CHEMISTRY LETTERS, pp. 283-286, 1979. Published by the Chemical Society of Japan

ANODIC CHLORINATION AND BROMINATION OF 3-SUBSTITUTED SYDNONE COMPOUNDS

Hsien-Ju TIEN,* Tsutomu NONAKA,** and Taro SEKINE**
*Department of Chemistry, National Cheng Kung University, Tainan,
Taiwan, Republic of China
**Department of Electronic Chemistry, Graduate School at Nagatsuta,
Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227

Anodic halogenation of 3-substituted sydnones was investigated using a platinum electrode in methanol containing halide ions from a synthetic aspect. The chlorination as well as the bromination did take place at the 4-position of sydnones in high yields rather than those in chemical procedures, while the fluorination and the iodination were unsuccessful.

4-Halosydnones are important compounds as a starting material for the syntheses of a number of sydnone derivatives.1) Many methods for preparing 3-substituted 4-chloro and 4-bromosydnones have been proposed.2-9) However, the yields for the halogenation are not so high because a sydnone ring is unstable to acid, alkali, and heat.

An electrochemical halogenation method established in this work was simple in experimental procedures and resulted in high yields and high purities10) of 4-halosydnones. This method may be superior to the chemical methods proposed previously.2-9)

Table 1 shows the electrolytic conditions for the halogenation and the results, compared to the chemical methods. Electrolysis was carried out in methanol at a constant potential using a platinum anode. The conversion of starting sydnones was confirmed to reach to almost 100% by IR spectroscopic analysis when electricity of about two faradays per one mole of the sydnones was passed. Methanol was a suitable solvent in comparison with aqueous acetone11) and acetonitrile, since the use of aqueous acetone decreased the yield of 4-holosydnones and the halogenation in acetonitrile failed.

The electrolytic fluorination of 3-phenylsydnone was unsuccessful12) because a platinum anode was passivated in a solution containing fluoride ions. In the iodination of sydnone an electrolytic current was smoothly passed without passivation, but the corresponding 4-iodosydnone could not be obtained.13) Products in the iodination were unidentified compounds containing iodine.

Based on the consumed electricity, the anodic halogenation of sydnones may be stoichiometrically represented by the following equation.14)

Table 1. Electrolytic Chlorination and Bromination of 3-Substituted Sydnones in Methanol[a] at a Platinum Anode

Starting sydnone	(mmol)	Supporting electrolyte	Anode potential V vs. SCE	Electricity passed C/mol	Yield of 4-halosydnone(II), %	
					Electrochemical method	Chemical method
Ia	(5.0)	$(CH_3)_4NCl$	1.15	1.93×10^5	90	50[b] 73[c] 75[d]
Ib	(2.5)	$(CH_3)_4NCl$	1.15	1.98×10^5	90	e)
Ic	(2.5)	$(CH_3)_4NCl$	1.15	1.98×10^5	83	e)
Id	(2.5)	$(CH_3)_4NCl$	1.15	1.98×10^5	76	e)
Ia	(5.0)	$(CH_3)_4NBr$	1.00	1.98×10^5	87	13[f] 77[g] 78[h,i] 80[j] 81[k] 84[k]
Ia	(2.5)	$NaBr \cdot 2H_2O$	0.75	1.98×10^5	100	13[f] 77[g] 78[h,i] 80[j] 81[k] 84[k]
Ib	(2.5)	$NaBr \cdot 2H_2O$	0.75	1.98×10^5	99	72[k] 74[g]
Ic	(2.5)	$NaBr \cdot 2H_2O$	0.75	1.98×10^5	93	58[k] 63[g]
Id	(2.5)	$NaBr \cdot 2H_2O$	0.75	1.98×10^5	95	54[k] 59[g]

a) Thirty five mili liters of methanol containing a supporting electrolyte in 0.3M concentration. was used as an anolyte.

b) Chlorinated with chlorine in dilute hydrochloric acid.[4]

c) Chlorinated with potassium chlorate in dilute hydrochloric acid.[4]

d) Chlorinated with chlorine in acetic anhydride at 0°C.[3]

e) Any chemical chlorination has not been reported.

f) Brominated with bromine in acetic anhydride at 0°C.[5]

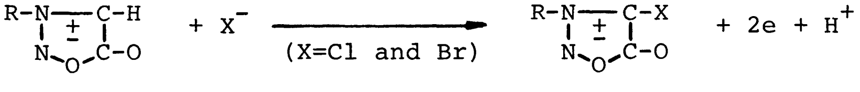
g) Brominated with sodium bromide in concentrated sulfuric acid.[9]

h) Brominated with bromine in ether-water in the presence of sodium hydrogencarbonate.[5]

i) Brominated with N-bromosuccinimide in chloroform.[5]

j) Brominated with bromine in ethanol in the presence of sodium hydrogencarbonate.[5]

k) Brominated with bromine in acetic acid in the presence of sodium acetate.[8,9]



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a: R=Phenyl
b: R=p-Tolyl
c: R=o-Tolyl
d: R=Benzyl

The present hologenation may proceed via anodically generated radical or cationic species,[16] since the electrolyses were carried out at a less positive potential than the oxidation potential of the sydnone ring.[21] A detailed mechanistic study of the anodic halogenation are in progress.

Experimental 3-Substituted sydnones used for the electrolysis were prepared by the method of Earl and Mackey.[23]

An H-type cell separated by a fritted glass was used. Both anode and cathode were platinum plate(1.5 x 1.5 cm). The initial electrolytic current in the controlled potential electrolysis was 100–140 mA and the current decreased slightly at the end of the electrolysis. The temperature of an anolyte was kept below 10°C during the electrolysis.

After the electrolysis, the anolyte was diluted with a large amount of water and the resulting precipitates, which were almost pure 4-halosydnone,[10] were filtered.

Of 4-halosydnones obtained, 3-phenyl-4-chloro,[3,4] 3-phenyl-4-bromo,[2,4,5,7-9] 3-(p-tolyl)-4-bromo,[9] 3-(o-tolyl)-4-bromo,[9] and 3-benzyl-4-bromosydnones[9] are known compounds and were identified with authentic samples by their IR spectra and melting points. Molecular structures of three new 4-chlorosydnones were confirmed by their IR spectra(KBr), NMR spectra(60 MHz, $CDCl_3$), mass spectra(70 eV), and elemental analyses. 3-(p-Tolyl)-4-chlorosydnone: Mp, 137°C(dp); IR, 1790(C=O) and 698 cm^{-1} (C-Cl); NMR, 2.53(s, 3H) and 7.54 ppm(s, 4H); Mass, m/e 212 and 210(M^+); Found, C 51.52, H 3.29, N 13.58, Cl 17.06%(Calcd for $C_9H_7N_2ClO_2$, C 51.32, H 3.37, N 13.30, Cl 16.83%). 3-(o-Tolyl)-4-chlorosydnone: Mp, 101-102°C; IR, 1785(C=O) and 700 cm^{-1} (C-Cl); NMR, 2.33(s, 3H) and 7.3-7.7 ppm(m, 4H); Mass, m/e 212 and 210(M^+); Found, C 51.63, H 3.28, N 13.42, Cl 18.11%. 3-Benzyl-4-chlorosydnone: Mp, 67-68°C; IR, 1770, 1750(C=O), and 690 cm^{-1}(C-Cl); NMR, 5.52(s, 2H) and 7.48 ppm(s, 5H); Mass, m/e 212 and 210(M^+); Found, C 50.82, H 3.32, N 13.39, Cl 17.60%.

References and Notes

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10) Any purification of the halosydnones was not necessary for elemental analysis and measurement of melting points.

11) About 10% of water was added to acetone in order to dissolve supporting salt.

12) No 4-fluorosydnone has been synthesized by chemical methods.

13) Sydnones are not iodinated directly by chemical methods. 3-Phenyl-4-iodosydnone was prepared by halogen exchange of 3-phenyl-4-bromosydnone.15)

14) A sydnone ring can be usually written in mesoionic and betaine forms.1) In this paper, the former form is employed as a matter of convenience.

15) M. Ohta and H. Kato, Nippon Kagaku Zasshi, 78, 1653(1957).

16) In the anodic halogenation of aromatic compounds,17) molecular halogen19) and halogen radical20) species were suggested as halogenating reagents.

17) A sydnone ring has a slight aromaticity and its electronic effect is dual.18)

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21) 3-Phenylsydnone can be oxidized at 1.50 V vs. SCE at a platinum electrode in methanol, acetic acid, and aqueous acetone.22)

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(Received January 22, 1979)