Aromatizing Oligomerization of 1,2-Di-isocyanoarene to Quinoxaline Oligomers

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The reaction of Grignard reagents with 1,2-di-isocyanoarene results in the formation of quinoxaline oligomers up to a hexa-oligomer, which may be derived from successive insertion of the two *ortho* isocyano groups of 1,2-di-isocyanoarene into the carbon–magnesium bond.

Isocyanides are known to be polymerzied by transition metal catalysts, especially by nickel(II) salts, to afford poly(*N*-substituted iminomethylenes).[1] The polymerization reaction proceeds *via* consecutive insertion reactions of co-ordinated isocyanides to a propagating species on the transition metal co-ordination sphere. On the other hand, various organometallic compounds of typical metals undergo an insertion reaction with isocyanide. As reported by Ugi[2] and Walborsky,[3] Grignard reagents reacted with isocyanide to give magnesium aldimines, of which the synthetic use has been

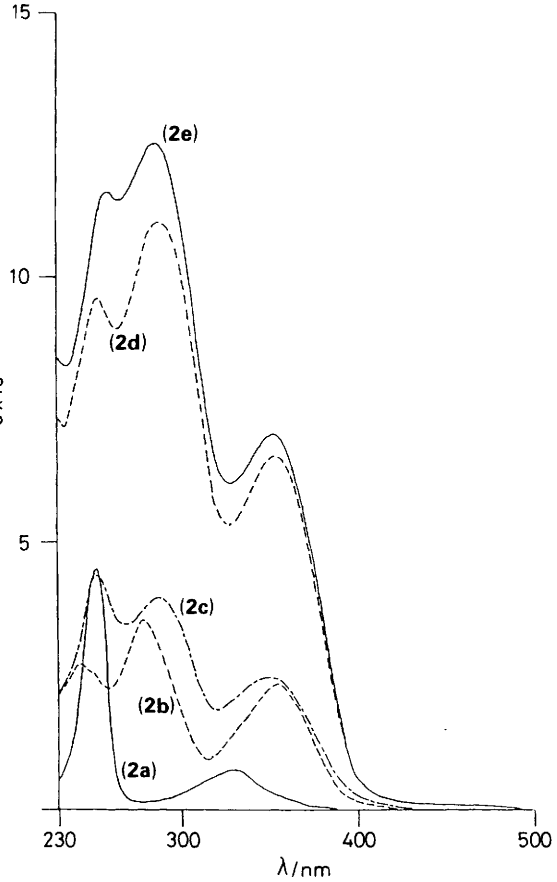
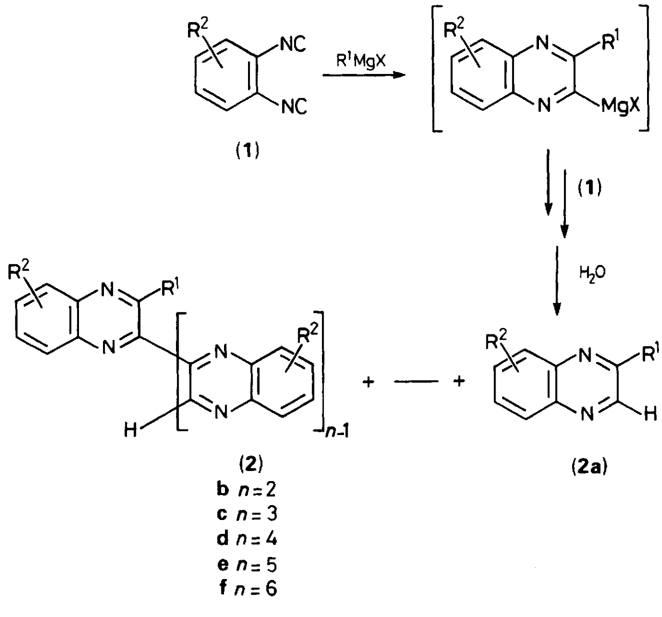


Figure 1. UV spectra of quinoxaline oligomers (2) (R^1 = Bu^n) in CH_2Cl_2.



Scheme 1

Table 1. Reaction of (**1**) with Grignard reagents.

		% Yield[a] of (**2**)					
R^1MgX	(**1**)/R^1MgX	(**2a**)	(**2b**)	(**2c**)	(**2d**)	(**2e**)	(**2f**)
Pr^{i}MgBr	3	5	3	7	5	8	3
Bu^{n}MgBr	2	2	4	8	10	10	—
Bu^{i}MgBr	2	5	6	6	4	6	3
Bu^{t}MgCl	2	12	3	3	3	4	—

[a] Yields of (**2**) are based on chromatographically isolated products (silica gel and/or polystyrene gel).

limited. However, successive insertions of isocyanides into a carbon-typical metal bond have been not extensively studied. We now report oligomerizations of 1,2-di-isocyano-3,4,5,6-tetramethylbenzene (**1**) promoted by Grignard reagents to give quinoxaline oligomers (**2**) up to hexa-oligomers.

1,2-Di-isocyano-3,4,5,6-tetramethylbenzene (**1**) was treated with Grignard reagents in tetrahydrofuran (THF) at 0 °C to give a variety of quinoxaline oligomers (**2**) after hydrolysis (Table 1). These oligomers were separated and isolated by preparative TLC on silica gel and/or recycling HPLC on polystyrene gel, and characterized by ^1H NMR and IR spectroscopy.† The parent peaks (M^+) of quinoxaline oligomers (**2a**—**f**) (R^1 = Bu^i) were observed in the mass spectra. The quinoxaline skeleton was regularly constructed by successive insertion of the two *ortho* isocyano groups into the carbon–magnesium linkage. Use of 1,2-di-isocyano-4,5-dimethylbenzene instead of (**1**) afforded the quinoxaline monomer (**2a**) with intractable polymeric products, which were not identified.‡ UV spectra of the quinoxaline oligomers (**2a**—**e**) (R^1 = Bu^n) revealed an interesting structural feature (Figure 1); quinoxaline monomer (**2a**) possessed an intense $\pi \rightarrow \pi^*$ transition band at 252 nm, while quinoxaline dimer (**2b**) showed additionally a red shifted absorption at 280 nm. The two absorptions may be ascribed to a single isolated quinoxaline chromophore and a conjugated dimeric quinoxaline chromophore, respectively. For trimer (**2c**), the absorption band of the conjugated quinoxaline chromophore moved to 290 nm due to a slight resonance contribution. However, tetramer (**2d**) and pentamer (**2e**) absorbed at the same position as trimer (**2c**) with an increased absorption intensity indicating that an effective resonance conjugation over more than three sequential quinoxaline rings in the polymer chain may be inhibited by steric interaction.

The oligomerization of 1,2-di-isocyanoarenes mentioned above may be interestingly compared by nickel catalysed polymerizations of 1,2-di-isocyanoarenes; *e.g.*, 1,2-di-isocyano-3,4,5,6-tetramethylbenzene was treated with a catalytic amount of nickel(II) salts to produce a light brown powder in high yield which is insoluble in common organic solvents. The IR spectrum of the polymer was very similar to that of the oligomer, suggesting that the polymer consists mainly of a quinoxaline unit. The polymer thus formed, although not fully characterized because of insolubility, is of interest in terms of potential technological properties.

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† *Spectral data* for (**2e**) (R^1 = Bu^t): ^1H NMR (200 MHz, $CDCl_3$) δ 1.64 (s, 9H), 1.89 (s, 6H), 1.93 (s, 3H), 1.96 (s, 3 H), 2.12 (s, 3 H), 2.16 (s, 6 H), 2.20 (s, 6 H), 2.24 (s, 3 H), 2.27 (s, 3 H), 2.28 (s, 3 H), 2.36 (s, 3 H), 2.37 (s, 6 H), 2.43 (s, 3 H), 2.74 (s, 3 H), 2.75 (s, 3 H), 2.81 (s, 3 H), 2.91 (s, 3 H), 9.89 (s, 1 H); IR (KBr) 2936, 2880, 1568, 1464, 1384, 1142, 1052, 822 cm^{-1}; mass spectrum, *m/z* 978 (M^+).

‡ A similar effect of *ortho* substitution of an isocyano group was also observed in the reaction of organozinc with 2,6-xylyl isocyanide and *o*-tolyl isocyanide.[4]

Further application of the present methodology to the synthesis of a soluble polymer having higher molecular weight is in progress in our laboratory.

Received, 28th September 1989; Com. 9/04167B

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