Temperature Variable Pyrolyses of 2,6-Disubstituted Phenyl Azidoformates

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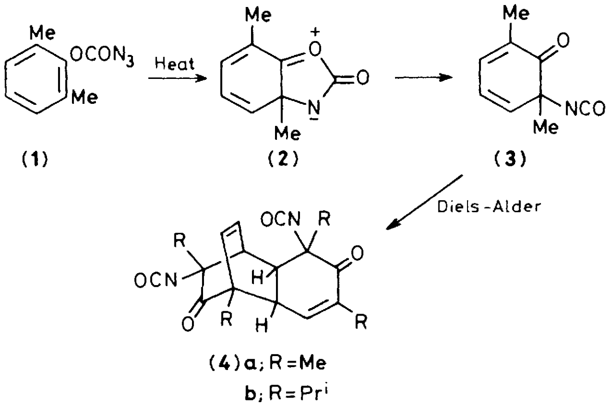
On pyrolysis, 2,6-di-isopropylphenyl azidoformate gives primarily a cyclohexadienone dimer, a benzoxazolone, or a benzoxazinone dependent upon temperature while 2-methyl-4,6-di-t-butylphenyl azidoformate gives 2-isocyanato-2-methyl-4,6-di-t-butylcyclohexa-2,4-dienone at lower temperature but 5-t-butyl-7-methylbenzoxazol-2-one at higher temperature.

We have recently noted the highly versatile cyclisations undergone by azidoformates on 'spray pyrolysis'.[1] In a number of these and related cases it is now evident that the reactions are remarkably temperature sensitive, the reactions being subject to kinetic and thermodynamic control. We herein report two typical and novel examples in the chemistry of aryl azidoformates.

We have already reported the formation of the dimer (**4a**) of the cyclohexadienone (**3**) by pyrolysis of the azide (**1**) as shown in Scheme 1.[1c]

In the case of the 2,6-di-isopropylphenyl azidoformate (**5**), the derived nitrene (**6**) has the choice of attacking the aromatic ring (path a) as before or of inserting into the attractive tertiary C–H bond (path b) to give the benzoxazinone (**7**). Thermolysis of the azide (**5**) in refluxing tetrachloroethane indeed gave both (**7**) and (**8**) in 21 and 29% yield respectively. In fact, as shown in Scheme 2, the reaction is temperature variable. In the vapour phase at 250 °C, the cyclohexadienone



(**4**)a; R = Me
b; R = Pr^i

Scheme 1

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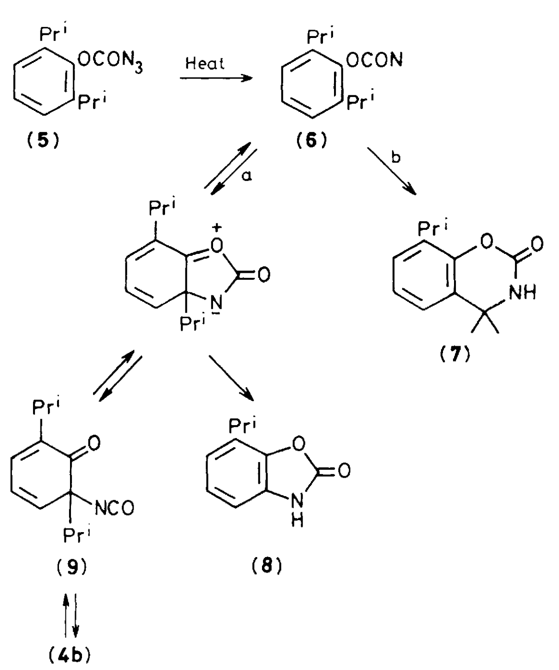
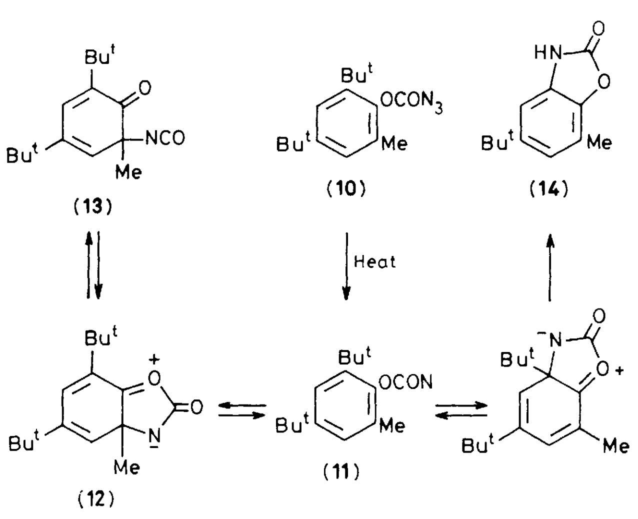


Scheme 2

dimer (**4b**) is the major product (26%) with minor amounts of (**7**) and (**8**) being formed also. At 300 °C, the benzoxazinone (**7**) becomes the major product (33%) again with the other two minor products, while at 500 °C, no dimer is isolated and the benzoxazolone (**8**) is primarily formed (46%). Thermolysis of the dimer (**4b**) in refluxing trichlorobenzene also yields the thermodynamically favoured products [(**7**) and (**8**)] both in 42% yield. *These results indicate that the dimer* (**4b**) *and nitrene* (**6**) *are in equilibrium* as shown in Scheme 2.

A second example arises when the unsymmetrically substituted azide (**10**) is pyrolysed. At 240 °C the azide yields solely the stable, monomeric cyclohexadienone (**13**) in 83% yield in the usual way. However, at 530 °C this product is almost absent and the benzoxazolone (**14**) is isolated in 81% yield, involving loss of isobutene. At intervening temperatures a mixture of the two products is observed as expected, once again the cyclohexadienone (**13**) is efficiently transformed into the benzoxazolone both in solution and in the vapour phase. These results again are best interpreted as involving a mobile equilibrium in which kinetic attack at the least hindered site proceeds at lower temperature, while under more energetic conditions the nitrene (**11**) attacks at the more hindered position (Scheme 3).



Scheme 3

These results suggest that a number of reported nitrene reactions would be worthy of reinvestigation as a function of temperature.

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1 Method: (a) M. Clancy, D. G. Hawkins, M. M. Hesabi, O. Meth-Cohn, and S. Rhouati, *J. Chem. Res.* (*S*), 1982, 78. Applications: (b) M. Clancy, M. M. Hesabi, and O. Meth-Cohn, *J. Chem. Soc., Chem. Commun.*, 1980, 1112; (c) O. Meth-Cohn and S.Rhouati, *ibid.*, 1980, 1161; (d) 1981, 241.