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A NOVEL REACTION OF ISOCYANATES WITH TRANSITION METAL ETHYNYL COMPLEXES

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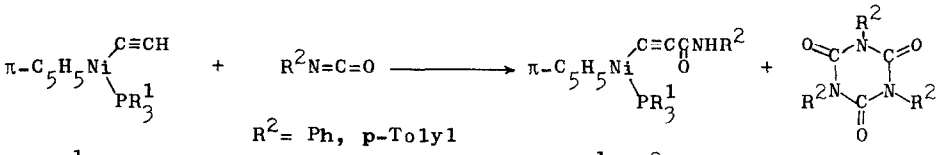
Reactions of nucleophilic olefins, such as enamines, ketenacetals, ketenaminals, etc., with isocyanates have received considerable attention recently(1). The olefins containing a β-hydrogen add to isocyanates to form unsaturated amides as linear adducts. Without the β-hydrogen in the olefins, 1,2-cycloaddition occurs to afford β-lactams.

However, a similar reaction of isocyanates with acetylenic compounds is not known. For example, the reaction of phenyl isocyanate with ethoxyacetylene gives 4-ethoxy-2-quinolone by 1,4-addition (2). On the other hand, it has been reported that the isocyanate reacts with alkynylmagnesium bromide or alkynyllead to form phenylpropiolic anilide (3) and 1,3,6-triphenyl uracil (4), respectively, by insertion into the metal-carbon bond. In this paper, we wish to report that aryl isocyanates reacted with some transition metal ethynyl complexes to give linear adducts by insertion into the ≡C-H bond.

A solution of phenyl isocyanate (0.33 g, 3 mmol) and triphenylphosphine-π-cyclopentadienyl-σ-ethynylnickel (5), Ia, (0.3 g, 0.73 mmol) in 10 ml of tetrahydrofuran was kept at room temperature under nitrogen for two days. Gradually the solution changed from dark green to brownish green. After removal of the solvent, the residue was chromatographed on almina. Elution with benzene-ethyl acetate (10:1) gave a mixture of the starting material, Ia, (20 mg) and triphenyl isocyanurate (130 mg). Elution with benzene-ethyl acetate (1:1) gave dark green crystals, IIa, (145 mg), which were recrystallized from n-hexane-benzene. IIa was found to be $C_{38}H_{32}NOPNi$, suggesting the structure of 1:1

adduct containing one molecule of benzene of crystallization, based on its elementary analysis. The infrared spectrum showed the presence of a triple bond and an amido group. The n.m.r. spectrum indicated a broad and a sharp singlet peaks at 4.06 and 4.75 τ in relative intensity 1;5, assigned to NH and cyclopentadienyl group, respectively. The assignment of the former was supported by the fact that the signal disappeared when the $CDCl_3$ solution was shaken with a few drops of D_2O. IIa could be prepared by the intermolecular dehydrohalogenation (6) of triphenylphosphine-π-cyclopentadienylnickel chloride (2.5 g, 5.93 mmol) and propiolic anilide (7) with diethylamine (2 ml) in a 57 % yield. These evidences indicated that the product IIa was triphenylphosphine-π-cyclopentadienyl-2-(phenylcarbamoyl)ethynylnickel.

Similar reactions occured when p-tolyl isocyanate was treated with Ia, and phenyl and p-tolyl isocyanates with Ib (8), respectively.



R^2= Ph, p-Tolyl

Ia, R^1= Ph

Ib, R^1= n-Bu

IIa, R^1= R^2= Ph

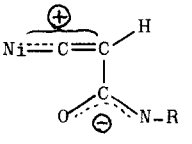
IIb, R^1= Ph; R^2= p-Tolyl

IIc, R^1= n-Bu; R^2= Ph

IId, R^1= n-Bu; R^2= p-Tolyl

On the other hand, substituted alkynylnickel complexes, π-$C_5H_5Ni(PPh_3)$-C≡CR (R= Ph, -C≡CH), were unreactive toward the isocyanates under the similar condition.

It might be thought that the reaction proceeds via a zwitterionic intermediate (III). Thus, a dπ-pπ multiple bonding (9) in the metal-carbon bond of the ethynyl complex may increase nucleophilicity on the β-carbon atom of the ethynyl group. Therefore, the electrophilic carbon atom of the isocyanate adds to the β-carbon atom to form the intermediate (III).



III

Then the migration of the hydrogen atom gives II.

Table 1. π-$C_5H_5Ni(PR^1_3)$-C≡CCONHR^2(S*)

	R^1	R^2	S*	color	Mp.	yield	Found (Calcd) % C	H	N	P
IIa	C_6H_5	C_6H_5	benzene	dark green	109°	35%	74.50 (75.02	5.22 5.30	2.39 2.30	5.16 5.09)
IIa	C_6H_5	C_6H_5	toluene	dark green	102-104°		75.15 (75.26	5.42 5.51	2.45 2.25	5.22 4.98)
IIb	C_6H_5	p-Tolyl	benzene	dark green	113-115°	24%	75.28 (75.26	5.42 5.51	2.37 2.25	5.24 4.98)
IIc	n-C_4H_9	C_6H_5	—	pale green	142-144°	27%	66.56 (66.41	8.57 8.14	3.04 2.98	6.71 6.59)
IId	n-C_4H_9	p-Tolyl	—	pale green	133-135°	64%	66.93 (66.96	8.53 8.23	3.01 2.89	6.46 6.39)

S* Solvent of crystallization

Table 2. Infrared and n.m.r. spectra of π-$C_5H_5Ni(PR_3)$-C≡CCONHR

	I R (cm^{-1})*1			N M R (τ)*2				
	ν NH	ν C≡C	ν C=O	aromatic H	NH*3	C_5H_5	n-C_4H_9	CH_3
IIa	3395	2080	1655,1640	2.1-3.2(m)	4.06	4.75(s)		
IIb	3400	2080	1645	2.1-3.2(m)	4.10	4.78(s)		7.80(s)
IIc	3265,3215	2090	1619	2.4-3.05(m)		4.70(s)	8.0-9.3(m)	
IId	3255,3200	2080	1629,1618	2.72(d),2.90(d)	2.80	4.71(s)	8.0-9.3(m)	7.81(s)

*1 Nujol mull *2 60 Mc. in $CDCl_3$ *3 Broad singlet

Reference

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