Nonagueous Potentiostatic Reduction of 9,9-Dichlorofluorene to Difluorenylidene

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Polarographic studies in nonaqueous systems are fruitful areas of study for chemists with interests in organic reaction mechanisms (1). To elucidate a mechanism of an organic reaction, it is quite often necessary to operate a controlled potential reduction on a larger scale than currents and time permit with conventional polarographic equipment. Berlin et al. (2) have used an apparatus designed for both conventional polarography and long-term controlled potential reductions (up to 10 days) in nonaqueous solutions; however, they were restricted to solute concentrations of 10^{-4} to $10^{-3}M$ solutions. In addition, the cell had to be hermetically sealed to prevent solvent evaporation, and their analyses of products were restricted to gas chromatography because of the small quantities formed.

Organic compounds, including organic halides, have been extensively studied by Wawzonek et al. (3-9) in nonaqueous solvents, but all of their work has been done with a large uncontrolled dc supply. Erickson (10, 11) et al. have studied the polarographic and controlled potential reduction of stereochemical isomers of cyclopropyl halides in ethanol, and Grimshaw et al. (12, 13) have studied the polarographic-potentiostatic reduction of 1-acetylnapthalene and benzyl bromides in nonaqueous solvents.

Since Wawzonek et al. (7) had previously shown that chlorocarbanions were precursors to carbenes in nonaqueous solvents via electrolytical reduction, albeit a very small yield, we elected to demonstrate that other gemdichloro compounds could be reduced via the same mechanism. The compound chosen for this study was 9,9-dichlorofluorene.

EXPERIMENTAL

Apparatus. A Heath Model EUW-401 polarograph with Heath Model EUW-19-2 operational amplifier was used to record the polarograms on a Bausch and Lomb 100-mV recorder (maximum sensitivity 10 mV with ¹/₂-sec full scale pen response on a 5-in. chart). Infrared spectra were recorded on a Beckman IR-8 spectrophotometer, and the NMR spectra were recorded on a Hitachi

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Perkin-Elmer R-20 high resolution NMR spectrometer.

The potentiostat used in this study was a modified design of Tackett and Knowles (14). We increased their output capacity by adding an additional power supply and filtering circuit to operate three additional field-effect current boosting transistors. This potentiostat could generate 90 mA of current through a 1000-ohm load, whereas Tackett and Knowles' potentiostat was restricted to 16 mA through a 500-ohm load. Interested readers may obtain a schematic of the potentiostat by writing the senior author (RCD).

Reagents. Fisher reagent grade N, N-dimethylformamide (DMF) was dried over anhydrous potassium carbonate and distilled through an 18-inch fractionating column of glass helices. The inside diameter of the column was 2 cm. Eastman reagent grade tetra-*n*-butylammonium bromide (0.175M) was used as the supporting electrolyte after recrystallizing the salt from anhydrous ethyl acetate until polarographically pure. Three or more recrystallizations were required. The 9,9-dichlorofluorene was prepared from 10 g (0.056 mole) of Eastman white label 9-fluorenone. The 9-fluorenone was added to 100 ml of toluene containing 22.2 g (0.145 mole) of phosphoryl chloride and 17.5 g (0.084 mole) of phosphorus pentachloride. The solution was refluxed on a steam bath for 3 hr. After the solvent was removed, 3.2 g of crude 9,9dichlorofluorene was recovered (25% yield). After recrystallizing from glacial acetic acid and once from n-pentane, the colorless, prism crystals had a mp of 101-102 °C. (Lit. mp 102.5 °C) (15).

Procedure. A current-voltage curve was recorded for a solution concentration of the order $1 \times 10^{-3}M$ with a concentration of 0.175M supporting electrolyte. The capillary had a drop time in distilled water of 3.99 sec at a mercury height of 60 cm. The $m^{2-3}t^{1-6}$ value for the capillary was 4.85.

A medium fine, sintered glass frit separated the catholyte from the anolyte in the large reduction cell. A small magnetic stirrer placed on top of the mercury pool cathode (7.00 cm²) vigorously stirred the solution throughout the reduction. A coiled 12-gauge platinum wire was used as the anode. The Ag/AgBr nonaqueous electrode (0.175M tetra-n-butylammonium bromide in DMF) served as the reference electrode. The cell resistance was approximately 500 ohm as measured from the anode potential (20 volts) and the initial cell current (40 mA). The reductions were carried out in an ice-water bath with temperature of the reduction solution at approximately +3 °C.

A 1.50-g sample of 9,9-dichlorofluorene was added to the cathode compartment which contained approximately 22 ml of a DMF solution with 0.175M tetra-n-butylammonium bromide. The analyte was approximately 18 ml of DMF containing 0.175Mtetra-n-butylammonium bromide. Both catholyte and anolyte were degassed for 20 min with purified nitrogen prior to the start of the reduction and were continuously degassed during the reduction. When the potentiostat was first turned on, the current registered 120 mA and gradually fell to 80 mA after 3.5 hr. After 5-6 hr, the potentiostat was turned off with the current reading at 10 mA.

During the course of the reduction, the cathode changed from a light yellow to orange which progressively intensified until the catholyte became an opaque brownish black color. The catholyte was diluted with 100 ml of water, and the dark brown organic precipitate was filtered and dried (0.51 g). The dried precipitate was recrystallized from absolute ethanol and produced 0.363 g of very bright orange needle-like crystals (34.7% yield) mp 186-190 °C. After an additional recrystallization from ethanol, the difluorenylidene mp was 193-195 °C. (Lit. mp 194-5 °C) (16). The IR

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Figure 1. Polarograms of 9,9-dichlorofluorene



Figure 2. i_d vs. $h^{1/2}$ graph for 9,9-dichlorofluorene

and NMR spectra compared favorably with that for difluorenylidene: IR $\bar{\nu}$ (cm⁻¹) (KBr) 3060, 1595, 1430, 1340, 765, 740, and 725; nmr (CDCl₃) δ 7.50 (m, 12H, ring hydrogens) and δ 8.25 (m, 4H, remaining ring hydrogens in positions 2, 2', 9, 9'). The IR spectrum reveals the double bond stretching vibrations at 1595 cm⁻¹ which was a weak to moderate bond. These data are in agreement with compounds which contain highly conjugated double bonds (17). The NMR spectrum reveals only aromatic hydrogens with 12 hydrogens centered at 7.50 Hz and 4 hydrogens (2, 2', 9, 9') centered at 8.25. Undoubtedly, these four downfield hydrogens are deshielded by the effects of both aromatic rings. The NMR spectrum was recorded with a TMS external standard.

RESULTS AND DISCUSSION

A potentiostat (see Apparatus section) was used in conjunction with the Heath polarograph Model EUW-401 to ascertain the reduction pathway for 9,9-dichlorofluorene. In Figure 1, the first half-wave potential vs: Ag/AgBr nonaqueous electrode (18) was 0.10 V. The second polarographic wave, which was somewhat complicated by a

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Figure 3. Cell used for potentiostatic reductions

maximum, occurred at -0.42 V and was less than half the height of the first wave. This behavior suggests the gemdichlorocompound was reduced through a carbene intermediate and parallels the experimental work reported by Wawzonek (7) for the polarographic study of polyhalogenated methanes, benzotrichloride and dichlorodiphenylmethane. Wawzonek had established that carbon tetrachloride reduced through a carbene intermediate which he trapped with tetramethylethylene in a large scale reduction. The dichlorocarbene intermediate was generated from the initial reduction product of carbon tetrachloride, the trichlorocarbanion. A similar reduction scheme is proposed for 9,9-dichlorofluorene:



The first reduction wave ($E_{1/2} = 0.10$ V) represents the reduction of the first chlorine atom which forms the 9chlorofluorene carbanion. This carbanion is the precursor to the strongly electrophilic carbene, fluorenylidene, which will reduce at the -0.10 V potential directly to the dianion of fluorene (See Equation 3). The reaction of the 9-chlorofluorene carbanion, at the surface of the electrode, is a rapid reaction because the diffusion current for the first wave is directly proportional to the square root of the mercury height. This phenomenon is characteristic of a polarographic wave that is diffusion controlled (19). (See Figure 2). Consequently, instead of observing two polarographic waves of equal height that correspond directly to the reduction of the first and second chlorines, respectively, one finds the first wave 2.3 times as high as the second because of the formation and subsequent reduction at the electrode surface of the carbene, fluorenylidene.

(19) P. Zuman, "Organic Polarographic Analysis," The Macmillan Co., New York, N.Y., 1964, p 23.

The second polarogram in Figure 1 illustrates the reduction of 9.9-dichlorofluorene in the presence of water. Water was added to increase the supply of protons which would readily protonate the 9-chlorofluorene carbanion, the precursor to the fluorenylidene carbene. Consequently, with the source of carbenes eliminated and the concurrent increase in the concentration of 9-fluorene, the height of the second wave would be enhanced. This is illustrated by the diffusion current of the second wave which is equal to the sum of the diffusion currents for the prewave at 0.00 V and the wave for the reduction of the first chlorine. The prewave undoubtedly represents a reaction of the reactive gem-dichlorocompound with mercury which is similar to what Wawzonek (7) observed with dichlorodiphenylmethane. One can observe the reaction of the 9.9-dichlorofluorene with mercury because, immediately above a quiet mercury pool, one can see a yellow solution forming which intensifies with time.

Polarographic evidence can infer that a carbene intermediate exists in solution, but it cannot provide absolute evidence. Therefore, we employed the potentiostat in a large scale reduction for the purpose of isolating a product from the carbene intermediate. The dimensions of the cell for the large scale reductions are given in Figure 3. The potentiostat was set to control the potential of the electrolytic reduction at -0.39 V. This was above the reduction potential of the first chlorine $(E_{1/2} = 0.10 \text{ V})$, but below the reduction potential of the second chlorine ($E_{1/2} = 0.42$ V). At this potential, the 9,9-dichlorofluorene would reduce to the 9-chlorofluorene carbanion. This carbanion could generate the fluorenylidene through the loss of a chloride ion or abstract a proton from the solvent to form 9-chlorofluorene. If fluorenylidene were generated, it would have two reaction pathways available: 1) reduce further at the pool of mercury to the dianion of fluorene or 2) dimerize to form difluorenylidene.



To enhance the formation of difluorenylidene, the solution above the mercury pool was stirred vigorously with a small magnetic stirrer. This, hopefully, would sweep the fluorenylidene away from the electrode surface and give it a chance to dimerize before reducing at the electrode surface to the dianion of fluorene.

Fluorenvlidene is known to dimerize to difluorenylidene (20) and, also, has been shown to have both electrons unpaired, e.g., a triplet ground state (21). Consequently,

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Table I. Half-Wave Potentials and Diffusion **Current Constants**

		1st wave		2nd wave	
Compound	Solvent	-E./2	$l_d a$	-E _{1/2}	l _d
9,9-Dichlorofluorene ^b	DMF	0.10	1.11	0.42	0.50
9,9-Dichlorofluorene ^b	DMF	0.28	1.15	0.54	1.03
	(10% H₂O)				
Difluorenylidene ^c	DMF	0.48	0.81	0.96	
$a_{l_d} = i_d / CM^{2/3} t^{1/6}$. 1.89 × 10 ⁻³ M.	Concentration 1	.00 × 10)-3M. (Concen	tration

proof that the carbene was generated in the polarographic reduction would depend on the isolation of the dimerized product, difluorenvlidene.

The polarographic half-wave potentials and diffusion current constants for 9,9-dichlorofluorene are given in Table I. Notice that the diffusion current constants are higher in the aqueous N,N-dimethylformamide (DMF). The reason for the larger diffusion current constants is the lower viscosity of the solvent which enhances the diffusion of the electroactive species (7). Also, in Table I are found the reduction potentials for difluorenylidene. This compound was run to verify that the difluorenylidene was stable at the potentiostatic reduction potential of -0.39 V.

In the large scale reduction of 9.9-dichlorofluorene, a 34.7% yield of difluorenylidene was recovered after recrystallizing the crude product from ethanol. The isolation of difluorenylidene establishes that the carbene, fluorenylidene, undoubtedly was generated from the 9-chlorofluorene carbanion at the dropping mercury electrode (DME). Also, the generation and subsequent reduction of this carbene at the DME explains why the first polarographic wave was larger than the second wave.

This polarographic and controlled potential electrolysis study demonstrates the ease with which organic reaction mechanisms can be studied with electroanalytical techniques. However, one need not restrict himself to reduction mechanisms because the anolyte can be used to study oxidation mechanisms. A controlled potential study of anthracene in acetonitrile provides an informative study of an oxidation mechanism (22).

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