A Novel Decyanogenative Coupling of α-Cyanoimines Mediated by Samarium. A Facile Route to α-Diketimines

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Conversion of α-cyanoimines **1** into α-diketimines **2** has been achieved successfully by using samarium diiodide in dry tetrahydrofuran in high yields without formation of anilinoanil **3**, 1,2-diamines **4** or anilides **5**.

Recently, samarium metal, its salts and organosamarium compounds have been widely employed as useful reagents or catalysts in organic synthesis.[1] Since the pioneering studies by Kagan[2] and co-workers demonstrated the particular effectiveness of SmI_2, which is a powerful single-electron transfer reductant in the lanthanide series, the utilisation of SmI_2 in synthetic organic chemistry has been dramatically documented.[3] The versatility of SmI_2 is emphasized by the fact that it can be used to generate both C-centered radicals and carbanions. It possesses excellent chemoselectivity in the reduction of carbonyl, alkyl halide, and α-heterosubstituted carbonyl substrates, promotes Barbier type coupling reactions, hetero-alkene coupling reactions, carbon–carbon fragmentation/ring expansion chemistry of some aliphatic 1,4-diketones,[4] radical cyclizations,[5] deoxygenative coupling of benzamides,[6] and mediates cascade radical cyclizations[7] in the synthesis of peoxylactone β etc. But samarium has not been employed for the dimerization of α-cyanoimines so far though it is used for the coupling of aldimines[8] to 1,2-diamines. In continuation to our studies on metal mediated organic transformations,[9] we report herein a novel one-pot procedure for the decyanogenative coupling of α-cyanoimines to form α-diketimines using samarium diiodide as a mediator. However, to our knowledge there are no literature reports on the coupling of α-cyanoimines into α-diketimines and this is the first ever report of this kind. Here the reaction proceeds efficiently in high yields at the reflux temperature of tetrahydrofuran. These α-diketimines are useful key intermediates for the preparation of 1,2-diketones by the acid hydrolysis.

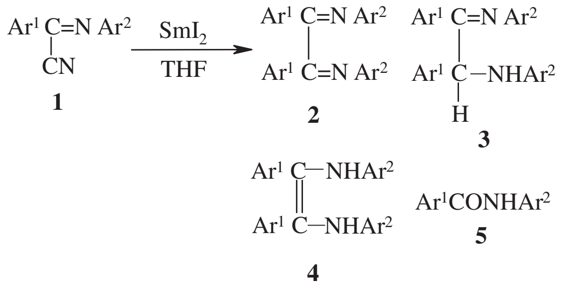
Walia[10] and Becker[11] have reported a alkalicyanide mediated oxidative dimerization of aromatic aldimines to α-diketimines, but it involves an aerial oxidation of dianilinostilbene or anilinoanil formed during the reaction course. In another report[12] benzil dianil has been obtained in 16% yield by heating aniline and benzil in the presence of P_2O_5 at 200 °C. Consequently, there is a need for the development of more selective method of general applicability. In a recent report Fujiwara *et al.*[13] have reported the dehydrogenative coupling of aldimines to vicinal diimines mediated by ytterbium. Though, several reports on the coupling of imines to 1,2-diamines are available[14] but the dehydrogenative coupling of imines to α-diimines are very rare. Our novel finding couples with ease a wide variety of α-cyanoimines directly to form the corresponding α-diketimines without formation of any anilinoanil **3** or dianilinostilbene **4** or anilides **5**.

In a typical procedure, to a solution of α-cyanoimine **1a** (0.412 g, 2 mmol) in dry THF (15 mL), was added two equivalent of freshly prepared[15] SmI_2 (2 mmol) and the mixture was refluxed for 18 h. After completion (monitored by tlc), THF was distilled off and diethyl ether (20 mL) was added to it. The organic layer was then washed with sodium thiosulphate solution and dried over anhydrous Na_2SO_4. Evaporation of the solvent on a rotary evaporator gives the α-diketimine **2a** in 80% yield, without formation of any side products as reported by earlier workers.[11,12] The structure of the diketimine thus obtained was unambiguously identified on the basis of its physicochemical data (IR, NMR, and MS) and finally by preparing 1,2-diketones by the acid hydrolysis of the corresponding α-diketimines.[16] **2a** mp 143–144 °C, ^1H NMR δ 7.10–7.35 (m, 20H, aromatics). M^+ 360; analysis $C_{26}H_{20}N_2$ calcd. C, 86.67; H, 5.55; N, 7.78, found C, 86.72; H, 5.60; N, 7.66. Similarly α-cyanoimines **1b**–**k** were reacted and the corresponding α-diketimines **2b**–**k** were obtained in good yields. The results and scope of this reaction are shown in the Table 1. Enhancing further the reaction time gave no improvement in yield but rather decomposition of starting material occured. An inspection of Table 1 shows that this method is fairly general and the substituents in Ar^1 and Ar^2 can vary considerably. The α-cyanoimines derived from benzaldehyde and other aromatic amines (besides aniline) such as 4-chloroaniline, 2 and 4-toluidine, 3 and 4-anisidines, smoothly underwent this reaction to afford the corresponding dianils in good yields. The reaction, however, fails with benzylidine cyclohexylamine, *p*-hydroxybenzylidineaniline and *p*-nitrobenzylidineanilines. It is notable that the cyanide ion catalyzed coupling

Table 1. SmI_2 catalyzed dimerisation of α-cyanoimines **1** into α-diketimines **2**

Product **2**	Ar^1	Ar^2	Time /h	M.p. /°C	Lit.M.p. /°C	Yield[a] /%
a	Ph	Ph	18.0	143–145	144–45[20]	80
b	*p*-Anisyl	Ph	19.0	149–151	150–151[20]	72
c	*p*-Chloro	Ph	15.0	156–157	155–156[10]	74
d	Ph	*p*-Anisyl	17.5	160–162	162–163[10]	80
e	*m*-Chloro	Ph	15.5	215–216	216–217[10]	72
f	*p*-Tolyl	Ph	18.5	147–149	147–148[20]	70
g	Ph	*p*-Tolyl	19.0	157–158	157–158[10]	70
h	Ph	*m*-Anisyl	16.0	134–135	134–135[10]	75
i	Ph	*p*-Chloro	19.0	170–172	172–173[20]	70
j	*o*-Tolyl	Ph	21.0	180–181	181–182[21]	50
k	Ph	*o*-Tolyl	21.0	145–146	145–147[21]	55

[a]Yields refer to pure isolated products, fully characterised by ^1H NMR and IR spectroscopy.



Scheme 1.

of benzylidine-*p*-toluidine in liquid ammonia gives a colorless crystalline dimer anilinoanil.[17] In contrast, with SmI_2 in THF we obtained directly the corresponding dianil **2g** instead of anilinoanil. Furthermore, the reaction conditions are tolerant to the ether group (Entries D and H) and aromatic chloro group, which showed selectivity to give the α-diketimines without any dechlorination (Entry I). Although the detailed mechanism is not clear at this stage, it is likely that the reaction starts by an electron transfer from samarium diiodide[18] to α-cyanoimine **1**. As cyanide is a good leaving group, first the reagent SmI_2 generates the radical by one electron reduction which then forms the organosamarium species followed by coupling with second equivalent of α-cyanoimines produced the α-diketimine **2** via a samarium diketimine complex intermediate.

In conclusion, we have provided a novel and efficient method for the coupling of α-cyanoimines into α-diketimines employing samarium diiodide in dry THF which involves a simple workup and will make a useful and important addition in the existing methodologies. The α-diketimines thus obtained can be easily hydrolysed in acidic media[16] to the corresponding 1,2-diketones in excellent yields. Of particular interest is that this procedure also provides a novel and convenient method for the synthesis of 1,2-dicarbonyl functionality, which has recently attracted[19] a growing attention.

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15 As the commercially available samarium diiodide is expensive and is also hygroscopic and air-sensitive, we freshly prepared this reagent in an inert atmosphere under very stringent conditions and used directly. For a typical case, iodine (5.1 g, 20 mmol) was added with stirring to a mixture of Sm powder (3.1 g, 22 mmol) in dry THF. The initial mild exothermic reaction subsided within several minutes to form a yellow suspension of SmI_3. The mixture was then refluxed with stirring. The colour of the suspension gradually turns to blue. Refluxing overnight gives 0.1 M/L of SmI_2.

16 A mixture of 1 g of dianil **2** and 10 mL of concd HCl acid was magnetically stirred for 14 h. The precipitated diketone was filtered and the melting point was compared with authentic samples for all the compounds.

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