

## REACTION OF N-MONOCHLOROAMINES WITH NICKEL CARBONYL

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It has been well known that several organic monohalides which contain unsaturated bonds (e.g.  $>C=C<$ ,  $>C=O$ ,  $-C\equiv N$ ) at the  $\beta,\gamma$ -position to the halogenes add to metal carbonyls oxidatively to give cationic complexes,  $RM(CO)_nX$  or  $KCOM(CO)_{n-1}X$ , which decompose to give coupling products R-R and ketones RCOR (or  $\alpha$ -diketones RCOCOR) (1). On the other hand, few studies of the reaction of N-chloroamines with metal carbonyls have been reported. Only one example is the reaction of N-dichloroamines with nickel carbonyl in wet benzene giving N,N'-dialkylureas (2). So it seems to be interesting to study whether compounds with heteroatom-halide bond, haloamine ( $RR'N-X$ ) or hypohalite ( $RO-X$ ), show analogous reactivity. In a previous paper, we have reported the formation of anionic carbamoylnickel complex,  $Li[(CH_3)_2NCONi(CO)_3]$ , by the reductive addition of lithium dimethylamide to nickel carbonyl (3).

In this paper we wish to report the formation of cationic carbamoylnickel complexes as precursors to urea derivatives by the oxidative addition of N-monochloroamines to nickel carbonyl.

To 75 ml ethereal solution of N-chlorodiethylamine (73 mmol) prepared from diethylamine hydrochloride and 10% aq. sodium hypochlorite in ether (4), was added dropwise 12.4 g (73 mmol) of nickel carbonyl in 20 ml of ether at 15° with stirring under nitrogen atmosphere. In the course of the reaction, grayish white precipitate was formed along with gas evolution (CO 3000 ml, after

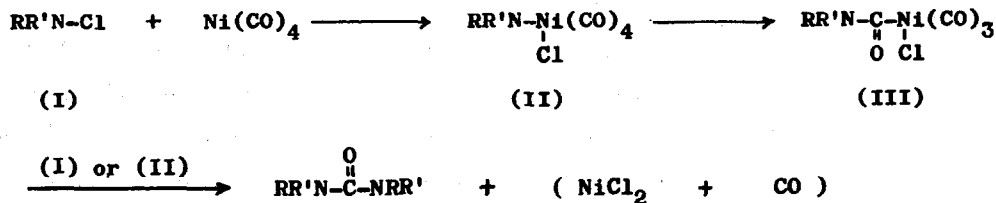
stirring for 20 hr at 15-20°). The reaction mixture was filtered. After removal of the ether the filtrate was distilled under reduced pressure to give 772 mg of oily liquid (120-135°/115 mm), which was analyzed by glpc (Polyester 2 m and PEG 20 M 2 m, 180°, He 10 ml/min) and found to contain 638 mg (10.1 %) of tetraethylurea, 192 mg (1.9 %) of diethylcarbamoyl chloride and a trace amount of ethyl diethylcarbamate. A coupling product, tetraethylhydrazine was not detected. The results are summarized in Table I.

Table I

R	R'	Solv.	°C	hr	RR'NCONRR' (%) <sup>*</sup>	Other products
CH <sub>3</sub>	CH <sub>3</sub>	Et <sub>2</sub> O	17-30	6	10.0	(CH <sub>3</sub> ) <sub>2</sub> NCOC1 (trace)
C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	"	15-20	20	10.1	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NCOC1 (1.9 %) (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NCOOC <sub>2</sub> H <sub>5</sub> (trace)
C <sub>2</sub> H <sub>5</sub>	H	"	20-30	15	17.2	
PhCH <sub>2</sub>	H	"	20-30	14	17.0	

\* Yields were calculated based on the used N-monochloroamines.

The mechanism of the formation of urea derivatives seems to be analogous to that of the reaction of organic monohalide with metal carbonyl, although the formation of the intermediates (II) and (III) have not yet been confirmed by irs studies.



The formation of dialkylcarbamoyl chloride is explained in terms of the decomposition of (III).

It has been well known that organotransition metal  $\sigma$ -complexes readily add

to unsaturated bonds (e.g.  $>C=C<$ ,  $-C\equiv C-$ ,  $>C=O$ ) (5,6,7). Anionic carbamoyl-nickel complex also adds to phenylacetylene to give succinamide derivative (3). Therefore, the intermediates, (II) and (III), were expected to cause the addition of amino or carbamoyl group to olefinic or acetylenic bond. But contrary to the expectation, the attempted reaction of N-chloroethylamine or N-chlorobenzylamine with nickel carbonyl in the presence of acrylonitrile or phenylacetylene gave urea derivative alone.

It is known that phenacyl bromide, one of  $\beta$ -haloketones, reacts with nickel carbonyl without CO insertion to give two types of dimerization products, 1,2-dibenzoylthane (in THF) and  $\Delta$ -phenacyl styrene oxide (in DMF) (8,9). But N-chlorobenzamide which is one of the nitrogen compounds corresponding to  $\beta$ -haloketone reacts with nickel carbonyl to give CO inserted product, N,N'-dibenzoylurea.

To a  $CHCl_3$  (60 ml) solution of  $PhCONHCl$  (3.9 g, 25 mmol) was added 4.2 g of nickel carbonyl (25 mmol) in 10 ml of  $CHCl_3$  at  $45^\circ$ . After stirring for 2.5 hr, yellow ochre precipitate (5.7 g) was formed and 2000 ml of CO was evolved. From  $Et_2O$  and  $CH_2Cl_2$  extracts of the precipitate, white crystals (3.91 g) were obtained after removal of  $Et_2O$  and  $CH_2Cl_2$ . The crystals gave by sublimation 1.15 g (38.0 %) of  $PhCONH_2$  (below  $80^\circ/0.2$  mm) and 1.76 g (52.5 %) of  $PhCONHCONHCOPh$  (remained at  $80^\circ/0.2$  mm). Dibenzoylurea was identified by mp ( $218^\circ$ , dec.); ir (10), mass, nmr spectra and elemental analysis.

The reaction of t-butyl hypochlorite with nickel carbonyl in n-hexane at room temp. under nitrogen atmosphere gave a trace amount of di-t-butyl carbonate and bluish purple precipitate. The precipitate seems to resemble to nickel(II) di-t-butyl alkoxide,  $Ni^X(OBu-t)_2$ , prepared from di-t-butyl peroxide and bis(cycloocta-1,5-diene)nickel by Schott and Wilke (11). Our studies of this complex are continuing and a more detailed discussion will be given in a forthcoming paper.

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