
Conjugated Heterocumulenes. Synthesis of C=C- and N=C-Conjugated Ketenimines through a Wittig-type Reaction and their Conversion into Hetero(carbo)cycles

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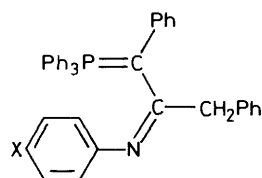
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N=C- and C=C-Conjugated ketenimines have been synthesized as key intermediates through a Wittig-type reaction of imino- or methylene-phosphoranes with isocyanates or diphenylketene, and have been converted into hetero(carbo)cycles *via* cycloadditions.

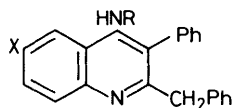
Compounds containing a cumulene entity coupled to further unsaturation are expected to have synthetic potential as a result

of their ability to take part in cycloadditions.¹ Our synthetic approach to unsaturated heterocumulenes consists of treating

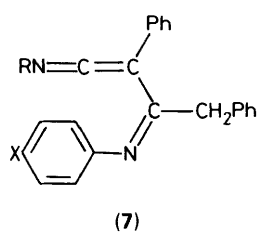
methylene- or imino-phosphoranes bearing an unsaturated group with easily accessible heterocumulenes such as isocyanates^{2,3} and *N*-sulphinylamines in a Wittig-type reaction.⁴ With this strategy,⁵ we now describe how conjugated ketenimines thus formed can be utilized as potent synthons for the construction of hetero(carbo)cycles.



- (1) X = H
(2) X = Me



- (3) X = H, R = Ph
(4) X = Me, R = *p*-Tolyl
(5) X = H, R = 2,6-Cl₂C₆H₃
(6) X = H, R = *c*-C₆H₁₁



(7)

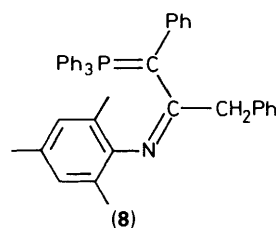
Wittig-type reaction of the imidoylphosphoranes (1) and (2) with isocyanates in refluxing toluene for 11–26 h gave the 4-aminoquinolines (3)–(6) in good yields.* It is likely that, initially, the aryl-N=C-conjugated C-ketenimines (7) are formed as intermediates and these then undergo 6π-electrocyclization with the aryl group as a 2π-component; subsequently aromatization occurs by way of a proton shift.

When the P-ylide (8) having a mesityl group at the nitrogen was employed in order to prevent the cyclization, 4-imino-tetrahydro-1,3-diazin-2-ones (9)–(12) were obtained. In this case, the conjugated ketenimine (13) behaved as an 1-azadiene to cycloadd onto the C=N bond of another molecule of isocyanate.†

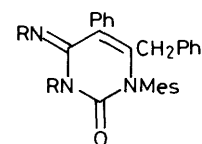
The reaction of (14) with isocyanates in refluxing benzene for 5 h gave the fluoranthenes (15)–(17) probably by electrocyclic ring closure of the ArC=C-conjugated C-ketenimines (18).

Treatment of the vinyliminophosphorane (19) with diphenylketene in refluxing benzene for 3 h afforded a 2*H*-1,3-oxazine (20), no intramolecularly cyclized product being detected. In this case the intermediate C=C-conjugated *N*-ketenimine (21) behaved as an 2-azadiene to cycloadd onto the C=O bond of a second molecule of diphenylketene.

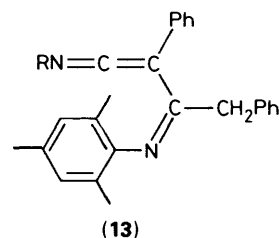
An alternative approach to C=C-conjugated *N*-ketenimines by the Wittig-type reaction was investigated by using (22) and β-styryl isocyanate (23). *N*-β-Styrylketenimine (24) was isolated as yellow cubes (88% yield) when an equimolar mixture of (22) and (23) was heated in benzene under reflux for 1 h.‡



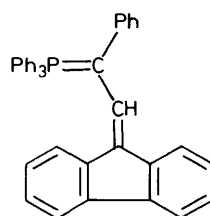
(8)



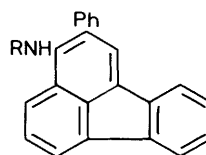
- (9) R = Ph
(10) R = *p*-Tol
(11) R = *p*-ClC₆H₄
(12) R = *p*-MeOC₆H₄



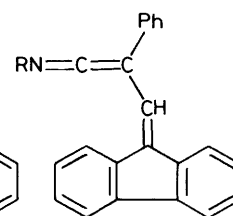
(13)



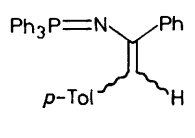
(14)



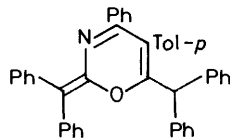
- (15) R = Ph
(16) R = *p*-Tol
(17) R = *p*-ClC₆H₄



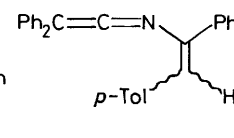
(18)



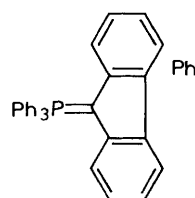
(19)



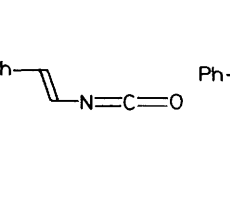
(20)



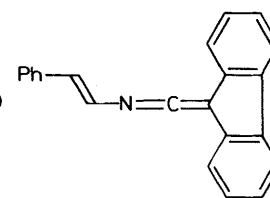
(21)



(22)



(23)



(24)

Experimental

A mixture of phenyl(*N*-phenylbenzylidoyl)methylenetriphenylphosphorane (1) (818 mg, 1.5 mmol) and phenyl isocyanate (1.6–3.6 mmol) in dry toluene (10 ml) was heated under reflux for 11 h. Evaporation of the solvent and purification of the residue by column chromatography [silica gel, benzene–dichloromethane (3 : 2)] and recrystallization from ether–hexane gave 2-benzyl-3-phenyl-4-anilinoquinoline (3) (510 mg, 88%) as colourless needles, m.p. 174–176 °C; ν_{max} (KBr) 3 400 cm⁻¹ (NH); δ_{H} (100 MHz, CDCl₃) 4.12 (s, 2 H, CH₂), 5.56 (s, 1 H, NH), and 6.58–8.12 (m, 19 H, ArH); δ_{C} (CDCl₃) 43.7 (CH₂) and 159.6 (C-2); m/z 386 (M^+ , 58%), 385 (100, $M^+ - 1$), and 294 (5, $M^+ - \text{NHPh}$).

* Attempts to isolate the expected ketenimine (7) resulted in failure because (1) and (2) were not sufficiently reactive toward the isocyanates under milder conditions, e.g. in refluxing benzene, where the eventual cyclization of (7) leading to (3)–(6) did not take place.

† The ketenimine (13) could not be isolated even when less than an equimolar amount of the isocyanate was added slowly to the ylide (8) in toluene under reflux or lower temperatures.

‡ *E* Geometry of the styryl group was conserved [J 13.5 Hz for (23) and (24)].

Table. Reaction of phosphoranes with isocyanates and diphenylketene

Phosphorane	Time (h)	Product*	Yield (%)
(1)	11	(3)	88
(2)	16	(4)	98
(1)	26	(5)	68
(1)	20	(6)	69
(8)	5	(9)	58
(8)	10	(10)	56
(8)	15	(11)	65
(8)	28	(12)	68
(14)	5	(15)	65
(14)	5	(16)	65
(14)	5	(17)	93
(19)	3	(20)	60
(22)	1	(24)	88

* M.p.s. and i.r. and ^1H and ^{13}C n.m.r. data for the products have been treated as a Supplementary publication [Sup. No. 56766 (3 pages)]. For details of the Supplementary publications scheme see Instructions for Authors (1989), *J. Chem. Soc., Perkin Trans. I*, 1989, Issue 1.

A solution of (8) (822 mg, 1.4 mmol) and phenyl isocyanate (3.2 mmol) in dry toluene (10 ml) was heated under reflux for 5 h. Evaporation of the solvent and column chromatography of the residue [silica gel, benzene-ethyl acetate (30:1)] gave (9) (58%) as yellow cubes (benzene-hexane); m.p. 197–200 °C (Found: C, 83.1; H, 6.1; N, 7.45. $\text{C}_{38}\text{H}_{33}\text{N}_2\text{O}$ requires C, 83.33; H, 6.07; N, 7.67%); ν_{max} 1 700 (CO), and 1 630 cm^{-1} (C=N); δ_{H} 1.84 (s, 6 H, *o*-CH₃), 2.24 (s, 3 H, *p*-CH₃), 3.32 (s, CH₂), and 6.16–7.28 (m, 22 H, ArH); δ_{C} 17.6, 21.0 (CH₃), 35.9 (CH₂), 148.4 (C=N), and 150.9 (CO); m/z 547 (M^+ , 70%), 546 (100, $M^+ - 1$).

A benzene solution of (14) (1.06 g, 2.0 mmol) and phenyl isocyanate (250 mg, 2.1 mmol) was refluxed for 5 h. Removal of the solvent and column chromatography of the residue [silica gel, benzene-dichloromethane (1:1)] afforded (15) (65%) as yellow needles (benzene-hexane); m.p. 193–194 °C (Found: C,

91.58; H, 5.25; N, 3.85. $\text{C}_{28}\text{H}_{19}\text{N}$ requires C, 91.02; H, 5.18; N, 3.79%); ν_{max} 3 400 cm^{-1} (NH); δ_{H} 3.44 (s, NH), and 6.78–7.86 (m, 18 H, ArH); m/z 369 (M^+ , 100).

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