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Mass Spectral and Pyrolytic Studies of Some 4,4-Disubstituted 1,4-Dihydro-2*H*-3,1-benzoxazin-2-ones

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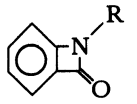
Pyrolysis of 4,4-diaryl-1,4-dihydro-2*H*-3,1-benzoxazin-2-ones at 230—240 °C gives 9-arylacridines and (2-aminophenyl)diarylmethanes. Their formation correlates well with the mass fragmentation of the respective parent compounds.

Benzazetin-2(1*H*)-ones (**1**) have been postulated as reactive intermediates in the pyrolysis and photolysis of isatoic anhydride and 3-substituted 1,2,3-benzotriazin-



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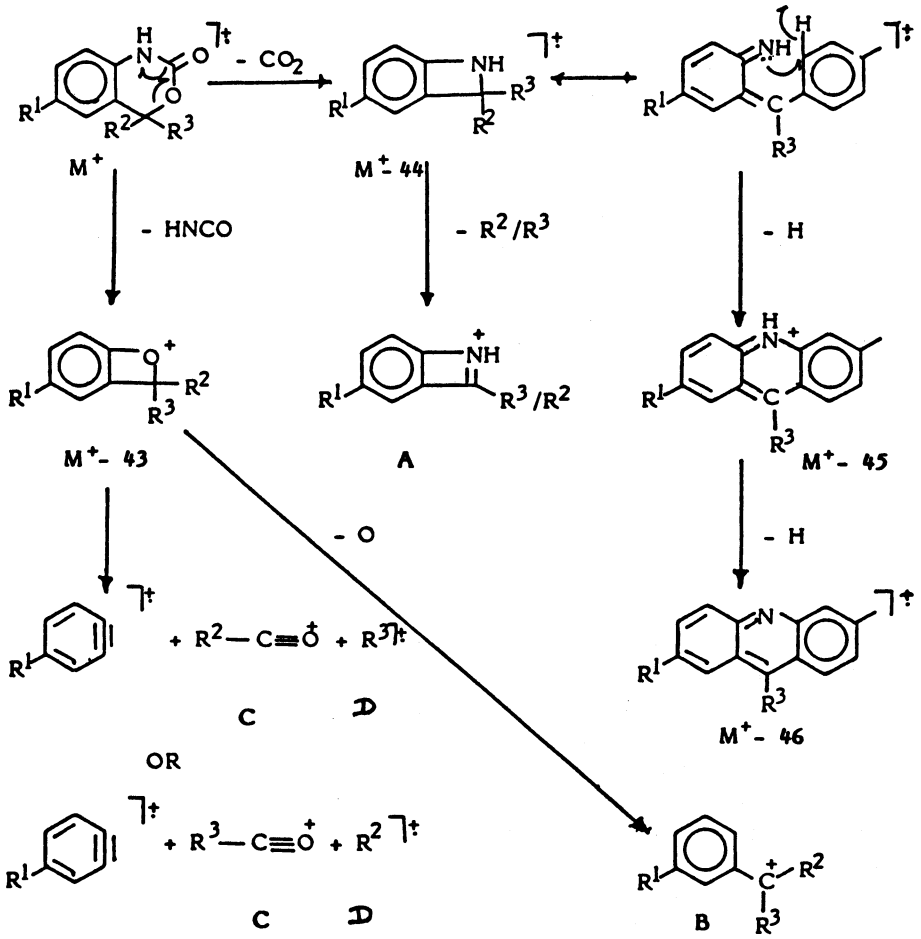
4(3*H*)-ones;[1,2] their formation during the mass fragmentation has also been observed. We had prepared some 4,4-diaryl-1,4-dihydro-2*H*-3,1-benzoxazin-2-ones (**2**) by Friedel-Crafts acylation of arenes with 2-isocyanatobenzoyl chlorides.[3,4] Their mass spectra show appearance of peaks at m/z M^+-44 and M^+-45 which are characteristic of these benzoxazinones **2**. In Table 1 are given prominent fragment ions with relative abundances and the fragmentation pattern is depicted in Chart 1.

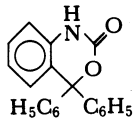
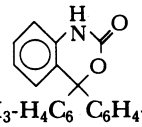
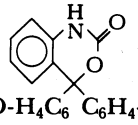
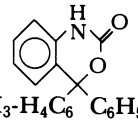
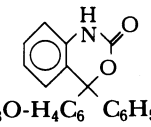
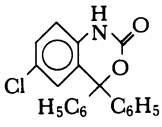
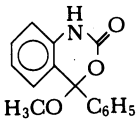
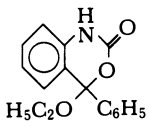
It is observed that these benzoxazinones decompose at their melting points and in view of the known corre-



	R^1	R^2	R^3		R^1	R^2	R^3
a)	H	C_6H_5	C_6H_5	e)	H	C_6H_5	C_6H_4-OCH_3 (*p*)
b)	H	C_6H_4-CH_3 (*p*)	C_6H_4-CH_3 (*p*)	f)	Cl	C_6H_5	C_6H_5
c)	H	C_6H_4-OCH_3 (*p*)	C_6H_4-OCH_3 (*p*)	g)	H	C_6H_5	OCH_3
d)	H	C_6H_5	C_6H_4-CH_3 (*p*)	h)	H	C_6H_5	OC_2H_5

Chart 1.

Table 1. Prominent Ions Found in the Mass Spectra of 4,4-Disubstituted 1,4-Dihydro-2*H*-3,1-benzoxazin-2-ones. Percentage of Relative Abundances are Mentioned in Parentheses

	Compound **2**	M+	M+−43	M+−44	M+−45	M+−46	Other fragment			
							A	B	C	D
a)		301 (2)	258 (10)	257 (47)	256 (100)	255 (14)	180 (30)	—	105 (5)	77 (10)
b)		329 (2)	286 (10)	285 (45)	284 (95)	283 (15)	194 (55)	270 (100)	119 (11)	91 (18)
c)		361 (2)	318 (15)	317 (50)	316 (100)	315 (62)	210 (65)	302 (47)	135 (11)	107 (15)
d)		315 (4)	272 (10)	271 (46)	270 (100)	269 (20)	194(30) 180(28)	256 (70)	119(12) 105(10)	77 (12)
e)		331 (2)	288 (10)	287 (40)	286 (100)	285 (30)	210(33) 180(26)	272 (40)	135(9) 105(11)	77(15) 107(5)
f)		335 (7)	292 (40)	291 (42)	290 (100)	289 (10)	214 (3)	—	105 (13)	77 (24)
g)		255 (4)	—	211 (59)	210 (100)	—	196 (37)	180 (35)	—	—
h)		269 (2)	226 (6)	225 (37)	224 (52)	223 (5)	196 (100)	180 (39)	—	—

lation of pyrolytic and electron impact reactions of some of the closely related compounds viz isatoic anhydride and 3-substituted 1,2,3-benzotriazin-4(3*H*)-ones, it is of interest to study the pyrolysis and photolysis of these 4,4-disubstituted benzoxazinones **2**; we report here the results of these investigations.

When the benzoxazinones (**2a, b, f**) are pyrolyzed at 230—240 °C without solvent, 9-arylacridines (**3a, b, f**) are obtained in 45—60% yield along with (2-aminophenyl) diarylmethanes (**4a, b, f**†) in 10—25% yield. These are separated by column chromatography and identified through their spectral data and comparison with authentic samples[6,7] wherever possible. The formation of **3** and **4** from the above pyrolysis reaction is depicted in Scheme 1.

It is likely that the two hydrogen atoms lost in the final step of formation of **3** add to the intermediate **5**. In order to verify this, the benzoxazinone (**2a**) is pyrolyzed in presence of hydrogen donors such as sodium borohydride and hydroquinone; however, no improvement in the yield of **4** is observed and products with the same relative distribution are obtained. Pyrolysis carried out in the presence of nucleophile e.g. methyl anthranilate also did not produce any additional product.

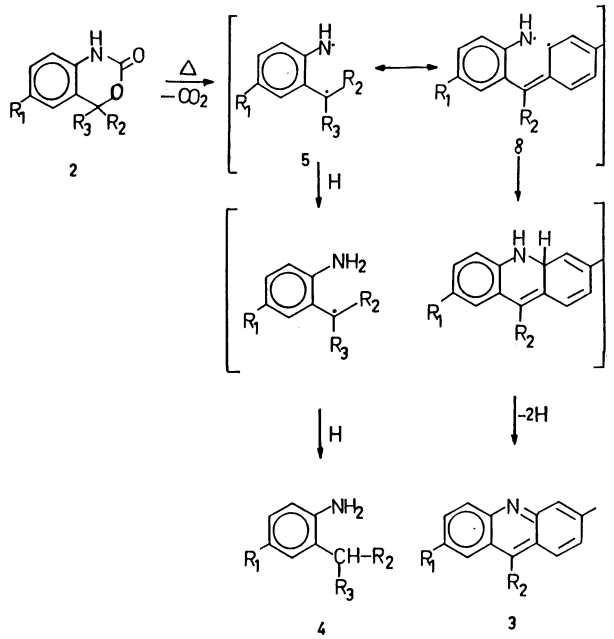
When 4-methoxy-4-phenyl-1,4-dihydro-2*H*-3,1-benzoxazin-2-one (**2g**) is pyrolyzed at 230 °C, it afforded 2-aminobenzophenone (**6**, 49%) and 6,12-diphenyldibenzo(*b,f*)(1,5)diazocine (**7**, 8.5%). The formation of dibenzodiazocine **7** seems to be through the dimerization of the

†**4f** was not isolated, but observed on TLC only.

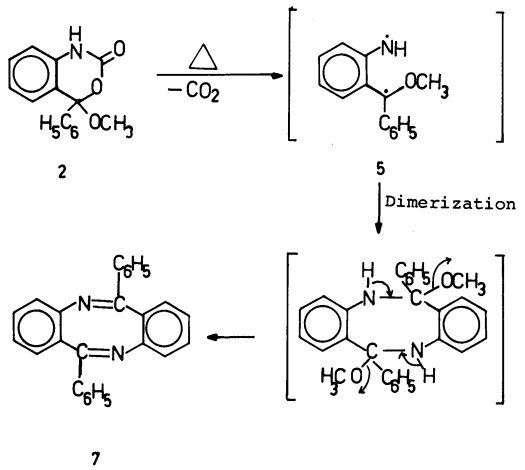
intermediate **5g** (Scheme 2) similar to the dimerization observed in the pyrolysis of isatoic anhydride and 1,2,3-benzotriazin-4(3*H*)-one reported earlier.[1,2]

Although these benzoxazinones **2** afforded the expected products on pyrolysis, they are found to be quite stable to photolysis and are recovered back unchanged after irradiation in a Hanovia reactor with a 400 W lamp for 24 h.

In the case of **2a, b, f,** no dimerization product is obtained, whereas dimerization products are invariably obtained in the reactions of isatoic anhydride and 3-substituted 1,2,3-benzotriazin-4(3*H*)-ones. This is probably due to the stabilization of the intermediate **5** by extended mesomeric interaction with the aromatic residue. No evidence for either the free radical or ionic mechanisms could be obtained as the product composition did not change when the pyrolysis is carried out in the presence of hydroquinone, a known free radical trap or sodium borohydride. However, in view of the correlation with the mass fragmentations, the free radical mechanism is preffered.[5] Formation of no other additional product in the presence of methylanthranilate supports this view. In the case of **2g** however, the intermediate **5g** dimerises to some extent and dibenzodiazocine **7** is obtained (Scheme 2).



Scheme 1.



Scheme 2.

Experimental

4,4-Disubstituted 1,4-dihydro-2*H*-3,1-benzoxazin-2-ones (**2**) are prepared according to the known procedure.[3,4] Yields are given after crystallization. Melting points reported are not corrected.

General Procedure of the Pyrolysis of 4,4-Disubstituted 1,4-Dihydro-2*H*-3,1-benzoxazin-2-ones (2): 4,4-Disubstituted 1,4-dihydro-2*H*-3,1-benzoxazin-2-ones (**2**) were pyrolyzed without solvent in an open mouth round bottomed flask at 230—240 °C for 3 h. After cooling, the mass was taken up in benzene (10 ml), filtered to remove the unreacted **2**, which remained insoluble and the filtrate was subjected to column chromatography on silica gel by successively eluting with benzene-hexane (1 : 1), benzene, and benzene-ethyl acetate (9 : 1) when (2-aminophenyl)diarylmethanes (**4**), 9-arylacridines (**3**) and some unreacted **2** were obtained in the same order of elution. These compounds were further purified by recrystallization.

Pyrolysis of 4,4-Diphenyl-1,2-dihydro-2*H*-3,1-benzoxazin-2-one (2a): The captioned compound **2a** (750 mg) was pyrolyzed as above; the following compounds were obtained:

(i) (2-Aminophenyl)diphenylmethane (**4a**) (180 mg, 28%), mp 127 °C (benzene-hexane), lit,[6] 126—128 °C; IR (Nujol) ν_{max} 3470, 3375, and 1610 cm^{-1}; MS *m/z* (rel intensity) 259 (M^+, 100), 258 (19), 182 (37), 181 (8), 180 (28), 167 (9), 91 (3). Found: C, 88.096; H, 6.552; N, 5.13%. Calcd for $C_{19}H_{17}N$: C, 88.031; H, 6.564; N, 5.405%.

(ii) 9-Phenylacridine (**3a**) (280 mg, 44%), mp 184 °C (benzene-hexane), lit,[7] 185 °C; MS *m/z* (rel intensity) 255.3 (M^+, 100), 254.3 (86.6), 253.3 (17.7), 252.3 (11.5), 251.2 (6.4), 227.2 (6.8), 226.2 (11.1), 127.2 (20.8), 126.2 (20.2), 113.2 (12.4). Found: C, 89.412; H, 5.098; N, 5.49%. No absorptions in the NH and carbonyl region are observed in the IR spectrum.

(iii) Unreacted **2a**. (130 mg).

Pyrolysis of 4,4-Di-*p*-tolyl-1,4-dihydro-2*H*-3,1-benzoxazin-2-one (2b): Analogously, pyrolysis of **2b** (350 mg) yielded.

(i) (2-Aminophenyl)di-*p*-tolylmethane (**4b**) (20 mg, 7%), semisolid, purified by passing over a short column of silica gel; IR (Nujol) ν_{max} 3450, 3360, 1610 cm^{-1}; MS *m/z* 287 (M^+, 100), 286 (11), 196 (40), 195 (19), 194 (57), 91 (49). Found: C, 87.52; H, 7.262; N, 4.87%. Calcd for $C_{21}H_{21}N$: C, 88.05; H, 7.317; N, 4.88%.

(ii) 2-*p*-Tolyl-3-methylacridine (**3b**) (210 mg, 70%), mp 143 °C (methanol); MS *m/z* (rel intensity) 283.3 (M^+, 100), 282.3 (18.2), 281.3 (5), 280.3 (4), 279.3 (1.6), 254.2 (2.4), 141.2 (29), 140.2 (2.7), 127.1 (19). Found: C, 89.049; H, 6.06; N, 4.8%. Calcd for $C_{21}H_{17}N$: C, 89.049; H, 6.007; N, 4.94%. IR spectrum shows no absorptions in the NH or carbonyl regions.

(iii) Unreacted **2b** (80 mg).

Pyrolysis of 6-Chloro-4,4-diphenyl-1,4-dihydro-2*H*-3,1-benzoxazin-2-one (2f): From the pyrolysis of the captioned compound **2f** (400 mg), were obtained 2-chloro-9-phenylacridine (**3f**) (210 mg, 64.5%), mp 133 °C (methanol); MS *m/z*

(rel intensity) 289.3 (M^+, 100), 288.3 (18.7), 254.3 (52), 253.3 (23.2), 252.3 (11.7), 251.3 (10), 227.2 (5), 144.8 (2.6), 127.2 (16.6), 125.8 (20.8). Found : C, 78.78; H, 4.087; N, 4.79%. Calcd for $C_{19}H_{12}ClN$: C, 78.893; H, 4.152; N, 4.847%. Its IR spectrum has no absorptions in the carbonyl or NH regions.

Unreacted **2f** (130 mg) from the column was recovered.

Pyrolysis of 4-Methoxy-4-phenyl-1,4-dihydro-2*H*-3,1-benzoxazin-2-one (2g): The above compound **2g** (500 mg) when pyrolyzed at 235 °C yielded.

(i) 6,12-Diphenyldibenzo[*b*,*f*][1,5]diazocine (**7**) (30 mg, 8.5%), mp 188 °C (methanol). Lit,[3] 186—188 °C, found to be identical with an authentic sample by mixed mp and superimposable IR spectrum.

(ii) 2-Aminobenzophenone (**6**) (190 mg, 49%), mp and mixed mp 106 °C (methanol).

(iii) Unreacted **2g** (75 mg).

Pyrolysis of 2a in Presence of Hydroquinone or Sodium Borohydride: The compound **2a** (300 mg, 0.001 mol) was pyrolyzed in presence of hydroquinone (1.1 g, 0.01 mol) at 235 °C for 3 h. After usual work up, were isolated **4a** (75 mg, 27%), **3a** (110 mg, 43%) and unreacted **2a** (50 mg).

Similar result wes obtained when the reaction is carried out in the presence of sodium borohydride also.

Pyrolysis of 2a in Presence of Methyl Anthranilate: A mixture of **2a** (300 mg, 0.001 mol) and methyl anthranilate (1.51 g, 0.01 mol) was heated for 3 h at 235 °C. After usual workup, was obtained **3a** (120 mg, 47%). **4a** was observed on TLC but could not be separated from the unreacted methyl anthranilate.

Photochemical Reaction of 4,4-Diphenyl-1,4-dihydro-2*H*-3,1-benzoxazin-2-one (2a): A solution of **2a** (300 mg) in methanol (400 ml) was irradiated with 400 W ultraviolet lamp in s Hanovia photochemical reactor, with Pyrex filter for 6 h. After one hour, the color of the solution changed to yellow. However, TLC at the end of 6 h showed no change, it was further irradiated for additional 18 h. Even then, no change was observed and the parent compound **2a** (275 mg, 90%) was recovered back after removal of solvent by distillation.

Similar observation of stability to UV irradiation was observed in the case of **2g** also.

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References

1) T. Kappe and W. Stadlbauer, "Advances in Heterocyclic Chemistry," ed by A. R. Katritzky and A. J. Boulton, Academic Press, New York (1981), Vol. 28, p. 140.

2) R. J. Kobylecki and A. McKillop, "Advances in Heterocyclic Chemistry," Vol. 19, 254 (1976) and references cited therein.

3) B. K. Misra, Y. R. Rao, and S. N. Mahapatra, *Indian J. Chem.*, **22B**, 1132 (1983).

4) B. P. Acharya and Y. R. Rao, *J. Chem. Res., (S)*, **1987**, 96; *J. Chem. Res. (M).*, **1987**, 1001.

5) We thank the referee for suggesting the free radical mechanism.

6) P. A. Petynuin and N. G. Panterova, *Zh. Obsch. Khim.*, **26**, 3191 (1956); *Chem. Abstr.*, **51**, 8745 (1957).

7) C. J. Bickelhaupt, P. D. Koe, R. Lourens, L. R. Mast, G. L. V. Mourin, H. Vermeer, and R. J. M. Weustink, *Tetrahedron*, **32**, 1921 (1976).