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THE REACTIONS OF N,N-DICHLOROAMINE AND -AMIDES WITH IRON CARBONYL COMPLEXES. METAL-ASSISTED NITRENE GENERATION

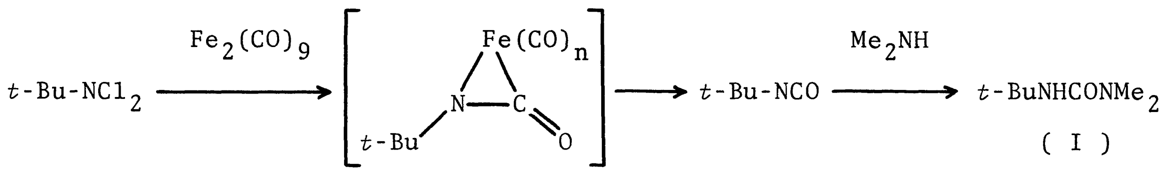
Hiroharu SUZUKI, Kenji ITOH, Isamu MATSUDA, and Yoshio ISHII
Department of Synthetic Chemistry, Faculty of Engineering,
Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464

Reactions of N,N-dichloroamine or -amides with diiron enneacarbonyl yield isocyanates *via* carbonylation of iron nitrenoid. N,N-Dichloro-*p*-chlorobenzamide gives complex whose composition is $(p\text{-Cl-C}_6H_4\text{-CO-N})_2\text{-Fe(CO)}_2\text{(maleic anhydride)Cl}_2$ in the reaction with maleic anhydride iron tetracarbonyl in an excellent yield.

The chemistry of nitrenes is a fascinating and active area for both experimental and theoretical chemists. In this letter, we report on metal-assisted nitrene generation from the reactions of N,N-dichloroamine or -amides with iron carbonyl complexes. N,N-Dichloroamine and -amide are expected to generate nitrenes in the reactions with iron carbonyl complexes in a similar manner to *gem*-dihaloalkanes for which some studies were achieved.1,2)

Reactions of N,N-Dichloroamine or -amides with Diiron Enneacarbonyl.

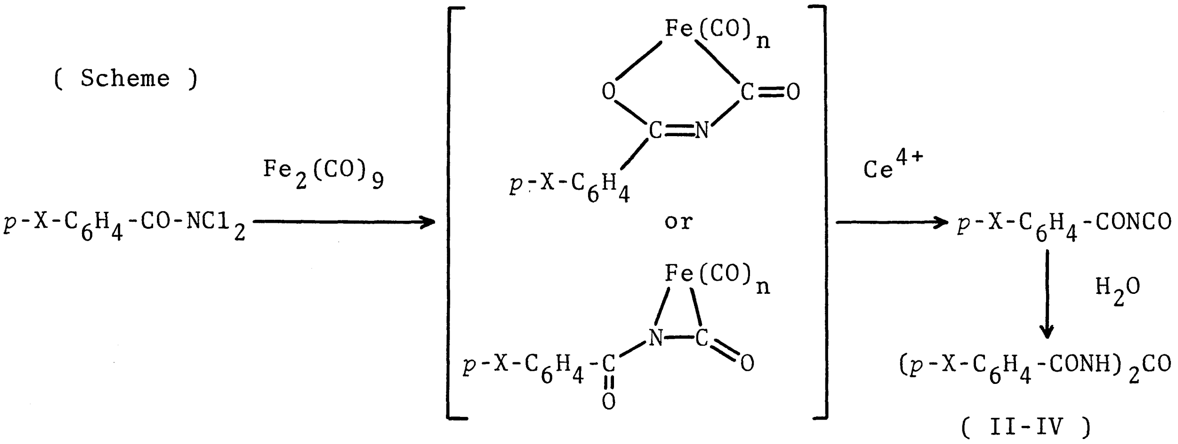
In the presence of equimolar amounts of olefinic or acetylenic acceptors (cyclohexene, norbornadiene, benzene, dimethyl maleate, dimethyl acetylenedicarboxylate, diphenylacetylene, etc.) a dilute solution of N,N-dichloro-*t*-butylamine (0.170g, 1.20 mmol, in 2 ml of benzene) was added to the diiron enneacarbonyl (0.408g, 1.12 mmol, suspended in 8 ml of benzene) at 0 °C under an atmosphere of argon. Analysis of reaction mixture indicates no sign of nitrene adduct formation with the above-mentioned acceptors at all. Infrarad spectrum of the reaction mixture showed a sharp and strong absorption band due to isocyanate skeleton at 2240 cm^{-1}. Addition of dimethylamine to this mixture gave N,N-dimethyl-N'-*t*-butylurea (I) in a 31% yield. This information suggests that the product is *t*-butyl isocyanate, which is yielded by carbonylation of first generated nitrene or nitrenoid as shown in eq. 1.



(eq. 1)

In spite of the presence of acceptor molecule, no nitrene adduct was obtained by the reaction of diiron enneacarbonyl with N,N-dichloro-*p*-toluamide, N,N-dichloro-*p*-chlorobenzamide, or N,N-dichloro-*p*-nitrobenzamide under similar conditions, too. However, diaroylureas (II-IV) were obtained in good yields as sole isolated products, when the reactions of diiron enneacarbonyl with those dichloroamides in benzene were carried out at room temperature and then followed by the treatment with ceric ammonium nitrate in 10% aqueous methanol solution. Mps and spectroscopic data of the ureas (II-IV) fitted in those of authentic samples derived from hydrolyses of corresponding isocyanates. Similar to the former case, these urea-formation are explained by the intermediacy of nitrenes or nitrenoids followed by carbonylation as shown in Scheme.

(Scheme)



(V)

At first step, nitrene or nitrenoid is formed by metal-assisted dehalogenation of N,N-dichloroamide followed by complexation with iron to give (V). Aroyl isocyanates liberate by oxidative demetallation with Ce^{4+}, and rapidly react with water to yield diaroylureas. Whole results on the reaction of N,N-dichloroamine or -amides with diiron enneacarbonyl are summarized in Table.

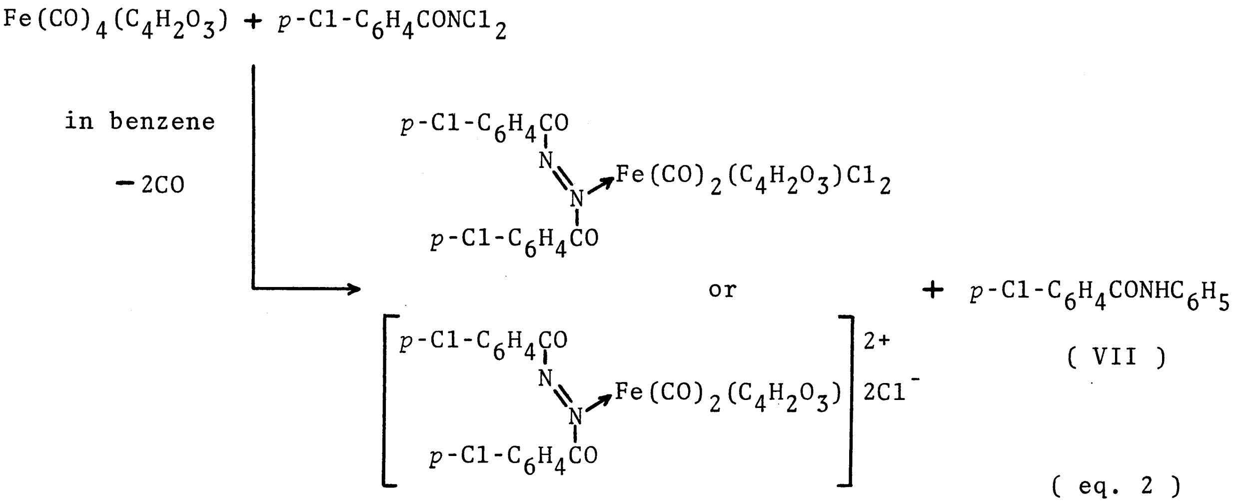
Table. Reaction of N,N-Dichloroamine and -amide with Diiron Enneacarbonyl in Benzene

Reactant	Product	Yield (isolated) (%)
t-Bu-NCl_2	*t*-BuNHCONMe_2 (I)	31
p-CH_3-C_6H_4-CO-NCl_2	(*p*-CH_3-C_6H_4-CO-NH)$_2$CO (II)	94
p-Cl-C_6H_4-CO-NCl_2	(*p*-Cl-C_6H_4-CO-NH)$_2$CO (III)	100
p-NO_2-C_6H_4-CO-NCl_2	(*p*-NO_2-C_6H_4-CO-NH)$_2$CO (IV)	50

Reaction of N,N-Dichloro-p-chlorobenzamide with Maleic Anhydride Iron Tetracarbonyl.

The reaction of N,N-dichloro-*p*-chlorobenzamide (0.137g, 0.612 mmol) with maleic anhydride iron tetracarbonyl (0.159g, 0.598 mmol) proceeded in benzene (20 ml) at room temperature with the evolution of about 2 moles of carbon monoxide. By column chromatographic separation on silica gel with acetone as solvent, white powder of diamagnetic complex (VI) (decomp. 124.0-126.0 °C, 80% yield) and N-phenyl-*p*-chlorobenzamide (VII) (mp. 197.0-198.0 °C, 14% yield) were obtained. The latter compound indicates the nitrene generation, because its formation is explained in terms of the insertion of an intermediate *p*-chlorobenzoylnitrene into C-H bond of solvent benzene. The yield of (VI) increased to 95% when *n*-hexane was used as the reaction solvent. The elevation of the yield of (VI) suggests that the amide formation and the complexation are competitive processes *via* common reaction intermediate, *i. e.* nitrene intermediates. Elemental analysis of complex (VI) indicated the composition $C_{20}H_{10}N_2O_7Cl_4Fe$, which was consistent with the formula of (*p*-Cl-C_6H_4-CO-N)$_2$Fe(CO)$_2$(maleic anhydride)Cl_2. In solid state infrared spectrum, (VI) showed five characteristic absorption band at 2050, 2020, 1820, 1746, and 1655 cm^{-1}. First two bands are attributed to the terminal $\nu_{C=O}$ bonding to iron, and carbonyl stretching vibrations of coordinating maleic anhydride appear at 1820 and 1746 cm^{-1}. The last one (1655 cm^{-1}) is reasonably assigned to amide carbonyl. The pmr spectrum of (VI) in $CDCl_3$ showed sharp singlet of olefinic protons (2H) of maleic anhydride at τ6.07 and the phenyl ring protons (8H) with AA'BB' coupling pattern centered at τ2.50. Surprisingly, complex (VI) was quite stable toward boiling methanol and oxidation with ceric ammonium nitrate. This indicates that (VI) is in a higher oxidation state.

As shown in eq. 2, two probable structures of (VI) might be formulated, and further structural elucidation is now in progress.



(VII)

(eq. 2)

(VI)

References

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