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THE THERMOLYSIS OF ORGANIC AND ORGANOMETALLIC ISOCYANATES. EVIDENCE FOR METAL-NITRENE COMPLEXES AND FOR NITRENOID DECOMPOSITION IN DIMETHYLSULPHOXIDE

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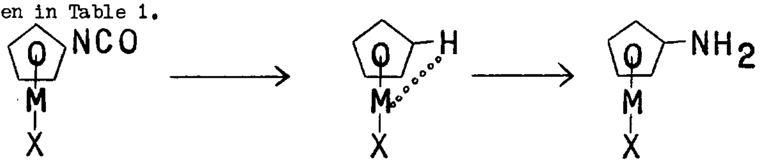
Only a few examples of the photochemical generation of nitrenes from isocyanates are known (1) and it is reported that phenyl isocyanate is thermally stable even at 700° (2). In contrast to the above we report that both ferrocenyl and cymantrenyl isocyanates (1 a and b) decompose smoothly in refluxing hydrocarbon solvents to give the corresponding amine and symmetrical urea in high yield. These results suggest that metal participation is involved in these reactions to give metal-nitrene complexes (2) which then abstracts hydrogen to give the amine (3) (Scheme 1). Subsequent reaction of (3) with its precursor leads to the formation of the symmetrical urea. Other experiments showed that organic isocyanates were stable under the reaction conditions used except in the case of p-nitrophenyl isocyanate which gave the symmetrical urea. The results are given in Table 1.



1. a. M=Fe, X=Cp 2. 3.

b. M=Mn, X=3CO

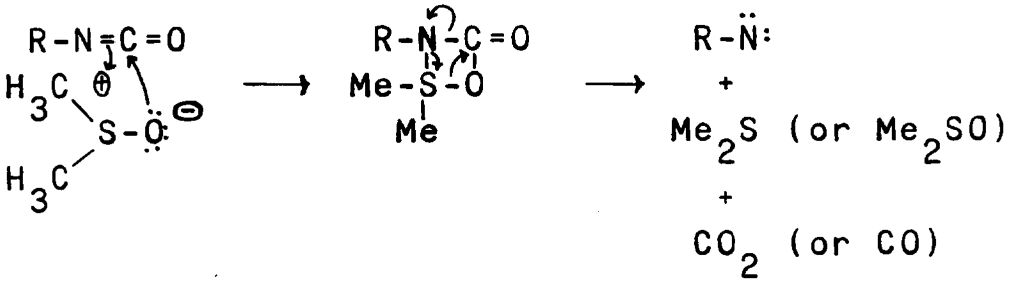
Scheme 1.

Table 1

Thermolysis of Isocyanates in Hydrocarbon Solvents

Isocyanate	Solvent	Reaction Conditions	Products	
			Amine(%)	Sym. Urea(%)
Ferrocenyl	C_6H_{12}	Reflux/3hrs/N_2		47.7
	C_6H_{10}	Reflux/3hrs/N_2		50
	C_6H_6	Reflux/3hrs/N_2		48.5
Cymantrenyl	C_6H_{12}	Reflux/4hrs/N_2	42.4	19.7
	C_6H_{10}	Reflux/4hrs/N_2	37.1	23
	C_6H_6	Reflux/4hrs/N_2	21.8	34.8
p-nitrophenyl	C_6H_{12}	Reflux/5hrs/N_2	-	20
	C_6H_{10}	Reflux/5hrs/N_2	-	12.5
	C_6H_6	Reflux/5hrs/N_2	-	20
Phenyl	C_6H_{12}	Reflux/5hrs/N_2	No Reaction	
	C_6H_{10}	Reflux/5hrs/N_2	No Reaction	
	C_6H_6	Reflux/5hrs/N_2	No Reaction	
α-Naphthyl	C_6H_{12}	Reflux/5hrs/N_2	No Reaction	
	C_6H_{10}	Reflux/5hrs/N_2	No Reaction	
	C_6H_6	Reflux/5hrs/N_2	No Reaction	
β-Naphthyl	C_6H_{12}	Reflux/5hrs/N_2	No Reaction	
	C_6H_{10}	Reflux/5hrs/N_2	No Reaction	
	C_6H_6	Reflux/5hrs/N_2	No Reaction	

Since dimethylsulphoxide (DMSO) is a well known nitrene trap the isocyanates were thermolysed in this solvent. Surprisingly, all of the isocyanates examined decomposed in this solvent at 80° to give a mixture of amine and symmetrical urea. The results are tabulated in Table 2. Since all the isocyanates decomposed, a different mechanism must be operative and it is likely that a nitrenoid intermediate is involved similar to that shown. (Scheme 2)



Scheme 2.

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Table 2

Thermolysis of Isocyanates in DMSO

Isocyanate	Reaction Conditions	Product	
		Amine(%)	Sym. Urea(%)
Phenyl	80°/3hrs/N_2	15.2	71.4
α-Naphthyl	80°/2hrs/N_2	15.8	82.6
β-naphthyl	80°/3hrs/N_2	11.8	82
p-nitrophenyl	80°/3hrs/N_2	26.6	66.3
Cymantrenyl	80°/4hrs/N_2	37.2	18.8
Ferrocenyl	80°/2hrs/N_2	11.8	41.4

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All new compounds have been fully characterised.

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