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IMPROVEMENT OF ARYL DIFLUOROMETHYL ETHERS AND THIOETHERS SYNTHESIS BY USING A NEW SOLID–LIQUID PHASE TRANSFER CATALYST

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Aryl difluoromethyl ethers and thioethers have been synthesized, in the 60s, by reacting a phenol (or a thiophenol) on chlorodifluoromethane, in the presence of a strong base (NaOH, RONa) and a protic medium (H_2O/dioxane, ROH). A difluorocarbene is involved.

However, this homogeneous procedure suffers from several limitations :

- extreme sensitivity of raw aryl difluoromethyl ethers and thioethers to traces of aqueous acids, making the work-up tricky,

- tedious elimination and recycling of dioxane.

So, we have developed a solid-liquid phase-transfer technique to circumvent these drawbacks. Phenols (or thiophenols) and chlorodifluoromethane, dissolved in a cheap aprotic solvent of low polarity, are contacted with solid caustic soda, in the presence of a new phase-transfer agent, really catalytic. Only filtration and distillation are needed.

If results are similar in both homogeneous and biphasic procedures for phenols, improved yields are obtained for thiophenols using phase transfer conditions. This observation is consistent with the presence of an aprotic solvent. Several exemples with substituted phenols and thiophenols are given.