Triphenylmethyldifluoramine: a stable reagent for the synthesis of *gem*-bis(difluoramines)†

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The conversion of ketones into geminal bis(difluoramines) can be achieved under mild two-phase reaction conditions by employing triphenylmethyldifluoramine as an *in situ* source of difluoramine.

The introduction of a difluoramine functionality into organic moieties and the properties of the obtained target compounds have been investigated intensively.[1] More recently a new class of high-energy containing materials, *gem*-bis(difluoramine)-substituted heterocyclic nitramines has gained much attention as high-energy oxidizers: HNFX (**1**)[2] and TNFX (**2**)[3] have been successfully synthesized from their corresponding ketone derivatives. Usually this transformation is achieved under strongly acidic conditions with an excess of condensed difluoramine (HNF_2),[4] an unpredictably shock-sensitive and thermally unstable, gaseous compound.[5] HNF_2 can be generated from different precursors, *e.g.* tetrafluorohydrazine,[6] *N,N*-difluorourea[7] or *N,N*-difluorocarbamates.[8] A short report on the synthesis of triphenylmethyldifluoramine (**3**) mentions its hydrolysis to HNF_2.[9] Except for **3**, a stable crystalline compound, all of the other HNF_2 precursors have only limited stability.

1   **2**   **3**
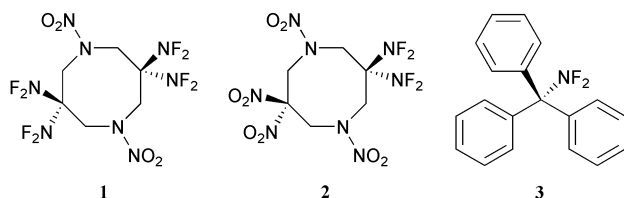
Compound **3** proved to be a convenient reagent for the conversion of ketones (**A**) into *gem*-bis(difluoramines) (**B**) thus circumventing the potential hazards associated with previous methodologies.

A → **B**

3 / oleum (30%) / CH_2Cl_2
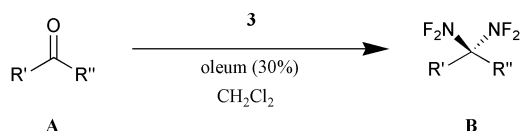
Triphenylmethyldifluoramine (**3**) is accessible from chloro-triphenylmethane and N_2F_4 in multi-gram quantities as stable, non-hygroscopic, colorless crystals.[9]† It can be stored without decomposition or any other hazards at ambient conditions. The complete characterization of **3** was carried out by IR, Raman, ^{1}H, ^{13}C and ^{19}F NMR spectroscopy. Additionally, we obtained single crystals suitable for a X-ray crystal structure determination.‡

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† Electronic supplementary information (ESI) available: optimized preparation of **3**, analytical data for **3**, **18**–**21** and a plot of the unit cell of **3**. See http://www.rsc.org/suppdata/cc/b2/b203811k/

The structural features of **3** are similar to those reported for *p*-bromophenyldiphenyl)methyldifluoramine.[10] The C–N distance of 1.523(2) Å found in **3** is longer than the corresponding distance of 1.481 Å in triphenylmethylamine.[11] The presence of two highly electronegative fluorines on the nitrogen atom reduces back-donation from the nitrogen lone pair, thereby decreasing the C–N bond order. The torsion angles from the difluoramine group to the *ipso*-carbon atoms of the phenyl rings, namely F1–N1–C1–C8 and F2–N1–C1–C2 are 56.4(1)° and 39.1(1)°, respectively, and reflect the deviation of these atoms from perfect staggering.
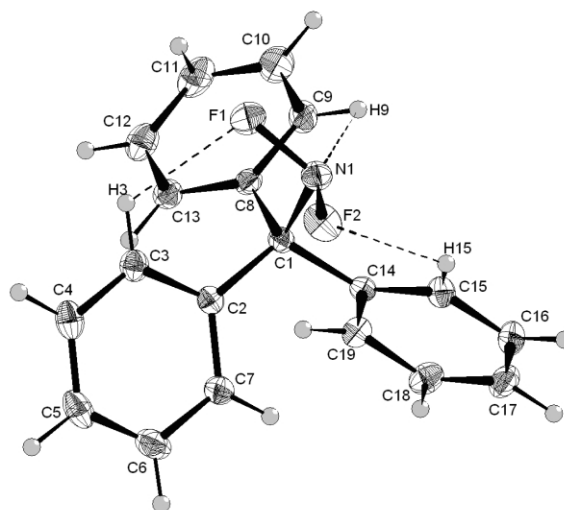
The closest intramolecular H···F contacts found in the crystal structure of **3** result from H3···F1 and F2···F15 at 2.281(16) and 2.334(16) Å, respectively. The closest intermolecular H···N contacts result from H15···N1 and H9···N1 at 2.408(16) and 2.553(16) Å, respectively. All these contacts are shorter than the sum of the van der Waals radii of nitrogen and hydrogen (1.55 + 1.20 = 2.75 Å) or fluorine and hydrogen (1.47 + 1.20 = 2.67 Å). A plot of the unit cell is provided with the ESI.†‡

We have investigated two-phase organic solvent/oleum media bis(difluoraminations) with **3** under mild reaction conditions for some model ketones. Typically a solution of the ketone (**A**) and 2.2 equivalents of **3** in CH_2Cl_2, $CHCl_3$ or $CFCl_3$ were added dropwise to the same volume of oleum (30%) at 0 °C. Due to the potential hazards of the intermediate HNF_2 and any labile products, all reactions were carried out on a small scale (~1 mmol). The completion of the reactions was confirmed by NMR spectroscopy (^{19}F, ^{1}H, ^{13}C). Thus, they were usually worked up after 15–20 min by pouring into ice/water, followed by extraction (CH_2Cl_2) and evaporation of the solvent from the dried organic phase.

The crude product contained only triphenylmethanol and the *gem*-bis(difluoramine) that (on a larger scale) can be purified by repeated crystallization, chromatography on neutral aluminum

Table 1 Conversion of ketones to *gem*-bis(difluoramines)

Entry	Ketone (**A**)	*gem*-Bis(difluoramine) (**B**)	Yield (%)	Ref.
1	Acetone (**4**)	2,2-Bis(difluoramino)propane (**12**)	90	4a
2	Cyclopentanone (**5**)	1,1-Bis(difluoramino)cyclopentane (**13**)	80	4a
3	Cyclohexanone (**6**)	1,1-Bis(difluoramino)cyclohexane (**14**)	80	4a
4	Cyclohexa-1,4-dione (**7**)	1,1,4,4-Tetrakis(difluoramino)cyclohexane (**15**)	85	4a
5	*N*-Acetylpiperidinone (**8**)	4,4-Bis(difluoramino)-*N*-acetylpiperidine (**16**)	85	14
6	**9a** (*n* = 1)	**17a**	*ab*	—
7	**9b** (*n* = 9)	**17b**	80[b]	—
8	**9c** (*n* = 10)	**17c**	85[b]	—
9	**10**	**18**	90[b]	—
10	**11a** (R = H)	**20a**	0[c]	—
11	**11b** (R = CH$_3$)	**20b**	0[c]	—

[a] Decomposition upon work-up; [b] Analytical data provided in the ESI†; [c] Only formation of the cage-systems **19a** (**19b**) in *ca.* 80% yield was observed.

oxide or distillation, respectively. The given yields are based on ^{1}H NMR data of the crude product containing only the *gem*-bis(difluoramine) (**B**) and triphenylmethanol. A variety of known (entries 1–5) as well as new (entries 6–11) difluoramine derivatives was prepared in good to excellent yields (Table 1).
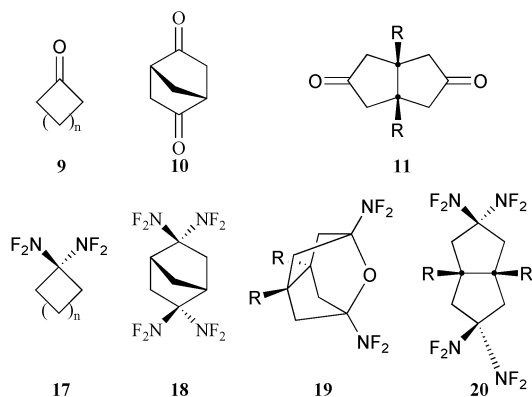
Although **17a** could not yet be isolated on this small scale, it represents the smallest alicyclic geminal bis(difluoramine) so far characterized. The bisketone **11a** (**11b**) could only be converted to the bridged hemiaminal **19a** (**19b**); neither a larger excess of **3** nor extended reaction time furnished the tetrakis(difluoramine) **20a** (**20b**).

Mechanistically, the reactions involve cleavage of **3** to the triphenylmethyl cation and difluoramine. The latter or the *in situ* product, difluorsulfamic acid, reacts with the ketone **A** to provide *gem*-bis(difluoramine) **B**. It is noteworthy that our reaction did not proceed in conc. H$_2$SO$_4$, although acidolysis of **3** was observed spectroscopically: the ^{19}F NMR signal of **3** disappeared and the trityl cation was observed in the ^{13}C NMR spectrum. Also employing other strong acids such as FSO$_3$H, CF$_3$CO$_2$H, CF$_3$SO$_3$H or CF$_3$SO$_3$H/(CF$_3$SO$_2$)$_2$O resulted in similar behavior. In the case of FSO$_3$H/SbF$_5$ only decomposition of **3** was observed. We have never been able to observe free or protonated difluoramine.[12] It is also possible that under the reaction conditions SO$_3$ in oleum—besides being a water scavanger – might react with **3** to form F$_2$NSO$_3$H as the ultimate difluoraminating reagent (*vide supra*). The triphenylmethyl cation might also act like a Lewis acid catalyst, polarizing the carbonyl group (Mukaiyama type activation[13]).

In conclusion, the readily preparable, stable triphenylmethyldifluoramine (**3**) can be conveniently employed for the efficient conversion of ketones (**A**) under mild reaction conditions to the respective geminal bis(difluoramines) (**B**). This is the first difluoramination methodology that avoids the use of neat HNF$_2$ and therefore minimizes its potential hazards. Work is underway to further investigate the reaction mecha-

nism, find alternative preparations of the reagent, and synthesize potential high-energy materials.

CAUTION: *gem*-Bis(difluoramines) are potentially shock-sensitive and thermolabile. They should be handled with care!

Notes and references

‡ *Crystal data*: the data were collected on a Bruker 3-circle platform diffractometer equipped with a SMART CCD detector with the χ-axis fixed at 54.74° from a fine-focus tube and an LT-3 apparatus for low temperature data collection: **3**, C$_{19}$H$_{15}$F$_2$N, M_r = 295.32, monoclinic, a = 10.3882(12), b = 9.8259(11), c = 14.6065(16) Å, β = 92.402(2)°, V = 1489.6(3) Å^3, T = 213(2) K, space group $P2_1/n$, Z = 4, D_c = 1.317 Mg m^{-3}, μ(Mo-Kα) = 0.094 mm^{-1}, 9649 reflections mesuared, 3035 unique (R_{int} = 0.0321). The final *wR2* was 0.1098 (all data). CCDC reference number 188416. See http://www.rsc.org/suppdata/cc/b2/b203811k/ for crystallographic data in CIF or other electronic format.

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