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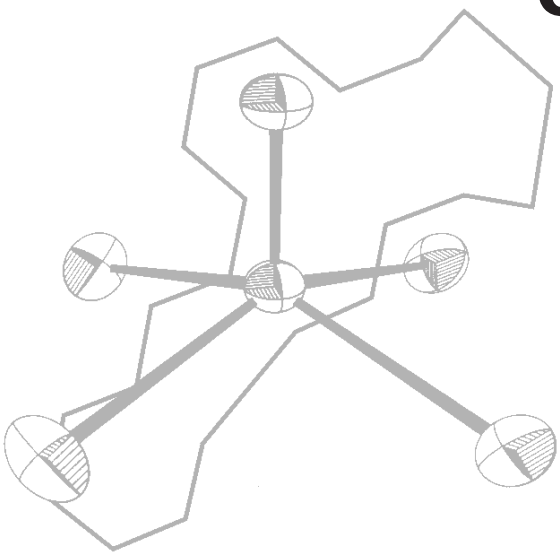

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A Comparison of the Flash Vacuum Pyrolysis Products of Some *N*-Acylbenzotriazoles and *N*-Acylbenzisoxazolones

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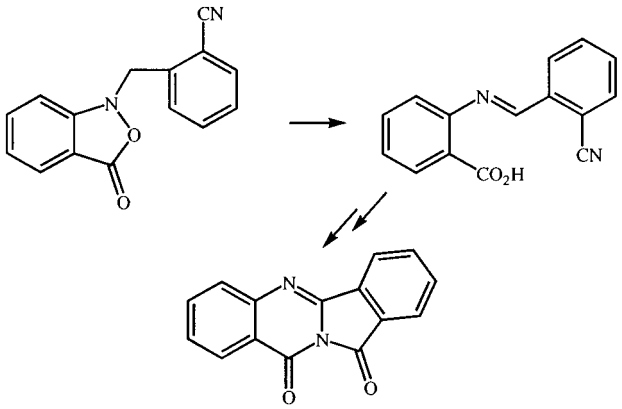
The flash vacuum pyrolysis (f.v.p.) products of 2-(1*H*-benzotriazol-1-ylcarbonyl)benzonitrile, methyl 2-(1*H*-benzotriazol-1-ylcarbonyl)benzoate and 1-(2-chloromethylbenzoyl)-1*H*-benzotriazole and the corresponding benzisoxazolones have been characterized. The benzotriazole derivatives gave compounds whose origin suggests the predominance of radical processes. At lower temperatures the benzisoxazolones gave benzoxazole products consistent with a singlet carbene intermediate, but which had triplet diradical properties at higher temperatures, leading to the formation of acridine from the chloromethyl compound. The major low-temperature f.v.p. product from the (chloromethylbenzoyl)benzisoxazolone was indolo[1,2-*b*]benzoxazole.

Introduction

In a recent paper[1] we examined the flash vacuum pyrolysis (f.v.p.) products of some (*ortho*-substituted) benzylbenzisoxazolones and the corresponding benzotriazoles, and found that the products of the latter were consistent with the intermediacy of diradicals. These pathways were most marked in the case of the 2-methoxycarbonylbenzyl analogue. We had hoped that the *N*-benzylbenzisoxazolones would undergo thermal decomposition by processes involving carbenoid intermediates,[2] but elimination to the imines was clearly the first step in their thermal reactions (Scheme 1). In order to avoid such elimination reactions, and to attempt to find any evidence for cyclizations of the type shown in Scheme 2, we have prepared the acyl compounds (1)–(6), and herein report their f.v.p. products, and a cursory examination of some photolysis products.



Scheme 1

Discussion

The 1-acyltriazoles (1)–(3) were prepared in high yield by treating the sodium salt of the benzotriazole with the corresponding acid chloride in tetrahydrofuran; only in the case of (3) was the N 1 acylated material accompanied by about 10% of the N 2 acylated isomer,[3] readily separated by crystallization. Previous work on the pyrolytic reactions of acylated benzotriazoles has always given low yields of products.[4–7] F.v.p. of compound (1) at 520° gave a mixture of oxazole (7) (16%), and 33% of a compound to which we have tentatively assigned the isoindolo[1,2-*d*] [1,2,3,5]benzotetraazepine structure (8). The structure of (8) is based only on mass and n.m.r. spectrometric evidence and its acidity, and would represent the first member of a new heterocyclic system. Compound (8), remarkably stable at 600°, is believed to be formed by radical recombination of the first formed diradical from (1), followed by addition of benzotriazole, itself formed by fragmentation of (1) (Scheme 3). The alternative zwitterionic intermediate (9), postulated in some thermal liquid phase reactions,[4,8] appears unlikely to us under the f.v.p. conditions employed.

The ester (2) underwent extensive decomposition under the pyrolysis conditions, and the only characterized product was the oxazole (10) (42%).

The triazole (3) underwent f.v.p. to give acridine hydrochloride (65%), with only traces of two other

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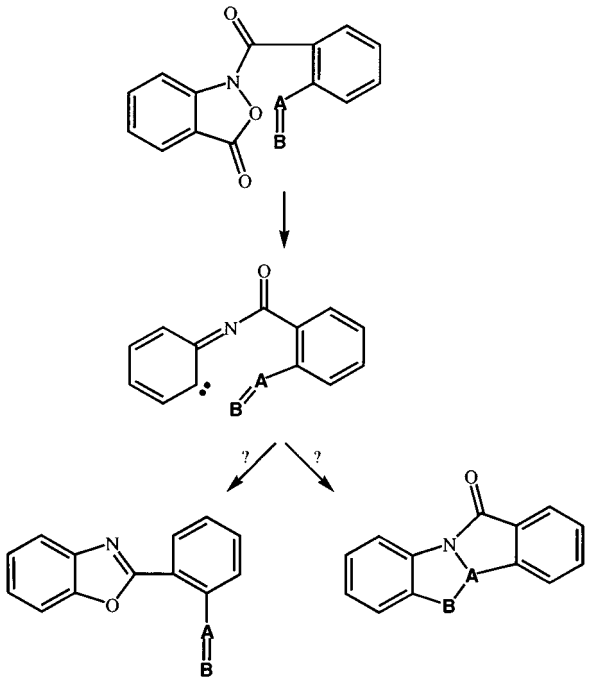
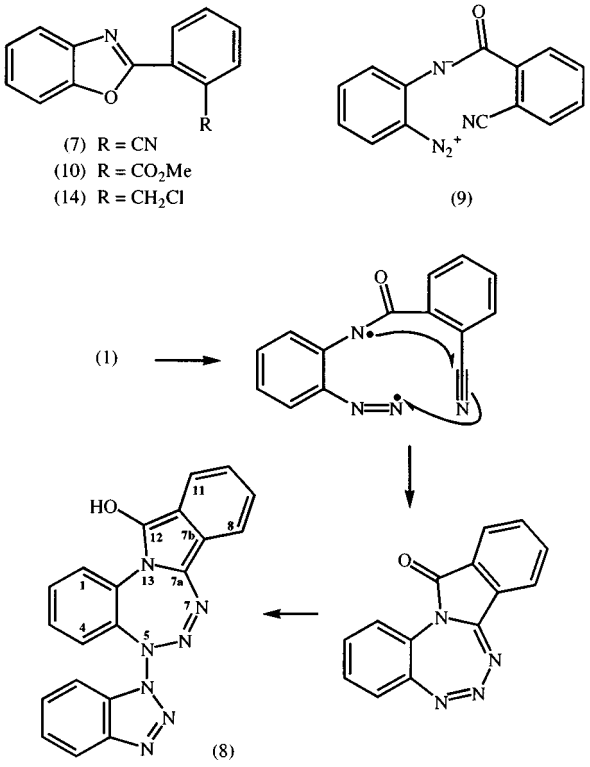


Scheme 2

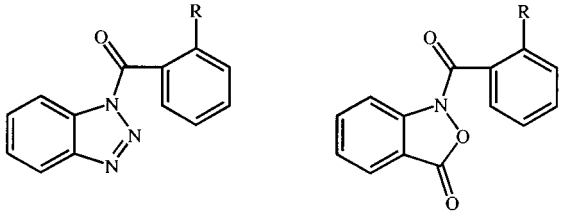


(7) R = CN
(10) R = CO_2Me
(14) R = CH_2Cl

(9)

(8)

Scheme 3

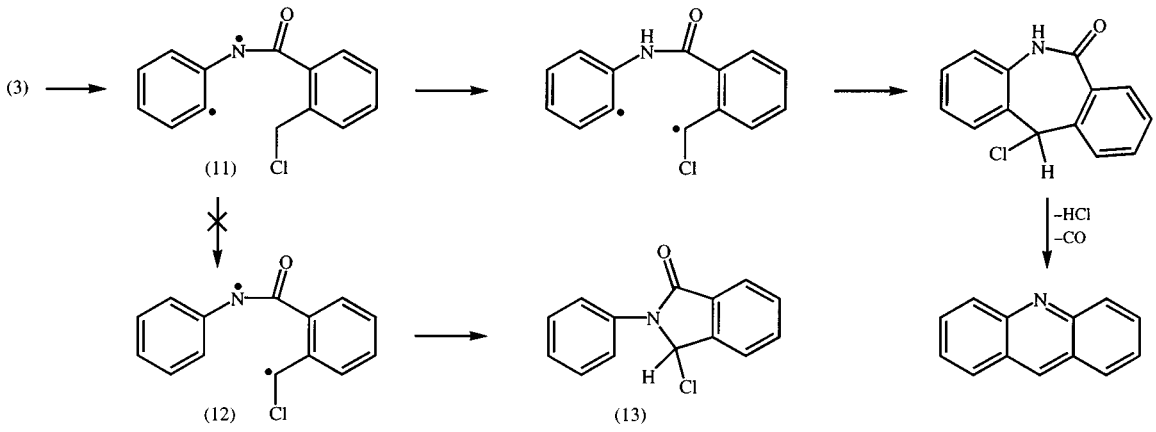


(1) R = CN
(2) R = CO_2Me
(3) R = CH_2Cl

(4) R = CN
(5) R = CO_2Me
(6) R = CH_2Cl

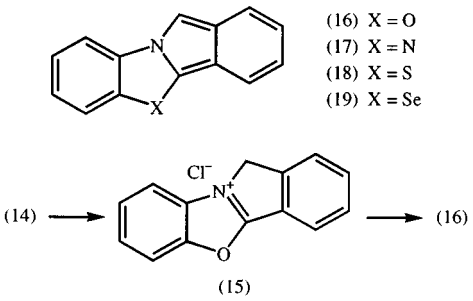
products. Evidence to be presented below suggests that the acridine is a product of the triplet diradical (11) (Scheme 4). The diradical (11), formed by loss of nitrogen, appears to prefer hydrogen atom transfer to the amidyl radical centre rather than to the aryl radical centre leading to (12), presumably for entropic reasons, as the bond strengths of N–H and Ar–H are comparable. In the event, no chlorophthalimidine (13) could be found by g.c.–m.s. investigation.

As has been previously observed,[2] the acylbenzisoxazolones, also prepared from their sodium salts and the corresponding acid chlorides in tetrahydrofuran, underwent f.v.p. at lower temperatures, and more cleanly, than the benzotriazoles. The benzisoxazolones (4) and (5) gave the oxazoles (7) and (10) in 72 and 83% yields respectively at 550°. The benzisoxazolone (6) gave the oxazole (14) in 11% yield at 520°; the major product (59%) was the novel tetracycle



Scheme 4

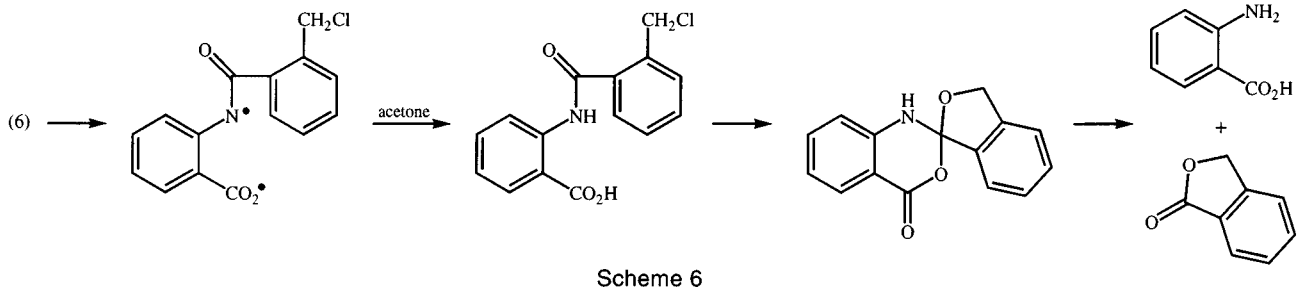
isoindolo[2,1-*b*]benzoxazole (16). While the syntheses of the nitrogen,[9] sulfur[10] and selenium[11] analogues (17)–(19) have been reported, and indeed they enjoy some industrial applications,[12] (16) does not appear to have been described. By analogy with the preparation of (18),[10] we suggest that, under the f.v.p. conditions, the relatively weak base (14) is converted into the salt (15), which is deprotonated under the high vacuum conditions (Scheme 5).



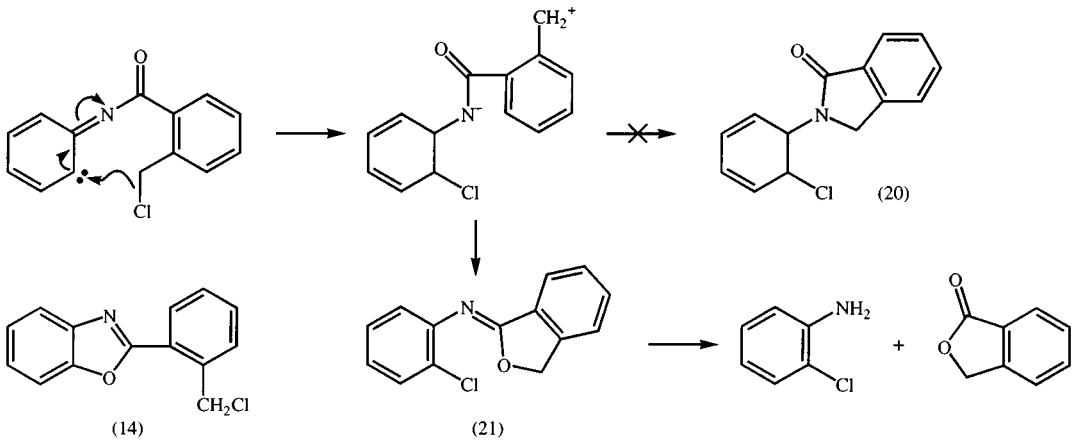
Scheme 5

When the f.v.p. of (6) was conducted at 650°, the product distribution was markedly different to that at 520°, above. While a trace of oxazole (14) was detected, the tetracycle (16) was now only a minor product (11%), the major product being acridine hydrochloride. This observation suggests that pyrolysis at the higher temperatures now gives predominantly a triplet carbene/diradical, leading to hydrogen atom transfer as observed with the benzotriazole. Finally, we wondered whether similar intermediates might be formed on photolysis in solution. When (6) was photolysed at 300 nm in acetone, conditions that favour oxazole formation from acylisoxazolones,[13] two compounds could be isolated; these were identified as phthalide (60%) and anthranilic acid (53%). These products could be expected from the diradical produced by homolysis of the N–O bond, which abstracts hydrogen from the solvent acetone (Scheme 6), but no acridine was obtained in this case. When the solvent was changed to acetonitrile, the photolysis products were a complicated mixture, in which only three components could be unambiguously identified, namely phthalide (38%), oxazole (14) (17%), and 2-chloroaniline (4%). The absence of reduction products in this case suggests to us that the products are arising from the carbene intermediate, as suggested in Scheme 7. While the formation of the phthalimidine (20) might have been expected, no evidence for its presence could be found by g.c.–m.s. The photolysis of *N*-benzoyltriazoles[14] generally leads mainly to hydrogen abstraction or cyclization to phenanthridin-6(5*H*)-one via radical intermediates (Scheme 8).

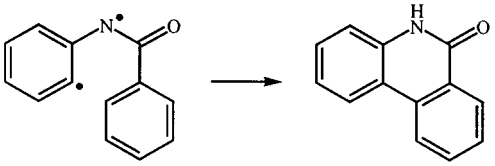
In conclusion, this work supports the conclusions of Yonezawa,[15] who suggests that the decomposition of triazoles, under both thermal and photochemical



Scheme 6



Scheme 7



Scheme 8

conditions, occurs by both singlet and triplet pathways. The benzisoxazolones generally decompose via singlet carbenes, at least at relatively low temperatures.

Experimental

Full experimental details were given in the preceding paper in this series.[1] All previously described compounds were identified by direct comparison with authentic materials, and synthesized by literature procedures.

*2-(1*H*-Benzotriazol-1-ylcarbonyl)benzonitrile (1)*

To a solution of 1*H*-benzotriazole (0·6 g, 5 mmol) and pyridine (7 drops) in dry dichloromethane (6 ml) was added a solution of 2-cyanobenzoyl chloride[16] (0·83 g, 5 mmol) in dry dichloromethane (12 ml). The mixture was refluxed under nitrogen for 5 h, cooled, further dichloromethane (20 ml) added, and the solution washed with water (3×20 ml). Removal of solvent gave a cream solid which was recrystallized from carbon tetrachloride to give white *needles*, m.p. 149° (1·02 g, 82%) (Found: C, 67·8; H, 3·1; N, 22·6%; $M^{+\bullet}$, 248·0703. $C_{14}H_8N_4O$ requires C, 67·8; H, 3·2; N, 22·6%; $M^{+\bullet}$, 248·0698). ^{1}H n.m.r. δ 7·59, td, *J* 7·5, 1·2 Hz, 1H; 7·71–7·95, m, 4H; 8·06, ddd, *J* 7·0, 1·2, 0·9 Hz, 1H; 8·18, dd, *J* 8·1, 1·2 Hz, 1H; 8·42, dd, *J* 8·1, 1·2 Hz, 1H. ^{13}C n.m.r. δ 113·05, 114·66, 116·53, 120·48, 127·01, 131·05, 131·62, 131·79, 132·37, 132·62, 134·05, 135·15, 146·17, 164·52. Mass spectrum *m/z* 248 (M, 14%), 221 (20), 220 (100), 192 (14), 129 (85), 101 (65), 74 (29).

*Methyl 2-(1*H*-Benzotriazol-1-ylcarbonyl)benzoate (2)*

To a solution of 1*H*-benzotriazole (357 mg, 3 mmol) and pyridine (5 drops) in dry dichloromethane (4 ml) was added a solution of 2-methoxycarbonylbenzoyl chloride (600 mg, 3 mmol) (made from methyl hydrogen phthalate[17] and thionyl chloride) in dry dichloromethane (2 ml). The mixture was stirred at 25° under nitrogen for 24 h. Dichloromethane (20 ml) was added, and the solution was washed with water (3×20 ml), dried, and the solvent removed. The resultant solid was recrystallized from ethanol to give the title compound as pale brown *needles*, m.p. 113° (718 mg, 85%) (Found: C, 64·2; H, 3·9; N, 15·0%; $M^{+\bullet}$, 281·0808. $C_{15}H_{11}N_3O_3$ requires C, 64·1; H, 3·9; N, 14·9%; $M^{+\bullet}$, 281·0801). ^{1}H n.m.r. δ 3·68, s, 3H; 7·55, ddd, *J* 8·2, 7·2, 1·0 Hz, 1H; 7·65–7·78, m, 4H; 8·11–8·18, m, 2H; 8·49, dt, *J* 8·4, 0·9 Hz, 1H. ^{13}C n.m.r. δ 52·56, 114·57, 120·27, 126·45, 128·56, 129·40, 130·16, 130·60, 131·01, 131·52, 132·77, 135·51, 146·23, 165·96, 169·56. ν_{max} 1726, 1597, 1487, 1442, 1385, 1327, 1290, 1231, 1151, 1083, 1052, 1004, 939, 884, 768, 771, 753, 714 cm^{-1}. Mass spectrum *m/z* 281 (M, 11%), 222 (16), 162 (100), 104 (9), 91 (11).

*1-(2-Chloromethylbenzoyl)-1*H*-benzotriazole (3)*

2-Chloromethylbenzoyl chloride was prepared in 87% yield from phthalide (1·34 g) and triphenylphosphine dichloride (3·3 g) by the method of Burton and Koppes.[18] ^{1}H n.m.r. δ 4·90, s, 2H; 7·42–7·75, m, 3H; 8·28, dd, *J* 7·75, 1·2 Hz, 1H.

A solution of 1*H*-benzotriazole (238 mg, 2 mmol) in dry tetrahydrofuran (4 ml) was added under nitrogen to a suspension of sodium hydride (80 mg, 60% suspension in oil, washed with dry tetrahydrofuran (2 ml)) in dry tetrahydrofuran (3 ml). After 10 min a solution of 2-chloromethylbenzoyl chloride (378 mg, 2 mmol) in dry tetrahydrofuran (4 ml) was added, and the mixture was stirred at 25° for 24 h. Dichloromethane (20 ml) was added, and the mixture washed with water (20 ml), dried, and the solvent removed. Recrystallization of the solid residue from ethanol removed *c.* 10% of the N 2 substituted isomer, and gave the title compound as white *needles* (450 mg, 83%), m.p. 144° (Found: C, 61·7; H, 3·6; N, 15·4%; $M^{+\bullet}$, 271·0511. $C_{14}H_{10}ClN_3O$ requires C, 61·9; H, 3·7; N, 15·5%; $M^{+\bullet}$, 271·0512). ^{1}H n.m.r. δ 4·81, s, 2H; 7·46–7·78, m, 6H; 8·17, dd, *J* 8·1, 1·2 Hz, 1H; 8·42, dd, *J* 8·1, 1·2 Hz, 1H. ^{13}C n.m.r. δ 43·41, 114·64, 120·33, 126·56, 128·09, 130·42, 130·61, 131·06, 131·79, 132·21, 137·64, 146·00, 167·10 (one quaternary C not visible). ν_{max} 1713, 1597, 1483, 1451, 1376, 1049, 939, 883 cm^{-1}. Mass spectrum *m/z* 271 (M, 5%), 243 (23), 242 (42), 241 (44), 208 (100), 180 (24), 179 (25), 154 (29), 152 (83), 124 (65).

2-(3-Oxo-1,3-dihydro-2,1-benzisoxazol-1-ylcarbonyl)benzonitrile (4)

A solution of 2-cyanobenzoyl chloride (166 mg, 1 mmol) in dichloromethane (4 ml) was added to a suspension of benzisoxazolone[19] (135 mg, 1 mmol) and pyridine (5 drops) in dry dichloromethane (5 ml). After 3·5 h at room temperature, the mixture was washed with water (2×5 ml), dried over sodium sulfate, and the solvent removed. The residue was recrystallized from ethanol to give white *needles* (210 mg, 80%), m.p. 180° (Found: C, 63·3; H, 2·7; N, 10·4%; $M^{+\bullet}$, 264·0535. $C_{15}H_8N_2O_3$ requires C, 63·2; H, 3·0; N, 10·1%; $M^{+\bullet}$, 264·0535). ^{1}H n.m.r. δ 7·69–7·93, m, 6H; 7·93, dd, *J* 8·1, 1·2 Hz, 1H; 8·28, dd, *J* 8·1, 1·2 Hz, 1H. ^{13}C n.m.r. δ 111·99, 115·65, 116·50, 125·90, 126·88, 129·73, 132·13, 132·61, 133·92, 135·00, 136·96, 144·95, 161·02, 163·41 (one quaternary C not visible). ν_{max} 2240, 1789, 1685, 1600, 1332, 958, 776, 769 cm^{-1}. Mass spectrum *m/z* 264 (M, 3%), 248 (5), 220 (5), 130 (100), 102 (23), 75 (17).

Methyl 2-(3-Oxo-1,3-dihydro-2,1-benzisoxazol-1-ylcarbonyl)benzoate (5)

A suspension of benzisoxazolone (135 mg, 1 mmol) and methyl 2-chlorocarbonylbenzoate (200 mg, 1 mmol) in dichloromethane (7 ml) was refluxed under nitrogen for 1 h. The solution was passed through a short plug of silica. The solid white residue obtained after evaporation was recrystallized from ethanol to give white needles (237 mg, 80%), m.p. 122° (Found: C, 64·9; H, 3·6; N, 4·7%; $M^{+\bullet}$, 297·0629. $C_{16}H_{11}NO_5$ requires C, 64·6; H, 3·7; N, 4·7%; $M^{+\bullet}$, 297·0637). ^{1}H n.m.r. δ 3·76, s, 3H; 7·46, ddd, *J* 8·1, 7·2, 0·9 Hz, 1H; 7·60, ddd, *J* 7·2, 1·5, 0·6 Hz, 1H; 7·62, td, *J* 7·5, 1·5 Hz, 1H; 7·71, td, *J* 7·5, 1·2 Hz, 1H; 7·86, ddd, *J* 8·4, 7·5, 1·2 Hz, 1H; 7·92, ddd, *J* 8·1, 1·2, 0·9 Hz, 1H; 8·1, ddd, *J* 8·1, 1·2, 0·9 Hz, 1H; 8·27, br d, *J* 7·2 Hz, 1H. ^{13}C n.m.r. δ 52·65, 111·99, 115·09, 125·73, 126·21, 127·91, 128·04, 130·21, 130·77, 133·02, 134·86, 136·78, 145·86, 163·84, 165·80, 165·92. ν_{max} 1786, 1719, 1697, 1465, 1367, 1332, 1288, 972, 754 cm^{-1}. Mass spectrum *m/z* 297 (M, 0·2%), 266 (1·6), 222 (1·7), 164 (9·7), 163 (100), 135 (3), 133 (2·5), 104 (4·2), 92 (4·7), 77 (13·3), 76 (9·7), 51 (1·5), 50 (3·4), 44 (6·7).

*1-(2-Chloromethylbenzoyl)benzisoxazol-3(1*H*)-one (6)*

A solution of benzisoxazolone (405 mg, 3 mmol) in dry tetrahydrofuran (3 ml) was added to a suspension of sodium hydride (120 mg, 60% suspension in oil, washed with dry tetrahydrofuran (2 ml)) in dry tetrahydrofuran (3 ml). After 10 min at room temperature under nitrogen, a solution of 2-chloromethylbenzoyl chloride (567 mg, 3 mmol) in dry tetrahydrofuran (3 ml) was added. The mixture was stirred at room

temperature for 4 h, dichloromethane (20 ml) added, and the mixture washed with water (20 ml). The organic phase was dried, concentrated, and the solution passed through a short column of silica. The resultant solid was recrystallized from ethanol to give white *needles* (623 mg, 77%), m.p. 139° (Found: C, 62·8; H, 3·6; N, 4·9%; $M^{+\bullet}$, 287·0353. $C_{15}H_{10}ClNO_3$ requires C, 62·6; H, 3·5; N, 4·9%; $M^{+\bullet}$, 287·0349). ^{1}H n.m.r. δ 4·78, s, 2H; 7·42–7·5, m, 2H; 7·53–7·57, m, 2H; 7·64, ddd, J 8·1, 1·2, 0·9 Hz, 1H; 7·84, td, J 8·1, 1·2 Hz, 1H; 7·93, ddd, J 7·5, 1·2, 0·9 Hz, 1H; 8·18, br d, J 8·1 Hz, 1H. ^{13}C n.m.r. δ 43·09, 112·10, 115·35, 125·71, 126·33, 128·34, 128·91, 130·37, 131·61, 131·71, 136·60, 136·62, 145·0, 163·36, 163·68. ν_{max} 1779, 1681, 1601, 1477, 1375, 1333, 1253, 973, 752 cm^{-1}. Mass spectrum m/z 289 (M, 0·6%), 287 (M, 1·8), 252 (1·2), 155 (47), 153 (100), 134 (18), 105 (53).

*Pyrolysis of 2-(1*H*-Benzotriazol-1-ylcarbonyl)benzonitrile (1)*

(i) *At 520°*. The nitrile (1) (100 mg) was subjected to flash vacuum pyrolysis (520°, 110°, 0·05 mmHg, 2 h). The contents of the cold trap were extracted with dichloromethane, to give 2-(benzoxazol-2-yl)benzonitrile (7) (14 mg, 16%), and evaporation of the ethanol extract of the pyrolysis tube gave a yellow base-soluble oil, tentatively identified as 5-(1*H*-benzotriazol-1-yl)-5*H*-isoindolo[1,2-*d*][1,2,3,5]benzotetrazepin-12-ol (8) (49 mg, 33%). ^{1}H n.m.r. δ 6·35, t, J 7 Hz, 2H; 6·63, d, J 10 Hz, 2H; 6·92, t, J 10 Hz, 1H; 7·05, d, J 10 Hz, 1H; 7·50, m, 3H; 7·65, m, 3H. ^{13}C n.m.r. δ 107·5, 114·0, 116·5, 120·0, 120·5, 120·8, 122·5, 125·8, 126·0, 132·8, 133·2, 134·6, 134·8, 135·0, 136·8, 142·0, 152·5, 170·0 (two peaks not observed). Mass spectrum m/z 367 (M), 341, 257, 217, 203, 136, 81.

(ii) *At 650°*. The nitrile (1) was pyrolysed under flash vacuum pyrolysis conditions (650°, 110°, 0·05 mmHg, 2 h). The product from the cold trap was purified by chromatography on silica to give 2-(benzoxazol-2-yl)benzonitrile (7) (25 mg, 32%) as a pale yellow *oil* (Found: $M^{+\bullet}$, 220·0637. $C_{14}H_8N_2O$ requires $M^{+\bullet}$, 220·0637). ^{1}H n.m.r. δ 7·38–7·46, m, 2H; 7·6–7·69, m, 2H; 7·75, td, J 8·1, 1·5 Hz, 1H; 7·83–7·89, m, 2H; 8·41, dd, J 8·1, 1·5 Hz, 1H. ^{13}C n.m.r. δ 110·88, 110·92, 117·62, 120·81, 125·0, 126·16, 129·14, 129·7, 131·06, 132·78, 135·06, 141·58, 150·65, 159·46. ν_{max} 2230, 1545, 1543, 1377, 1260, 1032, 815, 738 cm^{-1}. Mass spectrum m/z 220 (M, 100%), 192 (12), 178 (30), 151 (30), 128 (9), 92 (18).

*Pyrolysis of Methyl 2-(1*H*-Benzotriazol-1-ylcarbonyl)benzoate (2)*

The triazole (2) (100 mg) was pyrolysed as above (700°, 110°, 0·05 mmHg, 1 h). The product was obtained by passing the dichloromethane washing of the cold trap and pyrolysis tube through a short plug of silica, followed by radial chromatography (CH_2Cl_2/light petroleum, 1:1). Methyl 2-(benzoxazol-2-yl)benzoate (10) (38 mg, 42%) was isolated as a colourless oil, with properties identical to those described for the pyrolysis product of (5), below.

*Pyrolysis of 1-(2-Chloromethylbenzoyl)-1*H*-benzotriazole (3)*

The triazole (3) was pyrolysed as above (650°, 110°, 0·05 mmHg, 50 min). The products were obtained by washing the trap and pyrolysis tube with dichloromethane and water. The aqueous phase was basified with aqueous sodium hydroxide, and then extracted with dichloromethane to give acridine (42 mg, 62%), m.p. 100°, with spectroscopic data identical in all respects with those of an authentic sample.

Pyrolysis of 2-(3-Oxo-1,3-dihydro-2,1-benzoxazol-1-ylcarbonyl)benzonitrile (4)

The isoxazolone (4) (100 mg) was pyrolysed under f.v.p. conditions (520°, 110°, 0·05 mmHg, 4 h). A solution of the contents of the cold trap in dichloromethane was chromatographed on silica to give 2-(benzoxazol-2-yl)benzonitrile (7) (61 mg, 72%), whose spectroscopic data were identical with those of the compound obtained above.

Pyrolysis at 650° gave the same product, but the yield was reduced to 38%.

Pyrolysis of Methyl 2-(3-Oxo-1,3-dihydro-2,1-benzoxazol-1-ylcarbonyl)benzonitrile (5)

Compound 5 (100 mg) was pyrolysed under f.v.p. conditions (590°, 120°, 0·05 mmHg, 90 min). The product in the cold trap was dissolved in dichloromethane and filtered through a plug of silica. The solvent was removed, and the product (80 mg) was purified by radial chromatography (CH_2Cl_2)/light petroleum, 1:1), to give methyl 2-(benzoxazol-2-yl)benzoate (10) (71 mg, 83%) as a colourless *oil* (Found: $M^{+\bullet}$, 253·0738. $C_{15}H_{11}NO_3$ requires $M^{+\bullet}$, 253·0739). ^{1}H n.m.r. δ 3·85, s, 3H; 7·35–7·40, m, 2H; 7·54–7·67, m, 3H; 7·77–7·82, m, 2H; 8·04–8·08, m, 1H. ^{13}C n.m.r. δ 52·6, 110·6, 120·45, 124·64, 125·42, 126·58, 129·30, 130·12, 131·01, 131·16, 132·68, 141·95, 151·06, 162·15, 168·68. ν_{max} 1733, 1617, 1559, 1454, 1443, 1345, 1295, 1242, 1194, 1129, 1100, 1047, 761, 747, 703 cm^{-1}. Mass spectrum m/z 253 (M, 20%), 222 (41), 195 (34), 148 (66), 134 (20), 105 (50), 104 (100), 91 (8), 86 (18), 84 (28), 77 (24), 76 (96), 74 (23), 63 (13), 51 (13), 50 (45).

*Pyrolysis of 1-(2-Chloromethylbenzoyl)benzisoxazol-3(1*H*)-one (6)*

(i) *At 520°*. Isoxazolone (6) was pyrolysed under f.v.p. conditions (520°, 110°, 0·05 mmHg, 30 min). The crude product was separated by column chromatography (CH_2Cl_2), giving 2-(benzoxazol-2-yl)benzyl chloride (14) (10 mg, 11%) as a colourless *oil*, and isoindolo[2,1-*b*]benzoxazole (16) (43 mg, 59%) as a colourless *oil*. 2-(Benzoxazol-2-yl)benzyl chloride (14) (Found: $M^{+\bullet}$, 243·0448. $C_{14}H_{10}ClNO$ requires $M^{+\bullet}$, 243·0450). ^{1}H n.m.r. δ 5·39, s, 2H; 7·36–7·58, m, 4H; 7·62, td, J 8·1, 1·2 Hz, 1H; 7·69, dd, J 7·6, 1·2 Hz, 1H; 7·82, td, J 7·6, 1·2 Hz, 1H; 8·24, dd, J 7·6, 1·2 Hz, 1H. ^{13}C n.m.r. δ 44·67, 110·59, 115·76, 120·42, 124·61, 125·47, 127·70, 128·63, 130·09, 131·17, 131·35, 137·42, 142·20, 150·31. ν_{max} 1576, 1440, 1266, 1192, 1042, 835, 718 cm^{-1}. Mass spectrum m/z 245 (M, 34%), 243 (M, 100), 209 (17), 207 (82), 184 (20), 179 (14), 153 (15), 90 (11). Isoindolo[2,1-*b*]benzoxazole (16) (Found: $M^{+\bullet}$, 207·0688. $C_{14}H_9NO$ requires $M^{+\bullet}$, 207·0684). ^{1}H n.m.r. δ 6·66, s, 1H; 7·35, td, J 8·1, 1·2 Hz, 1H; 7·62–7·82, m, 4H; 7·97, dd, J 8·1, 1·2 Hz, 1H; 8·12–8·21, m, 2H. ^{13}C n.m.r. δ 84·69, 115·12, 119·64, 124·09, 124·71, 125·39, 131·06, 131·26, 131·78, 133·72, 135·92, 138·12, 138·92, 161·30. ν_{max} 1602, 1582, 1488, 1464, 1399, 1377, 1353, 1211, 1051, 1019, 756 cm^{-1}. Mass spectrum m/z 207 (M, 6%), 179 (12), 169 (20), 153 (10), 134 (53), 105 (100), 90 (8), 77 (78).

(ii) *At 650°*. Pyrolysis as above at 650° led to a product which was soluble in water, and another which was soluble in dichloromethane. The latter gave isoindolo[2,1-*b*]benzoxazole (16) (10 mg, 14%), identical with the sample obtained above. The aqueous phase was basified with sodium hydroxide and extracted with dichloromethane to give acridine as yellow crystals, m.p. 100° (39 mg, 62%) (Found: $M^{+\bullet}$, 179·0725. Calc. for $C_{13}H_9N$: $M^{+\bullet}$, 179·0735). The identity was confirmed by direct comparison of its spectroscopic properties with those of an authentic sample, and by g.c.–m.s. analysis. ^{1}H n.m.r. δ 7·45, td, J 7·5, 0·9 Hz, 2H; 7·71, td, J 7·5, 0·9 Hz, 2H; 7·88, dd, J 8·1, 1·2 Hz, 2H; 8·21, dd, J 8·1, 1·2 Hz, 2H; 8·63, s, 1H. ^{13}C n.m.r. δ 125·5, 126·43, 128·05, 129·23, 130·13, 135·86, 148·90.

*Photolysis of 1-(2-Chloromethylbenzoyl)benzisoxazol-3(1*H*)-one (6)*

(i) *In acetone*. A solution of the benzisoxazolone (6) (100 mg) in acetone (200 ml) was photolysed through a Pyrex filter under nitrogen for 24 h. Removal of the solvent and

partitioning of the residue between aqueous sodium carbonate and dichloromethane gave phthalide (29 mg, 60%) in the neutral fraction, and anthranilic acid (25 mg, 53%) in the acidic fraction. The identity of both compounds was established by infrared spectroscopy, ^{1}H and ^{13}C n.m.r. spectrometry and g.c.–m.s. comparison with commercially available samples.

(ii) *In acetonitrile*. A solution of the benzisoxazolone (6) (50 mg) in acetonitrile (200 ml) was irradiated through Pyrex under nitrogen for 24 h. Removal of solvent gave a brown solid which was analysed by ^{1}H n.m.r. spectroscopy and g.c.–m.s., and was shown to comprise phthalide (9 mg, 38%), 2-(benzoxazol-2-yl)benzyl chloride (14) (7 mg, 17%), and 2-chloroaniline (1 mg, 4%).

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