Synthetic Methods

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Synthesis of Trifluoroethyl-Substituted Ketones from Aldehydes and Cyclohexanones**

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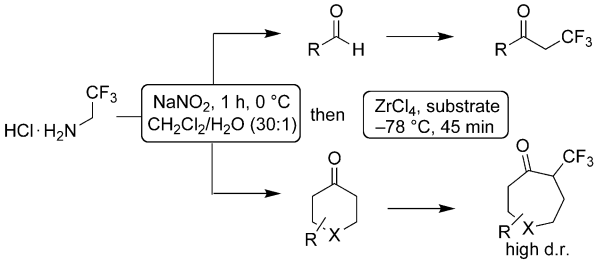
The demand for and applications of organofluoride compounds in pharmaceuticals and agrochemicals[1] has kindled interest in the development of convenient methods for their preparation. Trifluoromethyl-substituted aldehydes and ketones at the α-carbon center constitute particularly useful starting materials for the synthesis of a wide range of condensed, derived building blocks. The synthetic approaches to α-carbon trifluoromethyl-substituted carbonyl compounds rely on the reaction of enolates with intermediates generated from single electron-transfer processes or electrophilic CF_3-transfer reagents.[2,3] Carbonyl homologation reactions that employ fluorinated diazoalkanes provide alternative means for the introduction of CF_3 subunits.[4,5] Yet there is a lack of useful methods that rely on these for the preparation of trifluoroethyl-substituted ketones.[6,7] The absence of safe methods for the generation and handling of fluorinated diazoalkanes, in particular F_3CCHN_2, has been a hindrance to the development of this approach. Herein, we report the homologation of aldehydes and cyclohexanones employing F_3CCHN_2 generated in situ from $F_3CCH_2NH_2{\cdot}HCl$.[8,9] The method allows straightforward conversion of these substrates into trifluoromethyl-substituted ketones whose syntheses have not been previously reported. Key to the success of the process is the identification of $ZrCl_4$ as a suitable Lewis acid that is compatible with the conditions for generation of F_3CCHN_2 in situ.

The chemistry of trifluoromethyl diazomethane has not been extensively investigated, outside of its use in cyclopropanation reactions, because of the hazardous nature of this reagent. The handful of early reports involving this reagent prescribe its isolation and purification by distillation prior to its use, which comes with risk.[10] We have been interested in examining reactions utilizing trifluoromethyl diazomethane generated in situ without isolation. These boundary conditions have prompted the identification of catalysts that are competent in acidic, aqueous media. We have recently reported reactions that take advantage of F_3CCHN_2 generated in situ and its subsequent metal-catalyzed (Fe, Rh, Co) reactivity in aqueous media to afford trifluoromethyl-substituted cyclopropane and cyclopropene derivatives.[8] Our interest in the chemistry of F_3CCHN_2 has subsequently led us to examine it in aldehyde homologation processes.



In the initial screening, we were concerned with the ability to conduct the homologation reaction with F_3CCHN_2 generated in situ under operationally simple conditions. The use of F_3CCHN_2 in homologation reactions is not without precedence; however, reports on its reaction with aldehydes and ketones are rather limited in scope. Moreover the conditions and/or activating agents render the processes impractical and untenable. Thus in work limited to only two cyclohexanones, Mock and Hartman disclosed the use of large excess of Et_3OBF_4 as an activating agent.[4g–h] Only few examples have been reported involving aldehydes. Tordeux and Wakselman examined three aldehydes (pentanal, cyclohexane carbaldehyde, and benzaldehyde) in the homologation reaction with stoichiometric amounts of BF_3 or $SbCl_5$, and only pentanal afforded CF_3-substituted ketone (52% yield), and the rest furnished mixtures including oxiranes and other products.[7a] Activated aldehydes have also been the subject of limited investigations with a notable lack of success. Thus the reaction of ethyl glyoxylate proceeds in 41% yield[7b] after two days. The process employing chloral[7c] or fluoral was conducted in the dark for six weeks to provide products in undetermined yield for the former, as an inseparable mixture with the epoxides, and 5% yield for the latter.

Because of the lack of precedent for homologation reactions with F_3CCHN_2 under a more practical set of conditions, we examined whether the homologation of more useful set of aldehydes could be executed without recourse to isolation and handling of the diazoalkane. In this respect we were concerned about the use of Lewis acids under conditions for the generation of the diazoalkane from an amine with $NaNO_2$, because the process typically requires aqueous media and, significantly, itself leads to water formation ($F_3CCH_2NH_3Cl + NaNO_2 \rightarrow F_3CCHN_2 + 2H_2O + NaCl$).

We set reaction boundary conditions wherein $F_3CCH_2NH_2{\cdot}HCl$ and $NaNO_2$ were stirred for 1 hour at 0 °C in CH_2Cl_2/water (30:1) followed by cooling and addition of substrate and Lewis acid after 10 minutes. A wide range of Lewis acids were screened, including $BF_3{\cdot}OEt_2$, $SnCl_2$, $ZrCl_4$,

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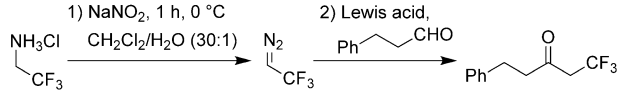
Table 1: Lewis acid screening.[a]



Entry	Lewis acid	Yield [%][b]	Entry	Lewis acid	Yield [%][b]
1	$BF_3{\cdot}Et_2O$	30	4	$ZrCl_4$	71
2	$AlCl_3$	32	5	$ZrCl_4$[c]	29
3	$SnCl_2$	n.r.	6	HCl	n.r.

[a] General procedure: $F_3CCH_2NH_3Cl$ (2.0 equiv) and $NaNO_2$ (2.4 equiv) stirred for 1 h at 0 °C in CH_2Cl_2/H_2O (30:1), followed by addition of Lewis acid (1.3 equiv) and substrate (0.22 mmol, 1 equiv) at −78 °C. [b] Yield based on ^1H NMR spectroscopy of the crude product. [c] Performed at 0 °C. n.r. = no reaction.

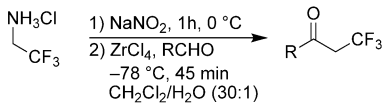
and $AlCl_3$ (Table 1). We were pleased to note that the homologation reaction can be conducted with a variety of Lewis acids in the absence of drying agents in mixtures of wet CH_2Cl_2 at −78 °C. We surmise that at this temperature the small amount of water freezes out, with phase separation effectively leading to anhydrous reaction media—this makes the use of strong Lewis acids possible as long as their heterogeneous hydrolytic decomposition with the ice is slower than the homologation process.[11] As control experiments, it is important to note that when the Lewis acid was added at higher temperature (0 °C),we observed rapid decomposition of the diazoalkane (Table 1, entry 5).

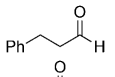
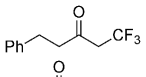
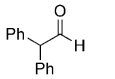
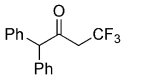
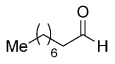
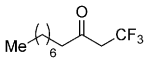
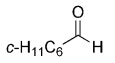
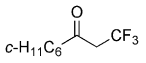
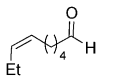
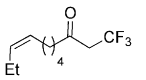
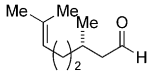
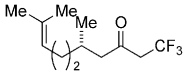
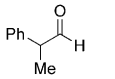
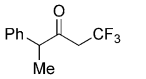
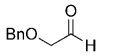
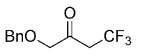
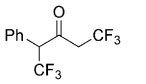
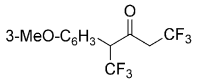
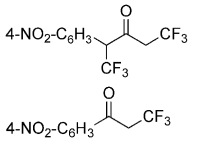
The use of $ZrCl_4$ as activator was selected for further optimization because it consistently gave good results. An experiment was conducted with HCl to examine if it mediates the homologation reaction, as it could arise from hydrolytic decomposition of $ZrCl_4$. However, its use led to recovery of starting material (Table 1, entry 6). Having identified suitable conditions we studied the scope of this reaction.

As can be seen in Table 2, a wide range of aliphatic aldehydes participate in the homologation reaction, to give product trifluoroethyl ketones in useful yields. However, aromatic aldehydes gave the product of double homologation to afford bis(trifluoromethyl)-substituted ketones (Table 2, entries 9–11). For example, benzaldehyde furnished **9** in a 67% yield (Table 2, entry 9). Interestingly, product **7** was prepared in enantioenriched form (>99% *ee*) without loss of optical purity, when the homologation reaction was conducted with the enantioenriched starting material (see the Supporting Information).

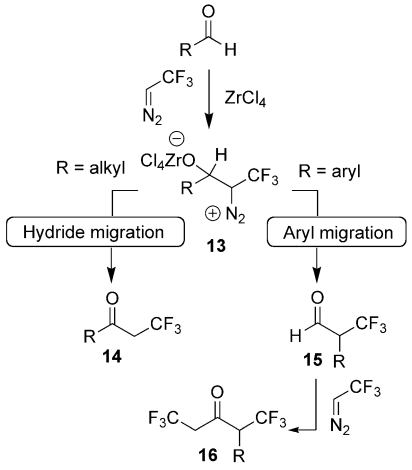
We hypothesize that the distinction between the aliphatic and aromatic substrates is grounded on the difference in the migratory aptitude of alkyl versus aryl groups (Scheme 1). In our working mechanism following activation by Lewis acid, aldehyde substrates undergo addition by F_3CCHN_2 to furnish adduct **13**. For aliphatic aldehydes hydride migration from **13** to give ketone **14** is favored over alkyl migration. By contrast for aromatic aldehydes the rate of aryl migration exceeds that of hydride migration, thus leading to aldehydes **15**. The aliphatic aldehyde so produced then undergoes a second round of addition to give the observed product of double homologation (**16**). The fact that an aromatic substrate that incorporates an electron-deficient arene (Table 2, entry 11) gives a considerable amount of the product of monohomologation (**12**) is consistent with this mechanistic proposal.

Table 2: Scope of the homologation reaction.[a]



Entry	Aldehyde	Product		Yield [%][b]
1			**1**	67
2			**2**	74
3			**3**	65
4			**4**	70
5			**5**	70
6			**6**	73
7			**7**	63
8[c]			**8**	47
9[c]	PhCHO		**9**	67
10[c]	3-MeO-PhCHO		**10**	76
11[c]	4-NO_2-PhCHO		**11** **12**	56[d] (1:1)

[a] Conditions: $F_3CCH_2NH_3Cl$ (2.0 equiv) and $NaNO_2$ (2.4 equiv) stirred for 1 h at 0 °C in CH_2Cl_2/H_2O (30:1), followed by addition of $ZrCl_4$ (1.3 equiv) and substrate (0.22 mmol, 1 equiv) at −78 °C. [b] Yield of isolated product. [c] Performed with $ZrCl_4$ (2.6 equiv), $F_3CCH_2NH_3Cl$ (4.0 equiv), and $NaNO_2$ (4.8 equiv). [d] Yield based on ^1H NMR spectroscopic analysis of the crude product. Bn = benzyl.

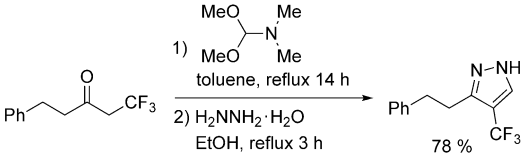


Scheme 1. Mechanistic proposal accounting for the difference between aliphatic and aromatic aldehydes.

With a practical protocol in hand for the homologation of aldehydes we investigated the reactivity of ketones under the same reaction conditions. Whereas acyclic ketones proved unreactive, cyclohexanones were smoothly converted into the corresponding trifluoromethyl-substituted cycloheptanones.[6] All the substrates bearing a substituent at position 4 on the cyclohexanone ring delivered the products in high diastereoselectivity and good yields. The observed selectivity for a similar reaction between diazoacetates and cyclohexanones has been correlated in the literature to the propensity of the substituent to lock the cyclohexanone in a conformation leading to equatorial attack of the diazo compound.[4l] We therefore assigned the relative configuration of the 2,5-substituted products (Table 3, entry 1–4 and 8) by analogy. To confirm this assignment, product **17** was reduced with excess sodium borohydride in MeOH to afford a crystalline derivative that was analyzed by X-ray crystallography and confirmed the predicted *trans* geometry (see the Supporting Information).[12] Even more interesting is the selectivity obtained with 2-substituted cyclohexanones. They led to the desired products with high regio- and diastereoselectivity. An X-ray crystal structure for ketone **22** was obtained to assign the relative configuration of these two products (**22** and **23**).[12] As far as we know, apart from trifluoromethyl cycloheptanone, all the products in Table 3 are unprecedented, thus revealing the high potential of this new reaction to generate new trifluoromethylated medium-size rings for drug discovery. The reaction is highly chemoselective and no by-products from multiple homologations were observed.

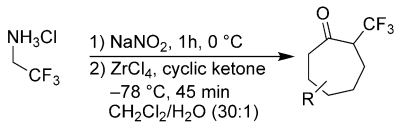
The method we have described gives rise to trifluoroethyl-substituted ketones that are potentially useful starting materials for a variety of transformations that can convert them into other useful building blocks. As an example, pyrazoles are extensively used in medicinal chemistry, and their synthesis from ketones is a well-established process. However, very few examples of the preparation of trifluoromethyl-substituted pyrazoles from trifluoroethyl ketones have been reported.[13] In this respect, treatment of the product from Table 2, entry 1 with dimethyl formamide acetal in toluene at reflux followed by hydrazine in ethanol afforded the corresponding trifluoromethyl-substituted pyrazole in 78% yield (Scheme 2). Overall, the combination of the new reaction method for the production of trifluoroethyl-substituted ketones with classical pyrazole syntheses approaches provides rapid access to trifluoromethyl-substituted pyrazoles from commercially available aldehydes.

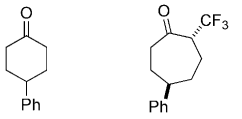
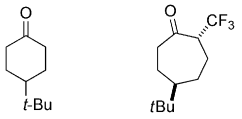
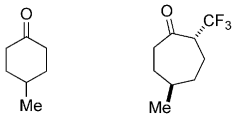
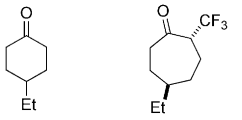
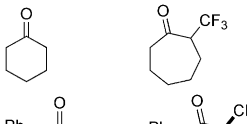
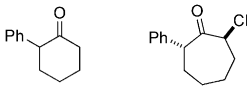
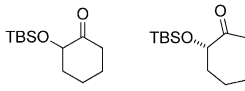
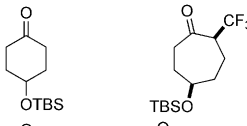
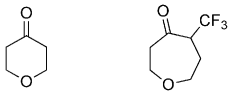
In summary, we have disclosed a new approach to prepare trifluoroethyl ketones that is notable for its convenience and ease of execution. The novelty of the approach is underscored by the observation that most of the products we document are unprecedented in the literature. These thus represent new fluorinated starting materials that may be elaborated into complex trifluoromethylated building blocks for drug discovery. An additional salient feature is the observations that the execution of wet reactions at lower temperature can effectively result in dry media, thus allowing transformations to proceed that would otherwise be impeded. The approach delineated for the preparation of trifuoromethylated ketones is complementary to other existing methods that have been recently documented. In a broader context, the development of processes that utilize reactive intermediates directly under the conditions for their generation opens many opportunities for design and discovery of new reactions. Studies towards



Scheme 2. Preparation of a trifluoromethyl-substituted pyrazole.

Table 3: Scope of the homologation reaction.[a]



Entry	Cyclic ketone	Product		Yield [%][b]	d.r.[c]
1			**17**	80	14:1
2			**18**	77	14:1
3			**19**	70	9:1
4			**20**	76	10:1
5			**21**	71	–
6			**22**	85	>20:1
7			**23**	85	>20:1
8			**24**	76	11:1
9[d]			**25**	65	–

[a] Conditions: $F_3CCH_2NH_3Cl$ (2.0 equiv) and $NaNO_2$ (2.4 equiv) stirred for 1 h at 0 °C in CH_2Cl_2/H_2O (30:1), followed by addition of $ZrCl_4$ (1.3 equiv) and substrate (0.22 mmol, 1 equiv) at −78 °C. [b] Yield of isolated product. [c] Based on analysis of the ^1H NMR spectrum of the crude product. [d] Performed with $ZrCl_4$ (3.9 equiv). TBS = *tert*-butyldimethylsilyl.

that aim are currently ongoing in our laboratory and will be reported as results become available.

Experimental Section

General procedure: Trifluoroethylamine hydrochloride (60 mg, 0.44 mmol, 2 equiv) and $NaNO_2$ (36 mg, 0.52 mmol, 2.4 equiv) are dissolved in a CH_2Cl_2/water mixture (3 mL/0.1 mL) and stirred for one hour in a sealed Schlenk in an ice bath. The mixture was then cooled to −78 °C in a dry-ice/acetone bath and stirred for 10 min, then the substrate (0.22 mmol) and $ZrCl_4$ (67 mg, 0.29 mmol, 1.3 equiv) are added. After 45 min, the mixture was quenched by the addition of MeOH (3 mL) followed by saturated aqueous $NaHCO_3$, extracted with CH_2Cl_2 (3 times), dried over $MgSO_4$, and evaporated in vacuo. After analysis of the crude residue by NMR spectroscopy, the crude mixture was purified by column chromatography on silica gel (pentane/diethyl ether) to afford product.

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