

<sup>35</sup>Cl NQR Study of *N,N'*-Dichloro-5,5-dimethylhydantoin and Related Compounds

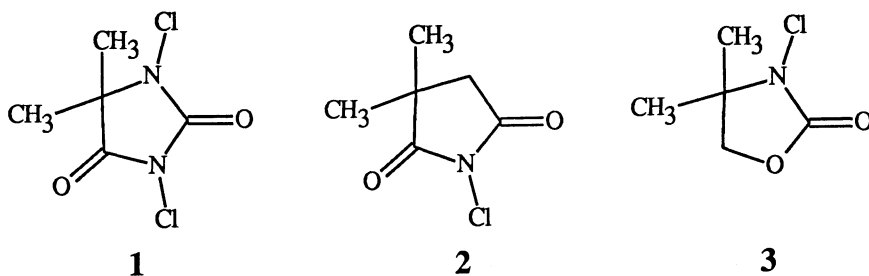
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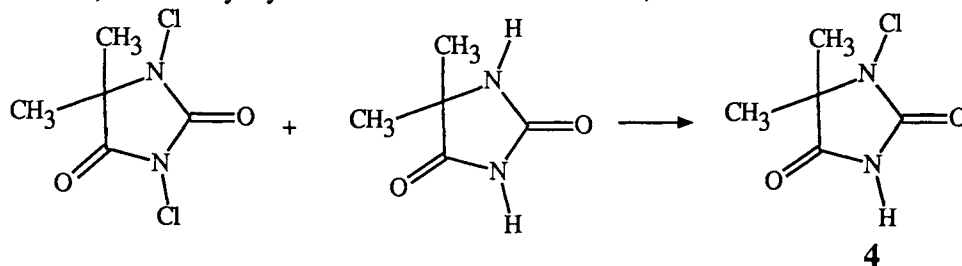
The <sup>35</sup>Cl NQR frequencies of *N,N'*-dichloro-5,5-dimethylhydantoin were assigned in comparison with those of *N*-chloro- $\alpha,\alpha$ -dimethylsuccinimide and *N*-chloro-4,4-dimethyl-2-oxazolidone. It turned out monochloro-5,5-dimethylhydantoin was a 1-chloro derivative

*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 <sup>35</sup>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.<sup>1)</sup> They assigned the lower frequency to the N-Cl bond adjacent to the C(CH<sub>3</sub>)<sub>2</sub>. In order to make sure this assignment <sup>35</sup>Cl NQR measurements were carried out for *N*-chloro- $\alpha,\alpha$ -dimethylsuccinimide (2) and *N*-chloro-4,4-dimethyl-2-oxazolidone (3) at liquid nitrogen temperature.

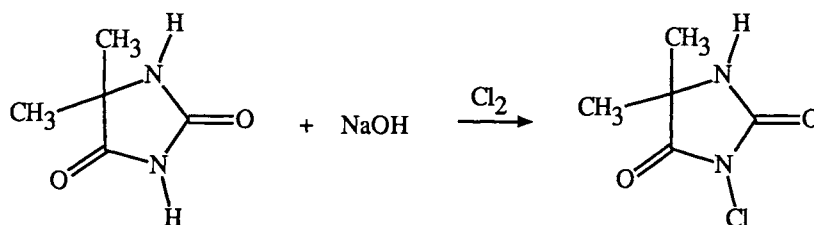
The N-Cl bond of compound 2 can be regarded as being corresponding to the N-Cl bond of compound 1 surrounded by the carbonyl groups, and that of compound 3 the N-Cl bond adjacent to the C(CH<sub>3</sub>)<sub>2</sub>. Their frequencies are shown in Table 1. The lower frequency observed in compound 1 is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



When compound **1** dissolves in water at pH 9, it decomposes rapidly and completely. It also reacts with 5,5-dimethylhydantoin in water as follows;<sup>2)</sup>



This reaction was carried out in both water and acetonitrile. These two products were the same materials. For this compound <sup>35</sup>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<sub>3</sub>)<sub>2</sub> 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.<sup>3)</sup> 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. <sup>35</sup>Cl NQR Frequencies

Entry	$\nu$ /MHz
<b>1</b>	53.639 55.960 <sup>a)</sup>
<b>2</b>	54.708
<b>3</b>	52.244 <sup>b)</sup>
<b>4</b>	53.561

a) Ref.1.  $\nu_1=53.648$ ,  $\nu_2=55.962$ MHz. b) Y.Nagao and S.Katagiri, *Bull.Chem.Soc.Jpn.*, **61**,1393(1988).

#### References

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- 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).

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