Pergamon

Tetrahedron Letters, Vol. 35, No. 15, pp. 2365-2368, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 $6.00+0.00

0040-4039(94)E0248-V

Electrochemical Reduction of Diaryl-1,2-Diketones in the Presence of Carbonimidoyl Dichlorides. A New Method for the Synthesis of Enediol Iminocarbonates.

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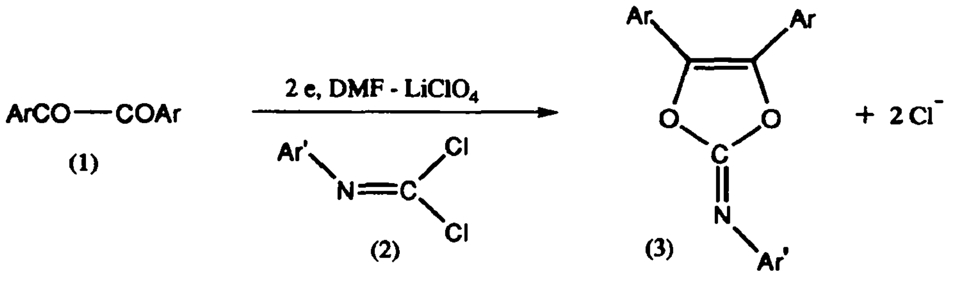
Abstract.-Selective cathodic reduction of diaryl-1,2-diketones in the presence of carbonimidoyl dichlorides provides a new and very convenient method for the synthesis of the title compounds.

Recently we reported a new method for the synthesis of isocyanides by electrochemical reduction of carbonimidoyl dichlorides[1]. Now, we have focused our interest on the study of the synthetic usefulness of using these dichlorides as electrophilic reagents to capture nucleophilic intermediates generated by cathodic reduction.

We herein report a new, efficient and simple method for the synthesis of N-substituted iminocarbonates (3), via selective cathodic reduction of diaryl-1,2-diketones in the presence of carbonimidoyl dichlorides which are easily available from isothiocyanates, isocyanates and N-monosubstituted formamides[2]. These reactions provide the corresponding products (3) in almost quantitative yields.



Carbonates and iminocarbonates of alcohols, diols and phenols have been known for a long time[3]. Carbonates derived from enediol species are usual intermediates of synthesis. Remarkable applications such as protective reagents of amine functional groups[4] as well as "electron-rich" dienophiles[5] have been reported. However, literature about enediol iminocarbonates is very scarce. This is perhaps because a convenient method for its synthesis has not been reported yet . Reaction of bis(tributylstannyloxy)ethenes with isothiocyanates is the only reported method of preparation[6]. This method requires the previous obtention of diethylaminotributylstannane by a complex and expensive procedure. Moreover, yields for the only two reported reaction examples[7] show a remarkable difference. In contrast, the present electrochemical procedure is far more convenient. Nearly quantitative yields in all the cases, easy availability of starting materials and simple experimental procedure are obviously valuable, noteworthy advantages.

Table 1. Preparation of enediol iminocarbonates (3) by cathodic reduction of diaryl-1,2-diketones (1) in the presence of carbonimidoyl dichlorides (2).

Entry	Ar	Ar'	Yield (%) [a]	m.p. (°C)
1	C_6H_5	C_6H_5	91	177-178
2	C_6H_5	4-Cl-C_6H_4	95	151-152
3	C_6H_5	2-Cl-4-Me-C_6H_3	92	185-186
4	4-MeO-C_6H_4	C_6H_5	85	152-153
5	4-MeO-C_6H_4	2-Cl-4-Me-C_6H_3	83	157-158
6	4-MeO-C_6H_4	4-Cl-C_6H_4	90	177-178
7	4-Br-C_6H_4	2-Cl-4-Me-C_6H_3	84	152-154
8	4-Br-C_6H_4	C_6H_5	92	147-148
9	4-Br-C_6H_4	4-Cl-C_6H_4	87	205-207

[a] yields in crystallized products. All compounds gave satisfactory IR, ^1H NMR, ^{13}C NMR, mass spectra, and elemental analyses[8].

Acylation and alkylation of diaryl-1,2-diketones have been reported previously[9] by cathodic reduction in the presence of carboxylic acid chlorides and anhydrides as well as in the presence of alkyl halides. It is generally neccesary to perform the electrolyses with an excess of the electrophilic reagent. However, this is the first time that an electrochemical reductive iminocarbonylation process is reported. Besides, it is also the first time that carbonimidoyl dichlorides have been used in electroorganic synthesis as nonelectroactive electrophilic reagents. It is also to be noticed that optima yields are obtained by just adding equimolecular amounts of reagents to the catholyte solution.

The results of a number of reactions are summarized in Table 1. The synthesis of the compound with entry number 1 had been reported previously[7]. The rest of the entries correspond to new iminocarbonates. NMR spectra of this class of compounds, especially ^{13}C NMR spectra, show a remarkable dependence upon temperature. When the temperature was increased simple spectra were recorded, whereas spectra became more complex when the temperature was lowered. This fact is attributed to a relatively unhindered rotation of the N-aryl group around the carbon-nitrogen double bond[10].

Typical Experimental Procedure. Electrolyses were carried out under a constant cathodic potential in a concentric cylindrical cell with two compartments separated by a circular glass frit (medium) diaphragm. A mercury pool (diameter 5 cm) was used as the cathode and a platinum plate as the anode. The catholyte was magnetically stirred. The temperature was kept at 18 °C by external cooling. The reductions were carried out[11] in DMF-$LiClO_4$, 0.2 M. Approximately 35 mL and 15 mL of this solution were placed in the cathodic and the anodic compartments, respectively. To prevent accumulation of electrogenerated acid in the anode compartment, anhydrous sodium carbonate (3 g) was placed in this compartment. Solutions of diaryl-1,2-diketones (1) (5 mmol) and carbonimidoyl dichlorides (2) (5 mmol) were electrolyzed under the following cathodic potentials: -0.95 V vs SCE (entries 2, 6, 9); -1.00 V (entries 1, 4, 8); -1.05 V (entries 3, 5,7) . The electricity consumption was 2 F . mol^{-1} for all cases. High purity products were isolated dropping the catholyte solution onto cold brine (200 mL) and filtrating or extracting the mixture with ether[12], which was washed with cold water and dried (Na_2SO_4). The directly collected solid crude products and that obtained after removing ether under reduced pressure were isolated in nearly quantitative yields[13] and were crystallized from acetonitrile.

Acknowledgements: We gratefully acknowledge the financial support of the Dirección General de Investigación Científica y Técnica (project number PB89-0442).

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7. The synthesis of compound with entry number 1 (Ar = C_6H_6, Ar' = C_6H_6, mp not reported) and further iminocarbonate (Ar = C_6H_6, Ar' = 4-Me-C_6H_4, mp 148-149 °C) has been reported in reference 6; yields 80% and 60% respectively.
8. The spectral data for entry 2 product (Ar = C_6H_6, Ar' = 4-Cl-C_6H_4) are reported as an example of spectroscopic properties of this class of compound: IR (nujol) 1744, 1233, 1069, 839, 760, 694 cm^{-1}; MS 70 eV m/z (rel. intensity) 349 (M^+ + 2, 1), 347 (M^+, 4), 166 (43), 165 (100), 125 (14), 105 (21), 77 (37); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ: 7.24 (d, 2H, J = 9.2 Hz), 7.29 (d, 2H, J = 9.1 Hz), 7.41 (m, 6H), 7.55 (br m, 2H), 7.61 (br m, 2H); ^{13}C NMR [75 MHz $(CD_3)_2SO$, 100 °C], δ: 124.61, 125.36*, 126.54*, 127.59, 128.78, 129.08*, 130.06*, 136.31*, 143.24, 149.87. *Each signal becomes a doublet when the temperature is lowered.
9. See for example: Simonet, J.; Lund, H. *Bull. Soc. Chim. Fr.* **1975**, 2547; Adams, C.; Kamkar, N. M.; Utley, J.H.P. *J. Chem. Soc., Perkin Trans. 2,* **1979**, 1767; Guirado, A.; Barba, A.; Hursthouse, M.B.; Arcas, A. *J. Org. Chem.* **1989**, 54, 3205; Guirado, A.; Barba, F.; Manzanera, C.; Velasco, M. *J. Org. Chem.* **1982**, 47, 142.
10. A kinetic study on inversion of configuration process is now in progress in our laboratory.
11. DMF was taken from a freshly opened bottle and dried with molecular sieve. $LiClO_4$ was anhydrous. Both were purchased from Fluka, and were used directly without purification.
12. Product corresponding to entry 7 was isolated by extraction.
13. IR and high field ^{1}H NMR spectra for crude and crystalline products were recorded showing negligible differences.

(*Received in UK* 17 *November* 1993; *revised* 28 *January* 1994; *accepted* 4 *February* 1994)