Tetrahedron Letters,Vol.24,No.22,pp 2223-2226,1983 0040-4039/83 $3.00 + .00
Printed in Great Britain

ELECTROGENERATED BASES VII[1]. NOVEL SYNTHESES OF ETHYL GLYOXALATE AND DIETHYL KETOMALONATE VIA ELECTROGENERATED SUPEROXIDE

M. Sugawara[2] and M.M. Baizer

Department of Chemistry
University of California, Santa Barbara, CA 93106

ABSTRACT: Using electrogenerated tetraalkylammonium superoxide plus oxygen ethyl cyanoacetate has been converted (a) directly to ethyl glyoxylate and (b) in a "one-pot" two-step synthesis to the oxomalonate.

As part of our program designed to develop organic syntheses based upon the utilization of electrogenerated bases (EGB), including superoxide, we have found that with the latter and oxygen sec-nitriles [Ph_2CHCN, 1, $Ph(CH_3)CHCN$, 2, Me_2CHCN, 3] are converted to their corresponding ketones (Ph_2CO, $PhCOCH_3$, Me_2CO) in excellent to moderate yields. Prim-nitriles ($PhCH_2CN$, 4, EtCN, 5, MeCN, 6) under similar conditions are converted directly to their corresponding acids; however, the intermediate aldehydes can be trapped as their diacetates if Ac_2O is included in the catholyte[1].

$$(X)(Y)\ CHCN \xrightarrow[-1.0V\ vs.\ SCE]{O_2} (X)(Y)\ C = O$$

1, X=Y=Ph	1', 95%
2, X=Ph, Y=Me	2', 72%
3, X=Y=Me	3', 20% + 74% 3

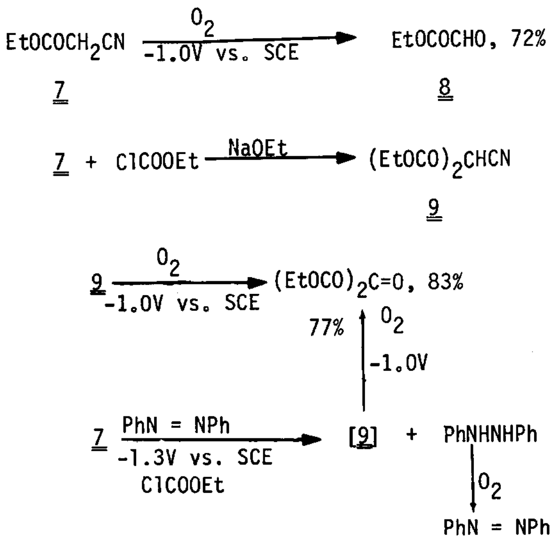
$$(X)\ CH_2CN \xrightarrow[-1.0V\ vs.\ SCE]{O_2}$$

	No Ac_2O XCOOH	Ac_2O $XCH(OAc)_2$
4, X=Ph	4', 89%	4", 54% + 27% 4
5, X=Me	5', 15% + 75% 5	5", 18% + 75% 5
6, X=H	6', low	6", low + 73% 6

The above reactions as well as those described here were carried out in conventional H-cells with a medium porosity sintered glass separator between the anode and cathode compartments. The cathode was Hg, the anode Pt and the solvent-supporting electrolyte system (SSE) very dry DMF (or MeCN)/n-Bu_4NBr. Pure oxygen was bubbled through the catholyte and reduced at ca. -1.0 V vs SCE; no organic substrate was reduced at this (potentiostatically controlled) voltage. A proposal for rationalizing these oxidative decyanations has been offered[1]; the first step is the deprotonation of the nitrile by superoxide functioning as an EGB.

It was of especial interest to determine whether the above methodology would be servicable[4] in the preparation of ethyl glyoxylate, 8, from a prim-nitrile ester precursor, 7, and of diethyl oxomalonate, 10, from a sec-nitrile ester, 9. Each of these products is valuable as an intermediate for further syntheses and has been the target of several recent investigations[5]. One of the newest recent methods of preparation involves ozonolysis respectively of diethyl maleate (65% yield of product) and diethyl ethylidenemalonate (62% of product)[5a].

The electrochemical syntheses of 8 from 7 and 10 from 9 were successful. The H-cell and electrode materials mentioned above were used. Each compartment had ca. 60 mL capacity and was charged with a 0.2 M solution of n-Bu_4NBr in dry MeCN. In addition, 5.0 mmol of ethyl cyanoacetate (7, Aldrich) and dry activated neutral[6] Al_2O_3 were



added to the catholyte and ca. 1 mL of cyclohexene to the anolyte (to trap anodically generated Br_2). After oxygen had been bubbled through the catholyte for a few minutes electrolysis at -1.0 V vs SCE was initiated and continued until 7 had completely disappeared (1.3 F/mol). The MeCN was removed from the catholyte *in vacuo*; the residue was triturated with dry ether and the insoluble electrolyte removed by filtration. Evaporation of the ether and vacuum distillation of the residue yielded 72% of 8 identical (gc, ir) to an authentic sample[7].

Two procedures were used for the preparation of 10. In the first, diethyl cyanomalonate 9 was prepared from $NCCH_2COOEt$ (Aldrich), ClCOOEt (Aldrich) and NaORt by a method which has been reported[8]. The electrolysis procedure and workup were similar to those described above for the preparation of 8 except that ca. 1 g of P_2O_5 was added to the ether solution of the product before vacuum distillation of 10, yield 83%[9]. In the second method $NCCH_2COOEt$ was alkylated to 9 in the catholyte by ClCOOEt using reduced azobenzene[10] as an EGB; the intermediate was then contacted *in situ* with electrogenerated superoxide. This sequence constituted a "one-pot" synthesis of 10. The cell containing the electrodes and SSE mentioned above were used. The catholyte, through which a stream of Ar was passed, was pre-electrolyzed at -1.6 V until the current dropped to 10 μA. This step served to remove traces of proton donor impurities. Azobenzene (5.1 mmol) and ethyl cyanoacetate (5.0 mmol) were added to the catholyte, cyclohexene to the anolyte. Then electrolysis was started at a cathode voltage of -1.3 V while ClCOOEt (5.0 mmol) was added dropwise[11] to the catholyte. After the passage of 1.8 F/mol all the cyanoacetate had been consumed and cyanomalonate had been formed. The electrolysis was interrupted while oxygen was bubbled through the catholyte for 0.5 hr then resumed at a cathode voltage at -1.0 V. After the passage of 0.4 F/mol the cyanomalonate had all been converted to oxomalonate. Removal of the MeCN, treatment with ether to segregate electrolyte, and separation of products in the ether solution yielded 77% of 10 (vacuum distillation) and 86% of azobenzene (residue).

An attempt to simplify further the "one-pot" synthesis of 10 by using superoxide as an EGB for both the alkylation and the oxidative decyanation steps yielded 10% of desired product.

Since potentiostats, potential controllers, and laboratory electrochemical cells are now available on an "off-the-shelf" basis, we consider the syntheses reported here convenient, facile, and simple[12].

Acknowledgment. We wish to thank the donors of the Petroleum Research Fund administered by the American Chemical Society for support of this work.

REFERENCES AND NOTES

1. Paper VI: M. Sugawara, M.M. Baizer, W.T. Monte and R.D. Little, Acta Chem. Scand., **xx**, xxxx (1983).
2. Permanent address: Department of Applied Chemistry, Yamagata University, Yonezawa, Yamagata-ken 992, Japan.
3. To whom inquiries should be addressed.
4. Many esters are only saponified by superoxide: J.S. Filippo, L.J. Romano, C.-I. Chern, and J.S. Valentine, J. Org. Chem. **41**, 586 (1976); see, however, P.M. Allen, U. Hess, C.S. Foote, and M.M. Baizer, Synth. Commun. **12**, 123 (1982)
5. (a) M.E. Jung, K. Shishido, and L.H. Davis, J. Org. Chem. **47**, 891 (1982); (b) M.M. Baizer, and R.D. Goodin, U.S. Pat. 4,351,951 of September 28, 1982.
6. B.S. Jensen and V.D. Parker, J. Chem. Soc. Chem. Commun. 367 (1974).
7. T.R. Kelly, T.E. Schmidt, and G. Haggerty, Synthesis, 544 (1972).
8. J.I. Cadogan, D.H. Hey, and J.T. Shark, J. Chem. Soc. C, 1973 (1966).
9. S. Astin, A.C.C. Newman, and H.L. Riley, J. Chem. Soc. 391 (1933).
10. Electroreduced azobenzenes have frequently been used as EGB's following the paper by P.E. Iversen and H. Lund, Tetr. Lett. 3523 (1969).
11. ClCOOEt does itself not reduce before -1.5 V.
12. Authors, including one of us (MMB), have occasionally used one or another of these adjectives in the titles of published syntheses. These characterizations sometimes reflect the authors' rather than the readers' degree of comfort with a given methodology.

(Received in USA 9 February 1983)