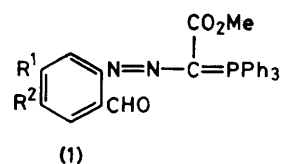


***ortho*-Formyl Substituted Arylazomethylenetriphenylphosphoranes: a Novel Facile Intramolecular Thermal Rearrangement with N=N Bond Fission**

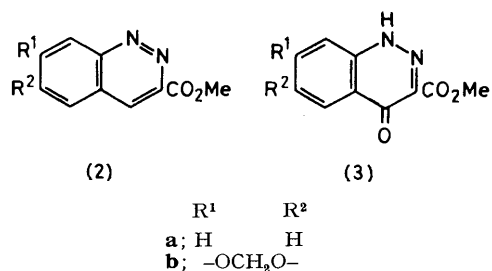
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Summary The arylazomethylenetriphenylphosphoranes (**1a**) and (**1b**) afford, in good yields, the quinazolin-4-one derivatives (**4a**) and (**4b**) via a facile thermally promoted rearrangement, with N=N bond cleavage and elimination of PPh₃.



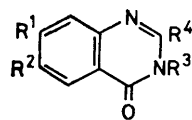
THE arylazomethylenetriphenylphosphoranes (**1**) are, formally, stabilized phosphorus ylides. Recently, Dalla Croce and Zaniboni have reported a new Wittig type synthesis of azoalkenes in which arylazomethylenetriphenylphosphoranes were generated '*in situ*' from the corresponding phosphonium salts with triethylamine.¹ Our interest in the chemistry of the title compounds² has led us to examine the possibility of intramolecular Wittig-type reactions in suitable substrates.

The starting materials (**1a**) and (**1b**) have been prepared via the nitrile imines;³ (**1b**) was also prepared via the phosphorus-methylene ylide, as proposed by Märkl.⁴ Reflux of compound (**1a**) in toluene under nitrogen for 20 min led to an amorphous product, m.p. 188—189 °C (from CH₂Cl₂-light petroleum), which was isomeric with



the starting material. This compound was further heated for 1 h in toluene and, instead of the expected cinnoline derivative (**2a**) and OPPh₃, furnished PPh₃ and the methyl quinazoline-2-carboxylate (**4a**), m.p. 209 °C (from

C₆H₆, 86% yield).† Analytical data for compound (**4a**) are consistent with molecular formula C₁₀H₈N₂O₃; ν_{\max} (Nujol) 3200, 3180, 3100, 1750, 1672, and 1618 cm⁻¹; δ (CDCl₃) 4.12 (3 H, s, OMe), 8.1—7.55 (3 H, m, aromatics), 8.47 (1 H, d, aromatic), and 10.46 (1 H, br s, NH).



(4)

	R ¹	R ²	R ³	R ⁴
a;	H	H	H	CO ₂ Me
b;	-OCH ₂ O-	H	H	CO ₂ Me
c;	-OCH ₂ O-	H	Et	H

When compound (**1b**) was heated at 70 °C in toluene for 2 h it gave PPh₃ and the methyl [1,3]dioxolo[4,5-*g*]-quinazolin-2-carboxylate (**4b**), m.p. 225 °C (from pyridine, 87%). Analytical data for compound (**4b**) are in accord with molecular formula C₁₁H₈N₂O₅; ν_{\max} (Nujol) 3190, 3160, 3110, 1765, and 1680 cm⁻¹; δ ([²H₅]pyridine) 3.9 (3 H, s, OMe), 6.0 (2 H, s, OCH₂O), 7.3 (1 H, s, aromatic), 7.81 (1 H, s, aromatic), and 8.68 (H₂O + NH).

The formation of PPh₃ instead of OPPh₃ and the presence of two C=O groups in both compounds (**4a**) and (**4b**) clearly show that the expected Wittig reaction did not take place. The structures of the 3-methoxycarbonylcinnolin-4-ones (**3a**) and (**3b**) do, to some extent, agree with the experimental data for the products (**4a**) and (**4b**),‡ but had to be discarded after comparison with authentic samples of compounds (**3a**) and (**3b**).

† In another experiment compound (**4a**) was obtained (86% yield) by refluxing [in toluene-acetonitrile (1:1)] methyl *ortho*-formylphenylhydrazono- α -chloroglyoxylate in the presence of NEt₃ (1 equiv.) and a catalytic amount of PPh₃. The nitrile imine generated *in situ* reacts with PPh₃ to give compound (**1a**) which then gives compound (**3a**) and PPh₃, which, in turn, reacts with the nitrile imine in a cyclic process.

‡ An example of an anomalous decomposition of the Wittig reaction intermediate leading to PPh₃ and a ketone has been reported (G. Wittig and W. Böll, *Chem. Ber.*, 1962, **95**, 2526).

¹ P. Dalla Croce and A. Zaniboni, *Synthesis*, 1977, 552.

² A. Alemagna, P. Del Buttero, E. Licandro, and S. Maiorana, *Gazz. Chim. Ital.*, 1981, **111**, 7.

³ P. Dalla Croce, P. Del Buttero, E. Licandro, and S. Maiorana, *Synthesis*, 1979, 299, and references therein.

⁴ G. Märkl, *Tetrahedron Lett.*, 1961, 807.

⁵ K. Suwinska and G. D. Andreotti, *Cryst. Struct. Commun.*, in the press.

On treatment with EtI and EtONa in EtOH at reflux, compound (**4b**) gave 3-ethyl[1,3]dioxolo[4,5-*g*]quinazolin-4(3*H*)-one (**4c**), m.p. 172—173 °C (from EtOH). Analytical data are in accord with molecular formula C₁₁H₁₀N₂O₃; ν_{\max} (Nujol) 1675 and 1630 cm⁻¹; δ (CDCl₃) 1.4 (3 H, t, MeCH₂), 4.07 (2 H, q, CH₂Me), 6.08 (2 H, s, OCH₂O), 7.03 (1 H, s, aromatic), 7.6 (1 H, s, aromatic), and 7.92 (1 H, s, aromatic). Hence, compound (**4b**) underwent alkylation, and also hydrolysis and decarboxylation of the methoxycarbonyl group.

Compound (**4c**) was obtained in well shaped crystals and was submitted to single crystal X-ray analysis,⁵ which revealed that it was a quinazolin-4-one derivative. Spectroscopic data of compounds (**4a**) and (**4b**) are also consistent with a quinazolinone structure, which has been subsequently confirmed by comparison with authentic samples prepared by known methods.

Thus the arylazomethylenetriphenylphosphoranes (**1a**) and (**1b**), with an *ortho*-CHO group, afforded, when heated, good yields of the quinazolinone derivatives (**4a**) and (**4b**) [equation (1)]. During these reactions a phosphorus-



containing intermediate was formed, which could sometimes be isolated (elucidation of the structure is difficult, but is under investigation) and is isomeric with the starting material. Through this intermediate an unexpectedly facile thermally promoted rearrangement takes place, with N=N bond cleavage, elimination of PPh₃, and formation of a quinazolinone ring.

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