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# AuBr<sub>3</sub>-Catalyzed Thiooxime-to-Carbonyl Conversion: From Chiral Aliphatic Nitro Compounds to Ketones without Racemization

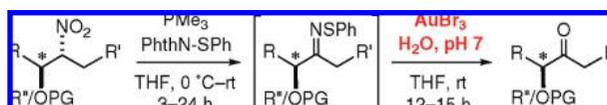
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## ABSTRACT



A new variant of the NO<sub>2</sub>-to-CO transformation (the Nef reaction) that occurs at room temperature under neutral conditions is uncovered. After the conversion of secondary nitroalkanes to phenylsulfenylketimines, these thiooximes are hydrolyzed quantitatively in situ, in THF–H<sub>2</sub>O at pH 7, by addition of AuBr<sub>3</sub> (but not with other MX<sub>n</sub>!). Adducts arising from asymmetric nitro-Michael and nitro-aldol reactions afford 1,4-diketones and  $\alpha$ -alkoxy ketones, respectively, with full retention of the configuration of the stereocenters  $\alpha$  to the CHNO<sub>2</sub>/C=N–SPh/C=O groups.

Many reactions of gold compounds have been described in the past recent years.<sup>1</sup> Here we report an unexpected application of Au<sup>3+</sup> complexes, which we have incidentally discovered during a screening of inorganic salts in the search for optimum conditions for the hydrolysis of sulfenylketimines to ketones.

(1) Among dozens of reviews on the uses of gold in organic chemistry (the new “gold rush”, mainly involving interactions of Au(I) with multiple C–C bonds in the key steps), see the following general summaries: (a) Corma, A.; García, H. *Chem. Soc. Rev.* **2008**, *37*, 2096. (b) Hashmi, A. S. K.; Rudolph, M. *Chem. Soc. Rev.* **2008**, *37*, 1766. (c) Arcadi, A. *Chem. Rev.* **2008**, *108*, 3266. (d) Li, Z.; Brouwer, C.; He, C. *Chem. Rev.* **2008**, *108*, 3239. For a mechanistic overview, see: (e) Soriano, E.; Marco-Contelles, J. *Acc. Chem. Res.* **2009**, *42*, 1026.

(2) For recent reviews of Nef-like reactions, see: (a) Wolfe, J. P. In *Name Reactions for Functional Group Transformations*; Li, J. J., Corey, E. J., Eds.; Wiley: Hoboken, 2007; p 645. (b) Ballini, R.; Palmieri, A.; Righi, P. *Tetrahedron* **2007**, *63*, 12099. (c) Ballini, R.; Petriani, M. *Tetrahedron* **2004**, *60*, 1017. Classical review on the use of TiCl<sub>3</sub>: (d) Mc Murry, J. E. *Acc. Chem. Res.* **1974**, *7*, 281. Many methods are too harsh for our purposes (to be applied to NO<sub>2</sub>-containing polyfunctional fragments, in advanced steps of total syntheses). We have sometimes used an oxidative variant (2KHSO<sub>5</sub>·KHSO<sub>4</sub>·K<sub>2</sub>SO<sub>4</sub>, Oxone): (e) Ceccherelli, P.; Curini, M.; Marcotullio, M. C.; Epifano, F.; Rosati, O. *Synth. Commun.* **1998**, *28*, 3057. However, the necessity of having an alkaline aqueous medium to ensure the presence of nitronate ions and to make Oxone partially soluble, as well as the sensitivity of several characteristic groups to peroxides, prevented us from using it in other cases.

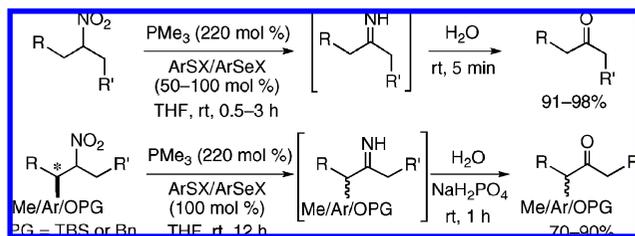
The conversion of secondary nitro alkanes to ketones is a well-known useful reaction, which connects nitrogen and carbonyl chemistry.<sup>2</sup> Very recently, we developed a smooth protocol that takes place at room temperature (rt) without strong bases or acids; trimethylphosphine and an activator (ArSSAr, PySeSePy, or PhthN–SePh) were the only reagents required (Scheme 1).<sup>3</sup>

In spite of the mild conditions, the procedure has the limitation that during the reduction of enantiopure nitro compounds, substituted at positions  $\alpha$  to the CHNO<sub>2</sub> groups, racemic ketones were obtained,<sup>3a</sup> as shown in the second equation of Scheme 1. Such a racemization occurs at the ketimine stage, via the enamines.<sup>3a,4</sup> To solve this handicap, we stopped the reduction cascade of nitro compounds (**1**) at sulfenylimines **2**, by means of our protocol that uses PMe<sub>3</sub> and *N*-(phenylsulfenyl)phthalimide (PhthN–SPh) in THF at rt.<sup>5</sup> As indicated in Scheme 2, the key point was then to

(3) (a) Burés, J.; Vilarrasa, J. *Tetrahedron Lett.* **2008**, *49*, 441. This method was based on (what we call) the BMZ reaction. (b) Barton, D. H. R.; Motherwell, W. B.; Zard, S. Z. *Tetrahedron Lett.* **1984**, *25*, 3707.

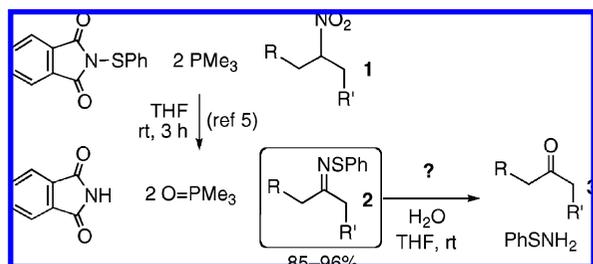
(4) This would not be the case if the imine/enamine equilibrium would occur preferably via the CH<sub>2</sub>R' moiety (e.g., for R' = Ar or EWG), but speaking in general the handicap was significant and restricted too much the application of our procedure.

**Scheme 1.**  $\text{PMe}_3$ -Mediated Conversion of Secondary Nitro Groups to Imines and Ketones



find a way to hydrolyze **2** to **3** in situ, without first cleaving the N–S bond.

**Scheme 2.** How to Hydrolyze Carefully *N*-(Phenylsulfenyl)-ketimines (*S*-Phenylthiooximes, **2**) to Ketones



Simple *N*-phenylsulfenylimines such as that of cyclohexanone undergo hydrolysis on moist silica, but those that are sterically crowded require strongly acidic media.<sup>6</sup> Since esters, acetals, and other protecting groups that could contain polyfunctional nitro derivatives would not survive under these conditions, and since chiral  $\alpha$ -substituted thiooximes and ketones may racemize at very low and high pH values, we imposed ourselves the limitation of operating without heating, in the absence of Brønsted acids<sup>7</sup> and as close as possible to pH 7.

A screening of the potential catalysts (Lewis acids, with thiophilic and relatively nontoxic transition-metal cations, which do not decompose in water) was undertaken with a model compound (**2a**),<sup>5</sup> in THF–H<sub>2</sub>O, as shown in Table 1.

Polymeric salts (MX) and, in general, inorganic compounds that are scarcely soluble in THF–H<sub>2</sub>O were inactive (as it was CuO, not included in Table 1), whereas CuBr<sub>2</sub> (entry 6), AuCl<sub>3</sub> (entries 17 and 18), AuBr<sub>3</sub> (entries 21–24),

(5) Burés, J. Isart, C. Vilarrasa, *J. Org. Lett.* **2007**, *9*, 4635. In Table 1, entry 4, the oxime should have been depicted as the *Z* isomer.

(6) (a) Most of our sulfenylimines underwent hydrolysis on warming with 1 M HCl or with Amberlite IR-120 (pH 2.2), but racemization or epimerization was then produced, as well as the cleavage of various protecting groups. (b) To our knowledge, only the cleavage of tritylsulfenylketimines, by an excess of AgNO<sub>3</sub> (and a different mechanism) has been described: Branchaud, B. P. *J. Org. Chem.* **1983**, *48*, 3531.

(7) By adding 1 M HCl or 1 M HBr to a THF solution of **2a**, hydrolysis to ketone **3a** was complete after stirring overnight. However, as mentioned, these conditions did not suit us, as we plan to apply the reaction on acid-sensitive polyfunctional substrates.

FeBr<sub>3</sub> (entries 34 and 35), and InBr<sub>3</sub> (entry 43) were the most active. These metallic ions, being harder Lewis acids than their respective M<sup>+</sup> and/or M<sup>2+</sup> ions, lower the pH of the medium (by partial hydrolysis). Part of their performance may be due to the inherently low pH of their aqueous solutions, but not exclusively. Moreover, it is remarkable that only AuBr<sub>3</sub>-derived species did not lose their activity when the reaction medium was partially or fully neutralized (AuBr<sub>3</sub> was even better than AuCl<sub>3</sub> in this regard, compare entry 24 to entry 20). As known, insoluble hydroxides or hydrated oxides of Cu(II), Fe(III), and In(III) were formed when the solutions of their MX<sub>n</sub> salts were neutralized. On the other hand, AuBr<sub>3</sub> did not give a precipitate when aqueous NaOH was added to neutralize the solution.<sup>8</sup> Thus, we attribute the activity of Au(III) to the formation of soluble [AuBr<sub>x</sub>(OH)<sub>y</sub>(**2a**)]<sup>3-x-y</sup> species where **2a** replaces one or two ligands of the inner sphere of the central atom. Coordination of Au(III) with the S atom and/or N–S group of thiooximes is plausible.<sup>9</sup>

At pH 7, when the amount of AuBr<sub>3</sub> was reduced to 0.3 (entries 25–27) and to 0.1 equiv (entry 28) the hydrolysis percentages fell. Given the price of gold and AuBr<sub>3</sub> the requirement of 0.5 equiv of catalyst would be a drawback for large-scale applications.

Since the hydrolysis coproduct (PhSNH<sub>2</sub>) is expected to be more basic and nucleophilic than **2a**, it may coordinate the central atom of the complex more strongly, “poisoning the catalyst”. To eliminate PhSNH<sub>2</sub> (and PhSNH<sub>2</sub>SPh and NH<sub>3</sub>)<sup>10</sup> we added isopentyl nitrite to the reaction mixture. At pH 7, isopentyl nitrite alone did not react with **2a**, but it did react with ArSNH<sub>2</sub> (checked independently).<sup>11</sup> The hydrolysis of **2a** was complete at pH 7 with 0.3 equiv of AuBr<sub>3</sub> and 0.4 equiv of RONO (overnight at rt). To our delight, with 0.8 equiv of RONO we could reduce the amount of AuBr<sub>3</sub> to 10 mol %.<sup>12</sup>

With optimum protocols for the hydrolysis of **2a** in hand, we subjected another simple nitro compound, racemic **1b**, and the stereopure or scalemic nitro derivatives (**1c–k**) shown in Table 2 to the cheapest protocol. Both steps—reduction of **1** to **2** and hydrolysis of **2**—were carried out in one pot. The commercially available THF solution of  $\text{PMe}_3$

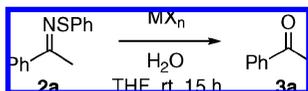
(8) (a) Baes, C. F.; Mesmer, R. E. *The Hydrolysis of Cations*; Wiley: New York, 1976; pp 279–285. (b) Usher, A.; McPhail, D. C.; Brugger, J. *Geochim. Cosmochim. Acta* **2009**, *73*, 3359 (a spectrophotometric study of aqueous Au(III) halide-hydroxide complexes). Also see ref 1a.

(9) On the other hand, oximes PhC(=N–OBn)Me and PhC(=N–OPh)Me are not hydrolyzed under the conditions of entry 24 of Table 1.

(10) Simple sulfenamides (RSNH<sub>2</sub>) may disproportionate to RSNHSR and NH<sub>3</sub>; (a) Bao, M.; Shimizu, M.; Shimada, S.; Tanaka, M. *Tetrahedron* **2003**, *59*, 303. (b) Davis, F. A.; Friedman, A. J.; Kluger, E. W.; Skibo, E. B.; Fretz, E. R.; Milicia, A. P.; LeMasters, W. C.; Bentley, M. D.; Lacadie, J. A.; Douglass, I. B. *J. Org. Chem.* **1977**, *42*, 967. For entries to the chemistry of sulfenamides, see: (c) Koval, I. V. *Russ. J. Org. Chem.* **2005**, *41*, 386. (d) Davis, F. A.; Mancinelli, P. A. *J. Org. Chem.* **1978**, *43*, 1797. Recent review of N–S bond-containing compounds: (e) Davis, F. A. *J. Org. Chem.* **2006**, *71*, 8993.

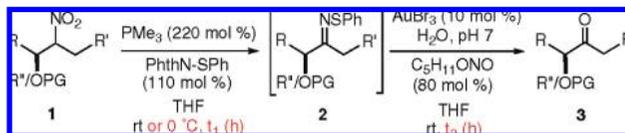
(11) (a) Any alkyl nitrite capable of nitrosating and hence decomposing ArSNH<sub>2</sub> and NH<sub>3</sub> should work. No PhSH was detected; according to TLC and <sup>1</sup>H NMR, PhSSPh was formed predominantly. (b) C<sub>5</sub>H<sub>11</sub>ONO alone reacted with **1a** at low pH (1.5 equiv was required to fully decompose **1a**, overnight at rt, pH 4.2), but not at all at pH 7.

(12) On the other hand, the addition of NaNO<sub>2</sub> (80 mol %) instead of C<sub>5</sub>H<sub>11</sub>ONO to the mixture of **2a** with AuBr<sub>3</sub> (10 mol %) at pH 7 did not improve the outcome of entry 28 of Table 1.

**Table 1.** Potential Catalysts for the Hydrolysis of **2a**<sup>a</sup>

entry	additive (MX <sub>n</sub> )	equiv	pH conditions	% of <b>3a</b>
1	Cu <sub>2</sub> Cl <sub>2</sub>	1.0		0–20 <sup>b</sup>
2	Cu <sub>2</sub> Cl <sub>2</sub>	1.0	buffered at pH 4.0	0–20 <sup>b</sup>
3	CuI	1.0		0
4	(CuOTf) <sub>2</sub> <sup>c</sup>	0.5		11
5	CuCl <sub>2</sub> ·2H <sub>2</sub> O	1.0		43
<b>6</b>	<b>CuBr<sub>2</sub></b>	<b>1.0</b>	<b>pH measured = 3.0</b>	<b>100</b>
7	CuBr <sub>2</sub>	0.5	pH measured = 3.5	71
8	CuBr <sub>2</sub>	0.1		23
9	CuBr <sub>2</sub>	1.0	buffered at pH 7.0	5
10	CuBr <sub>2</sub>	1.0	basified up to pH 10.0	0
11	Cu(OAc) <sub>2</sub>	1.0	pH measured = 5.5	16
12	Cu(acac) <sub>2</sub>	1.0		0
13	Cu(OTf) <sub>2</sub>	1.0		0
14	AgNO <sub>3</sub>	1.0		0
15	AgF	1.0		0
16	AuCl <sup>d</sup>	1.0		0
<b>17</b>	<b>AuCl<sub>3</sub></b>	<b>1.0</b>		<b>100</b>
<b>18</b>	<b>AuCl<sub>3</sub></b>	<b>0.5</b>	<b>pH measured = 0.9</b>	<b>100</b>
19	AuCl <sub>3</sub>	0.5	adjusted at pH 6.0	63
20	AuCl <sub>3</sub>	0.5	adjusted at pH 7.0	10
<b>21</b>	<b>AuBr<sub>3</sub></b>	<b>1.0</b>	<b>pH measured = 1.2</b>	<b>100</b>
<b>22</b>	<b>AuBr<sub>3</sub></b>	<b>0.5</b>		<b>100</b>
<b>23</b>	<b>AuBr<sub>3</sub></b>	<b>0.5</b>	<b>adjusted at pH 4.0</b>	<b>100</b>
<b>24</b>	<b>AuBr<sub>3</sub></b>	<b>0.5</b>	<b>adjusted at pH 7.0</b>	<b>100<sup>e</sup></b>
25	AuBr <sub>3</sub>	0.3	pH 4.6	67
26	AuBr <sub>3</sub>	0.3	pH 6.7	56
27	AuBr <sub>3</sub>	0.3	pH 8.9	6
28	AuBr <sub>3</sub>	0.1		26
29	ZnCl <sub>2</sub>	1.0		3
30	ZnBr <sub>2</sub>	1.0		11
31	FeCl <sub>2</sub>	1.0		23
32	CoCl <sub>2</sub> ·6H <sub>2</sub> O	1.0		0
33	NiCl <sub>2</sub> ·6H <sub>2</sub> O	1.0		0
<b>34</b>	<b>FeBr<sub>3</sub></b>	<b>1.0</b>	<b>pH measured = 0.2</b>	<b>100</b>
<b>35</b>	<b>FeBr<sub>3</sub></b>	<b>0.5</b>		<b>100</b>
36	FeBr <sub>3</sub>	0.1		24
37	FeBr <sub>3</sub>	1.0	adjusted at pH 4.0	8
38	Sc(OTf) <sub>3</sub>	1.0		62
39	LaCl <sub>3</sub> ·7H <sub>2</sub> O	1.0		0
40	CeCl <sub>3</sub> ·7H <sub>2</sub> O	1.0	adjusted at pH 7.0	0
41	CAN <sup>f</sup>	1.0	adjusted at pH 7.0	0
42	Yb(OTf) <sub>3</sub>	1.0		6
<b>43</b>	<b>InBr<sub>3</sub></b>	<b>1.0</b>	<b>pH measured = 0.0</b>	<b>100</b>
44	InBr <sub>3</sub>	1.0	adjusted at pH 7.0	0
45	none			0
46	silicagel			0
47	dil. HBr		pH 1.5	0
48	dil. HBr		pH 3.0	0

<sup>a</sup> To **2a** (0.3 mmol) in 1 mL of THF (unless otherwise indicated) a solution or suspension of the additive (possible catalyst) in 1 mL of H<sub>2</sub>O (pH 6.9–7.0) was added, and the mixture was stirred vigorously overnight; in some cases (indicated) the pH values were adjusted with 1 M NaOH (buffering effects were noted) or by addition of standard phosphate buffers. A Crison pHmeter was used. <sup>b</sup> We later confirmed that only commercial samples contaminated with CuCl<sub>2</sub> showed catalytic activity (no hydrolysis occurred with pure Cu<sub>2</sub>Cl<sub>2</sub>). <sup>c</sup> Commercially available Cu<sub>2</sub>(OTf)<sub>2</sub>·C<sub>6</sub>H<sub>6</sub>; identical result with commercial Cu<sub>2</sub>(OTf)<sub>2</sub>·C<sub>7</sub>H<sub>8</sub>. <sup>d</sup> AuCl is insoluble in H<sub>2</sub>O. <sup>e</sup> Identical result in 9:1 THF–H<sub>2</sub>O; the reaction was slower (85% of conversion) in 9:1 CH<sub>3</sub>CN–H<sub>2</sub>O. <sup>f</sup> Ce(NH<sub>4</sub>)<sub>2</sub>(NO<sub>3</sub>)<sub>6</sub>.

**Table 2.** From Chiral Nitro Derivatives to Ketones<sup>a</sup>

entry	substrate	reaction conditions <sup>b</sup>	ketone	isolated yield (%)
1		t <sub>1</sub> 3 t <sub>2</sub> 12		85
2		t <sub>1</sub> 12 t <sub>2</sub> 15		88
3		t <sub>1</sub> 24 <sup>c</sup> t <sub>2</sub> 15		81
4		0 °C, t <sub>1</sub> 24 t <sub>2</sub> 12 ≥98% ee		78 ≥98% ee
5		0 °C, t <sub>1</sub> 24 t <sub>2</sub> 12 ≥98% ee		78 ≥98% ee
6 <sup>d</sup>		0 °C, t <sub>1</sub> 24 t <sub>2</sub> 12 42% ee		75 42% ee
7 <sup>d</sup>		0 °C, t <sub>1</sub> 24 t <sub>2</sub> 12 46% ee		76 45% ee
8 <sup>d</sup>		t <sub>1</sub> 12 t <sub>2</sub> 12 (also 0 °C, t <sub>1</sub> 15, 0 °C, t <sub>2</sub> 30) 65% ee		78 62% ee
9		0 °C, t <sub>1</sub> 24 t <sub>2</sub> 12		65 >98% ee
10 <sup>e</sup>		t <sub>1</sub> 12 t <sub>2</sub> 12		85 >98% ee

<sup>a</sup> Unless otherwise indicated, both steps were carried out at rt. Workup: after dilution of the final THF–H<sub>2</sub>O solution with more water and extraction with CH<sub>2</sub>Cl<sub>2</sub> several times, only **3**, PhSSPh, and phthalimide derivatives were extracted (as Me<sub>3</sub>PO is very soluble in water and remains in the aqueous layer, together with the brownish gold complexes); PhSSPh was easily removed by filtration through silica (elution with hexane). Ee values were determined as explained in the Supporting Information. <sup>b</sup> t<sub>1</sub>, t<sub>2</sub>, and experiments carried out at 0 °C (instead of at rt) are indicated. <sup>c</sup> Six-hundred molar percent of PMe<sub>3</sub> and 300 mol % of PhthN-SPh were added. <sup>d</sup> Nitro compounds prepared by organocatalytic addition of nitroethane to the corresponding enones, with *trans*-2,5-dimethylpiperazine as the base. <sup>e</sup> **1k** as a 1:1 *syn/anti* mixture.

was used as the medium for the first step. After elimination of the slight excess of PMe<sub>3</sub> under vacuum, the aqueous neutral (buffered) solution of Au(III) and the alkyl nitrite were added and stirring was maintained at rt until the complete disappearance of **2**.

It is remarkable that the hydrolyses (second step) were always practically quantitative; in fact, only the starting

materials and expected hydrolysis products were detected by TLC and NMR.

On the other hand, the first step (when sulfenylketimines were formed, isolated, and purified by chromatography) took place in 80–90% yields. As an exception, in the **1j–2j–3j** sequence (entry 9) the yield was moderate, but it was due to the unavoidable formation of Beckmann fragmentation byproducts during the first step.<sup>5</sup> In fact, these secondary reactions are known to be inherent to all reactions involving oximes, thiooximes, etc., if stable cationic intermediates can be formed.

One advantage of our procedure is that it can be used to prepare chiral 1,4-dicarbonyl compounds from the organocatalytic conjugate addition of nitroalkanes to enones (entries 6–8). In the case of **3g** (entries 6 and 7), 2,5-dimethyl-3-phenylpyrrole was not formed at all.<sup>14</sup> Compounds arising from asymmetric nitro-aldol (Henry) reactions, such as those of entries 9 and 10, are also amenable to our protocol.

As final tests, we reduced the amount of AuBr<sub>3</sub> to 5 mol % and 2 mol %. We subjected **2a** to hydrolysis at pH 7 and rt as in Table 2, with 100 mol % of C<sub>5</sub>H<sub>11</sub>ONO. With 5 mol % of AuBr<sub>3</sub>, stirring for 30 h was sufficient for the complete disappearance of this sulfenylketimine and its full conversion to ketone **3a**. With 2 mol % of AuBr<sub>3</sub>, 5 days were required;<sup>15</sup> the hydrolysis was slower, as expected, but still feasible.

(13) (a) Hanessian, S.; Shao, Z.; Warrier, J. S. *Org. Lett.* **2006**, *8*, 4787, and references therein. (b) Mitchell, C. E. T.; Brenner, S. E.; Garcia-Fortanet, J.; Ley, S. V. *Org. Biomol. Chem.* **2006**, *4*, 2039. Instead of (*S*)-proline or a bicyclo[3.1.0]-derivative of Pro and instead of (*S*)-5-(pyrrolidin-2-yl)tetrazole, we used Seebach's bicyclic oxazolidinone (the amination of Pro and *t*-BuCHO). See: (c) Isart, C.; Burés, J.; Vilarrasa, J. *Tetrahedron Lett.* **2008**, *49*, 5414.

(14) Pyrrole formation is unavoidable in most reductions of  $\gamma$ -nitro ketones, since the intermediate oximes or imines react in situ with the CO groups (formation of five-membered rings). Cf. refs 2d and 3b. Zard et al. took advantage of this reaction to prepare various interesting pyrroles: (a) Quiclet-Sire, B.; Thevenot, I.; Zard, S. Z. *Tetrahedron Lett.* **1995**, *36*, 9469. (b) Barton, D. H. R.; Motherwell, W. B.; Simon, E. S.; Zard, S. Z. *J. Chem. Soc., Perkin Trans. 1* **1986**, 2243. (c) Barton, D. H. R.; Zard, S. Z. *Chem. Commun.* **1985**, 1098. Under the conditions of Scheme 1,  $\gamma$ -nitro acyclic ketones give pyrrole derivatives almost quantitatively.

(15) Experiments carried out in parallel, at rt and pH 7 as always, with only C<sub>5</sub>H<sub>11</sub>ONO or NaNO<sub>2</sub>, without AuBr<sub>3</sub>, did not affect **2a**.

Thus, the sulfenylimino groups can be hydrolyzed at neutral buffered pH and at rt only (to date) with 50 mol % of AuBr<sub>3</sub> or with 2–10 mol % of AuBr<sub>3</sub> and stoichiometric or substoichiometric amounts of RONO.

In summary, a very smooth two-step *one-pot procedure* for the conversion of secondary nitro groups to ketones has been disclosed. As pursued by the senior author for a long-time, it works at rt (or at 0 °C, if required) and *under neutral conditions*. The first step, the conversion of secondary nitro groups to sulfenylketimines,<sup>3a</sup> has been applied here successfully, for the first time, to various chiral compounds arising from organocatalytic reactions or stereoselective variants of venerable reactions. The second step—the hydrolysis of these sulfenylimines—involves the use of AuBr<sub>3</sub>, which among the large number of MX<sub>n</sub> salts examined is the only one that catalyzes such hydrolyses at pH 7. Therefore, for the first time to the best of our knowledge, we have taken advantage of a practical feature of AuBr<sub>3</sub>: the solubility and stability of [AuBr<sub>x</sub>(OH)<sub>y</sub>]<sup>3-x-y</sup> complexes, which permits thiooximes to coordinate with them and undergo the desired hydrolysis under the mildest possible conditions (compatible with  $\alpha$ -stereocenters and a plethora of protecting groups). As the first step was originally inspired in the BMZ reaction,<sup>3b</sup> the overall protocol might be called the Vilarrasa–BMZ Nef-type procedure or something similar.

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**Supporting Information Available:** Additional experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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