

OXIDATIVE α -ADDITION OF ISONITRILE BY USE OF MERCURIC SALTS
SYNTHESIS OF UREA AND URETHANE

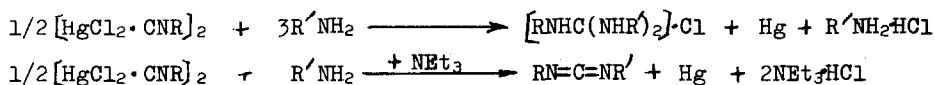
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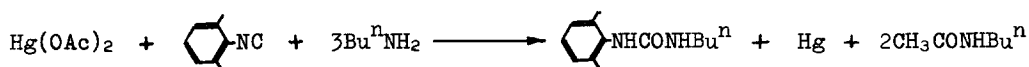
Isonitrile complexes of mercury(II) are considered to be a kind of organo-mercuric compound, and investigations of their reaction are interesting. Redox decomposition reaction of isonitrile complexes of mercuric salts was found to lead a variety of products depending on the anion, nucleophiles and the presence of tertiary amine. Previously, we reported the redox reaction of isonitrile-mercuric chloride with primary and secondary amines to give guanidine and carbodiimide as follows.⁽¹⁾



The present paper reports the redox reaction of isonitriles with mercuric salts in the presence of water, amine, ethanol and phenol to afford urea and urethane in high yields.

The reaction of isonitrile with amine by use of mercuric acetate proceeds very easily at room temperature. Thus n-butylamine was added to a stirred solution of 2,6-dimethylphenylisonitrile and mercuric acetate in dry tetrahydrofuran, and stirred at room temperature. Metal mercury precipitated in a few minutes and the reaction was complete within a half hour. The formation of N-n-butylacetamide was confirmed by glpc. Metal mercury was removed from the reaction mixture by filtration. Filtrate was evaporated to dryness, and was chromatographed on a silicagel column. Evaporation of the eluate and crystallization of the residue gave purified N-2,6-dimethylphenyl-Nⁿ-butylurea.

Data for typical conversions are summarized in Table 1.



On the contrary, in case of mercuric chloride N,N'-di-n-butyl-N''-2,6-dimethylphenylguanidine was obtained from 2,6-dimethylphenylisonitrile with n-butylamine at 66°C through redox reaction, but no redox reaction at room temperature. The reaction of 2,6-dimethylphenylisonitrile with n-butylamine by use of mercuric nitrate monohydrate gave metal mercury, corresponding urea and guanidine at room temperature. Such redox reaction did not occur even if at 66°C by using mercuric cyanide.

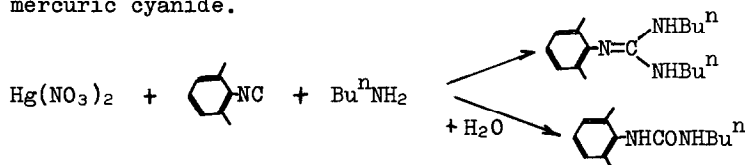


Table 1. Reaction of Isonitrile with Amine

| Isonitrile | Amine | HgX ₂ | Temp. (°C) | Time (hr) | Yield(mol% based on Hg(II)) | |
|--|---|----------------------|---------------|--------------|-----------------------------|-----------------|
| | | | | | Hg | Urea(Guanidine) |
| 2,6-Me ₂ C ₆ H ₃ NC | n-BuNH ₂ | Hg(OAc) ₂ | 25 | 0.5 | 97 | 88 |
| | | | 66 | 0.5 | 98 | 91 |
| | Hg(NO ₃) ₂ | 25 | 1 | 99 | 13 (43) | |
| | | HgCl ₂ | 25 | 1 | 0 | 0 |
| | | | 66 | 0.5 | 100 | 0 (97) |
| Hg(CN) ₂ | 25 | 1 | 0 | 0 | | |
| | 66 | 0.5 | 3 | 0 | | |
| t-BuNC | n-BuNH ₂ | Hg(OAc) ₂ | 25 | 1 | 92 | 64 |
| | C ₆ H ₅ NH ₂ | Hg(OAc) ₂ | 25 | 8 | 96 | 42 |
| 2,6-Me ₂ C ₆ H ₃ NC | Et ₂ NH ₂ | Hg(OAc) ₂ | 25 | 1 | 56 | 39 |
| | MeC ₆ H ₅ NH | Hg(OAc) ₂ | 25 | 1 | 43 | 40 |

HgX₂, 2.5mmol; RNC, 5mmol; RNH₂, 1ml.

Reaction of isonitrile with water by using mercuric salts gives symmetry urea. Water was added to a stirred solution of mercuric salt and 2,6-dimethylphenylisonitrile in tetrahydrofuran and stirred at room temperature. In case

of mercuric acetate and nitrate, 2,6-dimethylphenylurea and metal mercury were formed in high yields, but no product from mercuric cyanide. The reaction of phenylisonitrile and t-butylisonitrile with water by using mercuric chloride gave mercurous chloride and small amount of urea. The addition of triethylamine to this reaction system enhanced the redox reaction, thus metal mercury instead of mercurous chloride and corresponding urea were formed in high yields. Coordination of strong base to mercury(II) may be enhance the redox reaction. $\text{HgCl}_2(\text{CNC}_7\text{H}_7)_2$ is reported to decompose in hot ethanol solution to give di-p-tolylurea and mercurous chloride.⁽²⁾

Table 2. Reaction of Isonitrile with Water, Ethanol and Phenol

| Isonitrile | ROH | HgX_2 | Temp. (°C) | Time (hr) | Yield(mol% based on Hg(II)) | |
|--|----------------------------------|----------------------|---------------|--------------|---------------------------------------|-----------------|
| | | | | | Hg | Urea (Urethane) |
| 2,6-Me ₂ C ₆ H ₃ NC | H ₂ O | Hg(OAc)_2 | 25 | 5 | 72 | 61 |
| C ₆ H ₅ NC | H ₂ O | Hg(OAc)_2 | 25 | 5 | 98 | 95 |
| t-BuNC | H ₂ O | Hg(OAc)_2 | 25 | 1 | 92 | 51 |
| 2,6-Me ₂ C ₆ H ₃ NC | H ₂ O | $\text{Hg(NO}_3)_2$ | 25 | 1 | 92 | 47 |
| C ₆ H ₅ NC | H ₂ O | HgCl_2 | 25 | 1.5 | 0* | 35 |
| t-BuNC | H ₂ O | HgCl_2 | 25 | 1 | 0* | |
| C ₆ H ₅ NC | H ₂ O | HgCl_2^{**} | 25 | 1 | 88 | 78 |
| t-BuNC | H ₂ O | HgCl_2^{**} | 66 | 1 | 75 | 42 |
| 2,6-Me ₂ C ₆ H ₃ NC | H ₂ O | Hg(CN)_2 | 66 | 1 | 0 | 0 |
| 2,6-Me ₂ C ₆ H ₃ NC | EtOH | Hg(OAc)_2 | 66 | 2 | 61 | (49) |
| | C ₆ H ₅ OH | Hg(OAc)_2 | 66 | 1 | 66 | (59) |

* Hg_2Cl_2 was formed.

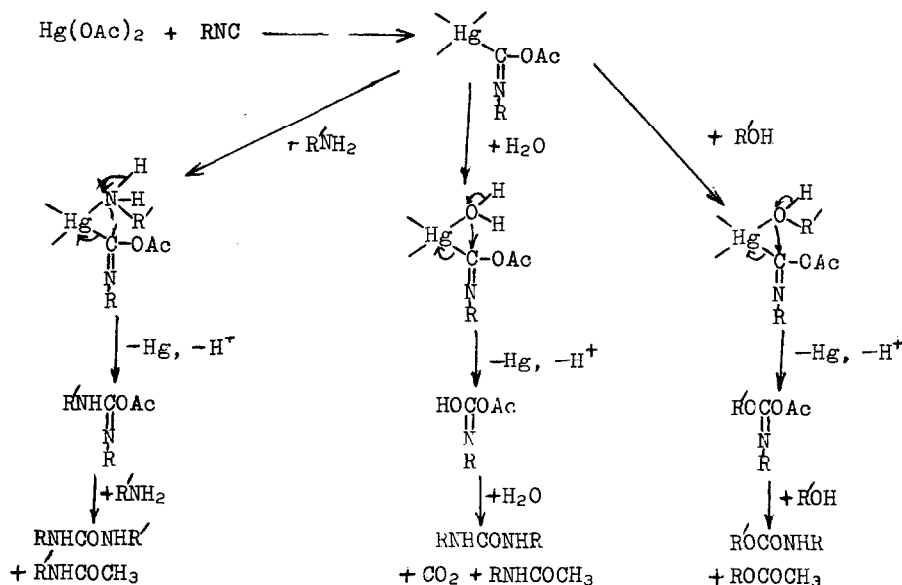
** In the presence of triethylamine.

HgX_2 , 2.5mmol; RNC, 5mmol; ROH, 1ml.

Under the similar reaction conditions, 2,6-dimethylphenylisonitrile reacts with mercuric acetate in the presence of ethanol and phenol to yield urethane and metal mercury as shown in Table 2. Recently, mercuric nitrate and thallium(III) nitrate is reported to oxidize isonitrile to urethane in the presence of methanol and isopropanol.⁽³⁾ Mercuric acetate is more effective and more versatile than mercuric nitrate and thallium(III) nitrate for synthesis of

urethane.

These urea and urethane are formed via oxymercuration of isonitrile followed by redox decomposition reaction as following scheme. Oxymercuration adduct was obtained from 2,6-dimethylphenylisonitrile with mercuric acetate in dry tetrahydrofuran.⁽⁴⁾



The reactivity of mercuric salt on these redox reaction is in the order, $\text{Hg(OAc)}_2 > \text{Hg(NO}_3)_2 > \text{HgCl}_2 \gg \text{Hg(CN)}_2$. This order is approximately accord with the redox potential and inverse accord with the covalency between mercury(II) and ligand. The reaction of 2,6-dimethylphenylisonitrile with n-butylamine by using Ag(OAc) , PdCl_2 , Tl(OAc)_3 and Pb(OAc)_4 was conducted to study the redox reaction, however no urea and nor guanidine was obtained in these cases. Mercury(II) has unique reactivity with isonitrile.

References

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