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Insertion across Chromium–Oxygen Bond

K. N. MAHENDRA, P. C. BHARARA and R. C. MEHROTRA

Chemical Laboratories, University of Delhi, Delhi, 110007, India

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A detailed survey of the literature reveals that the insertion of a number of ligands like isocyanates, isothiocyanates, carbodiimides, ketenes, sulphur dioxide, carbon disulphide *etc.* into M–O bond in the alkoxides of the non-transition elements have already been reported [1]. Such reactions are rarely known except those of titanium [2], zirconium [3] and niobium [4] alkoxides in the case of transition elements. In view of the above, it is considered worthwhile to study the reactions of chromium alkoxides with isocyanates.

Results and Discussion

Chromium alkoxides, $Cr(OR)_3$ (R = Me and Et) react exothermally with isocyanates, R'NCO (R' = Ph and α-naph) in stoichiometric ratios in benzene giving the insertion products as shown in Eq. 1

$$Cr(OR)_3 + nR'NCO \longrightarrow (OR)_{3-n}Cr[N(R')COOR]_n \quad (1)$$

[R = Me and Et; R' = Ph and α-Naph and n = 1–3]

All these reactions are completed only after refluxing the contents for about 3 to 5 hr due to the insolubility of the alkoxides in common organic solvents. The completion of the reaction is clearly

TABLE I. Insertion Products of Chromium Alkoxides with Phenyl and Naphthyl Isocyanates.

	Reactants (g)		Molar Ratio	Nature of Product	Analyses Found (Calc)	
	A	B			Cr%	N%
1.	0.46 A = $Cr(OEt)_3$	0.29	1:1	$(OEt)_2Cr[N(Ph)COOEt]$ greenish blue	16.89 (16.97)	4.30 (4.57)
2.	0.36	0.46	1:2	$(OEt)Cr[N(Ph)COOEt]_2$ greenish blue	12.46 (12.22)	5.93 (6.42)
3.	0.59	1.14	1:3	$Cr[N(Ph)COOEt]_3$ greenish blue	9.81 (9.54)	7.34 (7.71)
4.	0.86	0.78	1:1	$(OEt)_2Cr[N(Naph)COOEt]$ greyish green	14.23 (14.58)	3.86 (3.95)
5.	0.87	1.58	1:2	$(OEt)Cr[N(Naph)COOEt]_2$ greyish green	9.58 (9.89)	5.60 (5.32)
6.	0.61	1.67	1:3	$Cr[N(Naph)COOEt]_3$ greyish green	7.36 (7.48)	6.05 (6.04)
7.	0.58 A = $Cr(OMe)_3$	0.47	1:1	$(OMe)_2Cr[N(Ph)COOMe]$ greyish green	20.01 (19.68)	5.09 (5.22)
8.	0.56	0.91	1:2	$(OMe)Cr[N(Ph)COOMe]_2$ grey	13.30 (13.54)	7.20 (7.31)
9.	0.50	1.24	1:3	$Cr[N(Ph)COOMe]_3$ grey	10.25 (10.35)	8.10 (8.36)
10.	0.61	0.71	1:1	$(OMe)_2Cr[N(Naph)COOMe]$ greyish green	16.48 (16.54)	4.32 (4.45)
11.	0.48	1.12	1:2	$(OMe)Cr[N(Naph)COOMe]_2$ greyish green	10.67 (10.75)	5.56 (5.79)
12.	0.61	2.13	1:3	$Cr[N(Naph)COOMe]_3$ greyish green	7.80 (7.96)	6.20 (6.43)

TABLE II. Hydrolysis of $Cr[N(R')COOR]_3$.

Reactants	Nature of the Product	M.Pt.	N%	
			Found	Calc.
1. $Cr[N(Ph)COOEt]_3$ and H_2O	HN(Ph)COOEt white crystalline solid	52 °C	8.13	8.48
2. $Cr[N(Naph)COOEt]_3$ and H_2O	HN(Naph)COOEt white crystalline solid	79 °C	6.35	6.51
3. $Cr[N(Ph)COOMe]_3$ and H_2O	HN(Ph) COOMe white crystalline solid	–	10.05	9.26
4. $Cr[N(Naph)COOMe]_3$ and H_2O	HN(Naph)COOMe white crystalline solid	122 °C	6.70	6.96

indicated by the absence of the band at 2250 cm^{-1} (due to N=C=O) and the appearance of an intense band at 1700 cm^{-1} (due to ν C=O) in the final products.

All these products are colored solids, sparingly soluble in common organic solvents and highly sensitive to moisture. These insertion products on treatment with water in dioxane give urethanes of the general formula HN(R')COOR (R = Me and Et R' = Ph and α-naph) which are purified by crystallisation from benzene and identified by m.p. and elemental analysis. The hydrolysis reaction can be represented as follows.

$$Cr[N(R')COOR]_3 + 3H_2O \longrightarrow Cr(OH)_3 + 3NH(R')COOR \quad (2)$$

[R = Me and Et; R' = Ph and α-Naph]

Experimental

Stringent precautions were taken to exclude moisture in all the experiments. Phenyl isocyanate (b.pt. 164 °C) and naphthyl isocyanate (b.pt. 269 °C) were distilled twice before use. Chromium methoxide and ethoxide were synthesised by treating the corresponding lithium alkoxide with $CrCl_3 \cdot 3THF$ adduct [5].

Chromium was estimated as its oxide and nitrogen by the Kjeldhal method.

Reaction of Chromium Alkoxides with Isocyanates

To weighed amounts of chromium alkoxides in ~10 ml benzene was added the calculated amount of isocyanates in different molar ratios. These reactions are exothermic. The reaction mixture was then refluxed for about 3 hr in the case of ethoxides and for about 5 hr in the case of methoxides. The whole mass was then dried under reduced pressure for about 2 hr. Results are summarised in Table (I).

Hydrolysis of $Cr[N(R')COOR]_3$

To weighed amounts of $Cr\ N(R')COOR_3$ (R = Me and Et; R' = Ph and α-naph) in dioxane (40 ml) was added water (1 g). Chromium hydroxide was filtered out. The filtrate was concentrated and adding excess of water yielded a white solid which was crystallised from benzene. Results are tabulated in Table II.

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