Cycloadditions of Nitrile Oxides to Compounds containing Two-co-ordinate Phosphorus or Arsenic. Kinetic and Thermodynamic Regioselectivity

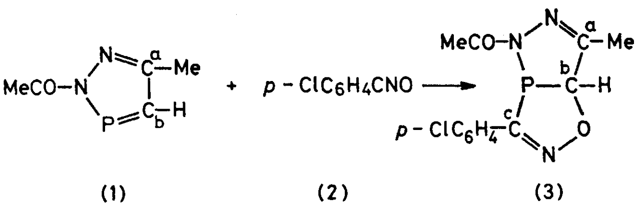
By ROBERT CARRIÉ* and Y. Y. C. YEUNG LAM KO
(Groupe de Physicochimie Structurale, Laboratoire no. 3, *E.R.A. no.* 389, *Université de Rennes,*
35042 *Rennes Cédex, France)*

and FRANCESCO DE SARLO and ALBERTO BRANDI
(Centro di studio sulla chimica e la struttura dei composti eterociclici e loro applicazioni, C.N.R., Istituto di
Chimica organica, Università di Firenze, Firenze 51021, *Italy)*

Summary Cycloaddition of *p*-chlorobenzonitrile oxide takes place only at the C=P bond of the diazaphosphole (**1**) yielding one regioisomer (**3**), and at the C=As bond of the diaza-arsole (**4**) yielding the analogous regioisomer (**5**) as the kinetic product, the other regioisomer (**6**) being the thermodynamic product.

THE reactivity of 1,3-dipoles towards the C=P double bond in two-co-ordinate phosphorus compounds has been studied in a few cases,[1,2] and the formation of a cycloadduct from the reaction of 1-diazo-2,2-dimethylpropane and bis-(trimethylsilyl)aminotrimethylsilylmethylenephosphorane has been reported very recently.[2]

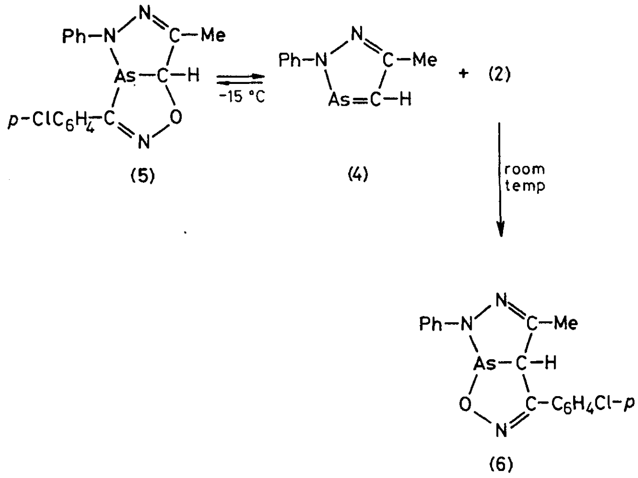
The diazaphosphole (**1**)[3] in benzene reacts easily with *p*-chlorobenzonitrile oxide (**2**) to give the 1:1 cycloadduct (**3**), which is stable at room temperature (yield 48%, m.p. 146 °C; $M^{\bullet +}$, found, *m/e* 295·025; calc. 295·028). The structure of the cycloadduct (**3**) is supported by comparison of its ^{13}C and ^{31}P n.m.r. data with data for the phosphole (**1**):† δ C^a: 157·1, $^2J_{PC}$ 2·9 for (**3**) and 159·0, $^2J_{PC}$ 12·7 for (**1**); C^b: 93·2, $^1J_{PC}$ 22·5 for (**3**) and 144·5, $^1J_{PC}$ 37·1 for (**1**); δ (^{31}P) 31·9 for (**3**) and 237·5 for (**1**). In addition, the large coupling constant between P and C^c in the adduct (**3**), δ (C^c) 158·0, $^1J_{PC}$ 55·4, clearly indicates not only the site, but also the orientation of the addition as well.



Scheme 1

M.O. parameters of the two reagents were evaluated by the CNDO/2 method.[4] The second-order perturbation energies[5] related to four possible interaction approaches (two orientations of the dipole for the two possible sites of addition, C=P and C=N) were consistent with the experimental results.

Treatment of the same nitrile oxide (**2**) with the diaza-arsole (**4**)[6] in toluene at room temperature afforded quantitatively the stable cycloadduct (**6**) (m.p. 180 °C; $M^{\bullet +}$, found, *m/e* 372·996; calc. 372·996). However, its regioisomer (**5**) was produced by carrying out the same reaction below −15 °C; m.p. 107—110 °C (decomp.); yield 43%. Structures (**5**) and (**6**) were ascribed to the isomeric cycloadducts on the basis of the ^1H and ^{13}C n.m.r. data for the CH group, compared with data for the diaza-arsole (**4**): δ (^{13}C) 154·6 for (**4**), 101·8 for (**5**), and 73·5 for (**6**); δ (^1H) 8·62 for (**4**), 6·13 for (**5**), and 5·16 for (**6**).‡



Scheme 2

In toluene solution at room temperature, the adduct (**5**) was quantitatively converted into the regioisomer (**6**). This isomerisation was shown to occur *via* retrocycloaddition by adding a slight excess of the diazaphosphole (**1**) to a cold solution of the adduct (**5**); at room temperature, a mixture of the cycloadduct (**3**) and the diaza-arsole (**4**) was obtained, no cycloadduct (**6**) being detected (^1H n.m.r.). A similar experiment, carried out with dimethyl acetylenedicarboxylate instead of the diazaphosphole (**1**), gave mainly the stable cycloadduct (**6**) together with a barely detectable amount of the adduct between the acetylenic ester and the *p*-chlorobenzonitrile oxide (**2**).

Reversibility in 1,3-dipolar cycloaddition reactions has been reported in some cases.[8,9] Its occurrence suggests that care must be taken in the interpretation of experimental results by the perturbation theory, in order to make sure that one is dealing with the kinetic rather than with the thermodynamic product.

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† Solvent $CDCl_3$; int. ref. Me_4Si (^{13}C) and ext. ref. 85% H_3PO_4 (^{31}P, downfield shifts +ve); *J* values in Hz, and δ values in p.p.m.

‡ *Cf.* values reported for CH between the two ring heteroatoms in some Δ^4-1,3-oxazolines: δ (^{13}C) 99·6—101·3; δ (^1H) 5·83—6·78.[7]

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