Pergamon

Tetrahedron Letters, Vol. 38, No. 43, pp. 7603-7604, 1997

0040-4039/97 \$17.00 + 0.00

PII: S0040-4039(97)01804-2

Sm or Zn-Induced Coupling Reactions. A Facile Route to 1,2-Diketones

Bipul Baruah, Anima Boruah, Dipak Prajapati and Jagir S Sandhu*

Regional Research Laboratory, Jorhat-785 006, Assam, India

Abstract: Coupling of keto cyanides 1 into 1,2-diketones 2 has been performed by the action of SmI_2 or ZnI_2 in tetrahydrofuran at ambient temperature in high yields.

Recently samarium metal, its salts and organosamarium compounds have been widely employed as useful reagents or catalysts in organic synthesis.[1] Since pioneering studies by Kagan and co-workers demonstrated the particular effectiveness of samarium diiodide as a strong one-electron transfer reducing agent,[2] the utilisation of SmI_2 in synthetic organic chemistry has been dramatically documented.[3] Herein we wish to report a novel one-pot procedure for the coupling of keto cyanides to form 1,2-diketones using samarium diiodide and/or zinc iodide as catalyst. The reaction proceeds efficiently in high yields at ambient temperature. However, to our knowledge there are no literature reports on the coupling of keto cyanides to form 1,2-diketones. Several methods for the synthesis of 1,2-diketones are reported which include acyloin condensation of esters with sodium metal,[4] coupling of acid chlorides[5] and selenium dioxide oxidation of various monoketones.[4,6] α-Diketones are also available through oxidative procedures such as the ene reaction of singlet oxygen with alkenes[7] or by the oxidation of acetylenes with $NaIO_4/RuO_2$.[8] Recently diethyl[1-alkyl(aryl)-1-(trimethyl siloxy)methyl]phosphonate was also employed[9]. However most of these methods have some disadvantages in relation to their general applicability, selectivity, availability, number of steps, operational convenience, or yields. As a result there is always a considerable interest in finding more selective methods. Our new method couples with ease a wide variety of acyl cyanides directly to form the corresponding 1,2-diketones and there was no evidence for the formation of any α-ketol type of byproducts.

$$\underset{\mathbf{1}}{\mathbf{RCOCN}} \xrightarrow[\mathbf{THF}]{SmI_2 \text{ or } ZnI_2} \underset{\mathbf{2}}{\mathbf{RCOCOR}}$$

In a typical procedure, benzoyl cyanide (0.13g, 1 mmol) dissolved in dry tetrahydrofuran (5ml) under nitrogen was added slowly to a solution of samarium diiodide (0.80g, 2 mmol) in tetrahydrofuran (10ml) and stirred at room temperature. The reaction starts immediately, as indicated by the fast disappearance of the characteristic blue-green color of SmI_2. After 25 mins., dil HCl was added and extracted with diethylether (3 x 20ml). The ether extract was washed with sodium bicarbonate solution, dried over sodium sulphate, and concentrated under reduced pressure to afford 2a in 80% yield exclusively. Similarly keto cyanides (1b-h) were reacted and the corresponding 1,2-diketones were obtained in 75-80% yields. The structures of the diketones were unambiguously identified on the basis of their physicochemical data (IR, NMR, MS). The results and scope of this reaction are shown in the table. Aliphatic keto cyanide 1h was also coupled with SmI_2 to directly form the 1,2-diketone, however the reaction completion time was about 90 mins. The reaction conditions are tolerant of the ester group (entry 1g) and of the ether in p-$MeOC_6H_4COCN$ (entry 1f). Furthermore, aromatic halides showed remarkable selectivity to give the diketone without any dehalogenation (entry 1b & 1c). When SmI_2 is replaced by inexpensive ZnI_2 the coupling proceeds effectively with only one equivalent of ZnI_2

compared with two equivalents of SmI_2 and the products were obtained in almost comparable yields. In most cases the reaction is over within (25-40) mins with SmI_2 however the reaction takes a little more time with ZnI_2. Further increasing the reaction time gave no significant improvement in yield but rather formation of the corresponding benzoin occurred.

Although the detailed mechanism of this reaction is not clear at this stage, it is likely that the reaction starts by an electron transfer from SmI_2 to RCOCN. The radical anion $(RCOCN)^{\bullet-}$ thus formed could be cleaved into $RCO^{\bullet}$and CN^-The radical $RCO^{\bullet}$can dimerise into 1,2-diketones or it can be reduced into an acyl anion species, which on acylation gives the corresponding diketones.[10] More detailed studies aimed at expanding the scope of the reaction and to understand its mechanism are in progress.

In conclusion, the present new method has some advantages over the existing methods and will make a useful and important addition. The main advantages of this new method are mild reaction conditions, reduced reaction times, lack of side products and better yields than the classical methods.

Table: SmI_2/ZnI_2 catalyzed coupling of keto cyanides into 1,2-diketones

entry	R	SmI_2[a] equivalents	Reaction time (mins)	Yield[b] %	ZnI_2 equivalents	Reaction time (mins)	Yields %
1a	C_6H_5	2	25	82	1	30	78
1b	$4\text{-}ClC_6H_4$	2	30	75	1	40	66
1c	$4\text{-}IC_6H_4$	2	35	80	1	45	70
1d	$4\text{-}MeC_6H_4$	2	35	75	1	50	68
1e	$4\text{-}NO_2C_6H_4$	2	40	70	1	65	70
1f	$4\text{-}MeOC_6H_4$	2	35	80	1	40	75
1g	$4\text{-}MeOOCC_6H_4$	2	35	75	1	45	70
1h	$n\text{-}C_8H_{17}$	2	90	65	1	75	65

[a] SmI_2 is prepared from samarium metal and 1,2-diiodoethane and stored in THF solution under an inert atmosphere. [b] All the yields refer to isolated chromatographically pure compounds.

References and Notes :

1. Recent reviews: (a) Molander, G. A., *Chem. Rev.,* **1992,** *92,* 29. (b) Inamoto, T., *In Comprehensive Organic Synthesis.;* Trost, B. M., Fleming, I., Eds. Pergamon: Oxford, **1991,** Vol. 4, pp 231-250. (c) Trost, B. M.., Fleming, I., Eds., Pergamon, Oxford, **1991**, Vol. 4, pp 251-282.
2. Girard, P., Namy, J-L., Kagan, H. B., *J. Am. Chem. Soc.,* **1980,** *102,* 2693.
3. For the deoxygenation of sulfoxides and epoxides see: Hasegawa, E., Curran, D. P., *J. Org. Chem.,* **1993,** *58,* 5008; Harada, Y., Inanaga, J., Yamaguchi, M., *J. Chem. Soc., Chem. Commun.,* **1989,** 276.; For the organohalo compounds see: Wipf, P., Venkatraman, S., *J. Org. Chem.,* **1993,** *58,* 3455; Curran, D. P., Totleben, M. J., *J. Am. Chem. Soc.,* **1992,** *114,* 6050; For the homocoupling of allylic or benzylic halides see : Collin, J., Namy, J. L., Dallemer, F., Kagan, H. B., J. Org. Chem., **1991,** *56,* 3118.
4. McElvain, S. M., *Org. React.,* **1948**, *4*, 256.
5. Using samarium diiodide see: Girard, P., Coutngnal, R., Kagan, H. B., *Tetrahedron Lett.,* **1981,** *22*, 3959; Souppe, J., Namy, J-L., Kagan, H. B., *Tetrahedron Lett.,* **1984,** *25,* 2869; Using pyrophoric lead see: Meszaros, L., *Tetrahedron Lett.,* **1967**, 4951; Using Li/ultrasound see: Han, H. B., Boudjouk, P., *Tetrahedron Lett.,* **1981,** *22,* 2757.
6. Rabjohn, N., *Org. React.,* **1949,** *5,* 331.
7. Adam, W., Griesbeck, A., Staab, E., *Tetrahedron Lett.,* **1986,** *27,* 2839.
8. Zibuck, R., Seebach, D., *Helv. Chim. Acta.,* **1988,** *71,* 237; For using zerovalent complexes of nickel see: Flood, T. C., *Tetrahedron Lett.,* **1977,** 3861.
9. Olah, G. A., An-hsiang, W., *J. Org. Chem.,* **1991,** 902.
10. Such type of dimerisation of photochemically prepared acyl radicals has been reported see: Barton, D. H. R., George, M. V., Tomoeda, M., *J. Chem. Soc.,* **1962,** *17,* 1967; For nucleophilic acylation see: Lapkin, I. I., Anvarovs, G. Y., Povarnltsyna, T. N., *J. Gen. Chem., USSR.* (English trans) **1966,** *36,* 1945.

(*Received in UK* 20 *June* 1997; *revised* 27 *August* 1997; *accepted* 29 *August* 1997)