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Synthesis of α-Diazo Carbonyl Compounds with the Shelf-Stable Diazo Transfer Reagent Nonafluorobutanesulfonyl Azide

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Dedicated to the memory of Prof. José Manuel Concellón.

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Abstract: Nonafluorobutanesulfonyl azide is a shelf-stable, cost-effective and general diazo transfer reagent for the efficient synthesis of α -diazo carbonyl compounds in excellent yields and in very short reaction times, under mild conditions. The diazo products can be readily isolated in pure form after a simple aqueous extractive work-up that avoids chromatographic purification in most cases. Because of its high efficiency and wide substrate scope, shelf-stability, relatively low cost, and ease of product purification, nonafluorobutanesulfonyl azide offers an advantageous alternative to other commonly used diazo transfer reagents.

Keywords: azides; diazo compounds; diazo transfer; ketones; sulfonyl azides

Diazo compounds are important substrates for the generation of carbenes, metal-complexed carbenoids and diazonium cations, which participate in useful chemical transformations including 1,3-dipolar cyclo-additions,^[1] cyclopropanations,^[1b,c,2] X–H insertion reactions (X=C, O, N, P, etc.),^[1b,c,3] phosphorus or sulfur ylide formation,^[4] and Pd-catalyzed cross-coupling reactions.^[5] One of the major routes for the synthesis of diazo compounds involves the base-assisted reaction of an active methylene group with a diazo transfer reagent.^[6] Many electron-deficient organo azide derivatives have been developed as diazo transfer reagents, most of them sulfonyl azides. Readily accessible *p*-toluenesulfonyl azide has been the reagent employed most frequently.^[7] With the objective to improve efficiency and safety and to ease product purification from the sulfonamide by-product, several alternative reagents have been investigated over the

years.^[8–23] The most recent additions to this arsenal include trifluoromethanesulfonyl azide (triflyl azide: TfN_3),^[20] imidazole-1-sulfonyl azide,^[21] 2-azido-1,3-dimethylimidazolium chloride,^[22] and benzotriazole-1-yl-sulfonyl azide.^[23] The beneficial use of ionic liquids in diazo transfer reactions has also been described recently.^[24] Nevertheless, there is still a need for alternative diazo transfer reagents with high shelf-stability and wide substrate applicability that also facilitate product isolation.

We have recently shown that nonafluorobutanesulfonyl azide (nonaflyl azide: NfN₃) is a shelf-stable and cost-effective diazo transfer reagent for the efficient synthesis of azides from primary amines.^[25] An additional advantage of this reagent is that the nonafluorobutanesulfonamide formed as by-product in the diazo transfer reaction can be easily removed from the crude reaction mixture by a simple aqueous extractive work-up under mildly basic conditions, facilitating the purification of the azide product that often does not require chromatography. Moreover, NfN₃ showed a better reactivity profile in these diazo transfer processes than its lower molecular weight analogue TfN₃, while not presenting the serious draw-backs of the latter.^[25] Thus, TfN₃ is an unstable and explosive compound that has to be prepared prior to use and should be handled always in solution.^[26] In addition, the reagent is obtained from the rather costly trifluoromethanesulfonic anhydride in variable yields and thus, in the absence of a cumbersome standardization of the crude reagent solution, it requires to be used in a large excess to guarantee a complete transformation of the substrate. By contrast, NfN_3 is readily prepared from the much cheaper and bulk reagent nonafluorobutanesulfonyl fluoride^[27] by reaction with NaN₃ in MeOH and is stable at room temperature as a neat compound, with a reported decomposition temperature of around 120 °C.^[27b] Zhu

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et al. have previously studied the reactions of NfN₃ with carbocyclic β-keto esters to give ring-opened diazo amido esters or ring-contracted amido esters, depending on the structure of the starting keto ester.^[28] More recently, while studying the reactivity of NfN₃ with enamines, the same group has found that ethyl acetoacetate gives ethyl diazoacetoacetate as the major product when treated with NfN₃ in the presence of morpholine.^[29] As a continuation of our previous work on the use of NfN₃ as a safe and efficient diazo transfer reagent,^[25a,b] we now describe its application to the synthesis of α -diazo carbonyl compounds under mild reaction conditions.

We first studied the effect of the base in the diazo transfer reaction using 1,3-diphenyl-1,3-propanedione (1a) as a model substrate. Thus, 1a was reacted with a small excess of NfN₃ (1.2 equiv.) and base (1.1 equiv.) in CH₂Cl₂ at room temperature (Table 1) to afford the expected diazo product 2a. As previously observed by Charette et al. for the case of TfN₃,^[20e] yields and reaction rates roughly correlate with base strength (Table 1). Gratifyingly, complete conversion of 1a (TLC analysis) was achieved in just 15 min with the stronger bases (Table 1, entries 3-5). However, longer reaction times and lower yields were obtained when we used weaker bases such pyridine or 2,6-lutidine (Table 1, entries 1 and 2).

We then investigated the scope of the diazo transfer reaction using a diverse set of α -substituted carbonyl compounds (Table 2), selecting Et_3N as the optimum base for its observed efficiency, lower cost, and easy removal by simple evaporation. 1,3-Diketones, 3-keto esters and malonates (entries 1-9) reacted smoothly within 15 min at room temperature to give the corresponding diazo compounds in very high yields in all cases examined. Diazo compounds 2 were isolated after repeated liquid-liquid extraction of the crude re-

Table 1. Effect of base on the diazo group transfer reaction of 1a with NfN₃.

	base (1.1 equiv.) O O
Ph + NfN ₃	CH ₂ Cl ₂ , r.t. Ph Ph + NfNH ₂
(1.2 equiv.) N ₂
1a	2a

Entry	Base	pK_a (MeCN) ^[a]	Time	Yield [%] ^[b]
1	pyridine	12.53	6 h	58
2	2,6-lutidine	14.13	2 h	71
3	Et ₃ N	18.82	15 min	94
4	$(i-Pr)_2NEt$	18.1 ^[c]	15 min	93
5	DBU	24.34	15 min	91

[a] Refers to the pK_a of the conjugated acid of the base measured in MeCN (ref.^[30]).

[b] Yield of isolated product.

[c] Ref.^[31] Table 2. Synthesis of α-diazocarbonyl compounds using nonaflyl azide.

$$R^{1} \xrightarrow{O} R^{2} \xrightarrow{H_{3}N_{1}(1.2 \text{ equiv.}),} CH_{2}CI_{2}, r.t., 15 \text{ min}} \qquad R^{1} \xrightarrow{O} R^{2}$$

Entry	Substrate	Product	Yield [%] ^[a]
1	Ph Ph Ph	Ph Ph Ph Ph Ph Ph Ph Ph	94
2	Me O Me	$Me \xrightarrow[N_2]{Me} Me$	98
3	Ph Me 1c	Ph N_2 $2c$	89
4	Me OMe	Me N ₂ 2d	90
5	Me OEt	Me OEt N ₂ 2e	88 (90) ^[b]
6	Me O- <i>t</i> -Bu	Me O- <i>t</i> -Bu N ₂ 2f	91
7	n-Pr OEt	$n-Pr \xrightarrow{O}_{N_2} OEt$	95
8	Ph OEt	$Ph \qquad OEt \\ N_2 \qquad 2h$	93
9	MeO OMe		92
10	NC OEt		81
11	Ph ^S Ph 1k	Ph ^S Ph N ₂ 2k	86
12	Ph ^{-S} OMe 11	Ph ^S N ₂ 2	87
13	MeO-P-OMe	MeO-P MeO N ₂ 2m	89

Table 2. (Continued)



^[a] Yield of isolated product.

^[b] Yield reported using morpholine instead of Et₃N (ref.^[29]).

action mixture in CH_2Cl_2 with a saturated aqueous solution of NaHCO₃ to remove the nonafluorobutanesulfonamide by-product. Residual nonafluorobutanesulfonamide was completely eliminated by sublimation during the concentration of the crude material at reduced pressure. This simple work-up afforded in most cases analytically pure diazo products without chromatography.

To further examine the scope and limitations of this method, we next investigated the diazotation of other α -substituted carbonyl compounds. α -Cyano- α -diazo carbonyl compounds are very versatile substrates that have been used for the synthesis of bis(oxazoles),^[32] 5-halo-,^[33] 5-hydroxy-^[34] and 5-amino-1,2,3-triazoles,^[35] in O–H insertion reactions^[36] and in cyclopropanations.^[20f,37] Under the standard reaction conditions, ethyl cyanoacetate gave the corresponding α -cyano- α diazo product 2j in 81% yield (Table 2, entry 10). Nonaflyl azide performed much better in this transformation than other recently described diazo transfer reagents (65% in 12 h with benzotriazole-1-yl-sulfonyl azide;^[23] 61% in 9 h with imidazole-1-sulfonyl azide;^[21] 79% in 14 h with TfN₃^[20e]). α -(Phenylsulfonyl) carbonyl compounds 1k and 1l (Table 2, entries 11 and 12) gave also the corresponding diazo products 2k and 2l, respectively, under the same conditions in good yield and, again, in much shorter reaction times than with other diazo transfer reagents recently developed. Thus, the synthesis of 2k using $TfN_3^{[20e]}$ and of **2l** using benzotriazol-1-ylsulfonyl azide^[23] required in both cases a reaction time of 14 h. Imidazole-1-sulfonyl azide, which is considered as a stable and inexpensive alternative to TfN₃, failed to give any diazo product with (phenylsulfonyl)acetates.^[21] The method is also applicable to the preparation of the Ohira–Bestmann reagent^[38] **2m** in very high yield (Table 2, entry 13) and again in shorter reaction times than with other diazo transfer reagents such as p-toluenesulfonyl azide (2 h),^[39] 4-acetamidobenzenesulfonyl azide (48 h),^[40] or 2-azido-1,3-dimethylimidazolinium chloride (1 hour).[22]

However, when we carried out the reaction with α nitro carbonyl compounds low yields of the desired α -



Scheme 1. Synthesis of α -nitro- α -diazocarbonyl compounds.

nitro-a-diazo carbonyl derivatives were obtained (Table 2, entries 14 and 15). Since complete transformation of the starting nitro compound was clearly apparent by TLC analysis of the crude reaction mixture, we ascribed these low yields to a probable degradation of the highly electrophilic diazo product in the presence of the base. In line with our hypothesis, better results were obtained when we employed a weaker and more hindered base such 2,6-lutidine (Scheme 1). A similar negative effect of the base was previously observed by Charette et al.^[20e] in the synthesis of α -cyano- α -diazo carbonyl compounds with TfN₃ when using Et_3N or Hünig's base [(*i*-Pr)₂NEt]. These authors have also shown that the yield of α nitro-a-diazo carbonyl products obtained with TfN3 could be further improved by adding the base at 0°C instead of room temperature^[20c] and the same would be expected to occur with NfN₃, although we have not tested these conditions with our substrates.

In conclusion, we have shown that nonafluorobutanesulfonyl azide is a shelf-stable, cost-effective and general diazo transfer reagent for the efficient synthesis of α -diazo carbonyl compounds in excellent yields and in very short reaction times. The reaction takes place under mild conditions and the desired diazo products can be readily isolated in pure form and in high yield after a simple extractive work-up that avoids chromatographic purification in most cases. For its high efficiency, wide substrate scope, shelf-stability, relatively low cost, and ease of product purification, nonaflyl azide is an advantageous alternative to other commonly used diazo transfer reagents, including the most recently described.^[20-23]

Experimental Section

Diazo Transfer Reactions

With Et_3N : To a solution of the corresponding carbonyl compound **1a–m** (0.80 mmol) in dry CH₂Cl₂ (1.5 mL) was added in sequence Et₃N (0.123 mL, 0.88 mmol), and per-fluorobutanesulfonyl azide (0.312 g, 0.96 mmol). After stirring the reaction mixture at room temperature for 15 min, a saturated aqueous solution of NaHCO₃ (4 mL) was added. The organic layer was separated and extracted with a saturated aqueous solution of NaHCO₃ (5×4 mL) to remove the nonafluorobutanesulfonamide by-product. After drying over anhydrous Na₂SO₄, the organic phase was concentrated at

reduced pressure. The corresponding diazo products 2a-m were obtained in pure form in most cases without any further purification.

With 2,6-lutidine: To a solution of the corresponding α nitro carbonyl compound **1n/10** (0.80 mmol) in dry CH₂Cl₂ (1.5 mL) was added in sequence 2,6-lutidine (0.13 mL, 1.12 mmol) and perfluorobutanesulfonyl azide (0.390 g, 1.20 mmol). The reaction mixture was stirred at room temperature for 30 min. The reaction was quenched with a saturated aqueous solution of NaHCO₃ (4 mL) and extracted with CH₂Cl₂ (3×8 mL). The organic layers were separated, dried over anhydrous Na₂SO₄, and concentrated at reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc 5:1) to give the corresponding α -nitro- α -diazocarbonyl compound **2n/20**.

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