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NEW METHODOLOGY FOR THE PREPARATION OF QUINAZOLINE DERIVATIVES VIA TANDEM AZA-WITTIG/HETEROCUMULENE-MEDIATED ANNULATION. SYNTHESIS OF 4(3H)-QUINAZOLINONES, BENZIMIDAZO[1,2-c]QUINAZOLINES, QUINAZOLINO[3,2-a]QUINAZOLINES AND BENZOTHIAZOLO[3,2-c]QUINAZOLINES[1]

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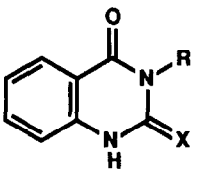
Abstract - *The aza-Wittig reaction of iminophosphoranes derived from N-substituted o-azidobenzamides, 2-(o-azidophenyl)-benzimidazole, -benzothiazole or -3,1-benzoxazin-4-one with heterocumulenes leads to functionalized quinazolines. Iminophosphoranes 9, derived from N-substituted o-azidobenzamides, react under mild conditions with isocyanates to form 4H-3,1-benzoxazine-4-imines 11 which are converted into 2-substituted-4(3H)-quinazolinones 12. Iminophosphoranes 9 also react with carbon disulfide and carbon dioxide to give the quinazolinones 13 and 14 respectively. Iminophosphorane 26, derived from 2-(o-azidophenyl)benzimidazole, reacts with isocyanates, carbon disulfide and carbon dioxide to form 6-substituted benzimidazo[1,2-c]quinazolines 27, 28 and 29 respectively. In benzene at room temperature, iminophosphorane 31, reacts with isocyanates yielding quinazolino[3,2-a]quinazolines 34. Compounds 34 can also be prepared from iminophosphorane 36 and isocyanates. Iminophosphorane 40 derived from 2-(o-azidophenyl)benzothiazole reacts with aliphatic and aromatic isocyanates or isothiocyanates to give 7H-benzothiazolo[3,2-c]quinazoline-7-imines 42. Iminophosphorane 40 also reacts with carbon dioxide or carbon disulfide to afford the corresponding isocyanate 43 or isothiocyanate 44. The molecular structures of 11d and 42a have been determined by X-ray diffraction methods.*

The quinazoline skeleton, when selectively functionalized, is a building block for the preparation of numerous alkaloids and substances capable of exhibiting a wide variety of biological activities. In the course of our

studies directed toward the iminophosphorane-mediated synthesis of heterocycles we had occasion to explore heterocyclization reactions based on a tandem aza-Wittig/electrocyclization strategy[2].

We now report a fundamentally new approach to the synthesis of a variety of quinazolines such as: 2-substituted 4(3H)-quinazolinones 1, benzimidazo [1,2-c]quinazolines 2, quinazolino[3,2-a]quinazolines 3 and benzothiazolo [3,2-c] quinazolines 4 .

Chart I



X= O, S, NR

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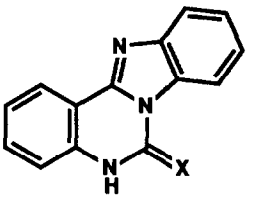

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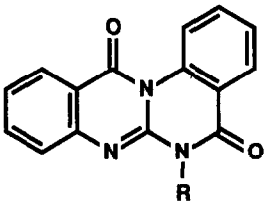

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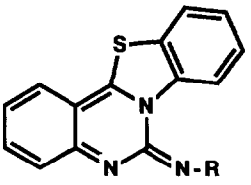

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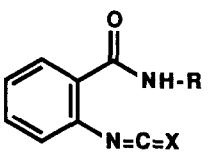
Our approach is centered on the aza-Wittig reaction of iminophosphoranes with isocyanates, carbon dioxide or carbon disulfide to give heterocumulenes of types 5, 6 and 7 which undergo cyclization to give a functionalized pyrimidine ring. To our knowledge this is the first reported annulation of a pyrimidine ring to an existing one from rings with an azido group adjacent to an amide or amidine one based on a tandem aza-Wittig/heterocumulene-mediated cyclization[3].



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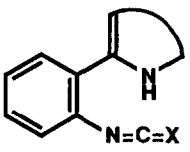

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4(3H)Quinazolinones. Crystal structure of compound 11d. In spite of considerable interest in 2-amino-4(3H)-quinazolinones as starting materials for pharmaceuticals and other biologically active compounds, no general and simple approach to this type of compound has been reported. It has only been briefly mentioned[4] that quinazoline-2,4(1H,3H)-diones by sequential treatment with phosphorus oxychloride and amines lead to 2-amino-4(3H)-quinazolinones. We report now a new and general method for the preparation of 2-amino-4(3H)-quinazolinones under mild and neutral conditions starting from N-substituted o-azidobenzamides via iminophosphoranes.

The N-substituted o-azidobenzamides 8 were prepared by previously reported procedures[5]. The preparation of the desired iminophosphoranes 9 was accomplished very easily through the classical Staudinger reaction[6] of o-azidobenzamides 8 with triphenylphosphine in dry methylene chloride at room temperature. The reaction of iminophosphoranes 9 with isocyanates (1:2 molar ratio) in dry methylene chloride at room temperature gave triphenylphosphine oxide and the corresponding 4H-3,1-benzoxazine-4-imines 11, the yield of the isolated products being higher than 74%.

The microanalytical data of compounds 11 correspond to two units of isocyanate per unit of starting material less one unit of triphenylphosphine oxide. An unambiguous structural assignment could not be achieved from the analytical and the deceptively simple spectral data alone, and X-ray crystallographic analysis was therefore performed. Table I gives the main geometrical characteristics of the molecule 11d according to the numbering scheme showed[7] in Fig. 1. Bond lengths indicate partial double bond character at the N3-C2 and C10-N17 bonds. The conformation is characterized by the torsion around N17-C18, the rest of the molecule being quite planar due, may be, to the N3.....H15 and O14.....H12C possible interactions. This conformation leaves O14 at 0.036(15) Å from the mean plane through the

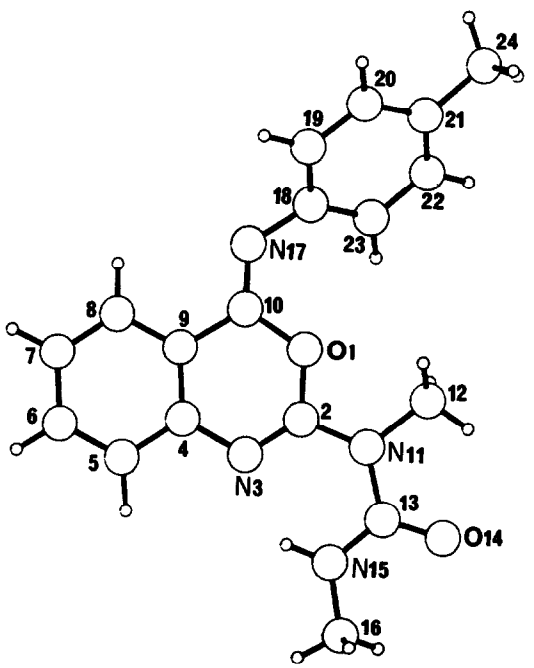
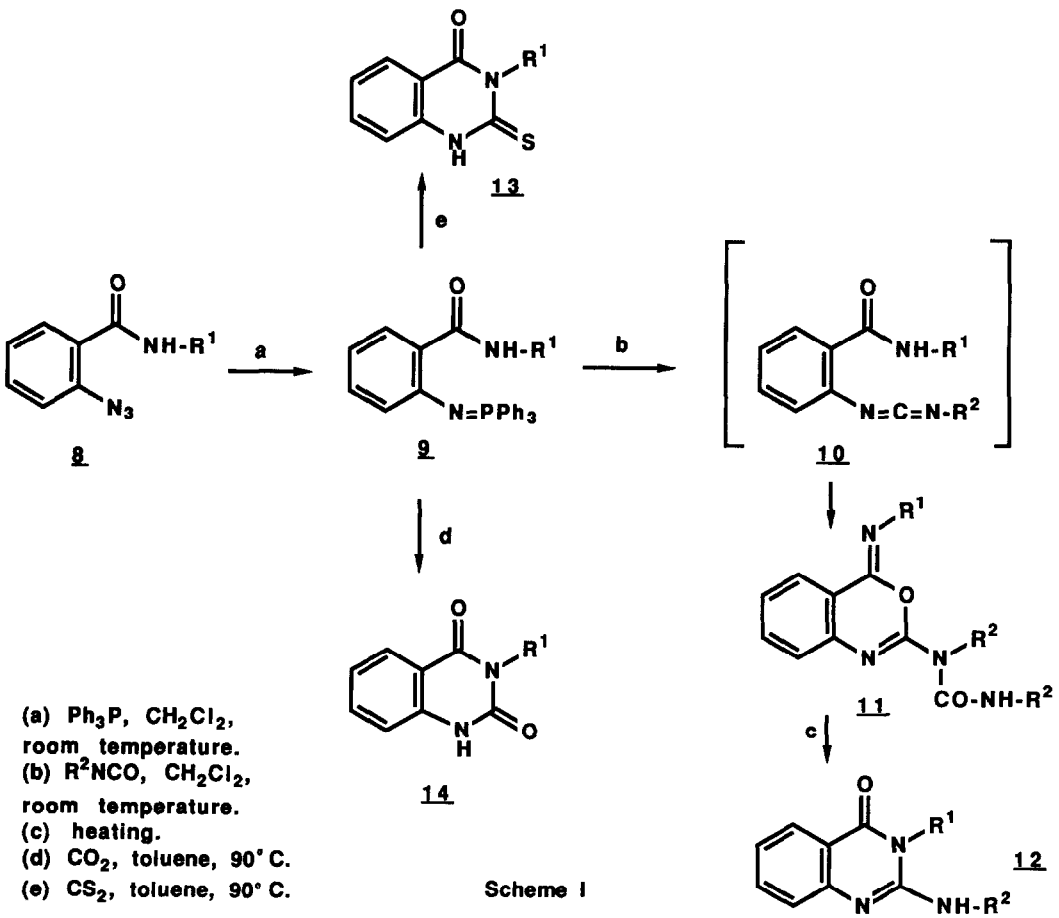


Fig. 1. Molecular structure with the numbering system used in the crystallography work for compound 11d.

central ring, O1, C2, ...C10, and 4.837(12) Å from the center of this ring, which is a bit puckered towards an envelope conformation flapping at C10.

When compounds 11 were heated in ethanol they underwent typical Dimroth rearrangements[8] followed by elimination of the isocyanate to furnish 2-aryl(alkyl)amino-4(3H)-quinazolinones 12 and the corresponding carbamates. Reaction of iminophosphoranes 9 with isocyanates in dry toluene at reflux temperature resulted in the formation of the corresponding 12 directly in good yields. When iminophosphorane 9 was treated with carbon disulfide in dry toluene at 90°C 3-substituted 2-thioxo-1,2,3,4-tetrahydroquinazolin-4-one 13 was formed in high yield. This synthetic approach may be useful in view of the pharmacological interest of this class of compounds[9]. Similarly, compounds 14 were prepared in good yield from iminophosphoranes 9 and carbon dioxide at 90°C in a sealed glass tube (Scheme I).

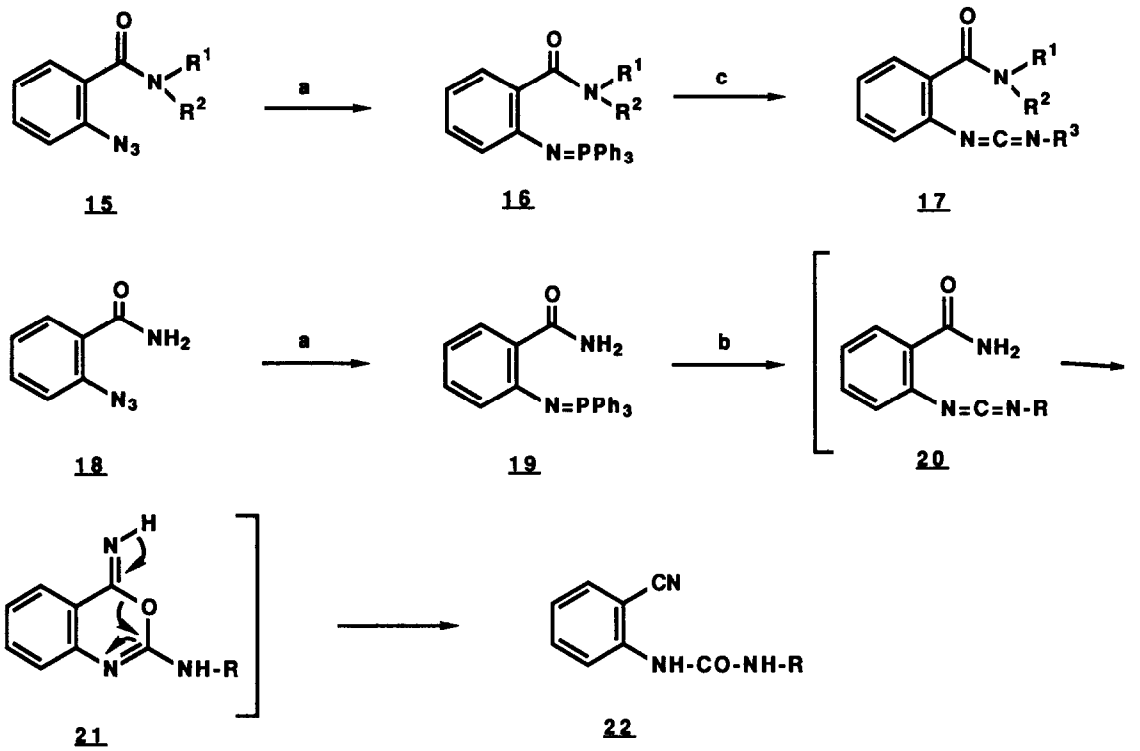


Scheme I

Table I. Selected geometrical parameters (Å, °) for compound 11d.

O1-C2	1.361(3)	O1-C10	1.397(3)
C2-N3	1.279(3)	C2-N11	1.369(3)
N3-C4	1.396(3)	C4-C9	1.389(3)
C9-C10	1.460(3)	C10-N17	1.258(3)
N11-C12	1.483(3)	N11-C13	1.429(3)
C13-O14	1.222(3)	C13-N15	1.319(3)
N15-C16	1.446(4)	N17-C18	1.418(3)
C2-O1-C10	121.0(2)	O1-C2-N11	110.1(2)
O1-C2-N3	125.1(2)	N3-C2-N11	124.8(2)
C2-N3-C4	117.9(2)	N3-C4-C9	122.1(2)
C4-C9-C10	118.2(2)	O1-C10-C9	115.5(2)
C9-C10-N17	123.7(2)	O1-C10-N17	120.8(2)
C2-N11-C13	125.0(2)	C2-N11-C12	119.4(2)
C12-N11-C13	115.6(2)	N11-C13-N15	117.6(2)
N11-C13-O14	118.5(2)	O14-C13-N15	123.9(2)
C13-N15-C16	121.5(2)		
C2-O1-C10-C9	-5.2(3)	C10-O1-C2-N3	3.0(3)
O1-C2-N3-C4	-0.1(3)	C2-N3-C4-C9	-0.2(3)
N3-C4-C9-C10	-2.3(3)	C4-C9-C10-O1	4.7(3)
N3-C2-N11-C12	175.5(2)	N3-C2-N11-C13	-6.3(4)
C2-N11-C13-O14	177.0(2)	C2-N11-C13-N15	-3.4(4)
N11-C13-N15-C16	179.0(2)	O1-C10-N17-C18	-0.6(4)
C10-N17-C18-C23	39.7(4)		
N15....N3	2.658(3)	N15-H15	0.90(3)
H15....N3	1.93(3)	C23-H23	0.96(3)
C23....O1	2.874(3)	C12.....O1	2.565(4)
H23....O1	2.47(3)	H12A.....O1	2.34(4)
C12-H12A	0.93(4)	C12.....O14	2.667(4)
C12-H12C	0.97(6)	H12C.....O14	2.15(5)

We believe that the mechanism of the conversion 9 ⟶ 11 involves initial aza-Wittig reaction between the iminophosphorane and the isocyanate to give a carbodiimide 10 as highly reactive intermediate which easily undergoes ring closure by nucleophilic attack of the hard end of the carboxamide group (the oxygen atom) on the hard electrophilic sp-hybridized carbon atom of the carbodiimide moiety to give the 3,1-benzoxazine ring with concomitant addition on the formed NH group of the second molecule of the isocyanate. This assumption is supported by the following facts: a) when iminophosphoranes 16 derived from N,N-disubstituted o-azidobenzamides were used, the reaction with aryl isocyanates led to the corresponding (o-carboxamido)phenyl aryl carbodiimide 17; b) the iminophosphorane 19 derived from o-azidobenzamide was converted into the corresponding o-ureidobenzonitrile 22 by action of aryl isocyanates (Scheme II). This putative intramolecular oxygen atom transfer in the converse reaction 20 ⟶ 22 has been studied in detail[10] and occurs through a 4H-3,1-benzoxazine 21 as intermediate; and c) as 12 was found to be inert to aryl isocyanates under the same reaction conditions, the second aryl group incorporation must be simultaneous to the ring cyclization; this is in good agreement with the results obtained when iminophosphorane 9 and aryl isocyanates react in equimolecular amounts to



(a) Ph_3P, CH_2Cl_2, room temperature. (b) RNCO, CH_2Cl_2, room temperature. (c) R^3NCO, CH_2Cl_2, room temperature.

Scheme II

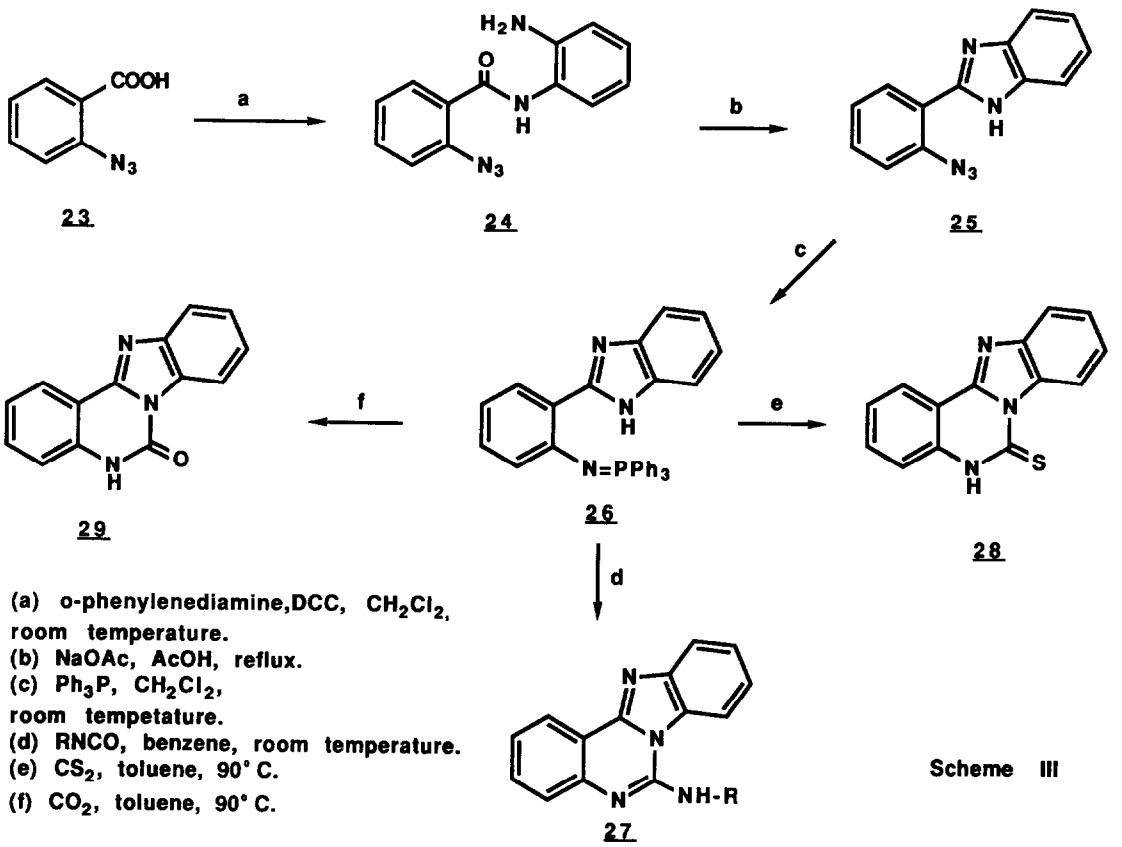
give 11 in moderate yields. Although reactions of carbodiimides with several amino compounds have been reported[11], to our knowledge this is the first example reported of heterocyclization based on the reaction of carbodiimides with carboxamides. Similarly, the formation of 13 and 14 can be understood as occuring by initial aza-Wittig reaction between iminophosphoranes 9 and carbon disulfide or carbon dioxide to give the corresponding isothiocyanate or isocyanate as intermediates[12] which cyclize spontaneously to give 13 or 14 respectively.

Benzimidazo[1,2-c]quinazolines.The above approach has also shown to be useful for the preparation of the otherwise not readily available benzimidazo[1,2-c] quinazoline ring system. Thus, compound 24, readily available from o-azidobenzoic acid 23 and o-phenylenediamine in the presence of DCC, reacted with sodium acetate in acetic acid to give 2-(o-azidophenyl)benzimidazole 25 in 72% yield. Compound 25 reacted with triphenylphosphine in dry ether at room temperature to give the iminophosphorane 26 in 84% yield. The reaction of iminophosphorane 26 with several aliphatic and aromatic isocyanates in dry

benzene at room temperature directly gave 6-alkyl(aryl)amino-benzimidazo [1,2-c]quinazolines 27 in good yields (Scheme III). The carbodiimide was indeed an intermediate in this reaction (as evidenced by IR) but never present in high concentration.

It is noteworthy that no general method for the preparation of 6-amino-benzimidazo[1,2-c]quinazolines has been reported.It has only been briefly mentioned[13] that 3,1-benzothiazine derivatives react with o-phenylenediamine to give 5,6-dihydro-6-thioxobenzimidazo[1,2-c]quinazolines.

When iminophosphorane 26 was treated with carbon disulfide or carbon dioxide in dry toluene at 90°C in a sealed glass tube, compounds 28 and 29 were formed respectively in high yields.



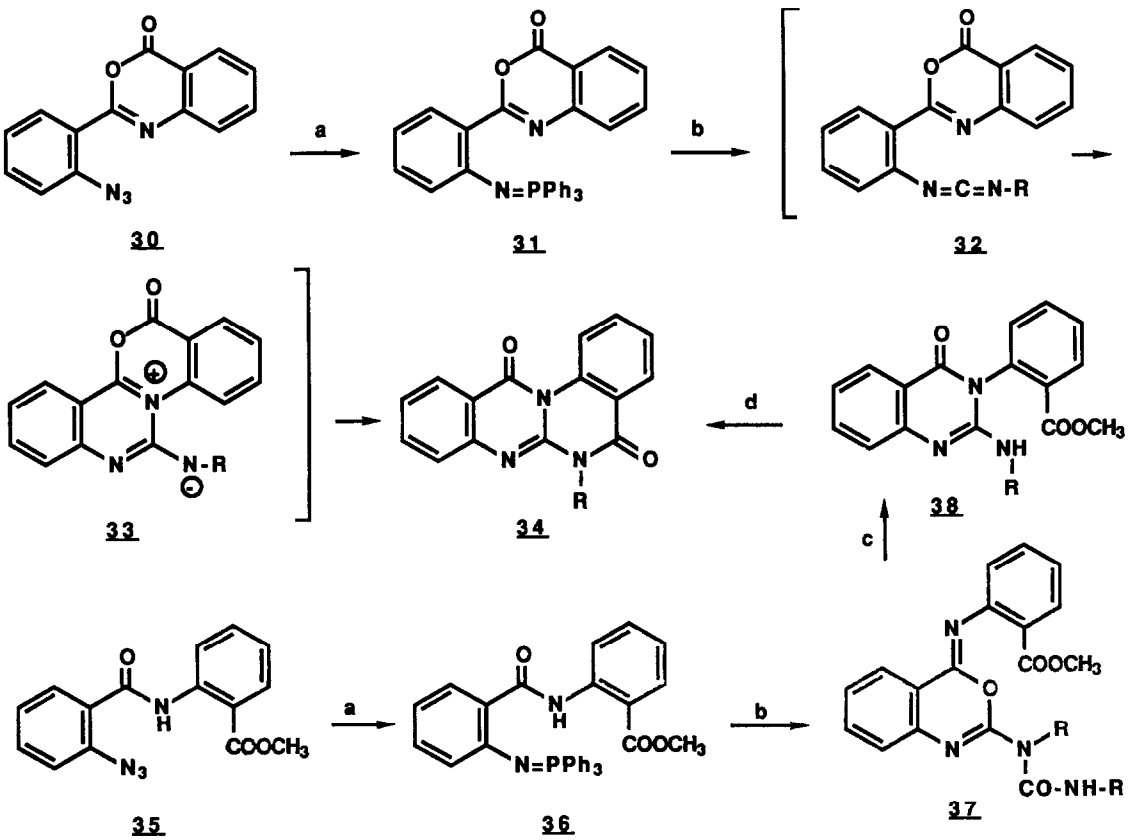
(a) o-phenylenediamine,DCC, CH_2Cl_2, room temperature.
(b) NaOAc, AcOH, reflux.
(c) Ph_3P, CH_2Cl_2, room tempetature.
(d) RNCO, benzene, room temperature.
(e) CS_2, toluene, 90° C.
(f) CO_2, toluene, 90° C.

Scheme III

Quinazolino[3,2-a]quinazolines.The 2-(o-azidophenyl)-4H-3,1-benzoxazin-4-one 30 was prepared by a previously reported procedure[14]. Compound 30 reacts with triphenylphosphine in dry methylene chloride at room temperature to give the iminophosphorane 31 in 93% yield. The reaction of iminophosphorane 31 with isocyanates at room temperature directly gave 6-substituted-12H-quinazolino [3,2-a]quinazoline-5(6H),12-diones 34, the yields of the isolated products

being higher than 70% (Method A). We believe that the mechanism of the conversion 31 ⟶ 34 involves initial aza-Wittig reaction between the iminophosphorane 31 and the isocyanate to give a carbodiimide 32 as intermediate which cyclized by nucleophilic attack of the nitrogen atom of the 3,1-benzoxazin-4-one on the sp-hybridized carbon atom of the carbodiimide group, to give 33 which undergoes a ring-opening/ring-closure sequence leading to 34.

Compounds 34 have also been prepared by an alternative route which involves the reaction of the o-azidobenzamide 35, readily available from o-azidobenzoyl chloride and methyl anthranilate, with triphenylphosphine in dry methylene chloride at room temperature to give the iminophosphorane 36 in 97% yield. The behaviour of this iminophosphorane towards isocyanates is similar to the previously described for iminophosphoranes 9. Thus, the reaction of 36 with isocyanates in dry methylene chloride at room temperataure led to 4-arylimino-3,1-benzoxazines 37. When compounds 37 were



(a) Ph_3P, CH_2Cl_2, room temperature. (b) RNCO, room temperature. (c) EtOH, reflux. (d) heating .

Scheme IV

heated at temperatures slightly above their melting points, they underwent a Dimroth-type rearrangement, followed by elimination of isocyanate and cyclization to give 34 (Method B). However, when compounds 37 were refluxed in ethanol the corresponding 2-arylamino-3-substituted-4(3H)-quinazolinones 38 were isolated, which were transformed by heating into 34 (Scheme IV).

Benzothiazolo[3,2-c]quinazolines. Crystal structure of compound 42a. The previously unreported benzothiazolo[3,2-c]quinazoline ring system has been prepared by the following approach: the 2-(o-azidophenyl)benzothiazole 39, available from 2-(o-aminophenyl)benzothiazole[15], reacted with triphenylphosphine in dry methylene chloride to give the iminophosphorane 40 in 86% yield. Reaction of iminophosphorane 40 with isocyanates or isothiocyanates in dry benzene at room temperature resulted in the formation of the corresponding benzothiazolo[3,2-c]quinazolines 42 directly as deep red crystalline solids in good yields.

To identify unambiguously compounds 42, an X-ray structure determination of compound 42a has been performed. Table II gives the main geometrical characteristics of 42a according to the numbering scheme shown[7] in Fig. 2. In 42a, a zwitterionic character is apparent, with double bonds at N18-C16 and C7-N18, which formally situate the positive charge at N8 and the negative one around N6. The substituent chain is almost orthogonal C7-N18-C19-O20= - 110.9(15)° with respect to the fused moiety. In this way, O21 is 1.267(12) Å from the least-squares plane C5, N6...C17 ring, and at 4.086(16) Å from its center. It seems worth noticing the different angular value at C2-N11-C13, in 11d, versus the analogous C7-N18-C19 in 42a. Compounds 11d and 42a build the respective crystals in different ways, as shown in Fig. 3.

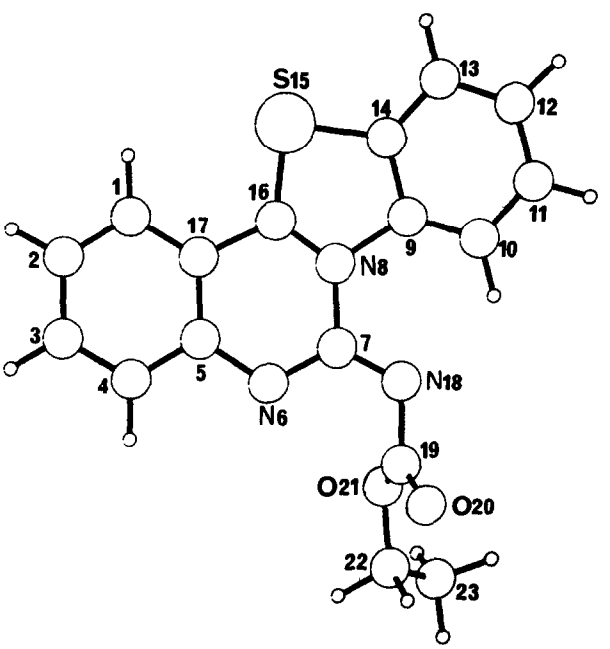
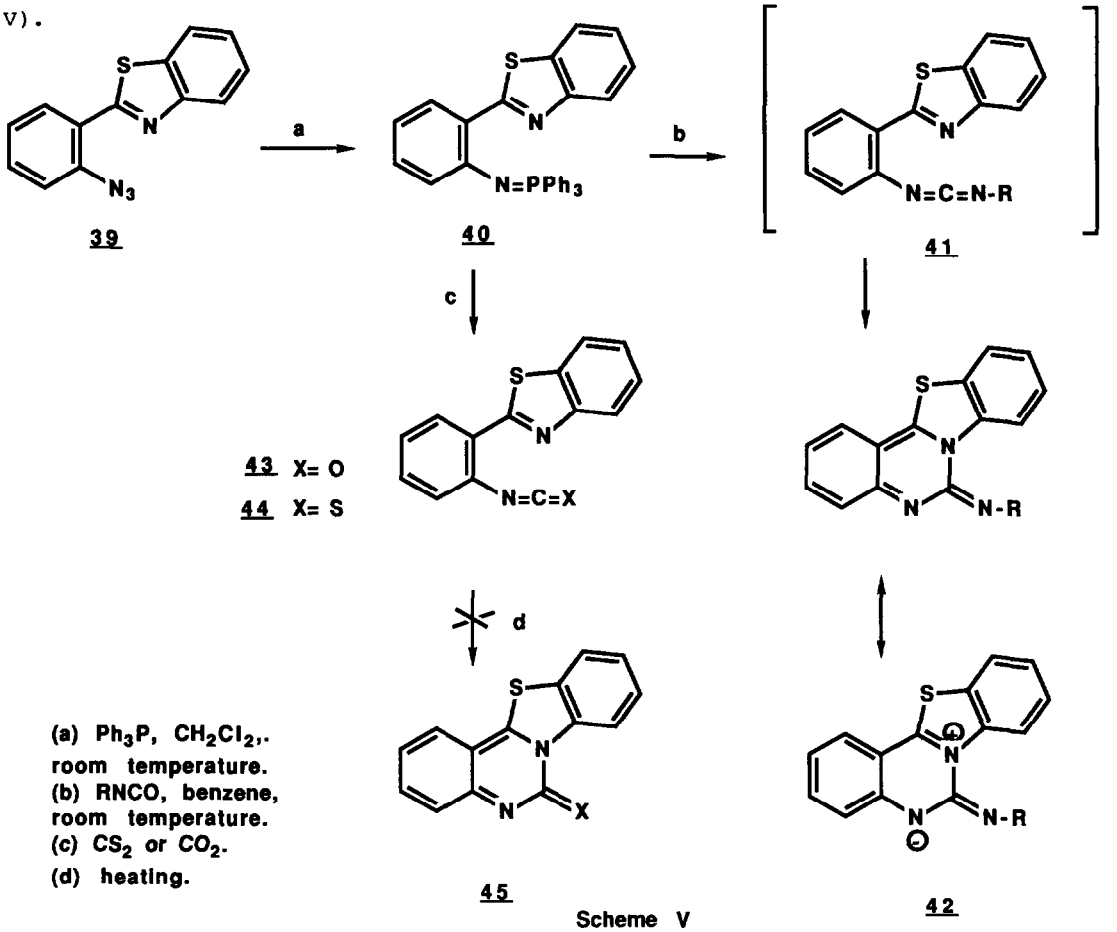


Fig. 2. Molecular structure with the numbering system used in the crystallography work for compound 42a.

We believe that the conversion 40 ⟶ 42 involves initial aza-Wittig reaction between the iminophosphorane 40 and the isocyanate to give a carbodiimide 41 as intermediate, which easily undergoes electrocyclic ring closure to give the fused quinazoline. This assumption is supported by the isolation of the isocyanate 43 and the isothiocyanate 44 in the reaction of iminophosphorane 40 with carbon dioxide or carbon disulfide respectively. Compounds 43 and 44, however, proved to be recalcitrant to cyclization by heating. They failed to form the benzothiazolo[3,2-c]quinazolines 45 (Scheme V).



Scheme V

The present study demonstrates that the tandem aza-Wittig/heterocumulene-mediated annulation strategy affords a new and general high-yield entry to a variety of substituted fused quinazolines. Due to the easy access of the starting materials, and due to the simplicity of the experimental one-pot procedure and extremely mild conditions, we think that the synthetic approach discussed here in many cases compares favorably with other existing methods. Application of this annulation approach to a number of other fused quinazolines can be anticipated.

Table II. Selected geometrical parameters (Å, °) for compound 42a.

C5-N6	1.390(16)	C5-C17	1.393(19)
N6-C7	1.349(15)	C7-N8	1.422(15)
C7-N18	1.281(17)	N8-C9	1.504(17)
N8-C16	1.271(18)	C9-C14	1.375(18)
C14-S15	1.767(12)	S15-C16	1.684(12)
C16-C17	1.474(18)	N18-C19	1.373(16)
C19-O20	1.186(18)	C19-O21	1.297(17)
O21-C22	1.447(20)	C22-C23	1.317(40)
N6-C5-C17	122.2(11)	C5-N6-C7	121.3(10)
N6-C7-N18	124.3(11)	N6-C7-N8	115.5(10)
N8-C7-N18	120.1(11)	C7-N8-C16	126.9(11)
C7-N8-C9	121.0(10)	C9-N8-C16	112.0(10)
N8-C9-C14	107.0(10)	C9-C14-S15	114.5(10)
C14-S15-C16	87.5(6)	N8-C16-S15	118.9(10)
S15-C16-C17	122.4(9)	N8-C16-C17	118.6(11)
C5-C17-C16	115.5(12)	C7-N18-C19	118.5(11)
N18-C19-O21	113.3(11)	N18-C19-O20	123.1(12)
O20-C19-O21	122.5(11)	C19-O21-C22	120.7(12)
O21-C22-C23	113.7(16)		
N6-C7-N18-C19	7.3(18)	C7-N18-C19-O20	-110.9(15)
C7-N18-C19-O21	81.4(15)	N18-C19-O21-C22	170.5(14)
C19-O21-C22-C23	-122.7(21)		
C10.....N18	2.844(16)	C10-H10	1.02(-)
H10.....N18	2.22(-)	O20.....C22	2.683(24)
O20.....H22B	2.27(-)	C22-H22B	1.05(2)

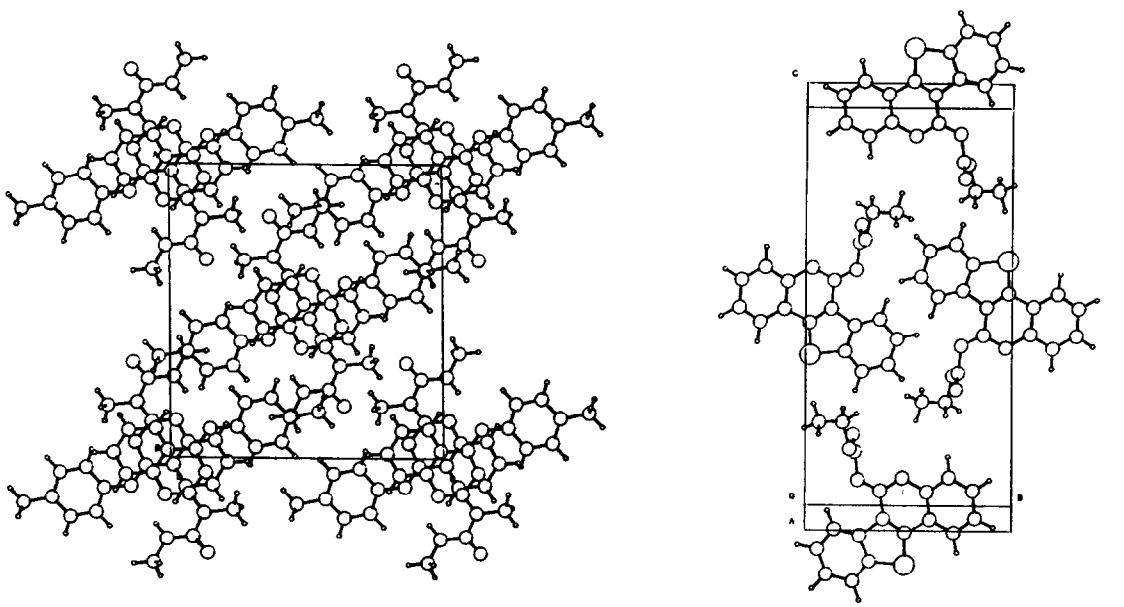


Fig. 3. (a) Packing of compound 11d projected along the b axis; (b) Packing of compound 42a projected along the a axis.

EXPERIMENTAL.

All melting points were determined on a Kofler hot-plate melting point apparatus and are uncorrected. I.R. spectra were obtained as Nujol emulsions on a Nicolet FT-5DX spectrophotometer. NMR spectra were recorded on one of the following spectrometers: Varian FT-80 (80 MHz) or Bruker AC-200 (200 MHz). Mass spectra were recorded on a Hewlett-Packard 5993C spectrometer. Microanalyses were performed on a Perkin-Elmer 240C instrument.

The crystallographic analises are summarized in Table III and the final atomic coordinates are presented in Tables IV and V. Lists of the structure factors, thermal components and hydrogen parameters have been deposited[16].The structures were solved by Direct Methods[17] and refined by least-squares procedures[18]. Empirical absorption correction[19] was carried out for compound 42a (Max-min transmission factors 1.86-0.63). All hydrogen atom were located on difference synthesis and included isotropically in the final stages of refinement (hydrogen parameters of compound 42a had to be kept fixed in the last cycles of refinement). Weigths were chosen as to give no trends in $\langle w\Delta^2F \rangle$ vs. $\langle |Fobs| \rangle$ and $\sin\theta/\lambda$. The atomic factors were taken from reference 20. All the calculations were performed on a VAX 11/750 computer.

Table III. Crystal analysis parameters at room temperature.

Compound	11d	42a
Formula	$C_{18}H_{18}N_4O_2$	$C_{17}H_{13}N_3O_2S$
Crystal habit	Colourless prism	Red prism
Crystal size (mm)	0.43x0.10x0.30	0.27x0.27x0.17
Symmetry	$P2_1/n$	$P2_1/c$
Unit cell determination:	Least-squares fit from 85 and 77 reflections ($\theta < 45°$)	
a(Å)	15.0297(5)	7.0672(3)
b(Å)	7.6376(2)	10.2310(7)
c(Å)	13.9678(6)	21.0004(25)
β(°)	90.997(3)	100.241(7)
V(Å^3)	1603.1(1)	1494.2(2)
Z	4	4
Dc(g.cm^{-3})	1.336	1.437
Mr	322.37	323.37
F(000)	680	672
μ(cm^{-1})	6.93	19.94
Technique	Four circle diffractometer, Philips PW1100 Bisecting geometry Graphite oriented monochromator: CuK_α ω/2θ scans, scan width: 1.6° Detector apertures 1.0x1.0°	
Total measurements	Up to 65 and 60° in θ respectively	
Speed	1 min./reflec.	
Independent reflections	2718	2362
Observed reflexions[3σ(I)]	1959	987
Standard reflections:	2 reflections every 90 minutes, no variation	
Number of variables	289	208
Final shift/error	0.17	0.01
Final ΔF peaks(e.Å^{-3})	0.18	0.64
Final R and R_w	0.049, 0.055	0.094,0.114

Table IV. FINAL ATOMIC COORDINATES AND THERMAL PARAMETERS AS IN: [a]

$U_{eq} = (1/3). \Sigma (U_{ij}.a^*_i.a^*_j.a_i.a_j.\cos(a_i,a_j))$

ATOM	x/a	y/b	z/c	$U_{eq}.10^4$
O1	0.5495(1)	0.3455(2)	0.3728(1)	484(5)
C2	0.6200(1)	0.3852(3)	0.4313(2)	425(6)
N3	0.6245(1)	0.3542(3)	0.5212(1)	493(6)
C4	0.5516(2)	0.2735(3)	0.5634(2)	452(7)
C5	0.5564(2)	0.2375(4)	0.6616(2)	552(8)
C6	0.4861(2)	0.1547(4)	0.7049(2)	594(9)
C7	0.4108(2)	0.1062(4)	0.6518(2)	619(9)
C8	0.4052(2)	0.1437(4)	0.5553(2)	571(8)
C9	0.4758(2)	0.2276(3)	0.5109(2)	455(7)
C10	0.4721(2)	0.2718(3)	0.4092(2)	459(7)
N11	0.6863(1)	0.4610(3)	0.3796(1)	479(6)
C12	0.6754(2)	0.4779(5)	0.2743(2)	603(9)
C13	0.7668(2)	0.5318(3)	0.4195(2)	492(7)
O14	0.8224(1)	0.5894(3)	0.3650(1)	748(7)
N15	0.7762(1	0.5319(3)	0.5135(2)	577(7)
C16	0.8559(2)	0.5983(5)	0.5602(2)	699(11)
N17	0.4039(1)	0.2515(3)	0.3568(1)	549(7)
C18	0.3964(2)	0.2993(3)	0.2589(2)	514(8)
C19	0.3141(2)	0.3610(5)	0.2284(2)	661(10)
C20	0.2975(2)	0.4040(5)	0.1339(2)	688(10)
C21	0.3619(2)	0.3833(4)	0.0655(2)	583(8)
C22	0.4440(2)	0.3204(4)	0.0962(2)	605(9)
C23	0.4623(2)	0.2789(4)	0.1916(2)	569(8)
C24	0.3419(3)	0.4202(6)	-0.0387(2)	759(12)

[a] *Compound 11d.*

Table V. FINAL ATOMIC COORDINATES AND THERMAL PARAMETERS AS IN: [b]

$U_{eq} = (1/3). \Sigma (U_{ij}.a^*_i.a^*_j.a_i.a_j.\cos(a_i,a_j))$

Atom	x/a	y/b	z/c	$U_{eq}.10^3$
C1	0.3051(18)	-0.2231(16)	0.4549(6)	78(6)
C2	0.3706(19)	-0.3241(14)	0.4933(9)	87(6)
C3	0.4038(19)	-0.3127(16)	0.5604(8)	87(6)
C4	0.3751(19)	-0.1979(15)	0.5887(6)	74(5)
C5	0.3137(15)	-0.0895(11)	0.5519(7)	61(5)
N6	0.2901(14)	0.0284(11)	0.5823(5)	67(4)
C7	0.2282(14)	0.1365(11)	0.5481(5)	51(4)
N8	0.1906(13)	0.1208(12)	0.4797(5)	69(4)
C9	0.1276(16)	0.2345(13)	0.4357(6)	63(5)
C10	0.0946(18)	0.3586(14)	0.4480(6)	70(5)
C11	0.0397(20)	0.4402(12)	0.3982(8)	82(6)
C12	0.0157(20)	0.4014(17)	0.3350(7)	89(6)
C13	0.0515(19)	0.2710(16)	0.3208(6)	78(5)
C14	0.1072(17)	0.1887(11)	0.3733(7)	66(5)
S15	0.1607(5)	0.0209(4)	0.3669(2)	78(1)
C16	0.2131(14)	0.0174(13)	0.4483(6)	63(4)
C17	0.2783(14)	-0.1023(13)	0.4847(7)	67(5)
N18	0.1948(16)	0.2462(11)	0.5733(5)	81(4)
C19	0.2437(20)	0.2604(11)	0.6392(6)	62(5)
O20	0.1283(14)	0.2702(9)	0.6736(4)	86(4)
O21	0.4242(15)	0.2867(12)	0.6585(4)	107(5)
C22	0.4952(34)	0.3244(26)	0.7249(8)	148(10)
C23	0.5819(48)	0.4388(28)	0.7307(10)	203(16)

[b] *Compound 42a.*

N-Substituted o-azidobenzamides[5] 8 and 35, 2-(o-azidophenyl)-4H-3,1-benzoxazin-4-one[14] 30, and 2-(o-azidophenyl)benzothiazole[15] 40 were prepared as described in the literature.

Preparation of Iminophosphoranes 9, 16 and 19.

A solution of triphenylphosphine (2.62 g, 10 mmol) in dry ether (25 ml) was added dropwise under nitrogen at room temperature to a well-stirred solution of the appropriate o-azidobenzamide 8, 15 or 18 (10 mmol) in dry methylene chloride (25 ml). The reaction mixture was stirred at room temperature for 3 h, and the solvent was removed off under reduced pressure at 25°C.The residual material was recrystallized from benzene/hexane (5:1) to give the corresponding iminophosphorane.

N-Methyl o-(triphenylphosphoranylidene)amino benzamide 9a. (60%), m.p. 225°C (white prisms). (Found: C, 75.91; H, 5.43; N, 6.68. $C_{26}H_{23}N_2OP$ requires: C, 76.08; H, 5.65; N, 6.82); i.r. (Nujol): 3190, 1636, 1591, 1558, 1446, 1343, 1275, 1110, 1019, 721, 689 and 602 cm^{-1}; δ ($CDCl_3$): 3.00 (d, 3H, J= 4.75 Hz, CH_3), 6.50-8.60 (m, 19H, aryl), 11.45 (s broad, 1H, NH); m/z (%): 410 (M^+, 16), 409 (30), 352 (41), 262 (11), 201 (27), 198 (22), 184 (15), 183 (100), 152 (20), 108 (24), 77 (29).

N-(p-Tolyl) o-(triphenylphosphoranylidene)amino benzamide 9b. (85%), m.p. 203-204°C (white prisms). (Found: C, 79.17; H, 5.63; N, 5.48. $C_{32}H_{27}N_2OP$ requires: C, 78.99; H, 5.59; N, 5.56); i.r. (Nujol): 3200, 1654, 1589, 1536, 1438, 1332, 1262, 1107, 757, 720 and 682 cm^{-1}; δ ($CDCl_3$): 2.32 (s, 3H, CH_3), 6.50-8.60 (m, 23H, aryl), 13.68 (s broad, 1H, NH); m/z (%): 486 (M^+, 15), 381 (18), 379 (71), 277 (13), 262 (20), 201 (82), 198 (12), 184 (19), 183 (100), 152 (20), 120 (12), 108 (28), 107 (24), 91 (10), 77 (29).

N,N-Dimethyl o-(triphenylphosphoranylidene)amino benzamide 16. (84%), m.p. 170°C (white prisms). (Found: C, 76.48; H, 6.19; N, 6.43. $C_{27}H_{25}N_2OP$ requires: C, 76.39; H, 5.94; N, 6.56); i.r. (Nujol): 1625, 1591, 1342, 1274, 1109, 1047, 752, 719 and 696 cm^{-1}; δ ($CDCl_3$): 2.97 (s, 3H, CH_3N), 3.23 (s, 3H, CH_3N), 6.45-7.95 (m, 19H, aryl); m/z (%): 424 (M^+, 63), 409 (31), 394 (28), 380 (29), 352 (45), 262 (44), 183 (100), 91 (44), 77 (25).

o-(Triphenylphosphoranylidene)amino benzamide 19. (63%), m.p. 208-209°C (colourless prisms). (Found: C, 75.66; H, 5.59; N, 6.83. $C_{25}H_{21}N_2OP$ requires: C, 75.74; H, 5.34; N, 7.01); i.r. (Nujol): 3260, 3190, 1653, 1589, 1320, 1280, 1109, 1013, 749 and 695 cm^{-1}; δ ($CDCl_3$): 6.05 (s broad, 1H, NH), 6.65-8.15 (m, 18H, aryl), 8.25-8.55 (m, 1H, aryl), 10.15 (s, 1H, NH); m/z (%): 396 (M^+, 58), 395 (21), 380 (17), 378 (44), 262 (43), 183 (100), 134 (26), 77 (31).

General Procedure for the Preparation of 2-Amino-4H-3,1-benzoxazin-4-imines 11

To a solution of the corresponding iminophosphorane 9 (2.5 mmol) in dry methylene chloride (25 ml) was added the appropriate isocyanate (5 mmol). The reaction mixture was stirred at room temperature for 24 h, the solvent was removed off under reduced pressure and the residual material was slurried in cold ethanol (5 ml) and stirred for 15 min, and the separated solid was collected by filtration and recrystallized from benzene/hexane (2:1) to give 11 as crystalline solids. The following derivatives 11 were obtained:

11a (R^1=CH_3, R^2= C_6H_5) (75%), m.p. 138-140°C (colourless prisms). (Found: C, 71.30; H, 4.81; N, 15.09. $C_{22}H_{18}N_4O_2$ requires: C, 71.34; H, 4.89; N, 15.12); i.r. (Nujol): 3219, 1710, 1693, 1630, 1596, 1562, 1347, 1297, 1274 and 760 cm^{-1}; δ ($CDCl_3$): 2.57 (s, 3H, CH_3-N), 7.00-8.30

(m, 14H, aryl), 12.79 (s broad, 1H, NH); m/z (%): 251 (M^+ - C_6H_5NCO, 26), 250 (18), 235 (8), 222 (10), 207 (8), 167 (12), 160 (10), 159 (100), 146 (10), 132 (8), 119 (42), 91 (24), 77 (10).

11b (R^1= CH_3, R^2= p-Cl-C_6H_4) (89%), m.p. 132-134°C (colourless prisms). (Found: C, 59.93; H, 3.55; N, 12.66. $C_{22}H_{16}Cl_2N_4O_2$ requires: C, 60.15; H, 3.67; N, 12.75); i.r. (Nujol): 3200, 1709, 1626, 1601, 1559, 1343, 1298, 1273, 1009, 976 and 771 cm^{-1}; δ ($CDCl_3$): 2.66 (s, 3H, CH_3-N), 6.70-8.25 (m, 12H, aryl), 12.83 (s, 1H, NH); m/z (%): 357 (8), 356 (10), 287 (9), 286 (10), 285 (30), 284 (17), 265 (20), 264 (36), 236 (7), 235 (32), 160 (7), 159 (75), 155 (29), 153 (100), 127 (20), 125 (54), 91 (26), 90 (60), 77 (13).

11c (R^1= CH_3, R^2= p-H_3CO-C_6H_4) (86%), m.p. 130-132°C (colourless prisms). (Found: C, 67.13; H, 5.19; N, 12.87. $C_{24}H_{22}N_4O_4$ requires: C, 66.96; H, 5.15; N, 13.01); i.r. (Nujol): 3199, 1706, 1694, 1628, 1604, 1565, 1509, 1296, 1276, 1246, 1225, 1179 and 833 cm^{-1}; δ ($CDCl_3$): 2.63 (s, 3H, CH_3-N), 3.82 (s, 3H, CH_3O), 3.87 (s, 3H, CH_3O), 6.75-8.05 (m, 12H, aryl), 12.49 (s, 1H, NH); m/z (%): 357 (5), 281 (12), 280 (5), 266 (5), 251 (6), 250 (6), 159 (22), 149 (100), 134 (62), 119 (5), 106 (40), 90 (10), 78 (21).

11d (R^1= p-H_3C-C_6H_4, R^2= CH_3) (74%), m.p. 157-159°C (colourless prisms). (Found: C, 66.92; H, 5.42; N, 17.41. $C_{18}H_{18}N_4O_2$ requires: C, 67.06; H, 5.63; N, 17.38); i.r. (Nujol): 3216, 1693, 1619, 1555, 1358, 1131 and 771 cm^{-1}; δ ($CDCl_3$): 2.42 (s, 3H, CH_3-N), 3.00 (d, 3H, J= 5 Hz, CH_3-NH), 3.20 (s, 3H, Ar-CH_3), 6.55-7.95 (m, 7H, aryl), 8.20-8.50 (m, 1H, aryl), 9.95 (s broad, 1H, NH); m/z (%): 322 (M^+, 17), 265 (M^+ - CH_3NCO, 35), 264 (100), 236 (15), 235 (74), 159 (60), 146 (12), 132 (12), 131 (17), 120 (22), 105 (11), 91 (56), 90 (33), 77 (11).

11e (R^1= p-H_3C-C_6H_4, R^2= C_6H_5) (86%), m.p. 142-144°C (colourless prisms). (Found: C, 75.43; H, 5.09; N, 12.39. $C_{28}H_{22}N_4O_2$ requires: C, 75.32; H, 4.96; N, 12.55); i.r. (Nujol): 3200, 1710, 1682, 1625, 1602, 1557, 1505, 1309, 1294, 1189, 976, 765 and 752 cm^{-1}; δ ($CDCl_3$): 2.28 (s, 3H, Ar-CH_3), 6.55-7.95 (m, 17H, aryl), 8.20-8.50 (m, 1H, aryl), 12.83 (s broad, 1H, NH); m/z (%): 327 (M^+ - C_6H_5NCO, 32), 326 (43), 236 (27), 235 (100), 221 (24), 220 (12), 208 (11), 207 (8), 192 (11), 180 (5), 167 (5), 91 (30), 90 (12), 77 (13).

11f (R^1= p-H_3C-C_6H_4, R^2= p-Cl-C_6H_4) (75%), m.p. 184-186°C (colourless prisms). (Found: C, 65.33; H, 4.18; N, 10.70. $C_{28}H_{20}Cl_2N_4O_2$ requires: C, 65.25; H, 3.91; N, 10.87); i.r. (Nujol): 3182, 1716, 1693, 1625, 1596, 1557, 1507, 1298, 1282, 1245, 1223, 1191, 986, 797 and 774 cm^{-1}; δ ($CDCl_3$): 2.40 (s, 3H, Ar-CH_3), 7.15-8.35 (m, 16H, aryl), 9.12 (s broad, 1H, NH); m/z (%): 363 (20), 362 (44), 361 (69), 360 (100), 236 (15), 235 (86), 220 (11), 192 (18), 117 (15), 116 (17), 99 (16), 91 (71), 90 (43), 77 (12).

11g (R^1= p-H_3C-C_6H_4, R^2= m-Cl-C_6H_4) (82%), m.p. 144-146°C (colourless prisms). (Found: C, 65.39; H, 4.16; N, 11.03. $C_{28}H_{20}Cl_2N_4O_2$ requires: C, 65.25; H, 3.91; N, 10.87); i.r. (Nujol): 3190, 1715, 1687, 1625, 1591, 1545, 1506, 1285, 1220, 1186, 1169, 772 and 689 cm^{-1}; δ($CDCl_3$): 2.32 (s, 3H, Ar-CH_3), 6.55-7.85 (m, 15H, aryl), 8.20-8.50 (m, 1H, aryl), 12.85 (s, 1H, NH); m/z (%): 363 (17), 362 (32), 361 (55), 360 (70), 236 (10), 235 (60), 192 (16), 180 (10), 166 (5), 144 (6), 117 (19), 116 (24), 111 (16), 99 (22), 91 (100), 77 (16).

11h (R^1= p-H_3C-C_6H_4, R^2= p-H_3C-C_6H_4) (84%), m.p. 168-170°C (colourless prisms). (Found: C, 76.18; H, 5.37; N, 11.67. $C_{30}H_{26}N_4O_2$ requires: C, 75.93; H, 5.52; N, 11.80); i.r. (Nujol): 3210, 1716, 1681, 1625, 1602, 1557, 1512, 1291, 1274, 1189, 1172, 979 and 778 cm^{-1}; δ

($CDCl_3$): 2.30 (s, 3H, Ar-CH_3), 2.35 (s, 3H, Ar-CH_3), 2.44 (s, 3H, Ar-CH_3), 6.55-7.75 (m, 15H, aryl), 8.20-8.50 (m, 1H, aryl), 12.71 (s broad, 1H, NH); m/z (%): 341 (10), 340 (11), 235 (29), 220 (10), 192 (10), 134 (15), 133 (100), 132 (51), 105 (16), 104 (42), 91 (22),.

11i (R^1= p-H_3C-C_6H_4, R^2= m-H_3C-C_6H_4) (90%), m.p. 126-128°C (colourless prisms) (Found: C, 76.12; H, 5.26; N, 11.63. $C_{30}H_{26}N_4O_2$ requires: C, 75.93; H, 5.52; N, 11.80); i.r. (Nujol): 3183, 1710, 1676, 1624, 1605, 1592, 1565, 1508, 1299, 1291, 1272, 1206, 1190, 1006, 778 and 694 cm^{-1}; δ ($CDCl_3$): 2.33 (s, 6H, Ar-CH_3), 2.39 (s, 3H, Ar-CH_3), 6.55-7.85 (m, 15H, aryl), 8.20-8.50 (m, 1H, aryl), 12.80 (s broad, 1H, NH); m/z (%): 342 (13), 341 (68), 340 (100), 250 (11), 236 (11), 235 (66), 220 (10), 192 (15), 180 (10), 152 (8), 131 (10), 117 (12), 116 (18), 91 (79), 90 (32), 77 (29).

11j (R^1= p-H_3C-C_6H_4, R^2= p-H_3CO-C_6H_4) (87%), m.p. 166-168°C (colourless prisms). (Found: C, 71.29; H, 5.03; N, 10.92. $C_{30}H_{26}N_4O_4$ requires: C, 71.13; H, 5.17; N, 11.06); i.r. (Nujol): 3233, 1704, 1687, 1626, 1601, 1560, 1510, 1294, 1275, 1261, 1247, 1219, 1189, 1178, 1167, 973, 823 and 774 cm^{-1}; δ ($CDCl_3$): 2.30 (s, 3H, Ar-CH_3), 3.84 (s, 3H, CH_3O), 3.90 (s, 3H, CH_3O), 6.55-7.40 (m, 16H, aryl), 12.63 (s, 1H, NH); m/z (%): 358 (17), 357 (80), 356 (100), 266 (10), 251 (8), 250 (5), 237 (10), 236 (13), 235 (58), 223 (10), 220 (10), 210 (10), 208 (12), 192 (15), 182 (10), 122 (15), 116 (20), 91 (57), 90 (30), 77 (15).

11k (R^1= p-H_3C-C_6H_4, R^2= m-H_3CO-C_6H_4) (81%), m.p. 124-126°C (colourless prisms). (Found: C, 72.95; H, 5.26; N, 10.89. $C_{30}H_{26}N_4O_4$ requires: C, 71.13; H, 5.17; N, 11.06); i.r. (Nujol): 3209, 1716, 1687, 1625, 1608, 1595, 1560, 1506, 1301, 1287, 1274, 1215, 1190, 1168, 993, 775 and 759 cm^{-1}; δ ($CDCl_3$): 2.31 (s, 3H, Ar-CH_3), 3.72 (s, 3H, CH_3O), 3.84 (s, 3H, CH_3O), 6.55-7.80 (m, 15H, aryl), 8.15-8.35 (m, 1H, aryl), 12.75 (s, 1H, NH); m/z (%): 357 (35), 356 (41), 236 (19), 235 (100), 220 (10), 208 (10), 192 (12), 179 (11), 116 (10), 91 (51), 77 (13).

General Procedure for the Preparation of 3-Substituted 2-Alkyl(aryl)amino-4(3H)-quinazolinones 12.

Method A.

A solution of the appropriate 4H-3,1-benzoxazin-4-imine 11 (5 mmol) in ethanol (50 ml) was heated at reflux temperature for 12 h. After cooling, the solvent was removed off under reduced pressure and the residue was slurried in cold hexane (20 ml), the separated solid was collected by filtration and recrystallized from the appropriate solvent to give 12 as crystalline solids.

Method B.

To a solution of the corresponding iminophosphorane 9 (5 mmol) in dry toluene (50 ml) was added the appropriate isocyanate (10 mmol). The reaction mixture was stirred at reflux temperature for 24 h. After cooling, the solvent was removed off under reduced pressure and the residual material was slurried in cold hexane (20 ml) and the separated solid was collected by filtration and recrystallized from the appropriate solvent to give 12.

12a 2-Phenylamino-3-methyl (97%), m.p. 208-210°C (white prisms from methanol). (Found: C, 71.55; H, 5.38; N, 16.61. $C_{15}H_{13}N_3O$ requires: C, 71.69; H, 5.21; N, 16.72); i.r. (Nujol): 3358, 1676, 1613, 1579, 1562, 1523, 1291, 1240, 766 and 693 cm^{-1}; δ (DMSO-d_6): 3.70 (s, 3H,

CH_3-N), 6.85-8.45 (m, 9H, aryl), 8.66 (s, 1H, NH); m/z (%): 251 (M^+, 98), 250 (100), 222 (46), 195 (14), 159 (11), 146 (60), 132 (19), 126 (12), 119 (28), 106 (10), 93 (50), 92 (36), 91 (38), 90 (50), 77 (53).

12b 2-(p-Chlorophenyl)amino-3-methyl (98%), m.p. 185-187°C (colourless prisms from methanol). (Found: C, 62.91; H, 4.37; N, 14.61. $C_{15}H_{12}ClN_3O$ requires: C, 63.05; H, 4.23; N, 14.70); i.r. (Nujol): 3386, 1659, 1602, 1585, 1571, 1539, 1292, 1233, 1192, 1013 and 763 cm^{-1}; δ (DMSO-d_6): 3.40 (s, 3H, CH_3-N), 6.85-8.25 (m, 8H, aryl), 8.87 (s, 1H, NH); m/z (%): 287 (M^+ + 2, 9), 286 (10), 285 (M^+, 30), 284 (100), 277 (17), 265 (20), 264 (36), 236 (7), 235 (32), 159 (75), 155 (295, 146 (16), 127 (20), 125 (54), 91 (26), 90 (60), 77 (13).

12c 2-(p-Methoxyphenyl)amino-3-methyl (96%), m.p. 232-234°C (colourless prisms from methanol). (Found: C, 68.43; H, 5.21; N, 15.19. $C_{16}H_{15}N_3O_2$ requires: C, 68.31; H, 5.37; N, 14.93); i.r. (Nujol): 3352, 1664, 1613, 1579, 1562, 1517, 1240, 826 and 769 cm^{-1}; δ (DMSO-d_6): 3.63 (s, 3H, CH_3-N), 3.82 (s, 3H, CH_3O), 6.75-8.20 (m, 8H, aryl), 8.60 (s, 1H, NH); m/z (%): 281 (M^+, 14), 280 (100), 266 (10), 252 (10), 251 (8), 250 (8), 159 (22), 150 (15), 149 (18), 134 (62), 106 (40), 90 (10), 78 (21).

12d 2-Methylamino-3-(p-tolyl) (93%), m.p. 160-162°C (colourless prisms from ether). (Found: C, 72.24; H, 5.79; N, 16.03. $C_{16}H_{15}N_3O$ requires: C, 72.43; H, 5.69; N, 15.84); i.r. (Nujol): 3375, 1674, 1612, 1589, 1515, 1311, 1152 and 772 cm^{-1}; δ ($CDCl_3$): 2.47 (s, 3H, Ar-CH_3), 3.00 (d, 3H, J= 5.0 Hz, CH_3-NH), 4.28 (m, 1H, NH), 7.25-8.35 (m, 8H, aryl);m/z (%): 265 (M^+, 35), 264 (100), 236 (15), 235 (74), 159 (60), 131 (17), 120 (22), 91 (56), 90 (33), 77 (11).

12e 2-Phenylamino-3-(p-tolyl) (97%), m.p. 193-195°C (white prisms from ether). (Found: C, 76.91; H, 5.42; N, 12.66. $C_{21}H_{17}N_3O$ requires: C, 77.04; H, 5.23; N, 12.83); i.r. (Nujol): 3141, 1682, 1613, 1589, 1567, 1536, 1513, 1247, 771, 763 and 689 cm^{-1}; δ ($CDCl_3$): 2.47 (s, 3H, Ar-CH_3), 6.07 (s, 1H, NH), 6.95-8.35 (m, 13H, aryl); m/z (%): 327 (M^+, 66), 326 (100), 277 (11), 236 (48), 235 (99), 221(56), 220 (31), 208 (26), 195 (16), 192 (24), 116 (15), 91 (70), 90 (37), 77 (47).

12f 2-(p-Chlorophenyl)amino-3-(p-tolyl) (92%), m.p. 187-189°C (colourless prisms from ether). (Found: C, 69.58; H, 4.66; N, 11.82. $C_{21}H_{16}ClN_3O$ requires: C, 69.71; H, 4.46; N, 11.61); i.r. (Nujol): 3313, 1676, 1608, 1579, 1562, 1540, 1319 and 768 cm^{-1}; δ ($CDCl_3$): 2.53 (s, 3H, Ar-CH_3), 6.10 (s, 1H, NH), 7.15-7.75 (m, 11H, aryl), 8.15-8.45 (m, 1H, aryl); m/z (%): 363 (M^+ + 2, 19), 362 (41), 361 (M^+, 55), 360 (80), 236 (12), 235 (67), 194 (6), 192 (18), 126 (10), 119 (6), 117 (23), 116 (28), 99 (23), 91 (100), 90 (60), 77 (18).

12g 2-(m-Chlorophenyl)amino-3-(p-tolyl) (99%), m.p. 187°C (colourless prisms from ether). (Found: C, 69.93; H, 4.59; H, 11.76. $C_{21}H_{16}ClN_3O$ requires: C, 69.71; H, 4.46; N, 11.61); i.r. (Nujol): 3268, 1668, 1607, 1587, 1578, 1568, 1538, 1303 and and 768 cm^{-1}; δ ($CDCl_3$): 2.50 (s, 3H, Ar-CH_3), 6.13 (s, 1H, NH), 6.95-8.35 (m, 12H, aryl); m/z (%): 363 (M^+ +2, 15), 362 (28), 361 (M^+, 46), 360 (64), 236 (11), 235 (70), 192 (18), 180 (10), 117 (16), 116 (25), 99 (17), 91 (100), 90 (61), 77 (19).

12h 2-(p-Tolyl)amino-3-(p-tolyl) (97%), m.p. 158-159°C (colourless prisms from ether). (Found: C, 77.52; H, 5.55; N, 12.16. $C_{22}H_{19}N_3O$ requires: C, 77.39; H, 5.61; N, 12.31); i.r. (Nujol): 3324, 1676, 1594, 1580, 1563, 1540, 1513, 1311, 1233, 812 and 771 cm^{-1}; δ ($CDCl_3$): 2.33 (s, 3H, Ar-CH_3), 2.50 (s, 3H, Ar-CH_3), 6.03 (s, 1H, NH), 6.95-7.85 (m, 11H, aryl),

8.15-8.35 (m, 1H, aryl); m/z (%): 341 (M^+, 65), 340 (100), 250 (22), 236 (15), 235 (96), 222 (20), 221 (17), 220 (39), 209 (27), 208 (30), 192 (26), 180 (18), 116 (18), 91 (81).

12i 2-(m-Tolyl)amino-3-(p-tolyl) (97%), m.p. 176-178°C (colourless prisms from ether). (Found: C, 77.61; H, 5.43; N, 12.22. $C_{22}H_{19}N_3O$ requires: C, 77.39; H, 5.61; N, 12.31); i.r. (Nujol): 3273, 1668, 1607, 1589, 1565, 1543, 1511, 1303, 1252, 768 and 703 cm^{-1}; δ ($CDCl_3$): 2.33 (s, 3H, Ar-CH_3), 2.47 (s, 3H, Ar-CH_3), 6.03 (s, 1H, NH), 6.85-7.85 (m, 11H, aryl), 8.05-8.45 (m, 1H, aryl); m/z (%): 341 (M^+, 73), 340 (100), 235 (54), 220 (105, 208 (10), 117 (15), 91 (64), 90 (25), 77 (19).

12j 2-(p-Methoxyphenyl)amino-3-(p-tolyl) (98%), m.p. 156-158°C (white prisms from ether). (Found: C, 74.16; H, 5.21; N, 11.68. $C_{22}H_{19}N_3O_2$ requires: C, 73.93; H, 5.36; N, 11.76); i.r. (Nujol): 3324, 1676, 1591, 1564, 1538, 1509, 1301, 1236 and 768 cm^{-1}; δ ($CDCl_3$): 2.10 (s, 3H, Ar-CH_3), 3.43 (s, 3H, CH_3O), 5.60 (s, 1H, NH), 6.45-8.05 (m, 12H, aryl); m/z (%): 357 (M^+, 81), 356 (100), 235 (39), 192 (13), 122 (16), 117 (17), 116 (20), 91 (91), 90 (43).

12k 2-(m-Methoxyphenyl)amino-3-(p-tolyl) (94%), m.p. 136-138°C (white prisms from ether). (Found: C, 73.84; H, 5.54; N, 11.87. $C_{22}H_{19}N_3O_2$ requires: C, 73.93; H, 5.36; N, 11.76); i.r. (Nujol): 3269, 1670, 1605, 1591, 1566, 1541, 1304, 1201, 812 and 768 cm^{-1}; δ ($CDCl_3$): 2.23 (s, 3H, Ar-CH_3), 3.51 (s, 3H, CH_3O), 5.83 (s, 1H, NH), 6.55-7.95 (m, 12H, aryl); m/z (%): 357 (M^+, 55), 356 (71), 251 (15), 236 (18), 235 (56), 192 (17), 180 (10), 178 (10), 117 (20), 116 (18), 92 (25), 91 (100), 90 (48), 77 (23).

3-Methyl-4-oxo-2-thioxo-1,2,3,4-tetrahydroquinazolinone 13.

The appropriate iminophosphorane 9 (R^1= CH_3) (1.02 g, 2.5 mmol) in dry toluene (25 ml), and excess of carbon disulfide (6 ml) were heated in a sealed tube at 90°C for 10 h. After cooling, the solvent was removed under reduced pressure and the crude product was slurried with ether (10 ml) filtrated, and recrystallized from toluene to give 13: yield 96%, m.p. 273-275°C as yellow prisms (lit.[21] 248-250°C).

3-Substituted 2,4-Dioxo-1,2,3,4-tetrahydroquinazolinones 14.

The appropriate iminophosphorane 9 (6 mmol), dry toluene (40 ml), and excess of solid carbon dioxide were heated in a sealed tube at 90°C for 15 h. After cooling, the solvent was removed off under reduced pressure and the crude product was slurried with ether (40 ml), filtered and recrystallized from toluene to give 14 as crystalline solids.

14a: yield 96%, m.p. 248-250°C (lit.[22] 244-245°C).

14b: yield 84%, m.p. 267-268°C (lit.[23] 266-267°C).

Reaction of Iminophosphorane 16 with Isocyanates.

To a solution of iminophosphorane 16 (R^1= R^2= CH_3) (0.85 g, 2 mmol) in dry methylene chloride (20 ml) was added p-tolylisocyanate (0.266 g, 2 mmol). The resultant mixture was stirred at room temperature for 6 h, the solvent was removed off under reduced pressure and the residual material was extracted with hexane (3 x 25 ml). The combined extracts were concentrated to dryness to give the carbodiimide 17 (R^1= R^2= CH_3, R^3= p-H_3C-C_6H_4) (85%) as viscous oil; i.r. (Nujol): 2140, 2106, 1636, 1602, 1398, 1200, 1064, 820 758 and 724 cm^{-1}; δ ($CDCl_3$): 2.36 (s, 3H, Ar-CH_3), 2.96 (s, 3H, CH_3-N), 3.16 (s, 3H, CH_3-N), 7.15-8.20 (m, 8H, aryl); m/z (%): 279 (M^+, 100).

Reaction of Iminophosphorane 19 with Isocyanates.

To a solution of iminophosphorane 19 (1.0 g, 2.5 mmol) in dry methylene chloride (25 ml) was added the appropriate isocyanate (2.5 mmol). The reaction mixture was stirred at room temperature for 24 h. Then the separated solid was collected by filtration, washed with ether (2 x 5 ml), dried and recrystallized from ethanol to give 22.

N-(o-Cyanophenyl)-N'-(p-chlorophenyl)urea 22a (89%), m.p. 230-231°C (colourless prisms). (Found: C, 62.13; H, 3.54; N, 15.33. $C_{14}H_{10}ClN_3O$ requires: C, 61.89; H, 3.71; N, 15.46); i.r. (Nujol): 3336, 3296, 2231, 1693, 1630, 1608, 1591, 1558, 1302 and 758 cm^{-1}; δ (DMSO-d_6): 7.25-8.25 (m, 8H, aryl), 8.91 (s, 1H, NH), 9.62 (s, 1H, NH); m/z (%): 273 (M^+ +2, 3), 271 (M^+, 9), 270 (10), 129 (18), 127 (69), 118 (100), 99 (11), 91 (13).

N-(o-Cyanophenyl)-N'-(p-tolyl)urea 22b (77%), m.p. 215-216°C (colourless prisms). (Found: C, 71.54; H, 5.38; N, 16.94. $C_{15}H_{13}N_3O$ requires: C, 71.69; H, 5.21; N, 16.72); i.r. (Nujol): 3330, 3267, 2231, 1710, 1647, 1608, 1585, 1552, 1305, 1295, 1237 and 758 cm^{-1}; δ (DMSO-d_6): 2.32 (s, 3H, Ar-CH_3), 7.05-8.05 (m, 7H, aryl), 8.10-8.35 (m, 1H, aryl), 8.78 (s, 1H, NH), 9.42 (s, 1H, NH); m/z (%): 251 (M^+, 16), 145 (5), 133 (17), 118 (100), 107 (35), 106 (45), 91 (16), 77 (19).

2-(o-Azidophenyl)benzimidazole 25.

o-Azidobenzoic acid (3.26 g, 20 mmol), o-phenylenediamine (2.16 g, 20 mmol) and dicyclohexylcarbodiimide (4.12 g, 20 mmol) in methylene chloride (75 ml) were stirred at 0°C for 30 min, then the mixture was allowed to warm at room temperature and stirred for 2 h. The precipitated solid was separated by filtration and the filtrate was concentrated under reduced pressure to dryness. The residual material was recrystallized from ethanol to give 24 (75%) as colourless needles, m.p. 145-147°C. (Found: C, 61.51; H, 4.56; N, 27.39. $C_{13}H_{11}N_5O$ requires: C, 61.65; H, 4.38; N, 27.65); i.r. (Nujol): 3409, 3262, 2123, 1095, 1636, 1602, 1528, 1296, 1155 and 752 cm^{-1}; δ (DMSO-d_6): 4.93 (s, 2H, NH_2), 6.55-8.15 (m, 8H, aryl), 9.73 (s, 1H, NH); m/z (%): 253 (M^+, 27), 225 (21), 208 (28), 197 (17), 196 (25), 185 (22), 169 (10), 120 (100), 119 (31), 93 (60), 92 (56), 90 (54), 77 (10).

To a solution of 24 (5.06 g, 20 mmol) in acetic acid (50 ml) was added sodium acetate (2.72 g, 20 mmol). The reaction mixture was refluxed for 1 h. After cooling, the solvent was removed off under reduced pressure to give a crude solid which washed with water (3 x 50 ml), dried and recrystallized from ethanol/water (1:1) gave 25 (72%) as yellow crystals, m.p. 187-189°C. (Found: C, 66.59; H, 3.64; N, 29.92. $C_{13}H_9N_5$ requires: C, 66.37; H, 3.86; N, 29.77); i.r. (Nujol): 2129, 1089, 1299 and 749 cm^{-1}; δ ($CDCl_3$): 7.15-7.95 (m, 7H, aryl), 8.65-8.90 (m, 1H, aryl), 9.23 (s, 1H, NH); m/z (%): 235 (M^+, 24), 208 (15), 207 (100), 206 (44), 181 (16), 179 (29), 156 (19), 129 (12), 103 (21), 92 (28), 91 (14), 77 (26).

2-(o-Triphenylphosphoranylideneamino)phenyl benzimidazole 26.

A solution of 2-(o-azidophenyl)benzimidazole 25 (3.52 g, 15 mmol) in dry methylene chloride (25 ml) was added dropwise at room temperature to a well stirred solution of triphenylphosphine (3.93 g, 15 mmol) in ether (25 ml). The reaction mixture was stirred at room temperature for 3 h. Then, the solvent was removed off under reduced pressure at 25°C and the remaining solid recrystallized from benzene/hexane (2:1) to give the titled iminophosphorane 26 (84%) as white prisms, m.p. 230-231°C. (Found: C, 79.53; H, 5.03; N,

9.19. $C_{31}H_{24}N_3P$ requires: C, 79.30; H, 5.15; N, 8.95); i.r. (Nujol): 1596, 1557, 1336, 1308, 1279, 1109, 743, 719 and 692 cm^{-1}; δ ($CDCl_3$): 6.65-8.15 (m, 23 H, aryl + NH), 8.65-8.85 (m, 1H, aryl); m/z (%): 469 (M^+, 100), 468 (54), 392 (67), 238 (19), 207 (17), 183 (60), 152 (10), 108 (20), 77 (17).

General Procedure for the Preparation of 6-Alkyl(aryl)amino-benzimidazo[1,2-c]quinazolines 27.

To a solution of iminophosphorane 26 (0.938 g, 2 mmol) in dry benzene (25 ml) was added the appropriate isocyanate (2 mmol). The reaction mixture was stirred at room temperature for 24 h. The solvent was removed off under reduced pressure and the crude solid was slurried with cold ethanol (5 ml) and stirred for 15 min. The solid was collected by filtration and recrystallized from ethanol to give 27 as crystalline solids. The following derivatives 27 were obtained:

27a 6-Isopropilamino (70%), m.p. 126°C (colourless needles). (Found: C, 74.12; H, 5.64; N, 20.38. $C_{17}H_{16}N_4$ requires: C, 73.89; H, 5.84; N, 20.27); i.r. (Nujol): 3245, 1628, 1601, 1565, 1553, 1216, 761 and 737 cm^{-1}; δ ($CDCl_3$): 1.50 (d, 6H, J= 6.4 Hz, $(CH_3)_2$-CH), 4.60 (m, 1H, CH), 5.20 (m, 1H, NH), 7.25-8.10 (m, 7H, aryl), 8.45-8.65 (m, 1H, aryl); m/z (%): 276 (M^+, 38), 261 (10), 235 (19), 234 (100), 219 (38), 207 (14), 90 (18).

27b 6-Cyclohexylamino (75%), m.p. 187°C (colourless needles). (Found: C, 76.09; H, 6.24; N, 17.63. $C_{20}H_{20}N_4$ requires: C, 75.92; H, 6.37; N, 17.71); i.r. (Nujol): 3426, 1627, 1603, 1566, 1533 and 726 cm^{-1}; δ ($CDCl_3$): 1.06-2.53 (m, 10H, CH_2), 4.33 (m, 1H, CH-N), 5.30 (m, 1H, NH), 7.25-8.15 (m, 7H, aryl), 8.65-8.75 (m, 1H, aryl); m/z (%): 316 (M^+, 12), 235 (18), 234 (100), 208 (22).

27c 6-Phenylamino (84%), m.p. 322-323°C (colourless prisms). (Found: C, 77.29; H, 4.73; N, 17.87. $C_{20}H_{14}N_4$ requires: C, 77.40; H, 4.55; N, 18.05); i.r. (Nujol): 3358, 3205, 1676, 1612, 1590, 1553, 750 and 695 cm^{-1}; δ (DMSO-d_6): 6.95-8.85 (m, 13H, aryl), 10.15 (s, 1H, NH); m/z (%): 310 (M^+, 75), 309 (100), 155 (10), 90 (15), 77 (17).

27d 6-(p-Tolyl)amino (87%), m.p. 261-263°C (colourless prisms). (Found: C, 77.62; H, 5.18; N, 17.39. $C_{21}H_{16}N_4$ requires: C, 77.75; H, 4.97; N, 17.27); i.r. (Nujol): 3205, 3148, 1675, 1608, 1596, 1160 and 748 cm^{-1}; δ (DMSO-d_6): 2.40 (s, 3H, Ar-CH_3), 7.35-8.95 (m, 12H, aryl), 10.13 (s, 1H, NH); m/z (%): 324 (M^+, 89), 323 (100), 308 (12), 307 (25), 161 (15), 159 (17), 90 (20), 77 (10).

27e 6-(m-Tolyl)amino (86%), m.p. 254-255°C (colourless prisms). (Found: C, 77.82; H, 4.81; N, 17.17. $C_{21}H_{16}N_4$ requires: C, 77.75; H, 4.97; N, 17.27); i.r. (Nujol): 3233, 3143, 1677, 1597, 1550 and 749 cm^{-1}; δ (DMSO-d_6): 2.40 (s, 3H, Ar-CH_3), 6.85-8.95 (m, 12H, aryl), 10.18 (s, 1H, NH); m/z (%): 324 (M^+, 80), 323 (100), 308 (15), 162 (10), 155 (18), 90 (20) 77 (10).

27f 6-(p-Methoxyphenyl)amino (74%), m.p. 250-251°C (colourless prisms). (Found: C, 73.92; H, 4.62; N, 16.61. $C_{21}H_{16}N_4O$ requires: C, 74.10; H, 4.74; N, 16.46); i.r. (Nujol): 3216, 3143, 1676, 1665, 1614, 1550, 1244, 762 and 753 cm^{-1}; δ (DMSO-d_6): 3.86 (s, 3H, CH_3O), 7.00-8.95 (m, 12H, aryl), 10.00 (s, 1H, NH); m/z (%): 340 (M^+, 98), 339 (28), 326 (22), 325 (100), 295 (10), 148 (20), 90 (27), 77 (10).

27g 6-(m-Methoxyphenyl)amino (70%), m.p. 247-249°C (colourless prisms). (Found: C, 74.23; H,

4.52; N, 16.35. $C_{21}H_{16}N_4O$ requires: C, 74.10; H, 4.74; N, 16.46); i.r. (Nujol): 3284, 1678, 1587, 1554, 1223, 1140 and 737 cm^{-1}; δ (DMSO-d_6): 3.88 (s, 3H, CH_3O), 6.65-8.85 (m, 12H, aryl), 10.20 (s, 1H, NH); m/z (%): 340 (M^+, 95), 329 (30), 325 (100), 296 (10), 295 (12), 148 (20), 90 (27), 77(10).

6-Thioxo(oxo)-5,6-dihydrobenzimidazo[1,2-c]quinazolines 28 and 29.

The iminophosphorane 26 (1.175 g, 5 mmol) in dry toluene (35 ml), and excess of carbon disulfide (10 ml) or solid carbon dioxide were heated in a sealed tube at 90°C for 12 h. After cooling, the solvent was removed off under reduced pressure and the crude product was slurried with ether (50 ml), filtered and recrystallized from toluene to give 28 and 29 respectively as crystalline solids .

28: yield 71%, m.p. 308-310°C (lit.[24] m.p. 284°C); m/z (%): 251 (M^+, 100).

29: yield 76%, m.p. 334-335°C (lit.[24] m.p. 334°C); m/z (%): 235 (M^+, 100).

Preparation of Iminophosphoranes 31 and 36.

Compounds 31 and 36 were prepared as described for iminophosphorane 26.

31 (93%), m.p. 164-165°C (colourless prisms from benzene/hexane). (Found: C, 76.92; H, 4.47; N, 5.78. $C_{32}H_{23}N_2O_2P$ requires: C, 77.10; H, 4.65; N, 5.62); i.r. (Nujol): 1750, 1637, 1604, 1593, 1315, 1120, 1109, 1127, 1099, 785, 754 and 715 cm^{-1}; δ ($CDCl_3$): 6.50-6.75 (m, 2H), 6.90-7.05 (m, 1H), 7.41-7.65 (m, 10H), 7.70-7.85 (m, 9H), 8.21-8.26 (m, 1H); m/z (%): 498 (M^+, 15), 352 (4), 277 (8), 262 (9), 236 (11), 201 (20), 199 (10), 183 (100), 152 (20), 146 (11), 108 (27), 107 (17), 90 (34), 77 (21).

36 (97%), m.p. 214-215°C (colourless prisms from benzene/hexane). (Found: C, 74.86; H, 4.92; N, 5.39. $C_{33}H_{27}N_2O_3P$ requires: C, 74.71; H, 5.13; N, 5.28); i.r. (Nujol): 3260, 1713, 1657, 1585, 1530, 1266, 1256, 1120, 1109, 756 and 720 cm^{-1}; δ ($CDCl_3$): 3.27 (s, 3H, CH_3O), 6.46-7.53 (m, 15H), 7.72-7.91 (m, 6H), 8.07-8.11 (m, 1H), 8.64 (d, 1H), 13.20 (s, 1H, NH); m/z (%): 530 (M^+, 6), 380 (16), 262 (14), 201 (48), 184(16), 183 (100), 146 (7), 120 (38), 108 (31), 90 (23), 77 (22).

Preparation of 3,1-Benzoxazine-4-imines 37.

These compounds were prepared as described for 3,1-benzoxazine-4-imines 11.

37a (R= p-H_3C-C_6H_4) (93%), m.p. 205-206°C (colourless prisms from benzene/hexane). (Found: C, 72.06; H, 4.93; N, 10.71. $C_{31}H_{26}N_4O_4$ requires: C, 71.80; H, 5.05; N, 10.80); i.r. (Nujol): 3358, 1720, 1708, 1629, 1602, 1560, 1514, 1296, 1284, 1271, 1185 and 747 cm^{-1}; δ ($CDCl_3$): 2.28 (s, 3H, Ar-CH_3), 2.31 (s, 3H, Ar-CH_3), 3.75 (s, 3H, CH_3O), 6.55-7.65 (m, 15H, aryl), 8.17 (dd, 1H, aryl), 12.35 (s, 1H, NH); m/z (%): 385 (M^+ - RNCO, 20), 352 (14), 326 (18), 279 (100), 146 (13), 133 (58), 92 (29), 91 (20), 77 (76).

37b (R= m-H_3C-C_6H_4) (89%), m.p. 158-159°C (colourless needles from benzene/hexane). (Found: C, 71.72; H, 5.19; N, 10.99. $C_{31}H_{26}N_4O_4$ requires: C, 71.80; H, 5.05; N, 10.80); i.r. (Nujol): 3296, 1713, 1696, 1629, 1607, 1593, 1576, 1300, 1290, 1249, 1211, 1079, 1007, 743 and 693 cm^{-1}; δ ($CDCl_3$): 2.16 (s, 3H, Ar-CH_3), 2.33 (s, 3H, Ar-CH_3), 3.74 (s, 3H, CH_3O), 6.55-7.75 (m, 15H, aryl), 8.18 (d, 1H, aryl), 12.39 (s, 1H, NH); m/z (%): 385 (M^+ - RNCO, 10), 353 (10), 337 (8), 192 (11), 134 (10), 133 (100), 132 (35), 104 (53), 91 (16), 77 (20).

37c (R= p-H_3CO-C_6H_4) (90%), m.p. 159-161°C (colourless prisms from benzene/hexane). (Found: C, 67.51; H, 4.89; N, 9.93. $C_{31}H_{26}N_4O_6$ requires: C, 67.63; H, 4.76; N, 10.17); i.r. (Nujol):

3345, 1720, 1703, 1628, 1602, 1554, 1512, 1298, 1285, 1249, 1221, 1079, 989 and 739 cm^{-1}; δ ($CDCl_3$): 3.75 (s, 3H, CH_3O), 3.77 (s, 6H, CH_3O), 6.55-7.65 (m, 15H, aryl), 8.19 (d, 1H, aryl), 12.27 (s, 1H, NH); m/z (%): 401 (M^+ - RNCO, 28), 369 (26), 368 (55), 343 (16), 342 (66), 251 (10), 236 (12), 208 (17), 192 (14), 184 (56), 179 (14), 163 (23), 149 (14), 146 (80), 103 (21), 102 (32), 90 (100), 77 (55).

General Procedure for the Preparation of 6-Substituted 12H-Quinazolino[3,2-a]quinazoline-5(6H),12-diones 34.

Method A.

To a solution of iminophosphorane 31 (0.99 g, 2 mmol) in dry benzene (10 ml) was added the corresponding isocyanate (2 mmol). The deep blue solution was stirred at room temperature for 6 h. Then the separated solid was collected by filtration, washed with cold ether (2 x 5 ml) and recrystallized from methylene chloride/ether (1:1) to give 34.

Method B.

3,1-Benzoxazin-4-imines 37 were dried at 50°C and were then heated in a sublimation apparatus at a temperature slightly above its melting point (200-250°C). The solid residue of the pyrolysis was recrystallized from methylene chloride/ether to give 34. The following derivatives 34 were obtained:

34a 6-Methyl (79%, Method A), m.p. 177-178°C (colourless prisms). (Found: C, 69.20; H, 3.81; N, 15.32. $C_{16}H_{11}N_3O_2$ requires: C, 69.31; H, 4.00; N, 15.15); i.r. (Nujol): 1706, 1693, 1600, 1591, 1563, 1290, 1050, 767, 681 and 608 cm^{-1}; δ ($CDCl_3$): 3.70 (s, 3H, CH_3-N), 7.26-7.87 (m, 5H, aryl), 8.22 (dd, 2H, aryl), 9.12 (d, 1H, aryl); m/z (%): 277 (M^+, 57), 249 (66), 248 (41), 220 (15), 159 (10), 131 (16), 130 (15), 124 (13), 102 (21), 90 (100), 77 (28).

34b 6-(m-Chlorophenyl) (71%, Method A), m.p. 257°C (colourless needles). (Found: C, 67.31; H, 3.18; N, 11.56. $C_{21}H_{12}ClN_3O_2$ requires: C, 67.48; H, 3.24; N, 11.24); i.r. (Nujol): 1696, 1605, 1588, 1564, 1393, 1347, 1280, 762 and 708 cm^{-1}; δ ($CDCl_3$ + TFA): 7.25-8.02 (m, 9H, aryl), 8.37 (m, 2H, aryl), 8.85 (d, 1H, aryl); m/z (%): 375 (M^+ + 2, 7), 374 (14), 373 (M^+, 21), 372 (35), 338 (5), 335 (7), 194 (3), 192 (18), 186 (10), 130 (16), 113 (13), 111 (45), 102 (36), 90 (100), 77 (14).

34c 6-(p-Tolyl) (77%, Method A; 88%, Method B), m.p. 295-297°C (colourless needles). (Found: C, 74.62; H, 4.16; N, 12.17. $C_{22}H_{15}N_3O_2$ requires: C, 74.77; H, 4.28; N, 11.89); i.r. (Nujol): 1701, 1604, 1587, 1564, 1389, 1341, 1278 and 683 cm^{-1}; δ ($CDCl_3$ + TFA): 2.45 (s, 3H, Ar-CH_3), 7.22-7.88 (m, 9H, aryl), 8.24 (d, 1H, aryl), 8.28 (d, 1H, aryl), 8.91 (d, 1H, aryl); m/z (%): 353 (M^+, 47), 352 (100), 337 (10), 235 (10), 177 (15), 133 (16), 116 (18), 91 (28), 77 (11).

34d 6-(m-Tolyl) (75%, Method A; 93%, Method B), m.p. 259°C (colourless prisms). (Found: C, 74.96; H, 4.08; N, 12.12. $C_{22}H_{15}N_3O_2$ requires: C, 74.77; H, 4.28; N, 11.89); i.r. (Nujol): 1702, 1691, 1602, 1586, 1562, 1391, 1349, 1280 and 763 cm^{-1}; δ ($CDCl_3$ + TFA): 2.44 (s, 3H, Ar-CH_3), 7.13-7.81 (m, 9H, aryl), 8.17 (d, 1H, aryl), 8.25 (d, 1H, aryl), 8.35 (d, 1H, aryl); m/z (%): 353 (M^+, 51), 352 (100), 337 (6), 220 (5), 192 (15), 177 (20), 161 (9), 133 (10), 116 (5), 102 (145, 91 (51), 90 (63), 77 (18).

34e 6-(p-Methoxyphenyl) (71%, Method A; 95%, Method B), m.p. 275-276°C (colourless prisms). (Found: C, 71.33; H, 3.92; N, 11.48. $C_{22}H_{15}N_3O_3$ requires: C, 71.54; H, 4.09; N, 11.37); i.r.

(Nujol): 1707, 1696, 1604, 1593, 1564, 1514, 1392, 1276, 1252 and 720 cm^{-1}, δ ($CDCl_3$ + TFA): 3.86 (s, 3H, CH_3O), 7.05-7.34 (m, 4H, aryl), 7.49-7.96 (m, 6H, aryl), 8.28 (dd, 1H, aryl), 8.80 (s, 1H, aryl); m/z (%): 369 (M^+, 62), 368 (100), 353 (10), 296 (5), 238 (5), 192 (7), 184 (10), 164 (7), 163 (8), 149 (11), 146 (11), 123 (7), 102 (11), 92 (10), 90 (39), 77 (15).

Preparation of 2-(m-Tolyl)amino-3-(o-methoxycarbamoyl)phenyl-4(3H)-quinazolinone 38.

This compound was prepared as described for 12 by Method A.

38 (94%), m.p. 164-165°C (colourless prisms). (Found: C, 71.52; H, 5.19; N, 10.65. $C_{23}H_{19}N_3O_3$ requires: C, 71.67; H, 4.97; N, 10.90); i.r. (Nujol): 3324, 1716, 1681, 1608, 1592, 1565, 1513, 1308, 1279 and 762 cm^{-1}; δ ($CDCl_3$): 2.30 (s, 3H, Ar-CH_3), 3.68 (s, 3H, CH_3O), 5.75 (s, 1H, NH), 6.91-7.78 (m, 10H, aryl), 8.14 (dd, 1H, aryl), 8.26 (dd, 1H, aryl); m/z (%): 385 (M^+, 15), 353 (27), 352 (56), 326 (37), 235 (21), 220 (10), 192 (21), 180 (20), 176 (38), 161 (19), 146 (43), 116 (25), 102 (28), 90 (100), 77 (52).

Preparation of Iminophosphorane 40.

This compound was prepared from the azide[15] 39 and triphenylphosphine as described for iminophosphorane 26.

40 (86%), m.p. 174-175°C (colourless needles from benzene/hexane). (Found: C, 76.38; H, 4.97; N, 5.55. $C_{31}H_{23}N_2PS$ requires: C, 76.52; H, 4.76; N, 5.77); i.r. (Nujol): 1591, 1551, 1350, 1303, 1114, 1016, 745 and 692 cm^{-1}; m/z (%): 486 (M^+, 27), 485 (19), 409 (19), 352 (11), 276 (10), 262 (7), 226 (11), 214 (14), 198 (8), 184 (16), 183 (100), 152 (14), 108 (20), 107 (13), 77 (8).

General Procedure for the Preparation of 7H-Benzothiazolo[3,2-c]quinazoline-7-imines 42.

To a well stirred solution of iminophosphorane 40 (0.97 g, 2 mmol) in dry benzene (20 ml) was added the appropriate isocyanate or isothiocyanate (2 mmol). The reaction mixture was stirred at room temperature for 24 h. Then, the solution was concentrated to dryness and the residual material was slurried with cold ethanol (10 ml). The resulting solid was collected by filtration, dried and recrystallized from benzene/hexane (1:1) to give 42 as crystalline solids. The following derivatives 42 were obtained:

42a 7-Ethoxycarbonylimino (51%), m.p. 224°C (red prisms). (Found: C, 62.91; H, 3.99; N, 12.86. $C_{17}H_{13}N_3O_2S$ requires: C, 63.14; H, 4.05; N, 12.99); i.r. (Nujol): 1685, 1600, 1280, 1240, 1180, 1140, 1050 and 740 cm^{-1}; δ ($CDCl_3$): 1.46 (t, 3H, J= 7 Hz; CH_3-CH_2), 4.46 (q, 2H, J= 7 Hz, CH_2O), 7.05-8.25 (m, 7H, aryl), 9.85-10.15 (m, 1H, aryl); m/z (%): 323 (M^+, 10), 280 (14), 278 (36), 267 (10), 253 (19), 251 (30), 250 (22), 237 (16), 225 (10), 224 (47), 209 (11), 139 (24), 134 (24), 116 (13), 109 (25), 108 (61), 102 (11), 90 (13), 82 (33), 69 (100).

42b 7-(p-Chlorophenylimino) (87%), m.p. 195-196°C (violet prisms). (Found: C, 66.48; H, 3.52; N, 11.39. $C_{20}H_{12}ClN_3S$ requires: C, 66.39; H, 3.34; N, 11.61); i.r. (Nujol): 1630, 1616, 1522, 1307, 1300, 749 and 602 cm^{-1}; δ ($CDCl_3$): 6.65-7.95 (m, 11H, aryl), 10.06-10.32 (m, 1H, aryl); m/z (%): 363 (M^+ + 2, 4), 362 (7), 361 (M^+, 12), 360 (14), 264 (16), 262 (26), 192 (12), 163 (12), 153 (12), 139 (11), 137 (12), 127 (26), 125 (62), 113 (15), 111 (40), 108 (22), 102 (22), 99 (21), 90 (53), 78 (100).

42c 7-(p-Tolylimino) (69%), m.p. 160-162°C (violet prisms). (Found: C, 73.62; H, 4.65; N,

12.57. $C_{21}H_{15}N_3S$ requires: C, 73.87; H, 4.43; N, 12.31); i.r. (Nujol): 1614, 1596, 1524, 1297, 1275 and 750 cm^{-1}; δ ($CDCl_3$): 2.40 (s, 3H, Ar-CH_3), 6.55-8.15 (m, 11H, aryl), 10.03-10.30 (m 1H, aryl); m/z (%): 341 (M^+, 2), 340 (3), 222 (58), 221 (13), 133 (14), 131 (12), 108 (6), 104 (22), 91 (100), 90 (12), 89 (19), 77 (30).

42d 7-(p-Methoxyphenylimino) (78%), m.p. 112-113°C (violet prisms). (Found: C, 70.77; H, 4.18; N, 11.98. $C_{21}H_{15}N_3OS$ requires: C, 70.57; H, 4,23; N, 11.76); i.r. (Nujol): 1608, 1591, 1564, 1510, 1295, 1273, 1232, 759 and 751 cm^{-1}; δ ($CDCl_3$): 3.90 (s, 3H, CH_3O), 6.55-8.15 (m, 11H, aryl), 10.03-10.29 (m 1H, aryl); m/z (%): 357 (M^+, 30), 342 (41), 255 (16), 254 (23), 252 (64), 239 (27), 226 (100), 225 (58), 198 (12), 157 (17), 139 (12), 113 (15), 109 (16), 108 (36), 92 (12), 77 (18).

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