CHEMISTRY LETTERS, pp. 1857-1858, 1991.

^{35}Cl NQR Study of *N,N'*-Dichloro-5,5-dimethylhydantoin and Related Compounds

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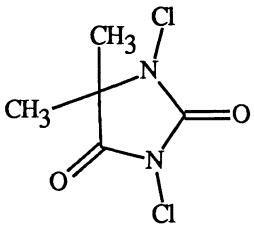
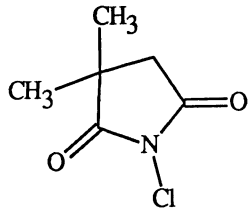
The ^{35}Cl NQR frequencies of *N,N'*-dichloro-5,5-dimethylhydantoin were assigned in comparision with those of *N*-chloro-α,α-dimethylsuccinimide and *N*-chloro-4,4-dimetyl-2-oxazolidone. It turned out monochloro-5,5-dimethylhydantoin was a 1-chloro derivative

N-Chloro imides(amides) are known as effective chlorinating or oxidizing reagents for olefins, alcohols and carbonyl compounds. Thus, it is interesting to investigate the character of the N-Cl bonds in *N*-chloro imides(amides). It is worthwhile to measure the ^{35}Cl NQR frequencies of *N*-chloro imides(amides), because these frequencies give the information on the bond character of N-Cl bonds. There are two N-Cl bonds in *N,N'*-dichloro-5,5-dimethylhydantoin (**1**). This compound showed two resonance signals at liquid nitrogen temperature as listed in Table 1. These frequencies agree with the result reported by Hart and Whitehead.[1] They assigned the lower frequency to the N-Cl bond adjacent to the $C(CH_3)_2$. In order to make sure this assignment ^{35}Cl NQR measurements were carried out for *N*-chloro-α,α-dimethylsuccinimide (**2**) and *N*-chloro-4,4-dimethyloxazolidone (**3**) at liquid nitrogen temperature.

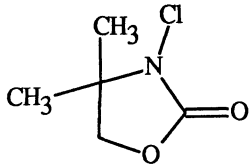
The N-Cl bond of compound **2** can be regarded as being corresponding to the N-Cl bond of compound **1** surrounded by the carbonyl groups, and that of compound **3** the N-Cl bond adjacent to the $C(CH_3)_2$. Their frequencies are shown in Table 1. The lower frequency observed in compound **1** is correponding to the N-Cl bond adjacent to the $C(CH_3)_2$ and in agreement with the assignment of Hart and Whitehead.



1

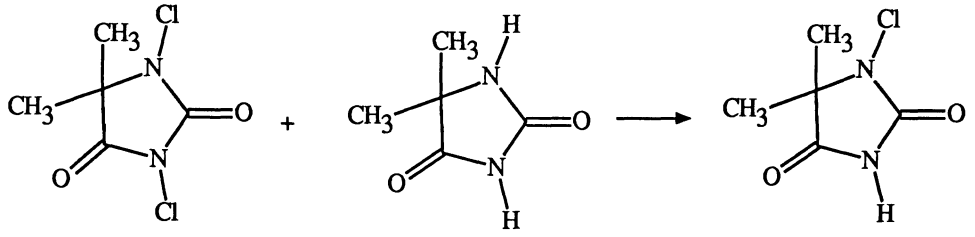


2



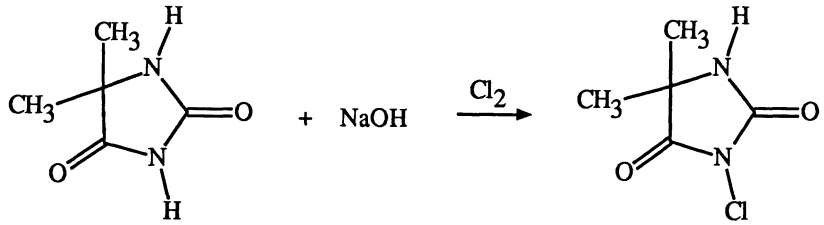
3

When compound **1** dissolves in water at pH 9, it decomposes rapidly and completely. It also reacts with 5,5-dimethylhydantion in water as follows;[2)]



4

This reaction was carried out in both water and acetonitrile. These two products were the same materials. For this compound ^{35}Cl NQR measurement was made. The frequency is shown in Table 1 and close to that of the N-Cl bond adjacent to the $C(CH_3)_2$ in compound **1**. Thus, this product can be undoubtedly regarded as being a 1-chloro derivative, **4**. The preparation of a 3-chloro derivative is reported by Ishii et al.[3)] as follows;



The reaction was carried out, but the yield was very small compared with that of the literature. IR spectrum of this compound, however, agreed with that of the 1-chloro derivative.

Table 1. ^{35}Cl NQR Frequencies

Entry	υ/MHz
1	53.639 55.960[a)]
2	54.708
3	52.244[b)]
4	53.561

a) Ref.1. υ_1=53.648, υ_2=55.962MHz. b) Y.Nagao and S.Katagiri, *Bull.Chem.Soc.Jpn.*,**61**,1393(1988).

Refarences

1) R.M.Hart and M.A.Whitehead, *Trans. Faraday Soc.*, **67**,1569(1971).

2) R.C.Petterson and U.Grzeskowiak, *J.Org.Chem.*, **24**, 1414(1959).

3) Y.Ishii, T.Ito, and S.Kato, *Kogyo Kagaku Zasshi*, **61**,1254(1958).

(Received August 12, 1991)