Formation of Aryl Isocyanates by Deoxygenation of Nitrosocarbonylarenes

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Summary The adducts of nitrosocarbonylarenes and 9,10-dimethylanthracene decompose in the presence of triphenylphosphine to give aryl isocyanates in high yield; kinetic evidence supporting the involvement of free nitrosocarbonylarenes in this process is presented.

C-NITROSO-COMPOUNDS react readily with phosphines to give the corresponding phosphine oxides and various nitrogenous products.[1] We report here the efficient conversion, by PPh_3, of the newly discovered,[2] transient nitrosocarbonylarenes (**1**) into aryl isocyanates (**2**).

The adducts (**3**) were prepared[2] by oxidation of the appropriate hydroxamic acids with $Et_4N^+IO_4^-$ in CH_2Cl_2 in the presence of 9,10-dimethylanthracene (DMA).† The reactions of (**3**) with PPh_3 (1 equiv.) proceeded cleanly in benzene at 80 °C to give DMA, $Ph_3P{=}O$, and the corresponding isocyanates (**2**). The yields of isocyanates were uniformly high (88—98% by g.l.c.) with a wide variety of

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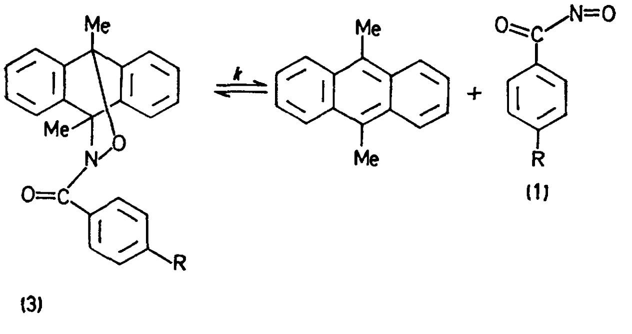
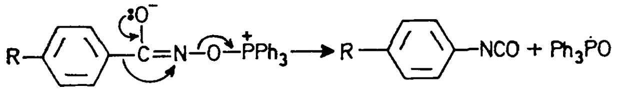
† DMA was most conveniently prepared by reduction of 9,10-bischloromethylanthracene (M. W. Miller, R. W. Amidon, and P. O. Tawney, *J. Amer. Chem. Soc.*, 1955, **77**, 2845) with $LiAlH_4$ in tetrahydrofuran.

aryl substituents (R = H, Cl, MeO, or NO_2); they were characterised by conversion into crystalline urea‡ derivatives.

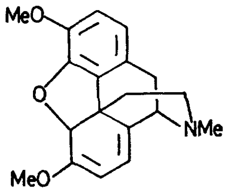


(3)

(1)



(6) (2)



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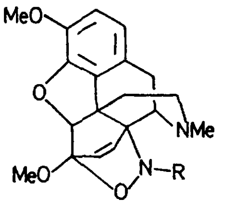

(5)

$Ph_3P{=}NCN$

(7)

The formation of isocyanates is believed to involve transient nitrosocarbonylarenes (**1**) for the following reasons. The reaction of (**3**; R = H) with PPh_3 in benzene at 60 °C was followed by the appearance of DMA (absorption at 385 or 400 nm). First-order kinetics were observed with a rate constant, $k = 6{\cdot}2 \times 10^{-5}\ s^{-1}$, independent of the initial concentration of PPh_3. Also, a similar first-order rate, $k = 5{\cdot}1 \times 10^{-5}\ s^{-1}$ (60 °C in benzene), was observed for the reaction of (**3**; R = H) with thebaine (**4**) to give the adduct[2] (**5**; R = PhCO) and DMA. These results are best explained by slow, rate-determining dissociation of (**3**; R = H) to give DMA and (**1**; R = H) which is rapidly captured by PPh_3 or thebaine. Attack of PPh_3 on (**1**; R = H) might give (**6**; R = H) (or the related, cyclic phosphorane) which could decompose with rearrangement to the observed products. The adducts (**3**; R = Cl, MeO, or NO_2) displayed similar, first-order decomposition in benzene at 60 °C; with thebaine, $k = 5{\cdot}2 \times 10^{-5}$ (R = Cl), $8{\cdot}7 \times 10^{-5}$ (R = MeO), and $4{\cdot}2 \times 10^{-5}\ s^{-1}$ (R = NO_2), and with PPh_3, $k = 3{\cdot}9 \times 10^{-5}\ s^{-1}$ (R = NO_2).

Further support for the independent existence of (**1**) came from analogy with the behaviour of the well characterised[3] species, nitrosyl cyanide, which formed a crystalline DMA-adduct,[4] m.p. 169—171 °C, analogous to (**3**). This decomposed in the presence of thebaine by first-order kinetics, $k = 7{\cdot}1 \times 10^{-5}\ s^{-1}$ (40 °C in benzene), to give DMA and the derivative[3] (**5**; R = CN) quantitatively. A similar first-order rate, $k = 6{\cdot}8 \times 10^{-5}\ s^{-1}$, was observed for the reaction of DMA–ONCN with PPh_3 (2 equiv.), the products being DMA, $Ph_3P{=}O$, and the known[5] compound (**7**).

The conversion of hydroxamic acids into isocyanates *via* the adducts (**3**) constitutes a variant on the classical Lossen rearrangement. A similar process has recently been reported[6] involving the reaction of hydroxamic acids with PPh_3 and diethyl azodicarboxylate. A protonated form of (**6**) is postulated as an intermediate but nitrosocarbonyl compounds do not appear to be involved in the overall transformation.

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‡ *N*-Phenyl- and *N*-n-propyl-*N'*-4-nitrophenylurea formed crystalline, 1 : 1 complexes with $Ph_3P{=}O$; the ^{31}P n.m.r. spectra in $CDCl_3$ showed chemical shifts, δ 31·6 p.p.m. (downfield from H_3PO_4), indicating no covalent bonding between phosphorus and the urea. (*Cf.* D. W. Allen, F. G. Mann, and J. C. Tebby, *J.C.S. Perkin I*, 1972, 2793).

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