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Recycle Waste Salt as Reagent: A One-Pot Substitution/Krapcho Reaction Sequence to α-Fluorinated Esters and Sulfones

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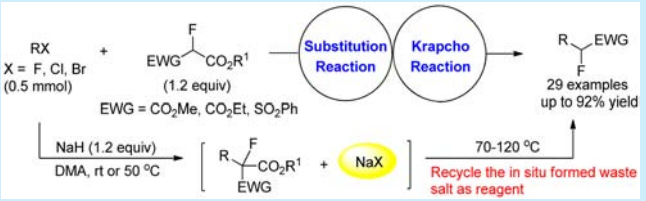
Supporting Information

ABSTRACT: A "one-pot" tandem substitution/Krapcho reaction is reported for the facile synthesis of α-fluorinated esters and sulfones, which utilizes the byproduct salt formed in the substitution step as an indispensible reagent to facilitate the Krapcho reaction step. This represents the first sustainable tandem reaction that internally recycles the waste salt formed in the upstream step as the reagent for the downstream step.



Because of the source-intensive nature of organic synthesis, it is very important to combine multistep syntheses into one-pot tandem reactions to reduce waste generation, save time, labor, energy, and materials, and minimize yield losses associated with the purification of intermediates.[1] In this context, there is an ever-increasing interest in developing novel tandem reactions that internally recycle waste produced in the upstream step to facilitate the downstream steps.[2] In 2003, Shibasaki reported the first example of such a type of tandem reaction, which ingeniously employed the byproduct Ph_3PO from the Wittig step as an effective additive to improve the reactivity and enantioselectivity of the downstream asymmetric epoxidation step.[3a] Since then, the independent works by Baba,[3b] Alaimo,[3c] Tian,[3d,e] Wu,[3f] Toy,[3g,h] and Coeffard and Greck[3i] have nicely demonstrated the possibility of internally recycling byproducts, and even excess reagents, from the upstream step of a tandem sequence to serve as a catalyst or a promoter for the downstream step, given careful design. As the byproduct of many reactions is essentially a kind of acid or base capable of facilitating certain reactions, there is ample room for the further development of such sustainable tandem reactions to effectively improve the atom-utilization of multistep syntheses because the internal reuse of byproduct avoids the use of extra substance, which in turn contributes to the reduction in waste generation.[4] Nevertheless, the corresponding research is still at its infancy, and successful examples are very limited.[2,3] Therefore, it is very important to design novel tandem sequences to discover new pathways that internally recycle various wastes and to provide an efficient and cost-effective synthesis of value-added products from simple materials by easy manipulation.

We have been engaged in developing tandem reactions for the synthesis of compounds that are interesting for medicinal research.[5] In particular, we are interested in coupling a reaction with low atom-efficiency into tandem reactions to internally utilize its byproduct to benefit the following reaction.[6] In this context, we have developed a tandem Wittig−conjugate reduction sequence which recycled Ph_3PO to activate $HSiCl_3$ for the conjugate reduction of enones, along with a Wittig−asymmetric cyanosilylation reaction which reused Ph_3PO as a necessary Lewis base catalyst for the cyanosilyaltion of enones.[6a] The tandem Wittig−conjugate reduction sequence further found its use in the chemoselective synthesis of α-CF_3 γ-keto esters from the corresponding β-CF_3 substituted enones, the selective conjugate reduction of which proved to be difficult by other methods.[6b] Based on these results, we further tried integrating salt-generating reactions such as substitution and coupling reactions into tandem sequences to internally reuse byproduct metal halides. Herein, we wish to report an unprecedented one-pot tandem substitution−Krapcho reaction that efficiently reuses the in situ generated metal halide for the dealkoxycarbonylative synthesis of α-fluorinated esters **6**.

The α-fluorinated esters **3** are a type of versatile building block to various fluorinated compounds.[7,8] In 1990, Burton reported a general method involving an alkylation of phosphorane **2** with primary alkyl iodides or activated alkyl bromides and the following hydrolysis (eq 1, Scheme 1),[9a] which allowed the synthesis of α-fluorinated esters bearing an alkyl, allyl or benzyl type substituent at α position in up to 59% yield by a one-pot operation. There are still other methods developed,[9] including nucleophilic fluorination of α-hydroxy ester derivatives[9b] and electrophilic fluorination of trimethylsilyl ketene acetals[9c,d] or other ester derivatives,[9e,f] but the scope of these methods was not as broad as Burton's protocol. Therefore, new general and efficient methods to differently substituted α-fluorinated esters, and in particular with α-allyl or α-propargyl groups, from easily available materials in a simple operation, are still highly desirable.

Considering readily available fluoromalonate **4** is highly reactive toward alkylation,[10] along with the fact that the Krapcho reaction requires using at least 1 equiv of a salt,[11] we designed a

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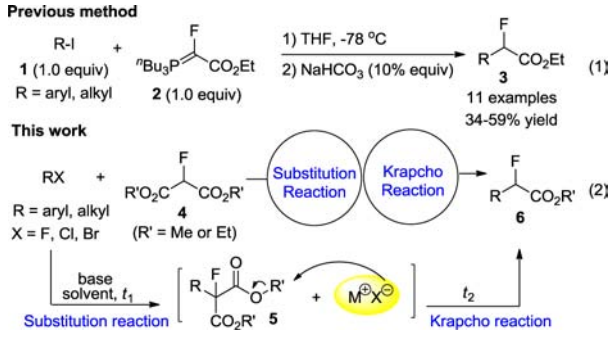
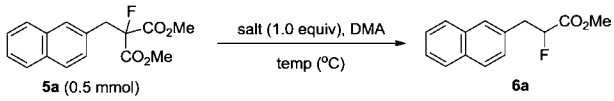
Scheme 1. Working Model



one-pot tandem substitution/Krapcho reaction for the modular syntheses of α-fluorinated esters from **4** and halides **1** (eq 2, Scheme 1), with our efforts in selective fluoroalkylation.[12] This sequence allows the reuse of byproduct salt to facilitate the following Krapcho reaction and offers the premise to synthesize α-fluorinated esters with various functional groups, owing to the almost neutral condition of Krapcho reaction. To examine this hypothesis, we first tried different salts in the dealkoxycarbonylation reaction of malonate **5a**, using *N*,*N*-dimethylacetylamide (DMA) as the solvent. In the absence of any salt, no reaction happened even at 120 °C (entry 1, Table 1), which confirmed the

Table 1. Screening of Different Salts



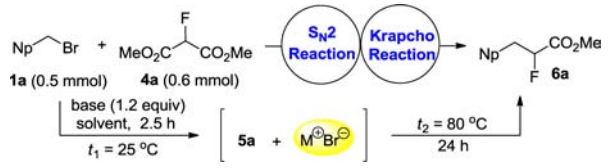
entry	salt	temp (°C)	time (h)	conv[a] (%)
1		120	24	nr
2	LiCl	100	4	100
3	LiBr	100	6	100
4	NaCl	100	24	82
5	NaBr	100	8	100
6	NaI	100	10	100
7	KCl	100	24	78
8	KBr	100	24	73
9	KI	100	13	100
10	NaBr	80	24	100

[a]Determined by ^{1}H NMR analysis of the crude mixture.

prerequisite role of a salt in the Krapcho reaction of **5a**. On the other hand, all reactions proceeded to some extent at 100 °C if adding any of the lithium, sodium and potassium halides we tried (entries 2−9). Finally, LiCl, LiBr, and NaBr proved to be better than NaCl and potassium halides, allowing the reaction to complete within hours. This result showed it is possible to use chlorides or bromides to develop the reaction. NaI and KI also worked well (entries 6 and 9), suggesting that, on demand, the more reactive but expensive organic iodides could be used in the alkylation step. It also turned out that in the presence of 1.0 equiv of NaBr the reaction worked well at 80 °C, albeit with a longer reaction time (entry 10).

While several salts could promote the Krapcho step, the development of the designed sequence was not as trivial as it first appeared. In principle, the efficiency of the whole sequence depended on a careful balance of the alkylation and downstream dealkoxycarbonylation, as the base used in the initial alkylation must give a suitable salt for the Krapcho step. Accordingly, we optimized the condition for the desired sequence, as shown in Table 2. The initial alkylation of bromide **1a** and fluoromalonate

Table 2. Optimization for Tandem Reaction



entry	base	solvent	isolated yield of **6a** (%)
1	Li_2CO_3	DMA	37
2	LiOH	DMA	49
3	LiOtBu	DMA	71
4	Na_2CO_3	DMA	66
5	NaOH	DMA	74
6	NaO^{t}Bu	DMA	78
7	NaH	DMA	80
8	NaH	DMF	75
9	NaH	DMSO	80

4a was run at 25 °C, using 1.2 equiv of base (equal amount to **4a**). The bromide **1a** was used in less amount than **4a** to avoid possible side reactions caused by excess halide at high temperature in the Krapcho step. Until the alkylation finished, the mixture was heated to 80 °C for the Krapcho reaction. It proved that base strongly affected the outcome of the sequence. While both LiCl and LiBr were efficient for the Krapcho reaction, all reactions mediated by three lithium bases gave product **6a** in lowered yield than the corresponding sodium bases (entries 1−3 vs 4−6). Finally, NaH (60% in mineral) proved to be the best, giving product **6a** in 80% yield (entry 7). It also revealed that both DMF and dimethyl sulfoxide (DMSO) were suitable for this sequence (entries 8 and 9) and almost no reaction took place in toluene or 1,4-dioxane.

On the basis of the above optimization, the scope of this tandem sequence was examined by running the reaction on a 0.5 mmol scale. The initial alkylation step was run at 25 or 50 °C for 2.5 h until full conversion of bromides **1**, and then the mixture was heated to indicated temperature until the completion of the following Krapcho reaction. By such a simple and operationally friendly procedure, a variety of α-fluoroesters **6a−i** with various α-substituents, benzyl type or simple aliphatic ones, could be obtained in good yield (entries 1−9, Table 3). In addition, differently substituted allyl or propargyl groups could be introduced, giving products **6k−v** in good yield. Noticeably, the synthesis of α-propargyl α-fluoroester was unprecedented. The broad substrate scope and high efficiency achieved by this simple one-pot sequence was impressive, as it enabled modular synthesis of α-fluoroesters from readily available materials without special care except for raising the temperature at the end of the alkylation step while reusing waste NaBr to facilitate the Krapcho step. The practicability of our protocol was further demonstrated by a gram-scale synthesis of product **6k**. By this sequence, a 7.5 mmol experiment readily gave the desired product **6k** in 72% yield (1.12 g), showing the good scalability of our protocol.

Importantly, multifunctional chloride **1w** also worked well to give α-fluoroester **6w** in 60% yield. This result showed chlorides were viable substrates for this tandem sequence, although the initial alkylation required higher temperature. It should be noted that it was difficult to prepare product **6w** via electrophilic

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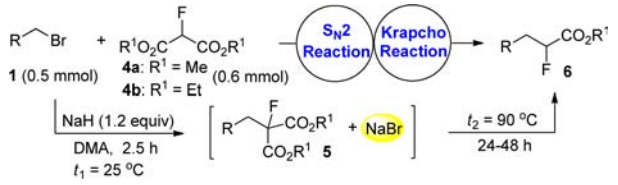
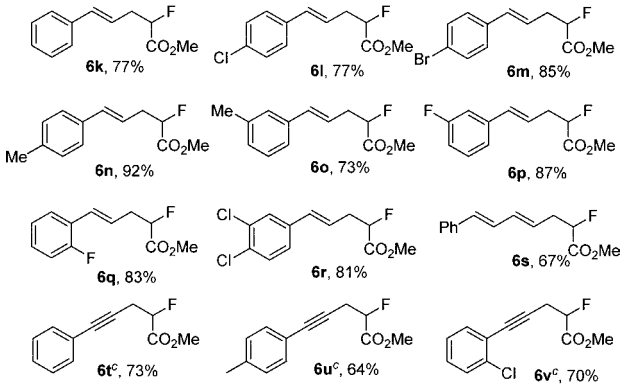
Table 3. Substrate Scope

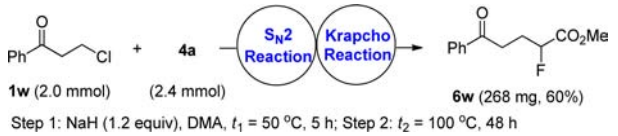


entry	R	1	4	6	yield[a] (%)
1[b]	2-naphthyl	1a	4a	6a	80
2[b]	1-naphthyl	1b	4a	6b	65
3[b]	4-ClC_6H_4	1c	4a	6c	78
4[b]	4-BrC_6H_4	1d	4a	6d	85
5[b]	9-anthracyl	1e	4a	6e	86
6[b]	2-thienyl	1f	4a	6f	79
7[d]	Bn	1g	4a	6g	85
8[d]	$BnCH_2$	1h	4a	6h	77
9[d]	$^nC_8H_{17}$	1i	4a	6i	76
10	2-naphthyl	1a	4b	6j	67

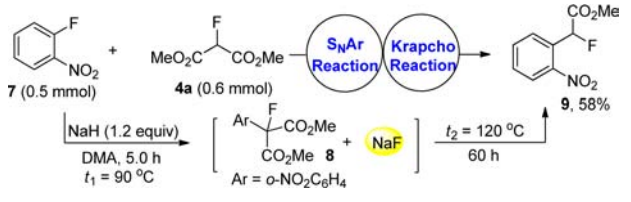
[a]Isolated yield. [b]t_2 = 80 °C. [c]t_2 = 70 °C. [d]t_1 = 50 °C.



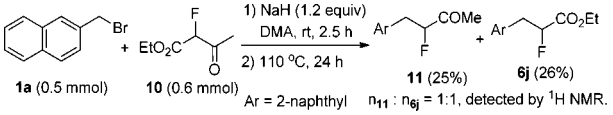
fluorination of ester derivatives due to the presence of the ketone moiety, which constituted an obvious advantage of our protocol.



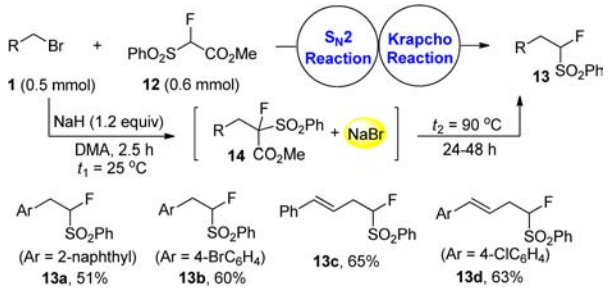
To our delight, the S_NAr reaction of nitrobenzene **7** and fluoromalonate **4a** could also be coupled into a one-pot tandem synthesis of α-fluoroester **9** in 58% yield. Recently, Sanford et al. reported the synthesis of product **9** via a stepwise synthesis involving S_NAr reaction, KOH-mediated decarboxylation, and an acid esterification.[13] Our tandem sequence showed improved efficiency by avoiding an extra step, two extractions, and the use of additional materials. However, NaF was not efficient enough to promote the Krapcho step,[14] and the scope of the tandem S_NAr/Krapcho sequence is still under investigation.



We further tried other fluorinated nucleophilies in this sequence. Ethyl α-fluoroacetoacetate **10** gave the corresponding α-fluoroketone **11** and α-fluoroester **6j** in almost 1:1 ratio by NMR analysis of the crude mixture, which could be separated by column chromatography.



The use of 2-fluoro-2-(phenylsulfonyl)acetate **12** allowed the synthesis of α-fluorinated sulfones **13** in acceptable yield. As compound **12** could be readily prepared from phenylsulfonylacetate,[15] our protocol provided a new method for the efficient synthesis of α-fluorinated sulfones **13**, versatile building blocks for the selective fluoroalkylation.[16]



In conclusion, we have developed a novel one-pot tandem substitution/Krapcho reaction sequence, which nicely demonstrated the possibility of internally recycling the in situ generated waste salt to facilitate the downstream step in a tandem reaction, given careful design. The thus-developed protocol constitutes a new efficient modular method for the synthesis of α-florinated esters and sulfones, versatile building blocks for the selective fluoroalkylation. The development of new one-pot tandem sequences that take advantage of the internally generated byproduct to facilitate the downstream steps is now ongoing in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

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Notes

The authors declare no competing financial interest.

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(14) While NaF failed to promote the Krapcho reaction of **5a** at 100 °C, it promoted that of **8** at 120 °C, with 42% conversion after 48 h by ^{1}H NMR analysis. This result suggested that the in situ generated NaF might be more efficient than adscititious NaF in promoting the Krapcho reaction.
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