when used as solvent.

SELECTED EXAMPLES OF REACTIONS IN SULFOLANE

Sulfolane is a dipolar aprotic solvent that offers many benefits in comparison to other dipolar aprotic solvents. It has remarkably low penetration through the human skin. Sulfolane has a high dipole moment, elevated relative permittivity, and a high Hildebrand solubility parameter. This means a high solvency power for reactions containing polarizable intermediates. Sulfolane is capable of strong solvation of cations by the oxygens in the sulfone group which increases the nucleophilicity of the corresponding, less solvated anions. With its high stability against strong acids and bases as well as its thermal stability sulfolane is a solvent that can be operated within a large range of reaction conditions.

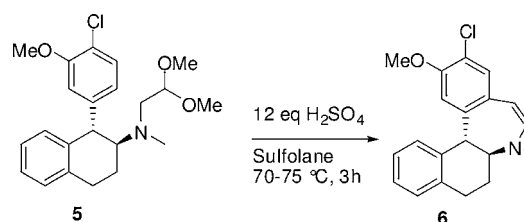
Due to the stability of sulfolane towards strong acidic conditions, also at high temperatures, it can be used not only

with strong acids but also together with reagents such as phosphorous tri- and pentachloride or thionyl chloride.

Twenty-one representative examples for the use of sulfolane as reaction medium are given in Schemes 2–22.

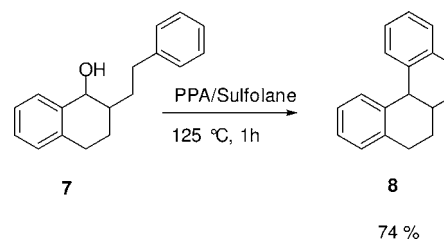
The best reaction conditions were found to be sulfuric acid (12 equiv) in sulfolane at 70–75 °C for 3 h for performing the cyclization of the sulfate salt of the free base **5** to produce the product **6**, although methanesulfonic acid (12 equiv) was found to be superior in the reaction with the oxalate salt of **5**. The use of the salt also removes impurities and improves the chiral purity of the reduced product. The use of sulfuric acid in sulfolane had no effect on the oxalate salt (Scheme 2).⁴

Scheme 2. Intramolecular Friedel–Crafts acylation



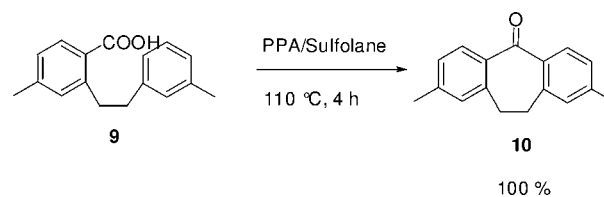
In 1967 Whiting et al. found that a 1:1 mixture of polyphosphoric acid (PPA) and sulfolane is a good reaction medium for the cyclization of the tetrahydronaphthol (**7**) to hexahydrobenzophenanthrene (**8**) at 125 °C for 1 h (Scheme 3).⁵

Scheme 3. Intramolecular Friedel–Crafts alkylation



Wild, et al. used a 1:4.2 mixture of sulfolane and PPA to cyclize acid **9** to the dibenzocycloheptadienone (**10**) at 110 °C for 4 h in 24 volumes of the mixture.⁶ The product **10** was obtained in quantitative yield (Scheme 4).

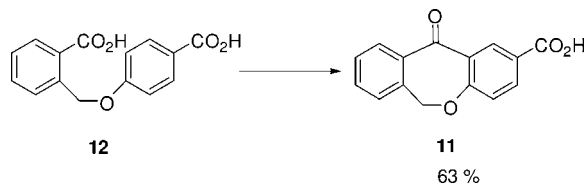
Scheme 4. Intramolecular Friedel–Crafts acylation

**Table 2. Toxicological data for sulfolane and four other commonly used, related dipolar aprotic solvents**

property	sulfolane	DMSO	NMP	DMF	DMAC
labeling R	22	36/37/38	36/38	61–20/21.1–36	61–20/21.1
labeling S	23.2–25	26 37/38	41	53.1–45	53.1–45
repr.	–	–	–	cat. 2	cat. 2
acute toxicity (g/kg rat oral)	1.9	14	3.6	2.8	4.3
skin permeability [mg/(m ² /h)]	0.2	176	171	98	107

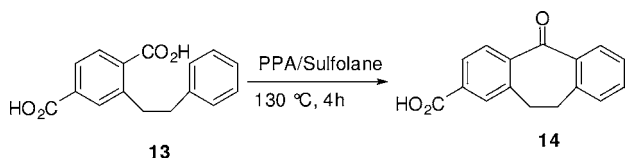
The dibenzo-oxepinone (**11**) was obtained in a novel direct cyclization of dicarboxylic acid (**12**). The cyclization was performed in 20 L/kg (volumes) of a 1:1 mixture of PPA and sulfolane at 100–110 °C for one hour. The product was obtained in 63% yield (Scheme 5).⁷

Scheme 5. Intramolecular Friedel–Crafts acylation



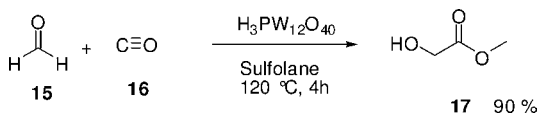
2-(2-Phenethyl)terephthalic acid (**13**) was cyclized with a 1:1.3 mixture of PPA and sulfolane at 130 °C for 4 h.⁸ Yield of the isolated product **14** was not reported (Scheme 6).

Scheme 6. Intramolecular Friedel–Crafts acylation



Liu et al. developed an efficient process for the synthesis of methyl glycolate (**17**) with heteropolyacids as catalyst in sulfolane as solvent.⁹ The catalytic carbonylation of paraformaldehyde (**15**) with carbon monoxide (**16**) and water with heteropolyacid catalysis was performed in an autoclave at 120 °C for 4 h. The process gave a 90% isolated yield of methyl glycolate. Reduction of the methyl glycolate gave ethylene glycol, a widely used, high-volume chemical product (Scheme 7).

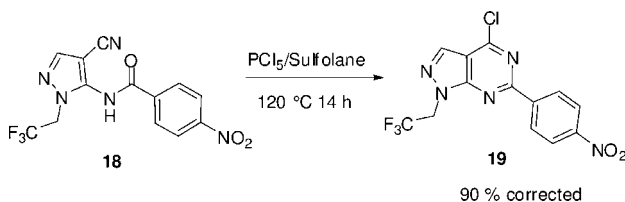
Scheme 7. Catalytic process towards methyl glycolate



Sulfolane was found to be the best solvent for a chloroimide cyclization of aromatic or heteroaromatic 2-acyl(amino)nitriles such as **18** with phosphorous pentachloride leading directly to the corresponding annulated 4-chloropyrimidines (**19**) in good to excellent yields (Scheme 8).¹⁰ The reaction is performed in sulfolane at 120 °C for 14 h. Other solvents did not give as clean a reaction and led to lower yields.

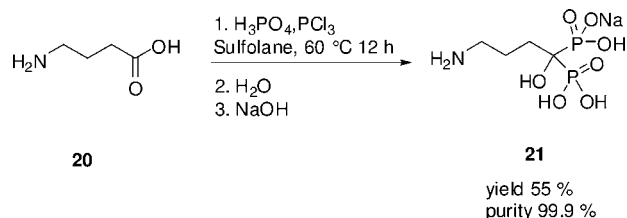
The phosphorylation of 4-aminobutyric acid (**20**) with phosphorous trichloride and phosphoric acid in sulfolane at

Scheme 8. Chloroimide annulation



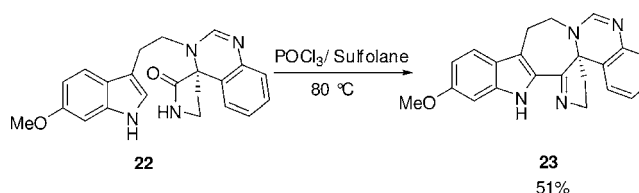
60–65 °C gives the 4-amino-1-hydroxybutylidene-1,1-bisphosphonic acid (**21**) in good yield.¹¹ The use of methanesulfonic acid was abandoned due to safety concerns. Methanesulfonic acid reacts with phosphorous trichloride that becomes self-heating at 85 °C (Scheme 9).

Scheme 9. Phosphonylation of 4-aminobutyric acid



Zhu et al. found that sulfolane was the solvent of choice for the phosphorous oxychloride-promoted Bischler–Napieralski reaction on the substrate **22** for the construction of the seven-membered ring in the product **23** (Scheme 10).¹² The reaction

Scheme 10. Difficult Bischler–Napieralski reaction in sulfolane

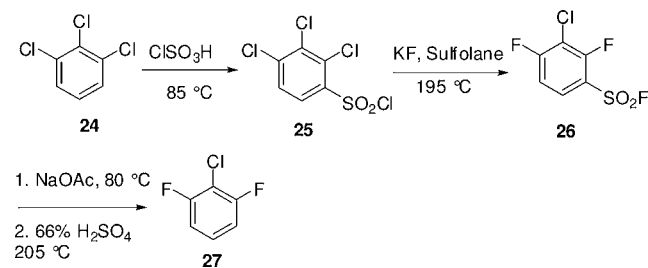


at 80 °C gave the product **23** in 51% yield. Standard condition as in toluene did not give any cyclization. In other polar solvents such as DMPU only 10% of the product **23** was obtained. The authors believe that sulfolane could find application in performing Bischler–Napieralski cyclization reactions which are difficult to realize otherwise.

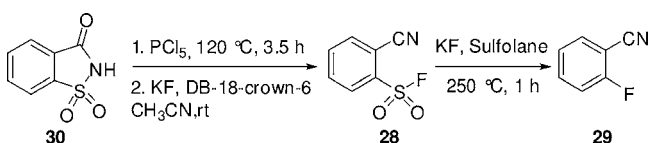
A new process for the synthesis of 1-chloro-2,6-difluorobenzene (**27**) from 1,2,3-trichlorobenzene (**24**) utilizes the selective formation of 2,3,4-trichlorobenzenes-1-sulfonyl chloride (**25**) to activate the two chlorine atoms in the ortho and para positions for a nucleophilic substitution with potassium fluoride in sulfolane at 195 °C, affording the intermediate **26**.¹³ After the fluorination the sulfonyl fluoride group is removed, giving the final product **27** (Scheme 11).

Van der Puy has found that heating of 2-cyano-benzene-1-sulfonyl fluoride (**28**) with spray-dried potassium fluoride in sulfolane at 250 °C gives 2-fluorobenzonitrile (**29**) in 84% yield.¹⁴ The 2-benzenesulfonyl fluoride (**28**) was obtained in a two-step process from saccharine (**30**) (Scheme 12).

Scheme 11. Selective haloexchange reaction

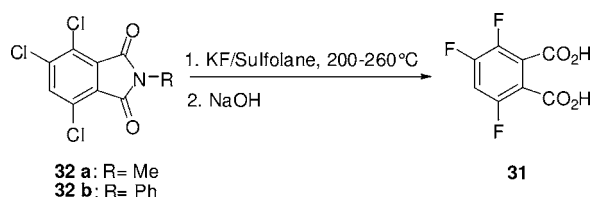


Scheme 12. Formation of 2-fluorobenzonitrile from saccharine



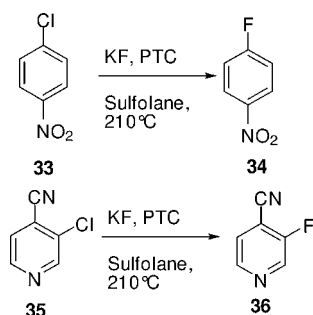
3,4,6-Trifluorophthalic acid (**31**) has been prepared in high yield by reaction of 3,4,6-trichloro-*N*-substituted phthalimides (**32**) with potassium fluoride at temperatures in the range of 200–260 °C in sulfolane, followed by hydrolysis of the imide. The reported phthalimides are *N*-methyl (**32a**) and *N*-phenyl (**32b**).¹⁵ The authors observed that the noncatalyzed process was more effective than a catalyzed process and that the methyl derivative (**32a**) gave a slightly higher yield of the desired product **31** (Scheme 13).

Scheme 13. Complete exchange of aromatic chlorines for fluorines



Cantrell has developed a method to transfer deactivated chloroaromatic compounds (**33**) to the corresponding deactivated fluoroaromatic compounds (**34**).¹⁶ The method is based on the use of a suspension of finely divided potassium fluoride in sulfolane obtained through dissolution of the fluoride in a methanol/sulfolane mixture. Addition of toluene and then removal of the two low-boiling solvents and water give a finely divided suspension of potassium fluoride in sulfolane. The exchange reaction was performed at 210–215 °C, giving the corresponding fluoroaromatic products in high yields. Also chloropyridine derivatives (**35**) were found to convert to the corresponding fluoropyridines (**36**) (Scheme 14).

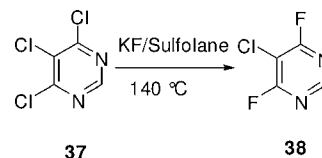
Scheme 14. Haloexchange reaction on electron-poor substrates



Ritzer et al. have developed a process for the synthesis of 5-chloro-4,6-difluoropyrimidine (**37**) from the reaction of potassium fluoride with 4,5,6-trichloropyrimidine (**38**) in sulfolane (Scheme 15).¹⁷

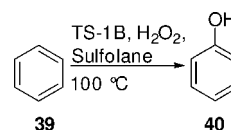
Bianchi et al. have reported on the direct hydroxylation of benzene (**39**) to phenol (**40**) with hydrogen peroxide over a

Scheme 15. Selective haloexchange reaction



modified titanium silicate as catalyst (Scheme 16).¹⁸ The reaction was performed in benzene. Although addition of

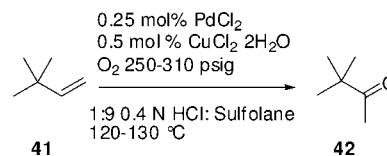
Scheme 16. Titanium-catalyzed oxidation of benzene



acetone as a cosolvent sped up the reaction 10 fold, the selectivity for phenol was only 43% at a conversion of hydrogen peroxide of 90%. After addition of sulfolane the selectivity for phenol increased dramatically up to 94% at a conversion of hydrogen peroxide of 97%. This can be explained through the properties of sulfolane. Sulfolane is a solvent with a high dipole moment and relative permittivity, thus having the peculiar property of being able to form complexes with phenolic compounds. These complexes are not stable enough to be isolated but can be identified in solution by IR spectroscopy.¹⁹

Aqueous sulfolane has been used as solvent in the rapid oxidation of 3,3-dimethylbut-1-ene (**41**) catalyzed by PdCl₂ (Scheme 17).²⁰ A mixture of the starting material, palladium

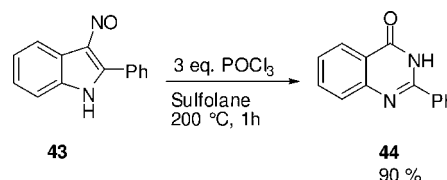
Scheme 17. Palladium-catalyzed oxygen oxidation



chloride, and cupric chloride was taken up in sulfolane and a small amount of dilute hydrochloric acid in an autoclave. The autoclave was pressurized with oxygen and heated up to 120–130 °C. With complete conversion the selectivity for 3,3-dimethylbutan-2-one (**42**) was 73%.

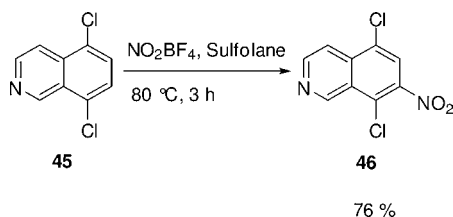
Yoneda et al. found that heating 3-nitroso-2-phenylindole (**43**) with 3 equiv of phosphorous oxychloride at 200 °C in sulfolane for 1 h afforded 2-phenylquinazoline-4(3*H*)-one (**44**) in 90% yield.²¹ Running the reaction in DMF under reflux conditions for 5 h afforded the wanted product only in 40% yield. This ring-expansion process proceeded probably through a second-order Beckmann rearrangement of the imino/oxime tautomer form of the starting material (Scheme 18).

Scheme 18. Rearrangement of 3-nitroso indole



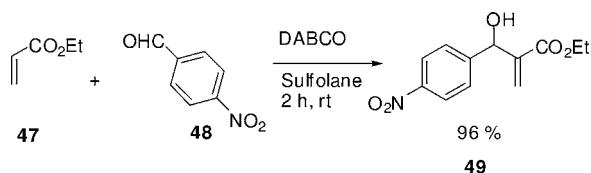
The nitration of 5,8-dichloroisoquinoline (**45**) is very difficult under standard conditions; either there is no conversion, or the reaction delivers a very low yield of the wanted product, in some cases with extremely long reaction times.²² Walker et al. found that nitronium salts as a neutral source of the nitronium ion gave an improved conversion of the 5,8-dichloroisoquinoline. The authors found sulfolane to be the solvent of choice; although dichloromethane could be used as a cosolvent, other solvents were either incompatible or led to no reaction. Although the best reaction conditions reported were 1.8 equiv of nitronium tetrafluoroborate with 2 equiv of trifluoromethanesulfonic acid in sulfolane at 80 °C for 2 h (93% isolated yield), the authors decided to use only 2.25 equiv of nitronium tetrafluoroborate in pure sulfolane without additives for 3 h at 80 °C. This process delivered the desired product 5,8-dichloro-7-nitroisoquinoline (**46**) in 76% yield on a 40 kg scale (Scheme 19).

Scheme 19. Nitration with nitronium tetrafluoroborate



Sulfolane has also successfully been used as solvent in the Morita–Baylis–Hillman reaction.²³ This reaction is a very important carbon–carbon bond-forming reaction between activated alkenes and aldehydes in the presence of tertiary bases used as catalysts, such as 1,4-diazabicyclo[2.2.2]octane (DABCO), to result in multifunctional products. However, this reaction traditionally suffers from low reactivity and limited substrate scope. Krishna et al. found that, instead of using the standard aqueous conditions, the use of dipolar aprotic solvents together with DABCO improves the conversion to the desired product and eliminates the problem with the hydrolysis of ethyl acrylate (Scheme 20). The investigated solvents were *N*-

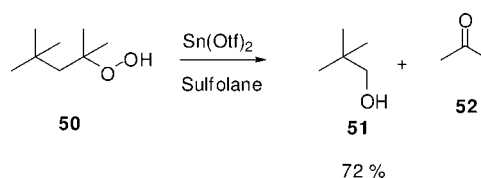
Scheme 20. DABCO-promoted Morita–Baylis–Hillman reaction to product 49



methylmorpholine, *N*-methylpyrrolidone, and sulfolane. From these, sulfolane was found to be the most efficient in the DABCO-promoted reaction between ethyl acrylate (**47**) and 4-nitrobenzaldehyde (**48**) to give the desired product (**49**).

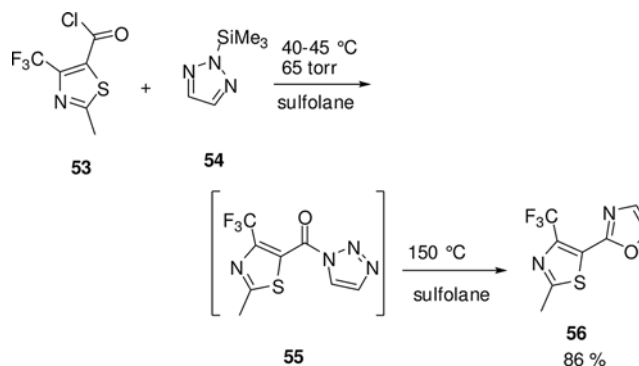
Metal triflates such as $\text{Sn}(\text{Otf})_2$ and $\text{La}(\text{Otf})_3$ have been found to act as efficient catalysts for cleaving 2,4,4-trimethylpentane-2-hydroperoxide (**50**) into neopentyl alcohol (**51**) and acetone (**52**) in sulfolane (Scheme 21).²⁴ Sulfolane was found to be superior to cyclohexane and 2-butanone, giving a much higher yield of neopentyl alcohol. If the Lewis acid was exchanged for sulfuric acid in sulfolane, a decrease in product yield was observed.

Scheme 21. Catalytic rearrangement of the hydroperoxide (50)



The reaction between 2-trimethylsilyl-1,2,3-triazole (**54**) and acid chlorides readily formed triazole amides. The triazole amides rearranged when they were heated to 150 °C in sulfolane for 2 h with the elimination of nitrogen to give 2-substituted oxazoles in high yields (Scheme 22).²⁵ The

Scheme 22. Rearrangement to the oxazole 56



rearrangement was sluggish in toluene or xylene with reaction times about 50 times longer. The reaction in sulfolane was also cleaner than for instance in DMF where dimethylamides were formed. The reaction can be performed with alkyl-, aryl-, and heteroaryl acid chlorides. In Scheme 22 the transformation of 5-chloro-2-methyl-4-(trifluoromethyl)thiazole (**53**), through the corresponding triazole amide (**55**), to the final product **56** is shown.

CONCLUSION

Sulfolane is a highly stable and attractive alternative to other more common dipolar aprotic solvents such as DMSO, DMF, DMAC, and NMP. Sulfolane is more toxic than the other solvents but has a very low skin penetration in comparison to that of the other solvents. A high skin penetration is not beneficial for organic solvents as dissolved toxic compounds might be transferred through the skin. Sulfolane has a high dipole moment, elevated relative permittivity, and a high Hildebrand solubility parameter. This means a high solvency power for reactions containing polarizable intermediates. Sulfolane is capable of strong solvation of cations by the oxygens in the sulfone group which increases the nucleophilicity of the corresponding, less solvated anions. With its high stability against strong acids and bases as well as its thermal stability sulfolane is a solvent that can be operated within a wide range of reaction conditions. This makes it the solvent of choice for different acidic reactions at elevated temperatures such as Friedel–Crafts acylations or Bischler–Napieralski condensations. Sulfolane has also found use in halo exchange reactions for the formation of various fluoroaromatic compounds. It has also been used as solvent for oxidations, nitrations, rearrangements, phosphorylations, and condensation reactions. As

sulfolane is not miscible with MTBE (as all other dipolar aprotic solvents are), it becomes an attractive solvent for reactions with an extractive workup by means of MTBE.

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Notes

The authors declare no competing financial interest.

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