

2,3-Benzoxazin-1-ones. Part I. Reactions of Aluminium Chloride, Sulphuric Acid, and Hydrazine Hydrate with 4-Aryl-2,3-benzoxazin-1-ones

By Fawzi G. Baddar,*† Amin F. M. Fahmy, and Nawal (Mrs.) F. Aly, Faculty of Science, Ain Shams University, Cairo, Egypt

4-Aryl-2,3-benzoxazin-1-ones (II) reacted with anhydrous aluminium chloride in hot nitrobenzene or chlorobenzene to give the corresponding *N*-arylpthalimides (V). However, reactions in benzene, toluene, and *p*-xylene gave the corresponding *o*-aroylanilides (VII). When heated with dilute sulphuric acid, and with hydrazine in acetic acid, the benzoxazinones (II) were converted into phthalic acid and 4-arylpthalazin-1-ones (IX), respectively.

o-AROYLBENZOIC ACIDS (Ia—c) were condensed with hydroxylamine hydrochloride in aqueous potassium hydroxide to give the 4-aryl-2,3-benzoxazin-1-ones (IIa—c),¹ which showed sharp i.r. bands at 1750, 1770, and 1790 cm⁻¹, respectively, characteristic of carbonyl groups in six-membered heterocyclic compounds (*cf.* δ -lactones).²

Action of Anhydrous Aluminium Chloride.—The benzoxazinones (IIa—c) reacted with anhydrous aluminium chloride in hot nitrobenzene or chlorobenzene to give the corresponding *N*-arylpthalimides (Va—c), respectively. These products were identical with authentic specimens and their i.r. spectra exhibited doublets, as expected for coupled carbonyl groups in cyclic imides³ (Table I).

† *Present address:* Department of Chemistry, Kuwait University, Kuwait.

¹ (a) R. E. Rose, *J. Amer. Chem. Soc.*, 1911, **33**, 389; (b) J. M. Sprague, F. C. Novello, A. A. Deans, U.S.P. 3,322,631 (*Chem. Abs.*, 1968, **68**, 114,434d).

However, similar reactions in hot benzene, toluene, or *p*-xylene gave *o*-aroylanilides (VIIa—c), (VIId—f), and (VIIg—i), respectively. These compounds were identified by their i.r. spectra [ν_{\max} 1700—1660s (aromatic CO), and 3340—3200br cm⁻¹ (bonded NH of aromatic anilides)⁴ (Table 2)], their u.v. spectra [λ_{\max} 265—270 nm (ϵ 6200—10,400) (Table 2)], and hydrolysis of (VIIa) with 70% sulphuric acid to give *o*-benzoylbenzoic acid (Ia) and aniline.

The mechanisms proposed for these reactions are summarised in the Scheme. The alternative route in which (II) reacts with the aromatic solvent substrate before Beckmann rearrangement is less probable, since *N*-arylpthalimides (Va—c) are formed when the unreactive solvents nitrobenzene and chloro-

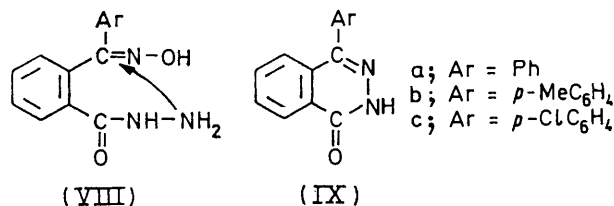
² L. J. Bellamy, 'Infrared spectra of Complex Molecules,' Methuen, London, 1960, p. 179.

³ W. R. Roderick and W. G. Brown, *J. Amer. Chem. Soc.*, 1957, **79**, 5196.

⁴ Ref. 2, p. 205.

benzene are used, indicating that the carbonium ion (IV) is an intermediate. This conclusion is supported by the fact that 3-phenyliminophthalide [*cf.* (III)] undergoes Friedel-Crafts reaction with benzene to give (VIIa),⁵ and rearranges to *N*-phenylphthalimide (Va) when heated at 250°.⁶ The readiness of (II) to undergo internal Beckmann rearrangement in the presence of a Lewis acid is substantiated by the ease of conversion of the 4-aryl-2,3-benzoxazin-1-ones (IIa—c) into phthalic acid when refluxed with sulphuric acid. This could only take place by an internal Beckmann rearrangement, which converts (II) into the corresponding

4-arylphthalazin-1-ones (IX). These compounds were identical with authentic specimens and showed i.r. absorption at 1700—1690s (CO) and 3180—3170br cm⁻¹ (NH) (Table 3). The reaction may proceed *via* the intermediate oxime hydrazone (VIII). Benzophenone



oxime reacts with hydrazine hydrate in acetic acid to give the corresponding hydrazone.⁸

EXPERIMENTAL

I.r. (KBr discs) and u.v. spectra (ethanol) were measured with Unicam SP 1200 and Perkin-Elmer 4000 A spectrophotometers, respectively.

4-(*p*-Tolyl)-2,3-benzoxazin-1-one (IIb).—Prepared according to ref. 1a, this compound formed pale yellow crystals (83%), m.p. 158—160° (from ethanol) (Found: C, 76.0; H, 4.4; N, 5.7. C₁₅H₁₁NO₂ requires C, 75.9; H, 4.6; N, 5.9%).

Action of Anhydrous Aluminium Chloride on 4-Aryl-2,3-benzoxazin-1-ones (II).—A mixture of the benzoxazinone (II) (0.1 mol), and anhydrous aluminium chloride (0.3 mol) in the solvent (100 ml) was heated under reflux for 15 min. The complex formed was decomposed with ice-cold dilute hydrochloric acid. The solvent was removed by steam distillation and the residual solid was filtered off; the products (V) obtained with nitrobenzene or chlorobenzene as solvent are reported in Table 1; those (VII) obtained with benzene, toluene, or *p*-xylene are reported in Table 2.

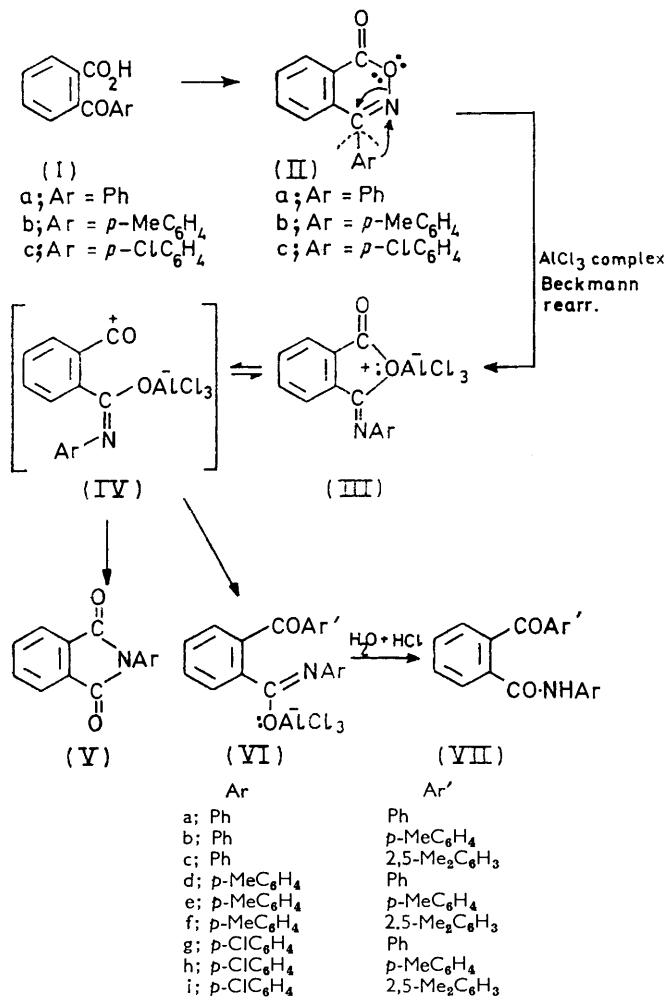
TABLE 1

I.r. spectra of *N*-arylphthalimides (V)

Reactant	Product	Yield (%)	M.p. (°C)	$\nu_{C=O}/\text{cm}^{-1}$
(IIa)	(Va)	90	204—205 ^a	1780, 1710
(IIb)	(Vb)	90	201—202 ^b	1780, 1715
(IIc)	(Vc)	90	194—195 ^a	1790, 1715

Action of Sulphuric Acid on 4-Aryl-2,3-benzoxazin-1-ones (IIa—c) and on *o*-Benzoylbenzanilide (VIIa).—A mixture of the benzoxazinone (II) (2 g) and 70% sulphuric acid (20 ml) was refluxed for 1 h. After cooling, the solid was filtered off and recrystallized from ethanol to give phthalic acid (80%), m.p. and mixed m.p. 206°. When *o*-benzoylbenzanilide (VIIa) was similarly treated it gave *o*-benzoylbenzoic acid (Ia) and aniline.

Action of Hydrazine Hydrate on 4-Aryl-2,3-benzoxazin-1-ones (IIa—c).—A solution of the benzoxazinone (II) (0.1 mol) in glacial acetic acid (50 ml) was treated dropwise with an excess of hydrazine hydrate (12 ml) and left for 1 h



SCHEME

aryliminophthalide.⁷ This is then hydrolysed to phthalic acid. Attempts to isolate the intermediate imine were fruitless.

Action of Hydrazine Hydrate.—When the benzoxazinones (IIa—c) were treated with hydrazine hydrate in glacial acetic acid they gave the corresponding

⁵ R. Pummerer and G. Dorfmueller, *Ber.*, 1912, **45**, 294.

⁶ D. Y. Curtin and L. L. Miller, *J. Amer. Chem. Soc.*, 1967, **89**, 641.

⁷ F. H. Thorpe, *Ber.*, 1893, **26**, 1262, 1795.

⁸ F. Just, *Ber.*, 1886, **19**, 1206.

⁹ (a) M. L. Sherrill, F. L. Schaeffer, and E. P. Shoyer, *J. Amer. Chem. Soc.*, 1928, **50**, 477 and 484 give m.p.s 207 and 192°, respectively; (b) A. Michael, *Ber.*, 1877, **10**, 577 gives m.p. 200°.

TABLE 2
 2-Aroylbenzanilides

Reactant	Solvent *	Product	Yield (%)	M.p. (°C) †	Found (%)				Formula	Required (%)				ν_{NH} / cm ⁻¹	$\nu_{\text{C=O}}$ / cm ⁻¹	$\lambda_{\text{max.}}$ / nm	ϵ
					C	H	Cl	N		C	H	Cl	N				
(IIa)	B	(VIIa)	74	190—191	79.7	4.9	5.1	4.7	C ₂₀ H ₁₃ NO ₂	79.7	4.9	4.7	4.7	3200	1680	265	6200
	T	(VIIb)	78.8	213—215	79.4	5.2	4.6	4.4	C ₂₁ H ₁₇ NO ₂	80.0	5.4	4.4	4.4	3250— 3200br	1690	265	6400
	X	(VIIc)	70	201—202	79.6	6.3	4.6	4.25	C ₂₂ H ₁₉ NO ₂	80.2	5.8	4.25	4.25	3340	1680	270	6600
(IIb)	B	(VIId)	88	192—194	79.7	5.9	4.2	4.4	C ₂₁ H ₁₇ NO ₂	80.01	5.4	4.4	4.4	3260— 3220br	1680	265	5800
	T	(VIIe)	82.2	303—304	80.6	6.1	4.2	4.25	C ₂₂ H ₁₉ NO ₂	80.2	5.8	4.25	4.25	3260— 3200br	1680	265	6000
	X	(VIIf)	89.2	185—187	83.2	6.6	4.6	4.1	C ₂₃ H ₂₁ NO ₂	82.8	6.1	4.1	4.1	3290	1685	270	6950
(IIc)	B	(VIIg)	83.3	210—212	71.2	4.0	4.3	10.8	C ₂₀ H ₁₄ ClNO ₂	71.51	4.2	4.7	10.6	3280	1690	265—270	7500
	T	(VIIh)	82	207—208	72.0	4.6	9.7	4.1	C ₂₁ H ₁₆ ClNO ₂	72.1	4.6	10.1	4.0	3240— 3200br	1680	265—270	7500
	X	(VIIi)	89.4	188	72.3	5.1	9.9	4.0	C ₂₂ H ₁₈ ClNO ₂	72.6	4.95	9.7	3.9	3340— 3300	1690	270	10,400

* B = Benzene, T = toluene, X = *p*-xylene. † Recrystallised from toluene.

 TABLE 3
 4-Arylphthalazin-1-ones

Product	Yield (%)	M.p. (°C)	Found (%)		Calc. (%)		ν_{NH} / cm ⁻¹	$\nu_{\text{C=O}}$ / cm ⁻¹
			C	H	C	H		
(IXa) ^a	80	236* ^{10a}	75.0	5.0	75.6	4.5	3180	1700
(IXb) ^b	85	246* ^{10b}	76.6	5.1	76.3	5.1	3170	1690
(IXc)	90	268† ^{10c}					3170	1680

* From ethanol. † From acetic acid.

^a C₁₄H₁₀N₂O. ^b C₁₅H₁₂N₂O.

with occasional shaking. The solid was filtered off and crystallized from a suitable solvent (Table 3) to give the corresponding 4-arylphthalazin-1-one (IX), identical with that obtained by the reaction of the appropriate *o*-aroylbenzoic acid (I) with hydrazine hydrate.¹⁰

[3/067 Received, 11th January, 1973]

¹⁰ V. Rothenburg, *J. prakt. Chem.*, 1895, **51**, (a) 151; (b) 153; (c) N. P. Buu-Hoi, N. Hoan, and N. H. Khai, *Rec. Trav. chim.*, 1950, **69**, 1083.