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NOTES

Insertion reactions of niobium alkoxides with phenylisocyanate

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INSERTION reactions of alkoxides of a few metals and metalloids with isocyanates, isothiocyanates, ' carbodiimides, ketens, sulphur dioxide and carbon disulphide have been investigated during the last decade [1–6]. We report the reaction of niobium alkoxides with phenylisocyanate and isothiocyanate. These have been carried out under strictly anhydrous conditions and the products obtained have been characterized by elemental and i.r. analyses.

EXPERIMENTAL

Niobium alkoxides (methoxide[7], isopropoxides[7] and tert.-butoxide[8]), phenylisocyanate and isothiocyanate were distilled before use. Anhydrous benzene was used as a solvent. Niobium was estimated as niobium pentaoxide by direct ignition of the compound after digestion with ammonia and nitric acid. Nitrogen was estimated by Kjeldahl procedure.

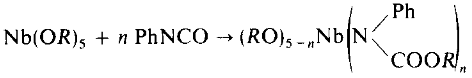
Calculated quantities of alkoxide in benzene solution were treated with phenylisocyanate and the progress of the reaction was followed by the disappearance of the N=C=O band (2275–2250 cm^{-1}) and the appearance of a new strong absorption band (1710 ± 20 cm^{-1}) due to the group (O=C) in the i.r. spectrum.

The results of these reactions are summarized in Table 1.

RESULTS

Phenylisocyanate reacts with niobium methoxide, ethoxide and *iso* propoxide to give mono-, di-, tri-, tetra- or penta-products according to the general equation:

Table 1. Insertion products of phenylisocyanate and niobium alkoxides with their i.r. spectra



$$\mathrm{Nb}(\mathrm{O}R)_5 + n\,\mathrm{PhNCO} \rightarrow (R\mathrm{O})_{5-n}\mathrm{Nb}\left(\mathrm{N}\begin{matrix}\diagup \mathrm{Ph} \\ \diagdown \mathrm{COO}R\end{matrix}\right)_n$$

R	*n*	Solvent	Method*	B.P.°C/mm (% yield)	% Nb Found	% Nb Required	% N Found	% N Required	Remarks	I.R.CO abs. (cm^{-1})
Me	1	Benzene	A	130/0·1 (60)	25·5	25·3	3·6	3·8	Yellow liquid	1710 s
Me	2	Benzene	A	Disprop.	19·4	19·1	5·4	5·7	Yellow liquid	1725 s
Me	3	Benzene	A	Disprop	15·6	15·3	6·8	6·9	Black sticky solid	1725 vs
Me	4	Benzene	B	Disprop	13·3	12·8	7·5	7·7	Orange red viscous solid	1730 s†
Me	5	Benzene	B	Disprop	11·1	11·0	7·9	8·3	Brown solid	1705 vs†
Et	1	Benzene	A	145/0·3 (75)	21·7	21·2	3·1	3·2	Yellow liquid	1720 s
Et	2	Benzene	A	Disprop	17·0	16·6	5·2	5·0	Yellow liquid	1725 s
Et	3	Benzene	A	Disprop	13·8	13·7	6·2	6·2	Yellow liquid	1710 s
Et	4	Benzene	B	Disprop	12·1	11·7	6·6	7·0	Yellow liquid	1725 vs
Et	5	Benzene	B	Disprop	10·9	10·2	7·2	7·7	Brown sticky solid	1700 vs
Pr^i	1	Benzene	A	100/0·2 (80)	18·9	18·3	2·3	2·8	Colourless liquid	1710 s
Pr^i	2	Benzene	A	Disprop	15·3	14·8	4·1	4·5	Yellowish solid	1690 s†
Pr^i	3	Benzene	A	Disprop	13·3	12·5	5·8	5·6	Black visual solid	1695 vs†
Pr^i	4	Benzene	B	Disprop	10·9	10·7	6·3	6·6	Brown visual solid	1710 vs†
Pr^i	5	Benzene	B	Disprop	10·1	9·5	6·9	7·1	Brown visual solid	1705 s
Bu^t	1	Benzene	A	Sublimes at 130–140/0·1 (50)	16·4	16·1	2·4	2·4	White solid	1690 vs*

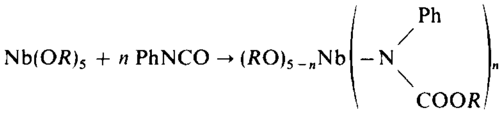
s = strong; vs = very strong

*See Experimental Section.

†In nujol—otherwise neat.

(A) Evaporation of the solvent;

(B) Evaporation of the solvent after refluxing in anhydrous condition for about 5–6 hr at (90–100°C).



$$\mathrm{Nb(OR)_5 + n\,PhNCO \rightarrow (RO)_{5-n}Nb\left(-N\begin{matrix}\diagup Ph\\ \diagdown COOR\end{matrix}\right)_n}$$

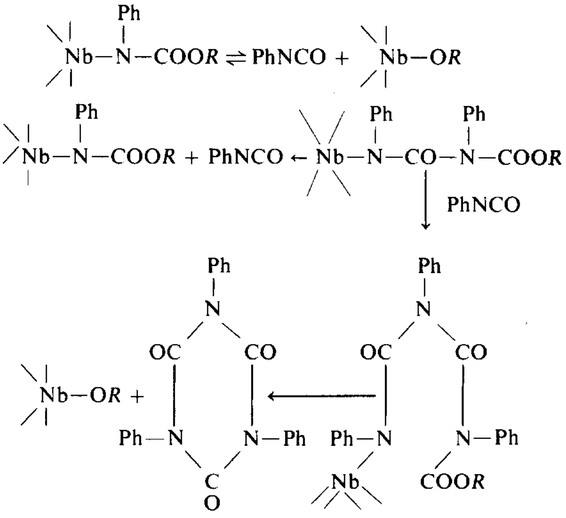
(R = Me, Et or Pr^i; n = 1–5).

Insertion of up to 3 mole of *iso*cyanate occurs readily at room temperature, but the reaction went further under refluxing conditions. With niobium tert.-butoxide, however, the reaction is slow and the second stage of the reaction does not appear to be completed even under refluxing conditions.

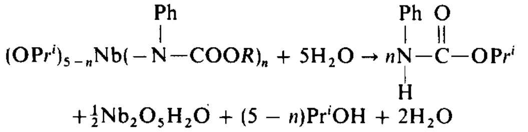
The mono-insertion products of phenylisocyanate are thermally stable and can be distilled under reduced pressure but the di- and higher insertion products tended to disproportionate under similar conditions.

Multiple insertion (similar to that reported by Meth-Cohn[9] for titanium alkoxides) was also observed when niobium *iso*propoxide was added to a large excess of phenylisocyanate. The trimerization of phenylisocyanate took place in about two weeks. The i.r. spectrum of the trimer (m.p. 294°C; yield 90 per cent) did not show any N–H band, but displayed a strong amide carbonyl absorption around 1690 $\mathrm{cm^{-1}}$.

Crystals of triphenyl *iso*cyanurate were also formed when the liquid insertion products were stored for a few weeks. This behaviour resembles that of the corresponding titanium compounds and tributyl tin methoxide[10] and can be explained on similar lines:

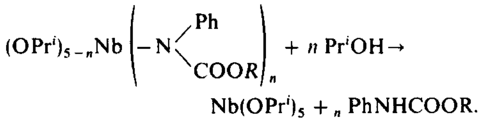


Freshly prepared insertion compounds with niobium *iso*propoxide when subjected to hydrolysis gave *iso*propyl N-phenyl-carbamate (a urethane) according to the general equation:



$$\mathrm{(OPr^i)_{5-n}Nb(-\underset{}{\overset{Ph}{N}}-COOR)_n + 5H_2O \rightarrow n\underset{H}{\overset{Ph}{N}}-\overset{O}{\overset{\|}{C}}-OPr^i + \tfrac{1}{2}Nb_2O_5H_2O + (5-n)Pr^iOH + 2H_2O}$$

The product $\mathrm{\underset{H}{\overset{Ph}{N}} - \overset{OPr^i}{C} = 0}$ (m.p. 88°C; Found: N, 7·7 per cent; calcd for $\mathrm{NHPhCOOPr^i}$: N, 7·8 per cent) can be recrystallized unchanged from a mixture of petroleum ether and benzene. In the i.r. spectrum of the urethane, the absorption peaks due to (N–H) and (C═O) stretch appeared at (3300 $\mathrm{cm^{-1}}$) and (1690 $\mathrm{cm^{-1}}$) respectively. Similarly alcholysis of insertion products gave the urethane and the corresponding niobium alkoxide:



$$\mathrm{(OPr^i)_{5-n}Nb\left(-N\begin{matrix}\diagup Ph\\ \diagdown COOR\end{matrix}\right)_n + n\,Pr^iOH \rightarrow Nb(OPr^i)_5 + {}_n\,PhNHCOOR.}$$

With phenylisothiocyanate, no insertion into Nb–O bond of niobium alkoxides was observed even after considerable ageing and refluxing in benzene.

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