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# A SIMPLE METHOD FOR PREPARATION OF 1-CYANO-1,2-DIAMINOETHYLENE DERIVATIVES THROUGH NICKEL-ISOCYANIDE COMPLEXES

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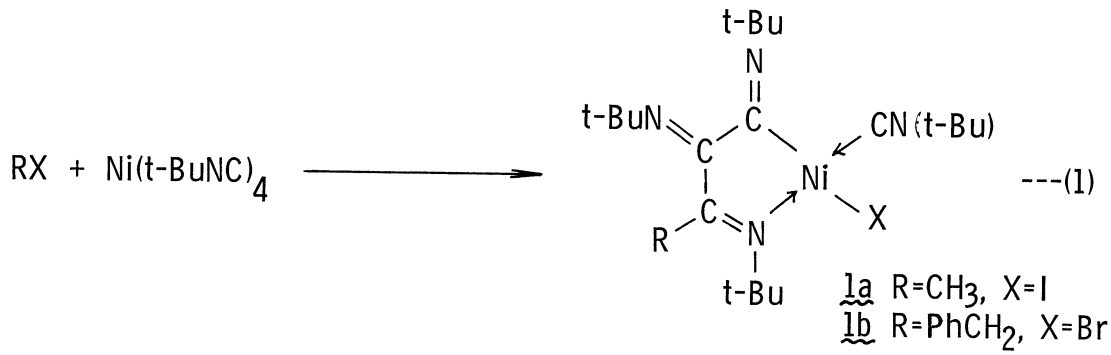
1-Cyano-1,2-diaminoethylene derivatives, R-C(NH-t-Bu)=C(NH-t-Bu)CN were found obtainable from isocyanide oligo-insertion complexes, $R[C{=}N(t\text{-}Bu)]_3NiX(t\text{-}BuNC)$, by reaction with protic reagents, e.g. dimethylglyoxime. N,N'-Di-t-butyl-C-acylglycinamide, RCO-CH(NH-t-Bu)CONH-t-Bu, was also isolated from the same reaction in wet conditions.

Catalytic carbonylations of olefins via CO insertion into a metal-carbon bond or stoichiometric reactions of metal-alkyl complexes with CO have been well-known and constitute important synthetic methods. The CO insertion appears to be limited only to mono-insertion and formation of a pyruvoyl ($CH_3$-CO-CO-) complex[2)] by di-insertion has never been realized. In contrast, isocyanides readily enter into a successive insertion into an active metal-alkyl bond[3,4)] and form an oligo-insertion product[4)] or polyisocyanide[3)] depending on the identity of metal complexes and on the reaction conditions. Recently we have reported an unique isocyanide insertion forming an interesting chelate complexes as illustrated below.[4)]

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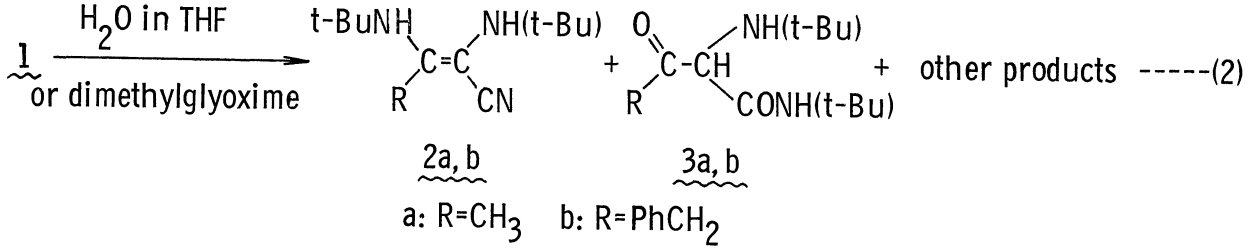
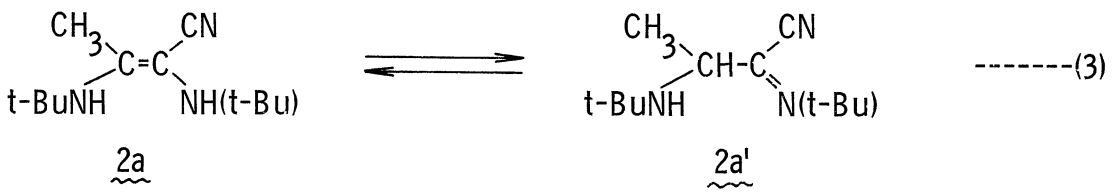
The reaction seems to be quite general as it is extendable to a variety of alkyl halides and alkyl isocyanides. Transformation of 1 into some difficultly accessible oligoimino compounds may be possible.

Here we report formation of some novel oligoamino compounds through decomposition of the oligo-insertion complex, 1. A related catalytic reaction of t-butyl isocyanide to form di-aminoethylenes is reported separately.

Thus a solution of 1a was decomposed with water in aq. THF(80%) at room temperature during 2 days giving a dark colored suspension. Chromatographic separation (silica gel) of the ether extract gave mainly two compounds. One is an unsaturated amino-nitrile, 2a, mp 63°C, bp 95°C/1 mmHg(yield 5%) and the other is an amino acid derivative 3a, bp 60°C/2 mmHg(yield 20%).[5] 2a was also obtained in an improved yield by decomposition of 1a with an equimolar amount of dry dimethylglyoxime in dry benzene or ether (20% yield). Probable structures of 2a and 3a




are deduced from their spectral data (Table I).* The $^1$H nmr spectrum of 2a which shows the presence of two non-equivalent t-butyl and NH groups together with a magnetically isolated methyl group. Consistently the infrared spectrum of 2a suggests the presence of NH, C=C, and CN groups. The mass spectral pattern is also interpretable with the structure. A cis-trans isomerism in 2a is possible but nothing is known at present. The compound 2a prepared through two steps from $Ni(t\text{-}BuNC)_4$ (cf. eq. (1) and (2)) presents a very remarkable structure of diaminoethylene group (diamino reducton)[6] which may be in equilibrium with α-amino-imine structure (2a') by prototropy (eq. 3). However, the infared spectrum shows the absence of C=N group. The observed $\nu_{C\equiv N}$ frequency is too low for the α-amino-imine structure. The nmr spectrum shows a sharp singlet for the methyl. These features exclude the α-amino-imine structure (2a') even in solution. In addi-



tion to the possible reducing ability of diamino-ethylene part, 2a has an active methyl group. These reactive groups may cause a variety of reactions and the observed low yield after purification is then attributable to this reactivity.

The second major product, 3a, has an acetyl and a carboxamide partial structures as revealed by its ir spectrum. The nmr spectrum clearly shows two non-equivalent t-butyl and NH groups together with a methyl, a feature similar to that observed for 2a. The mass spectrum clearly shows fragment peaks formed by a loss of $CH_3CO$, and two t-Bu groups. These spectral properties indicate the proposed N,N'-di-t-butyl-C-acetylglycinamide structure as the most probable one for 3a. The decomposition of 1b with dimethylglyoxime in benzene also gave the corresponding diaminoethylene 2b and glycinamide 3b in poor yields. 2b was the main isolable product when the reaction was carried out under exclusion of moisture whereas 3b was obtained in a somewhat wet reaction system. The loss of one N-t-butyl group

Table I. Spectroscopic Data of Organic Products Obtained from $CH_3[C=N(t\text{-}Bu)]_3NiI(t\text{-}BuNC)$.

| | 2a | 3a |
|---|---|---|
| Mass, $M^+$ at m/e | 209 | 228 |
| IR $\nu_{max}$ (Nujol or Liquid) in $cm^{-1}$ | 3320($\nu_{N-H}$) | 3250 broad($\nu_{N-H}$) |
| | 3330($\nu_{N-H}$) | |
| | 2175($\nu_{C\equiv N}$) | 1718($\nu_{C=O}$, acetyl) |
| | 2165($\nu_{C\equiv N}$) | 1680($\nu_{C=O}$, amide) |
| | 1605($\nu_{C=C}$) | 1515($\delta_{N-H}$, sec. amide) |
| NMR(in $CDCl_3$) $\delta$, ppm(TMS) | 1.12(s,9H,t-Bu) | 1.00(s,9H,t-Bu) |
| | 1.29(s,9H,t-Bu) | 1.30(s,9H,t-Bu) |
| | 1.60*(br,1H,NH) | 2.42(s,3H,$CH_3$) |
| | 2.18(s,3H,$CH_3$) | 3.90*(s,1H,NH) |
| | 6.15*(br,1H,NH) | 7.62*(br,2H,NH,CH) |
| UV $\lambda_{max}^{EtOH}$(in nm($\varepsilon$)) | 277(16,000) | ——— |

*) The signals indicated by an asterisk are exchangeable with deuterium upon addition of $D_2O$.

from the oligo-imino chelate ligand in the formation of 2a or 2b thus seems to be due to acidity of dimethylglyoxime in dry non-polar solvents.[7] The t-butyl group eliminated was found as isobutene in the gas phase of the reaction. On the other hand hydrolytic elimination of a molecule of $t\text{-BuNH}_2$ is responsible for the formation of 3a or 3b. It is tempting to consider a possible mechanism of formation of 2 or 3. In spite of our repeated attempts to simplify the product distibution by changing conditions, the complexity of the reaction could not be reduced. Therefore, a considerable amount of experimental work should be payed to clarify detailed mechanisms.

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3) See for example, Y. Yamamoto and N. Hagihara, Bull. Chem. Soc. Japan, 39, 1084(1966); Y. Yamamoto and H. Yamazaki, Ibid., 43, 2653(1970); Y. Yamamoto, H. Yamazaki, and N. Hagihara, J. Organometal. Chem., 18, 189(1969).

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5) Elemental analysis of these new compounds agreed well with the calculated values.

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