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Phosphono-Substituted Isoindolines and Indoles from 2,3- and 2,4-Benzoxazin-1-ones

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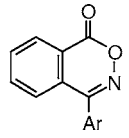
ABSTRACT: *Reactions of 2,3-benzoxazinone* **1** *and 2,4-benzoxazinone* **2**, *with trialkyl phosphites* **3a–c** *provide access to new phosphono-substituted isoindolines* **6a–f** *and indoles* **19a–e**, *respectively. Phosphono-substituted 2,3-benzoxazines* **5a–c** *were also obtained in the first reaction. Bisisoindolinylidene (***7***) was, however, isolated in low yields when* **1** *was heated with triethyl or triisopropyl phosphite at 100°C whereas at 170°C* **7** *was obtained as the major product (~53%). On the other hand, the reaction of* **1** *or* **2** *with dialkyl phosphonates* **4a–c** *proceeded in the presence of aqueous solution of NaOH (5%) to give the respective alkylated product* **14a–c** *or* **20a–c**. © 2003 Wiley Periodicals, Inc. Heteroatom Chem 15:77–84, 2004; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10216

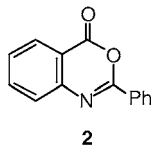
INTRODUCTION

Much attention has been given to the preparation of phosphono-substituted heterocyclic compounds [1–4] largely because of their possible relevance to the mechanism of certain enzymatic events [5,6]. The P=O is an important analogue of the carbonyl group and can serve as a transition state mimic owing to the additional ligand allowed by sp^3 hybridization. Therefore, the synthesis of phosphono-substituted heterocycles was extensively studied [7].

In a recent study [8], we described the synthesis of several isoquinoline derivatives of pharmacological value by treating 4-(4-methylphenyl)-2,3-benzoxazin-1-one (**1**) with different types of alkylidenephosphoranes. This result intrigued us to design and to synthesize a series of novel phosphono-substituted *N*-heterocycles from the reactions of 2,3-**1** and 2,4-benzoxazin-1-ones **2** with trialkyl phosphites **3a–c**. The study was extended to cover the reactions of **1** and **2** with dialkyl phosphonates **4a–c**.



1, Ar = C_6H_4-Me-*p*



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RESULTS AND DISCUSSION

The reaction of **1** with trimethyl phosphite (**3a**) was successfully completed (TLC) by using an excess of the phosphite as solvent and heating the mixture for 15 h at 105°C. Chromatographic separation of the product mixture yielded dimethyl 4-(4-methylphenyl)-2,3-benoxazin-1-yl-phosphonate (**5a**, 30%), dimethyl 3-(4-methylphenyl)-2-methyl-isoindolyl-phosphonate (**6a**, 18%), and dimethyl 3-(4-methylphenyl)isoindolyl-phosphonate (**6b**, 22%). Oxazinone **1**, when heated with triethyl-or triisopropyl phosphite (**3b,c**) at 100–105 °C for 12 h, gave a low yield of bisisoindolinylidene (**7**) (~10%), in addition to the respective phosphonates **5b,c** (18%), **6c,e** (~27%), and **6d,f** (~15%). However, at higher temperatures, **3b,c** reacted with **1** to give **7** as the major product (~52%) together with the phosphonates **6d,f** (~18%). No significant

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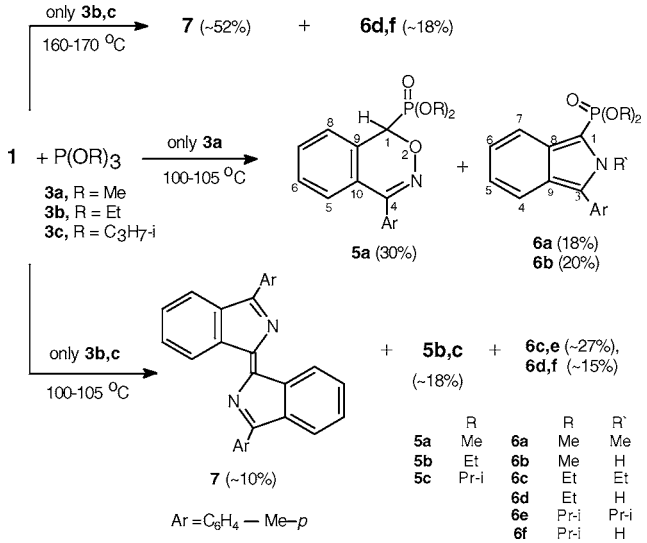
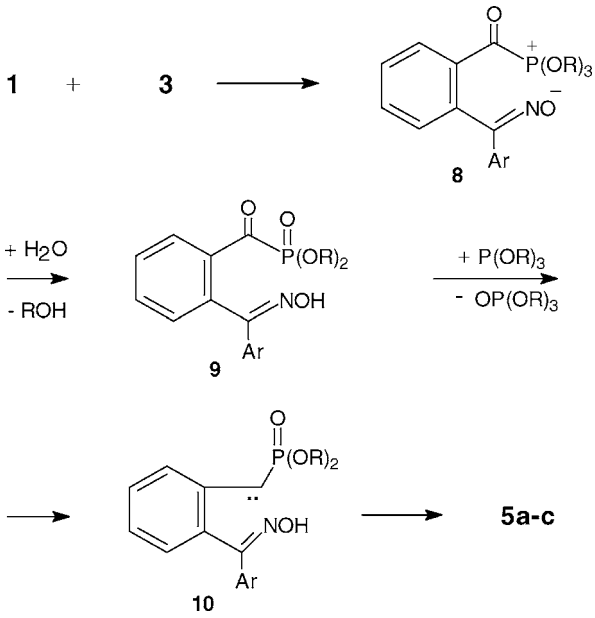
amount of phosphonates **5b,c** or **6c,e** was detected (Scheme 1).

Schemes 2 and 3 try to explain the observed reactions. The primary nucleophilic attack [8,9] of the phosphite on C-1, with subsequent ring opening of **1**, gives the zwitterion **8** [8,9]. Stabilization of **8** may be attained in two different ways. The first one is by partial hydrolysis of **8**, which affords the keto phosphonate **9**. Deoxygenation followed by cyclization of the proposed carbene intermediate **10** gives the phosphonates **5a–c**. Formation of the carbene intermediate and its transformation into similar phosphono-substituted heterocycles has been previously reported for the reaction of α-keto phosphonates with trialkyl phosphites [10,11].

The second pathway for stabilization of **8** is the intradeoxygenation of the nitroso function, yielding 3-oxoisoindole **11** (also known as 3-oxoisoindoline) with concomitant extrusion of trialkyl phosphate. Reductive cyclization of the nitroso function with phosphites has been reported [11a]. The reaction of **11** with a second phosphite species would lead to the formation of the ylidic phosphonate **13a–c** via the carbene intermediate **12**. Trialkyl phosphites are known to be efficient traps for carbenes, leading to ylide formation [12]. While the trismethoxyphosphonium ylide **13a** tended to rearrange to the corresponding phosphonate **6a** under the conditions needed for this formation, trisethoxy- and trisisopropoxy ylide analogs **13b,c** were much more resistant to such rearrangement. Therefore, a competing side reaction was observed for the case of **13b,c**, leading to the formation of **7**. This arose because of the ability of **13b,c** to function as Wittig reagents and to intercept the 3-oxoisoindole **11**. At relatively



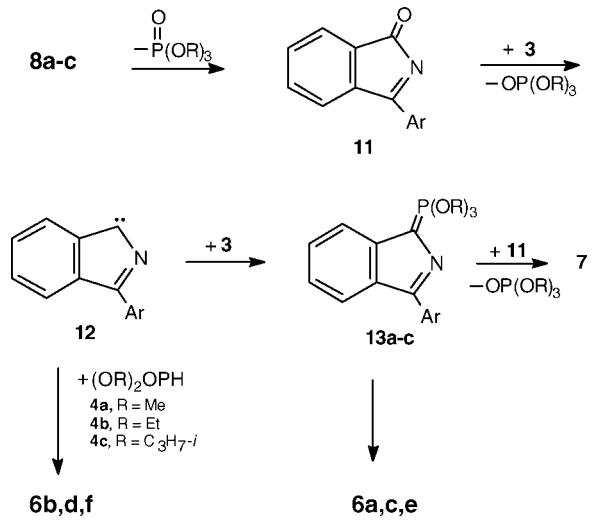
SCHEME 1



SCHEME 2

high temperature (160–170 °C), the Wittig reaction between **13b,c** and **11** predominates to give **7** as the major product. Notwithstanding, an alternative pathway for the formation of **7** by direct dimerization [10c] of the carbene **12** cannot be ruled out. The attack by three-valence phosphorus on the carbonyl-oxygen of cyclic anhydrides, phthalyl anhydride, was previously reported by Ramirez et al. [10b,c]. The reaction resulted in a deoxygenation coupling of the substrate through the carbene intermediate.

Finally, the hypothesis that a carbene **12** is generated during the reaction of trialkyl phosphites with oxazinone **1** is sufficient to explain the formation of isoindolinyl-1-phosphonates **6b,d,f** (R^1 = H). It



SCHEME 3

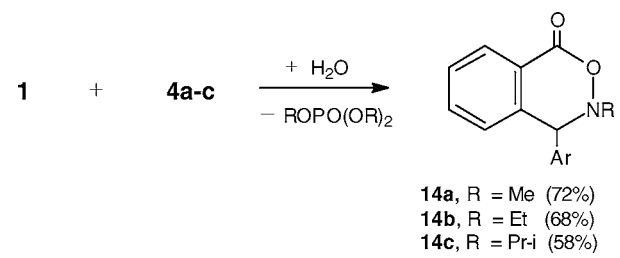
seemed likely that such products resulted from a small amount of water or of dialkyl phosphonates **4a–c** being present in the reaction mixture. It is noteworthy that, the formation of **6** in 1,2-addition rather than the expected 1,1-addition is consistent with the literature. Thus, stabilization of isoindolines by steric protection, particularly in the presence of substituents at the 1- and 3-positions, is well established [13].

In the absence of trialkyl phosphite, the reaction of **1** with dialkyl phosphonates **4a–c** proceeded only when a trace amount of aqueous solution NaOH (5%) was present in the medium, giving the respective 4-(4-methylphenyl)-3-alkyl-4*H*-2,3-benzoxazin-1-one **14a–c** as a sole reaction product in 60–70% yield (Scheme 4).

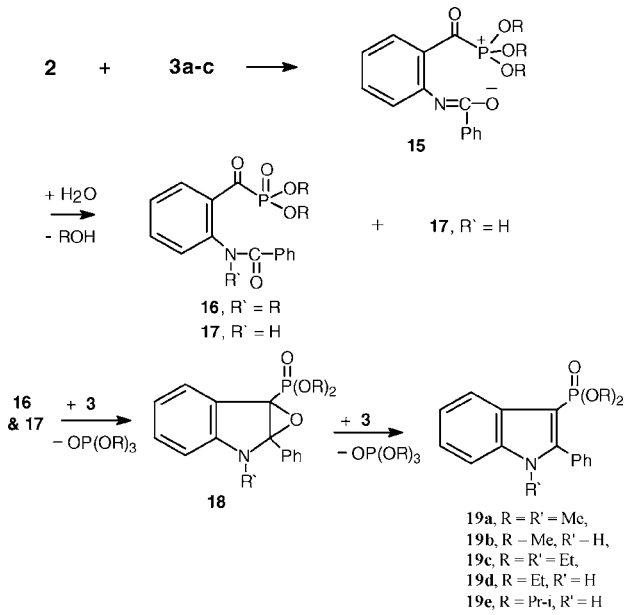
In summary, the findings from the reactions of 2,3-oxazinone **1** with alkyl phosphites, which have been reported in the present investigation, or with alkylidene phosphoranes that were reported in the earlier work [8], highlight the initial attack by the nucleophilic tri- and pentavalent phosphorus reagents on the carbonyl-carbon in **1**. However, the mode of further transformations would vary with the electronic characteristics of the phosphorus reagent. Considering the previous report [8], the common feature of the reactions of phosphorus ylides with **1** seemed to be proceeding via an ionic mechanism. Conversely, the involvement of the carbene intermediate in the reactions of **1** with TAP is the driving force for the formation of the final products **5–7**. Furthermore, the formation of only the dialkyl phosphonates **6b,d,f**, only from the reaction of **1** with TAP is a conclusive evidence for the involvement of the carbene intermediate **12**. Dialkyl phosphonates themselves acted as reducing agents [10c] toward **1** (Scheme 4). Other features of interest in the results of the reactions of **1** and **3a–c** are (a) The bisisoindolinyl condensation required elevated temperatures and (b) TMP was a very poor reagent. This was attributed to a lower reaction temperature and to a relatively rapid disappearance of the phosphite, which had been converted into dimethyl methyl phosphonate [$P(O)Me(OMe)_2$] or hydrolyzed to dimethyl phosphonate. However, yields are lower and the side-reactions (formation of **5a** and **6b**) are more noticeable.

We next studied the reactions between **2** and alkyl phosphites **3** and **4**, and the products obtained are depicted in Schemes 5 and 6. Thus, oxazinone **2** and trimethyl phosphite (TMP, **3a**), when heated at 100–105 °C for 12 h, gave dimethyl 2-phenyl-*N*-methylindolyl-3-phosphonate (**19a**) and dimethyl 2-phenylindolyl-3-phosphonate (**19b**) in equal yields (~32%). Similarly, the reaction products of **2** with triethyl phosphite (TEP, **3b**) were assigned analogous structures **19c** (42%) and **19d** (28%). Conversely, the reaction of **2** with triisopropyl phosphite (**3c**) afforded only the vinyl phosphonate **19e** (68%). Treatment of **19b** with methyl iodide in acetone, in the presence of anhydrous potassium carbonate, afforded the expected product **19a** (Scheme 5).

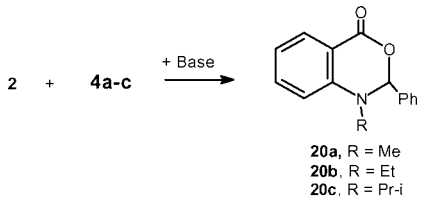
The formation of **19a–e** resulted from the initial production of the dipolar species **15** [14,15], which is an analog to the intermediate **8** (Scheme 2). Further intramolecular group translocation gave the intermediate **16**, whereas a partial hydrolysis yielded **17**. The absence of *N*-isopropyl derivative was not unexpected since the bulky isopropyl group could impede the Arbusov reaction. Reaction of **16** with a second phosphite species **3** afforded the epoxide intermediate **18** [11a]. Deoxygenation of **18** by further phosphite molecule yielded the products **19a,c**. Deoxygenation of epoxides to olefins with phosphites has been reported [16]. In the same manner, the phosphonates **19b,d,e** ($R^1 = H$) were derived from the intermediate **17**.



SCHEME 4



SCHEME 5



SCHEME 6

In a systematic study, the reaction of **2** with dialkyl phosphonates **4a–c** was completed in the presence of a trace amount of aqueous solution (5% NaOH) to give the respective 3-alkyl-4-phenyl-4H-2,4-benzoxazin-1-one **20a–c** (50–60%) (Scheme 6), similar as in Scheme 4.

The structures suggested for all new compounds are in good agreement with their analytical and spectroscopic data.

Finally, the present work describes an efficient and simple synthesis of a variety of phosphonate derivatives in satisfactory yields. This general method consists of suitable application of the appropriate phosphite ester with benzoxazinones. Furthermore, the new isoindole-phosphonates **6a–f** and indole-phosphonates **19a–e** might be useful for pharmaceutical and biological purposes as it is widely realized that the activity of certain natural products, drugs, and pesticides owes much to the presence of an isoindoline nucleus [17,18] or indole species in their molecules [19].

EXPERIMENTAL

The melting points are uncorrected. The IR spectra were recorded on a Perkin Elmer spectrophotometer model 297 (Grating), using KBr discs. The ^{1}H and ^{13}C NMR spectra were run in $CDCl_3$ or DMSO-d_6 as solvents on a Jeol-270 MHz instrument, using $SiMe_4$ as an internal reference. The ^{31}P NMR spectra were recorded relative to external H_3PO_4 (85%) with a Varian CFT-20 instrument. The mass spectra were performed at 70 eV on a Shimadzu GCS-QP 1000 EX spectrometer provided with a data system. The appropriate precautions in handling moisture-sensitive compounds were observed. Solvents were dried by standard techniques. Light petroleum refers to the fraction 40–60°C.

Reaction of **1** *with Trimethyl Phosphite (***3a***)*

A mixture of 1.00 g (4.21 mmol) **1** [20] and 5 ml **3a** was heated at 100–105°C for 15 h. After removal of the volatile materials under reduced pressure, the residue was purified by chromatography on silica gel using hexane-$CHCl_3$ as the eluent to give compounds **6a, 5a**, and **6b**, respectively.

Dimethyl 3-(4-methylphenyl)-*N*-methylisoindolyl-phosphonate (**6a**) was obtained (9:1 v/v) as colorless crystals (250 mg, 18%), m.p. 110–112°C (from pentane). Found: C, 65.53; H, 6.05; N, 4.19; P, 9.34. $C_{18}H_{20}NO_3P$ (329.35) requires C, 65.64; H, 6.12; N, 4.25; P, 9.41%; ν_{max} (KBr) (cm^{-1}) 2920 (H_3C—N), 1252 (P=O), 1080 (P—O—C); δ_H ($CDCl_3$): 2.42 (s, 3H, H_3C—Ph), 3.27 (s, 3H, H_3C—N), 3.89 (d, $J_{H.H}$ 11.2 Hz, 6H, H_3COP), 7.42-7.48 (m, 3H, *H*—Ph), 7.52–7.58 (m, 3H, *H*—Ph), 7.95, 8.25 (2dd, $J_{H.H}$ 2.7 Hz, 2H, *H*—Ph); δ_c ($CDCl_3$): 22.2 (CH_3—Ph), 31.2 (CH_3—N), 55.4 (d, $J_{C.P}$ 6.6 Hz, CH_3O—P), 127.31 (d, $J_{C.P}$ 145 Hz, 1-*C*—P), 123.5, 124.2, 126.7, 127.3, 129.6, 131.5, 136.8 (3-*C*—Ar, C_6H_4, and C_6H_4—Me); δ_p ($CDCl_3$) 29.77; *m/z* (EI) (%): 329 (33) [M^+], 314 (22), 223 (36), 205 (100), 109 (64), 91 (16).

Dimethyl 4-(4-methylphenyl)-1*H*-benzoxazin-1-yl-phosphonate (**5a**) was obtained (7:3 v/v) as colorless needles (419 mg, 30%), m.p. 122–124°C (from cyclohexane). Found: C, 61.69; H, 5.41; N, 4.14; P, 9.28. $C_{17}H_{18}NO_4P$ (331.3) requires C, 61.63; H, 5.48; N, 4.23; P, 9.35%; ν_{max} (KBr) (cm^{-1}) 1610 (C=N), 1256 (P=O), 1082 (P—O—C); δ_H ($CDCl_3$): 2.41 (s, 3H, H_3C—Ph), 3.88 (d, J_{HP} 11.2 Hz, 6H, H_3COP), 4.39 (d, J_{HP} 18 Hz, 1H, 1-C*H*—P), 7.44–7.49 (m, 3H, *H*—Ph), 7.53–7.61 (m, 3H, *H*—Ph), 7.98, 8.34 (2dd, *J* 2.5, 3.6 Hz, 2H, *H*—Ph); δ_C ($CDCl_3$): 22.4 (CH_3—Ph), 42.4 (d, $J_{C.P}$ 136.8 Hz, 1-*C*—P), 55.8 (d, $J_{C.P}$ 7.5 Hz, CH_3O), 124.3, 124.8, 126.3, 127.8, 128.9, 131.5 (C_6H_4 and C_6H_4—Me), 133.4 (4-*C*—Ar); δ_p ($CDCl_3$): 29.47; *m/z* (EI) (%): 331 (42) [M^+], 330 (27), 314 (36), 223 (18), 221 (17), 205 (100), 109 (68), 91 (13).

Dimethyl 3-(4-methylphenyl)isoindolyl-1-phosphonate (**6b**) was obtained as colorless crystals (290 mg, 22%), m.p. 136–138°C ($CHCl_3$-light petroleum, 1:1). Found: C, 64.83; H, 5.61; N, 4.47; P, 9.72. $C_{17}H_{18}NO_3P$ (315.3) requires C, 64.76; H, 5.75; N, 4.44; P, 9.82%; ν_{max} (KBr) (cm^{-1}) 3267 (NH), 1262 (P=O), 1081 (P—O—C); δ_H ($CDCl_3$): 2.43 (s, 3H, H_3C—Ph), 3.88 (d, J_{HH} 11.2 Hz, 6H, H_3COP), 7.27–7.35 (m, 3H, *H*—Ph), 7.44–7.68 (m, 3H, *H*—Ph), 7.93, 8.36 (2dd, J_{HH} 2.7 Hz, 2H, *H*—Ph), 12.26 (s br, 1H, N*H*, deuterium exchangeable); δ_C ($CDCl_3$) 22.2 (CH_3—Ph), 55.6 (d, $J_{C.P}$ 7.5 Hz, CH_3—O—P), 127.5 (d, $J_{C.P}$ 143 Hz, 1-*C*—P), 123.5, 124.3, 126.4, 127.1, 129.5, 131.2, 136.2 (3-*C*—Ar, C_6H_4, and C_6H_4—Me); δ_p ($CDCl_3$) 29.92; *m/z* (EI) (%): 315 (62) [M^+], 314 (24), 223 (55), 205 (100), 109 (60), 91 (20).

Reaction of **1** *with Triethyl Phosphite (***3b***)*

A mixture of 1.00 g (4.21 mmol) **1** and 5 ml **3b** was heated at 100–105°C for 12 h (TLC). Excess of

the phosphite was removed under reduced pressure and the residue was chromatographed on silica gel, gradient eluting from 1% to 10% $CHCl_3$ in hexane, yielded compounds **6c, 5b, 6d**, and **7**, respectively.

Diethyl 3-(4-methylphenyl)-*N*-ethylisoindolyl-1-phosphonate (**6c**) was obtained (9:1 v/v) as colorless crystals (438 mg, 28%), m.p. 98–100°C (from cyclohexane). Found: C, 67.98; H, 7.11; N, 3.72; P, 8.25. $C_{21}H_{26}NO_3P$ (371.41) requires C, 67.91; H, 7.05; N, 3.77; P, 8.34%; ν_{max} (KBr) (cm^{-1}) 2915 (—N—Et), 1255 (P═O), 1055 (P—O—C); δ_H ($CDCl_3$): 1.35 (dt, $J_{H.H}$ 7.5, $J_{H.P}$ 2.7 Hz, 6H, H_3C—C—OP), 1.44 (t, $J_{H.H}$ 6.5 Hz, 3H, H_3C—C—N), 2.49 (s, 3H, H_3C—Ph), 3.56 (q, J_{HH} 6.5 Hz, 2H, H_2C—N), 3.89 (dq, J_{HH} 7.5 Hz, $J_{H.P}$ 3.5 Hz, 4H, H_2C—OP), 7.41–7.49 (m, 3H, *H*—Ph), 7.50–7.53 (m, 3H, *H*—Ph), 7.93, 8.28 (2dd, J_{HH} 2.4, 2.8 Hz, 2H, *H*—Ph); δ_C ($CDCl_3$): 15.8 (CH_3CH_2N), 16.2 (d, $J_{C.P}$ 5.5 Hz, CH_3-C—O—P), 22.3 (CH_3—Ph), 40.7 (CH_2N), 61.5 (d, $J_{C.P}$ 7.5 Hz, CH_2OP), 121.6 (d, $J_{C.P}$ 145 Hz, 1-*C*—P), 123.5, 124.4, 126.7, 127.6, 129.2, 131.8, 136.8 (3-*C*—Ar, C_6H_4, & C_6H_4-Me); δ_p ($CDCl_3$) 29.77; *m/z* (EI) (%): 371 (29) [M^+], 342 (47), 251 (27), 205 (100), 137 (58), 91 (18).

Diethyl 4-(4-methylphenyl)-1*H*-benzoxazin-1-ylphosphonate (**5b**) was obtained (7:3 v/v) as colorless needles (242 mg, 16%), m.p. 115–117°C (from benzene-pentane, 1:2 v/v). Found: C, 63.59; H, 6.11; N, 3.84; P, 8.55. $C_{19}H_{22}NO_4P$ (359.36) requires C, 63.50; H, 6.17; N, 3.90; P, 8.62%; ν_{max} (KBr) (cm^{-1}) 1605 (C═N), 1258 (P═O), 1100 (P—O—C); δ_H ($CDCl_3$) 1.38 (dt, $J_{H.H}$ 7.5, $J_{H.P}$ 2.7 Hz, 6H, H_3C—C—OP), 2.38 (s, 3H, H_3C—Ph), 3.95 (dq, J_{HH} 7.5, $J_{H.P}$ 3.4 Hz, 2H, H_2COP), 4.47 (d, $J_{H.P}$ 18 Hz, 1H, 1-C*H*—P), 7.47–7.49 (m, 3H, *H*—Ph), 7.50–7.51 (m, 3H, *H*—Ph), 7.97, 8.31 (2dd, J_{HH} 2.5 Hz, 2H, *H*—Ph); δ_C ($CDCl_3$): 16.4 (d, $J_{C.P}$ 5.5 Hz, CH_3—C—O), 22.4 (CH_3—Ph), 44.3 (d, $J_{C.P}$ 139.3 Hz, 1-*C*—P), 61.4 (d, $J_{C.P}$ 7.4 Hz, CH_2—OP), 123.7, 124.2, 126.3, 127.6, 128.3, 131.5, 136.7 (4-*C*—Ar, C_6H_4, & C_6H_4—Me); δ_p ($CDCl_3$): 30.41; *m/z* (EI) (%): 359 (21) [M^+], 358 (11), 251 (40), 221 (20), 205 (100), 137 (22), 91 (19).

Diethyl 3-(4-methylphenyl)isoindolyl-1-phosphonate (**6d**) was obtained as colorless crystals (245 mg, 17%), m.p. 128–130°C (from CH_2Cl_2). Found: C, 66.55; H, 6.42; N, 4.03; P, 9.10. $C_{19}H_{22}NO_3P$ (343.36) requires C, 66.46; H, 6.46; N, 4.08; P, 9.02%; ν_{max} (KBr) (cm^{-1}) 3245 (NH), 1245 (P═O), 1085 (P—O—C); δ_H ($CDCl_3$): 1.38 (dt, $J_{H.H}$ 7.2, $J_{H.P}$ 2.9 Hz, 6H, H_3C—C—OP), 2.39 (s, 3H, H_3C—Ph), 4.01 (dq, J_{HH} 7.2, $J_{H.P}$ 3.4 Hz, 6H, H_2COP), 7.42–7.44 (m, 3H, *H*—Ph), 7.48–7.49 (m, 3H, *H*—Ph), 7.97, 8.28 (2dd, J_{HH} 2.7 Hz, 2H, *H*—Ph), 12.22 (s br, 1H, N*H*, deuterium exchangeable); δ_C ($CDCl_3$): 15.95 (d, $J_{C.P}$ 5.5 Hz, CH_3—C—O), 22.37 (CH_3—Ph), 62.8 (d, $J_{C.P}$ 7.2 Hz, CH_2OP), 127.2 (d, $J_{C.P}$ 145.8 Hz, 1-*C*—P), 122.4, 124.1, 126.7, 127.3, 129.5, 131.3, 136.4 (3-*C*—Ar, C_6H_4, & C_6H_4—Me); δ_p ($CDCl_3$): 30.62; *m/z* (EI) (%): 343 (39) [M^+], 342 (14), 251 (22), 205 (100), 137 (66), 91 (11).

Bisisoindolinylidene (**7**) was obtained (1:9 v/v) as yellow leaflets (155 mg, 9%), m.p. 188–190°C (from C_2H_5OH). Found: C, 87.87; H, 5.43; N, 6.88. $C_{30}H_{22}N_2$ (410.50) requires C, 87.78; H, 5.40; N, 6.82%; ν_{max} (KBr) (cm^{-1}) 1624 (C═C, exocyclic), 1595 (C═N); δ_H (d_6-DMSO) 2.32, 2.40 (2s, 2 × 3H, H_3C—Ph), 7.27–7.95 (m, 16H, *H*—Ph); *m/z* (EI) (%): 410 (100) [M^+], 319 (24), 228 (38), 205 (71), 182 (14).

When the same reaction (**1** + **3b**) was repeated in boiling triethyl phosphite for 10 h, only **6d** and **7** were isolated in 20 and 50% yields, respectively.

Reaction of **1** *with Triisopropyl Phosphite (***3c***)*

Similarly compounds **6e, 5c, 6f**, and **7** were isolated upon heating a mixture of 1.00 g (4.21 mmol) **1** and 5 ml **3c** at 105–110°C for 12 h; followed by the usual working up.

Diisopropyl 3-(4-methylphenyl)-*N*-isopropylisoindolyl-1-phosphonate (**6e**) was obtained (9:1 v/v) as colorless crystals (435 mg, 24%), m.p. 92–94°C (from diethyl ether-light petroleum, 1:1 v/v). Found: C, 69.77; H, 7.72; N, 3.32; P, 7.58. $C_{24}H_{32}NO_3P$ (413.45) requires C, 69.72; H, 7.79; N, 3.39; P, 7.49%; ν_{max} (KBr) (cm^{-1}) 2915 (—N—C*H*Me_2), 1248 (P═O), 1050 (P—O—C); δ_H ($CDCl_3$): 0.88 (d, $J_{H.H}$ 6.3 Hz, 6H, $(H_3C)_2$CHN), 1.26 (d, $J_{H.H}$ 6.3 Hz, 12H, $(H_3C)_2$CO), 2.42 (s, 3H, H_3C—Ph), 3.51 (sept, J_{HH} 6.3 Hz, 1H, NC*H*Me_2), 3.87–3.98 (d.sept, $J_{H.P}$ 7.5 Hz, 2H, OC*H*$Me)_2$), 7.47–7.49 (m, 3H, *H*—Ph), 7.51–7.52 (m, 2H, *H*—Ph), 7.96, 8.29 (2dd, $J_{H.H}$ 2.5 Hz, 2H, *H*—Ph); δ_p ($CDCl_3$): 27.43; *m/z* (EI) (%): 413 (15) [M^+], 470 (36), 279 (14), 205 (100), 165 (55), 91 (33).

Diisopropyl 4-(4-methylphenyl)-1*H*-benzoxazin-1-yl-phosphonate (**5c**) was obtained (8:2 v/v) as colorless needles (295 mg, 18%), m.p. 109–110°C (from cyclohexane). Found: C, 55.19; H, 6.70; N, 3.54; P, 8.08. $C_{21}H_{26}NO_4P$ (387.41) requires C, 55.11; H, 6.76; N, 3.62; P, 8.00%; ν_{max} (KBr) (cm^{-1}) 1587 (C═N), 1258 (P═O), 1080 (P—O—C); δ_H ($CDCl_3$): 1.32, 1.37 (2d, $J_{H.H}$ 6.3 Hz, 12H, $(H_3C)_2$CHOP), 4.16–4.22 (d sept, $J_{H.P}$ 7.5 Hz, 2H, OC*H*Me_2), 4.46 (d, $J_{H.P}$ 15.6 Hz, 1H, 1-C*H*—P), 7.38–7.40 (m, 3H, *H*—Ph), 7.49–7.51 (m, 3H, *H*—Ph), 7.90, 8.28 (2dd, $J_{H.H}$ 2.4 Hz, 2H, *H*—Ph); δ_C ($CDCl_3$): 20.6, 20.9 (2d, $J_{C.P}$ 6.0 Hz, $(CH_3)_2$C—O), 22.77 (CH_3—Ph), 46.3 (d, $J_{C.P}$ 156 Hz, 1-*C*—P), 123.1, 124.8, 126.5, 129.2, 130.7, 131.3, 137.6 (4-*C*—Ar, C_6H_4, and C_6H_4—Me); δ_p ($CDCl_3$): 29.5; *m/z* (EI) (%): 387 (37) [M^+], 386 (23), 370 (14), 221 (20), 205 (100), 165 (58), 91 (15).

Diisopropyl 3-(4-methylphenyl)isoindolyl-1-phosphonate (**6f**) was isolated (7:3 v/v) as colorless

crystals (200 mg, 13%), m.p. 112–113°C (from diethyl ether). Found: C, 67.85; H, 7.01; N, 3.71; P, 8.42. $C_{21}H_{26}NO_3P$ (371.43) requires C, 67.91; H, 7.06; N, 3.77; P, 8.34%; ν_{max} (KBr) (cm^{-1}) 3260 (NH), 1252 (P=O), 1060 (P–O–C); δ_H ($CDCl_3$): 1.36 (d, $J_{H.H}$ 6.3 Hz, $J_{H.P}$ 2.7 Hz, 12H, $(H_3C)_2CHOP$), 2.39 (s, 3H, H_3C–Ph), 4.03–4.08 (d sept, $J_{H.P}$ 10.3 Hz, 2H, $OCHMe_2$), 7.41–7.44 (m, 3H, *H*–Ph), 7.48–7.49 (m, 3H, *H*–Ph), 7.93, 8.32 (2dd, $J_{H.H}$ 2.6 Hz, 2H, *H*–Ph), 12.28 (s.br, 1H, *H*N, deuterium exchangeable); δ_p ($CDCl_3$): 30.20; *m/z* (EI) (%): 371 (40) [M^+], 370 (21), 279 (18), 205 (100), 165 (55), 91 (18).

Bisisoindolinylidene (**7**) was next obtained (1:9 v/v) in a pure form (170 mg, 10%), m.p., and mixed m.p., and comparative IR and mass spectra with that previously obtained.

When the same reaction (**1** + **3c**) was repeated at the boiling temperature of triisopropyl phosphite for 10 h, only **6f** and **7** were isolated in 18 and 55% yields, respectively.

Reaction of **1** *with Dialkyl Phosphonates* **4a–c**

To a mixture of 1.00 g (4.21 mmol) **1** and dimethyl-, diethyl or diisopropyl phosphonate (**4a–c**) (6.00 mmol) in 20 ml toluene was added 2 ml of freshly prepared NaOH solution (5%). The reaction mixture was refluxed for 10 h. After the removal of the volatile materials in vacuo, the oily residue left behind was treated with light petroleum ether. The solid product, thus obtained was crystallized from the appropriate solvent to give **14a, 14b**, or **14c**.

4-(4-Methylphenyl)-*N*-methyl-4*H*-2,3-benzoxazin-1-one (**14a**) was isolated as pale yellow crystals (675 mg, 72%), m.p. 132–134°C (from *n*-hexane). Found: C, 75.94; H, 5.92; N, 5.44. $C_{17}H_{17}NO_2$ (253.3) requires C, 75.87; H, 5.97; N, 5.53%; ν_{max} (KBr) (cm^{-1}) 2920 (N-Me), 1758 (C=O); δ_H ($CDCl_3$): 2.47 (s, 3H, H_3C–Ph), 3.17 (s, 3H, H_3C–N), 4.64 (s, 1H, 4-C*H*), 7.41–7.42 (m, 3H, *H*–Ph), 7.48–7.50 (m, 3H, *H*–Ph), 7.92, 8.28 (2dd, $J_{H.H}$ 2.5 Hz, 2H, *H*–Ph); δ_C ($CDCl_3$): 24.4 (CH_3–Ar), 31.4 (CH_3–N), 42.6 (4-*C*), 121.8, 122.6, 124.2, 124.6, 126.8, 130.9, 133.4 (C_6H_4 & C_6H_4–Me), 182.4 (1-*C*=O); *m/z* (EI) (%): 253 (100) [M^+], 252 (13), 237 (29), 221 (55), 205 (37), 91 (13).

4-(4-Methylphenyl)-*N*-ethyl-4*H*-2,3-benzoxazin-1-one (**14b**) was obtained as pale yellow crystals (766 mg, 68%), m.p. 115–117°C (from cyclohexane). Found: C, 76.32; H, 6.33; N, 5.18. $C_{17}H_{17}NO_2$ (267.32) requires C, 76.38; H, 6.41; N, 5.24%; ν_{max} (KBr) (cm^{-1}) 2915 (N–Et), 1764 (C=O); δ_H ($CDCl_3$): 1.33 (t, $J_{H.H}$ 6.4 Hz, CH_3–C–N), 2.44 (s, 3H, H_3C–Ph), 3.82 (q, $J_{H.H}$ 6.4 Hz, 2H, H_2C–N), 4.65 (s, 1H, 4-C*H*), 7.42–7.45 (m, 3H, *H*–Ph), 7.48–7.49 (m, 3H, *H*–Ph), 7.92, 8.26 (2dd, $J_{H.H}$ 2.5 Hz, 2H, *H*–Ph); δ_C ($CDCl_3$): 15.8 (CH_3CH_2–N), 22.1 (CH_3–Ph), 43.6 (CH_2–N), 47.2 (4-*C*HAr), 121.7, 122.4, 124.9, 126.1, 127.2, 130.6, 131.7 (C_6H_4 & C_6H_4–Me), 178.6 (1-*C*=O); *m/z* (EI) (%): 267 (100) [M^+], 266 (29), 237 (22), 221 (36), 205 (67), 91 (18).

4-(4-Methylphenyl)-*N*-isopropyl-4*H*-2,3-benzoxazin-1-one (**14c**) was obtained as pale yellow crystals (685 mg, 58%), m.p. 122–124°C (from acetone). Found: C, 76.89; H, 6.86; N, 4.92. $C_{18}H_{19}NO_2$ (281.35) requires C, 76.84; H, 6.81; N, 4.98%; ν_{max} (KBr) (cm^{-1}) 2935 (N–C_3H_7), 1770 (C=O); δ_H ($CDCl_3$) 1.58 (d, $J_{H.H}$ 7.2 Hz, 6H, $(CH_3)_2$-CHN), 2.42 (s, 3H, H_3C–Ph), 3.98 (sept., $J_{H.H}$ 7.2 Hz, 1H, $HCMe_2N$), 4.68 (s, 1H, 4-C*H*), 7.45–7.47 (m, 3H, *H*–Ph), 7.48–7.49 (m, 3H, *H*–Ph), 7.92, 8.31 (2dd, $J_{H.H}$ 2.7 Hz, 2H, *H*–Ph); *m/z* (EI) (%): 281 (100) [M^+], 280 (20), 237 (26), 221 (30), 205 (60), 91 (22).

Reaction of **2** *with Trialkyl Phosphites* **3a–c**

A mixture of 1.00 g (4.48 mmol) **2** [21] and 5 ml trialkyl phosphite (trimethyl-, triethyl, or triisopropyl phosphite (**3a–c**) was heated at 100–110°C for 12 h. After removal of the excess phosphite, the residue was chromatographed on silica gel using hexane-$CHCl_3$ as the eluent.

Reaction with **3a**

Dimethyl 3-phenyl-*N*-methylindolyl-1-phosphonate (**19a**) was obtained (9:1 v/v) as colorless crystals (438 mg, 31%), m.p. 98–100°C (from diethyl ether). Found: C, 64.84; H, 5.73; N, 4.38; P, 9.91. $C_{17}H_{18}NO_3P$ (315.32) requires C, 64.76; H, 5.75; N, 4.44; P, 9.82%; ν_{max} (KBr) (cm^{-1}) 2918 (Me-N), 1235 (P=O), 1086 (P–O–C); δ_H ($CDCl_3$): 3.65, 3.69 (2d, $J_{H.H}$ 10 Hz, 6H, $(H_3CO)_2P$), 7.48–7.57 (m, 3H, *H*–Ph), 7.68–7.82 (m, 3H, *H*–Ph), 8.23, 8.46 (2d, $J_{H.H}$ 2.7 Hz, *H*–Ph); δ_C ($CDCl_3$): 33.2 (N–CH_3), 54.72, 55.3 ($2 \times CH_3OP$), 105.7 (d, $J_{C.P}$ 136.8 Hz, 2-*C*–P), 122.2, 122.6, 124.1, 124.5, 126.6, 126.9, 129.1, 131.8 (C_6H_5 & C_6H_4), 142.5 (2-*C*–Ph); δ_p ($CDCl_3$) 33.41; *m/z* (EI) (%): 315 (15) [M^+], 300 (11), 206 (23), 191 (38), 109 (24), 105 (100).

Dimethyl 3-phenylindolyl-1-phosphonate (**19b**) was obtained (8:2 v/v) as colorless crystals (445 mg, 33%), m.p. 147–149°C (from C_2H_5OH). Found: C, 63.72; H, 5.28; N, 4.60; P, 10.34. $C_{16}H_{16}NO_3P$ (301.29) requires C, 63.78; H, 5.35; N, 4.65; P, 10.28%; ν_{max} (KBr) (cm^{-1}) 3279 (NH), 1248 (P=O), 1028 (P–O–C); δ_H ($CDCl_3$): 3.74, 3.78 (2d, $J_{H.H}$ 10.6 Hz, 6H, $(H_3CO)_2P$), 7.47–7.57 (m, 3H, *H*–Ph), 7.66–7.84

(m, 3H, *H*—Ph), 8.15, 8.46 (2d, $J_{H.H}$ 2.75 Hz, 2H, *H*—Ph), 11.84 (s, 1H, *H*N, deuterium exchangeable); δ_p ($CDCl_3$): 33.26; *m/z* (EI) (%): 301 (42) [M^+], 192 (23), 109 (24), 105 (100).

Methylation of the Phosphonate **19b**

To a stirred solution of 0.5 g (1.58 mmol) **19b** in 20 ml dry acetone was added 1.00 g of anhydrous K_2CO_3. Stirring was continued at room temperature for 1 h. Freshly distilled 0.3 g CH_3I (2.16 mmol) was then added and the mixture was gently heated under reflux for 8 h. The inorganic and volatile materials were removed to give a semi-solid, which solidified after being triturated with cold pentane to give 272 mg (52%) **19a**, m.p. and mixed m.p. and comparative IR and mass spectra with that previously obtained.

Reaction with **3b**

Diethyl 3-phenyl-*N*-ethylindolyl-1-phosphonate (**19c**) was obtained (9:1 v/v) as colorless crystals (672 mg, 42%), m.p. 62–64°C (from pentane). Found: C, 67.11; H, 6.72; N, 3.84; P, 8.74. $C_{20}H_{24}NO_3P$ (357.4) requires C, 67.21; H, 6.77; N, 3.92; P, 8.67%; ν_{max} (KBr) (cm^{-1}) 1922 (Et—N), 1238 (P═O), 1080 (P—O—C); δ_H ($CDCl_3$): 1.23 (t, $J_{H.H}$ 6.5 Hz, 3H, H_3C—CN), 1.40–1.45 (m, 6H, H_3C—C—OP), 3.9 (q, 2H, H_2C—N), 4.24–4.28 (2q (m), 4H, H_2C—OP), 7.58–7.63 (m, 3H, *H*—Ph), 7.79–8.05 (m, 3H, *H*—Ph), 8.69, 8.72 (2d, $J_{H.H}$ 2.5 Hz, 2H, *H*—Ph); δ_C ($CDCl_3$): 15.7, 16.2, 16.5 [CH_3-C—N & (H_3C—$CO)_2$], 44.3 (H_2C—N), 59.4, 61.8 (POCH_2), 98.9 (3-*C*—P), 118.2, 121.2, 122.2, 124.8, 125.9, 129.6, 133.6, 137.4 (2-*C*—Ph), C_6H_4, and C_6H_5); δ_p ($CDCl_3$): 32.85; *m/z* (EI) (%): 357 (22) [M^+], 328 (13), 220 (55), 191 (30), 137 (18), 105 (100).

Diethyl 3-phenylindolyl-1-phosphonate (**19d**) was obtained (8:2 v/v) as colorless crystals (410 mg, 27%), m.p. 108–110°C (from cyclohexane). Found: C, 65.71; H, 6.07; N, 4.17; P, 9.49. $C_{18}H_{20}NO_3P$ (329.35) requires C, 65.64; H, 6.12; N, 4.25; P, 9.41%; ν_{max} (KBr) (cm^{-1}) 3260 (NH), 1240 (P═O), 1110 (P—O—C); δ_H ($CDCl_3$): 1.41, 1.44 (2dt, $J_{H.H}$ 6.7 Hz, $J_{H.H}$ 3.1 Hz, 6H, (H_3C—$CH_2O)_2$P), 4.22, 4.25 (2q, $J_{H.P}$ 11.2 Hz, 4H, H_2C—O), 7.53–7.56 (m, 3H, *H*—Ph), 7.62–7.66 (m, 3H, *H*—Ph), 8.11, 8.12 (2d, $J_{H.H}$ 2.5 Hz, 2H, *H*—Ph), 12.06 (s, 1H, *H*N, deuterium exchang.); δ_p ($CDCl_3$): 31.31; *m/z* (EI) (%): 329 (36) [M^+], 328 (16), 191 (29), 138 (18), 105 (100).

Reaction with **3c**

Diisopropyl 3-phenylindolyl-1-phosphonate (**19e**) was obtained (7:3 v/v) as colorless crystals (1.00 g, 68%), m.p. 147–149°C (from acetone). Found: C, 67.28; H, 6.71; N, 3.84; P, 8.65. $C_{20}H_{24}NO_3P$ (357.4) requires C, 67.21; H, 6.77; N, 3.92; P, 8.67%; ν_{max} (KBr) (cm^{-1}) 3278 (NH), 1228 (P═O), 1008 (P—O—C); δ_H ($CDCl_3$): 1.16, 1.18 (2d, $J_{H.H}$ 6.2 Hz, 12H, ($H_3C)_2CH$), 4.73–4.79 (d.sept, $J_{H.H}$ 6.2 Hz, $J_{H.P}$ 7.5 Hz, 2H, OCHMe$_2$), 7.54–7.58 (m, $J_{H.H}$ 4 Hz, 3H, *H*—Ph), 7.79–7.95 (m, 3H, *H*—Ph), 8.69, 8.72 (2d, $J_{H.H}$ 4 Hz, 2H, *H*—Ph); δ_C ($CDCl_3$): [21.6 (d, $J_{C.P}$ 6.5 Hz), 22.8 (d, $J_{C.P}$ 5 Hz, OCH($CH_3)_2$], 70.6 (dd, $J_{C.P}$ 5.5 Hz, OCH($CH_3)_2$), 110 (d, $J_{C.P}$ 145 Hz, 3-*C*), 122.4, 125.2, 125.7, 126.1, 131.6, 139.4, 144.5 (2-*C*, C_6H_4, and C_6H_5); δ_p ($CDCl_3$): 31.81; *m/z* (EI) (%): 357 (52) [M^+], 356 (18), 191 (43), 166 (33), 105 (100).

IV-Reaction of **2** *with Dialkyl Phosphonates* **4a–c**

To a mixture of 1.00 g (4.48 mmol) **2** and dimethyl-, diethyl-, or diisopropyl phosphonate (**4a–c**) (6.00 mmol) in 20 ml toluene, was added 2 ml of freshly prepared NaOH solution (5%). The reaction mixture was refluxed for 10 h. After the removal of the volatile materials in vacuo, the residue was crystallized from the appropriate solvent to give **20a, 20b**, or **20c**, respectively.

N-Methyl-3-phenyl-3*H*-2,4-benzoxazin-1-one (**20a**) was obtained as colorless needles (568 mg, 53%), m.p. 105–107°C (from cyclohexane). Found: C, 75.35; H, 5.41; N, 5.79. $C_{15}H_{13}NO_2$ (239.28) requires C, 75.30; H, 5.48; N, 5.85%; ν_{max} (KBr) (cm^{-1}) 2920 (N-Me), 1764 (C═O); δ_H ($CDCl_3$): 3.31 (d, $J_{H.H}$ 2.2 Hz, 3H, H_3C—N), 5.01 (q, 1H, 3-C*H*—Ph), 7.47–7.96 (m, 8H, *H*—Ph); δ_C ($CDCl_3$): 32.2 (H_3C—N), 49.5 (3-*C*H—Ph), 118.6, 120.9, 121.2, 123.5, 125.4, 125.9, 126.28, 133.47 (C_6H_4 and C_6H_5), 205.6 (1-*C*═O); *m/z* (EI) (%): 239 (78) [M^+], 224 (26), 162 (50), 147 (32), 77 (100).

N-Ethyl-3-phenyl-3*H*-2,4-benzoxazin-1-one (**20b**) was obtained as colorless needles (680 mg, 60%), m.p. 85–86°C (from pentane). Found: C, 75.82; H, 5.90; N, 5.47. $C_{16}H_{15}NO_4$ (253.30) requires C, 75.82; H, 5.97; N, 5.53%; ν_{max} (KBr) (cm^{-1}) 2915 (N—C_2H_5), 1764 (C═O); δ_H ($CDCl_3$): 1.55 (t, $J_{H.H}$ 7 Hz, 3H, H_3C—CH_2—N), 3.92 (q, $J_{H.H}$ 7 Hz, 2H, CH_2—N), 5.03 (s, 1H, 3-C*H*—Ph), 7.47–7.98 (m, 8H, *H*—Ph); *m/z* (EI) (%): 253 (100) [M^+], 237 (18), 224 (12), 208 (30), 176 (40), 147 (55), 77 (82).

N-isopropyl-3-phenyl-3*H*-2,4-benzoxazin-1-one (**20c**) was obtained as colorless crystals (590 mg, 50%), m.p. 98–100°C (from light petroleum). Found: C, 76.43; H, 6.33; N, 5.17. $C_{17}H_{17}NO_2$ (267.33) requires C, 76.38; H, 6.41; N, 5.24%; ν_{max} (KBr) (cm^{-1}) 2933 (N—C_3H_7), 1760 (1-C═O); δ_H ($CDCl_3$): 1.62 (d, $J_{H.H}$ 8.0 Hz, 6H, i-H_3C—C—N), 4.40 (sept,

$J_{H,H}$ 8.0 Hz, 1H, C*H*—N), 7.45–8.11 (m, 8H, *H*—Ph); *m/z* (EI) (%): 267 (100) [M^+], 251 (11), 237 (42), 190 (31), 177 (22), 160 (9), 77 (78).

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