CHEMISTRY LETTERS, pp. 1087-1090, 1977. Published by the Chemical Society of Japan

ELECTROCHEMICAL GENERATION OF CARBALKOXYNITRENES FROM N,N-DICHLORO CARBAMATES[1]

Toshio FUCHIGAMI and Tsutomu NONAKA
Department of Electronic Chemistry, The Graduate School
Tokyo Institute of Technology, Meguro-ku, Tokyo 152

Carbalkoxynitrenes (II) can be generated from N,N-dichloro carbamates (methyl, ethyl) (I) by electrolysis, as shown by the formation of 2-(carbalkoxyamino)-1,4-dioxane (III) in the electroreduction of (I) in the presence of dioxane.

Nitrenes are unique in reactivity and important key intermediates for organic synthesis. It is well known that the most common route to the nitrene is thermally or photochemically induced loss of molecular nitrogen from an azide.

In our previous papers,[2,3] we described that a sulfonylnitrene could be generated by cathodic reduction of N,N-dichlorotoluene-p-sulfonamide (dichloramine-T) and proposed the mechanism for the cathodic process.

In this work, we have investigated the possible generation of carbalkoxynitrenes (II) by the electrochemical reduction of N,N-dichloro carbamates (I).

The generation of (II) was verified by the formation of 2-(carbalkoxyamino)-1,4-dioxane (III) in the electroreduction of (I) in the presence of dioxane, since it is well known that the C-H insertion reaction is a distinctive nitrene reaction.[4]

Results and Discussion

Constant current electrolyses were carried out in acetonitrile at variuos kinds of cathode materials and about 2×10^5C/mol of electricity was passed. Electrolytic results are summerized in Table.

As shown in Table, C-H insertion products (III) were expectedly formed by electrochemical reduction of (I), however the yields were generally low and carbamates (IV) were obtained in quantity. Because the yields of (III) were so low that they could not be isolated from the mixture of products, the identification of (III) was carried out by using a gas chromatography. The retention times for (III) in the mixture of the products were equal to those for the independently synthesized authentic samples$^{5)}$ under a variety of gas chromatographic conditions. In addition, the mass fragmentations$^{6)}$ of (III) were completely identical with those of the authentic samples.

Table. Results for the electrolysis of (I)

R	Cathode material	Ratio (V/V) Dioxane/Acetonitrile	Current density (A/dm^2)	Amount of current (C/mol)	Yield (%)	
					(III)	(IV)
Me	Pt	7/3	2.6	2.1×10^5	5	25
Me	Pt	7/3	4.0	2.1×10^5	7	36
Et	Pt	7/3	2.0	2.6×10^5	2	63
Et	Pt	7/3	2.6	2.1×10^5	6	63
Et	Zn	7/3	2.6	2.1×10^5	3	40
Et	C	7/3	2.6	2.1×10^5	4	53
Et	Pt	17/3	2.6	2.1×10^5	4	72
Et	Pt	7/3	4.0	2.1×10^5	5	43

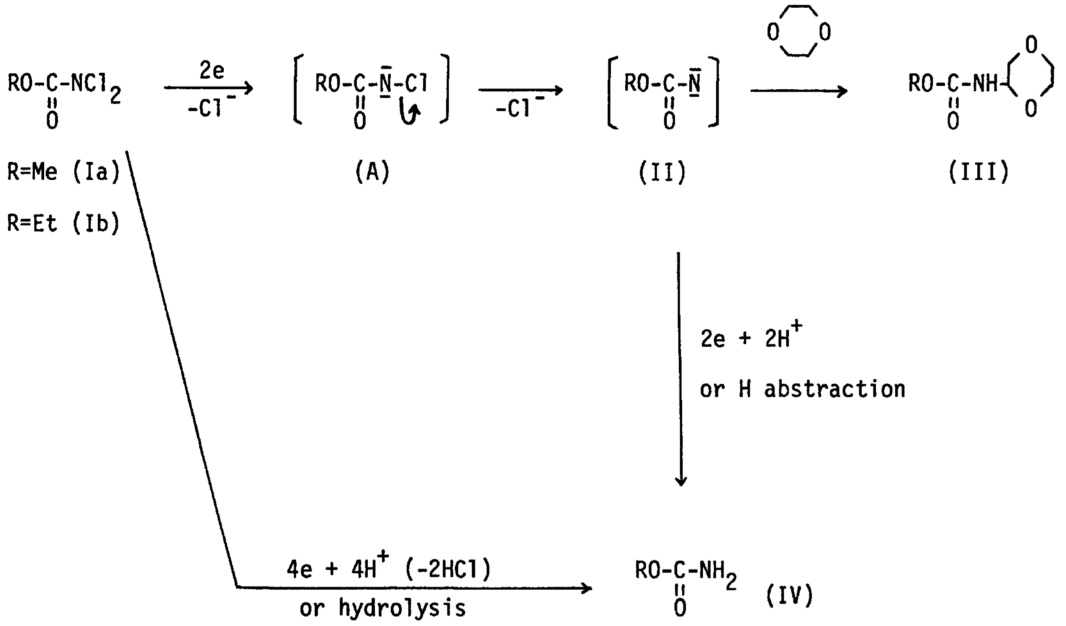
Both N,N-dichloro carbamates (I) gave (III) in approximately the same yields. The yields of (III) depended on current density. Platinum was a suitable cathode for the formation of (III). Zinc was not found to be suitable, though it was an effective catalyzer for the generation of a nitrene from N,N-dichlorotoluene-p-sulfonamide.$^{7)}$ No N,N'-dicarbalkoxyhydrazine (a coupling product of two carbamate radicals) could be detected by a gas chromatography.

The formation reaction of (II) and (III) might proceed in the following scheme.

The addition of two electrons and removal of a chloride ion produce an anion. Further removal of another chloride ion from the resulting anion (A) may form a nitrene intermediate (II). The nitrene thus formed probably inserts a C-H bond of dioxane if dioxane is in the neighborhood of (II). In the absence of dioxane in the neighborhood, further reduction of (II) may result in the formation of the carbamate (IV), because (II) is an electron-defficient species.

The carbamate was also formed in the hydrolysis of (I) under electrolytic conditions. Hydrogen abstraction of (II) would be conceivable for the formation of (IV).

Reaction scheme



Experimental

Electrolysis: An H-type cell devided with a sintered glass diaphragm was used. Platinum, zinc, and carbon plates (4x3 cm) were used as a cathode. . The catholyte and anolyte were 50 ml of 1.1 M $LiClO_4 \cdot 3H_2O - CH_3CN$ solution containing dioxane. To the catholyte was added 15 mmol of (I) and then a constant current was supplied. The electrolysis was carried out in the dark at 10°C. The detailed electrolytic conditions are shown in Table.

Analysis of Products: After electrolysis, the catholyte was evaporated under reduced pressure below 25°C, and then the residue was mixed with water. The aqueous solution was extracted repeatedly with dichloromethane and the combined extracts were dried over anhydrous sodium sulfate.

The solution was subjected to gas chromatographic analysis.

The identification was carried out by comparison of retention times for (III) and the independently synthesized authentic samples$^{5)}$ under a variety of gas chromatographic conditions: column packing, apiezon grease L and silicone DC HV grease; column temperature, 150, 170, and 190°C.

2-(Carbomethoxyamino)-1,4-dioxane (IIIa) was prepared by the photolysis of methylazidoformate in the presence of dioxane according to a method similar to that described by Nozaki et al.$^{5)}$ Yield, 11%; bp 115-117°C/6 Torr. (Found: C, 44.43; H, 6.85; N, 8.33%. Calcd for $C_6H_{11}NO_4$: C, 44.72; H, 6.88; N, 8.69%). m/e 161 (M^+).

References

1) Organic N-Halogen Compounds. Part 11.
Part 10: T. Fuchigami and K. Odo, Bull. Chem. Soc. Jpn., 50, 1791 (1977).
Electrochemical Generation of Unstable Nitrogen Species. Part 2. Part 1: ref. 2, 3.
2) T. Fuchigami, T. Nonaka, and K. Iwata, J. Chem. Soc. Chem. Commun., 1976, 951.
3) T. Fuchigami, K. Iwata, and T. Nonaka, J. Chem. Soc., submitted for publication.
4) D. S. Breslow, "Nitrenes", ed. by W. Lwowski, Interscience Publishers, New York, p. 287 (1970).
5) H. Nozaki, S. Fujita, H. Takaya, and R. Noyori, Tetrahedron., 23, 45 (1967).
6) The mass spectra of (III) were measured by a gas chromatograph-mass spectrometer.
7) D. S. Breslow and M. F. Sloan, Tetrahedron Lett., 1968, 5349.

(Received July 6, 1977)