Major Fragmentation Pathways on Electron Impact of Some Aryl *N*-Arylbenzimidates, Chapman Rearrangement Products, and Acridones

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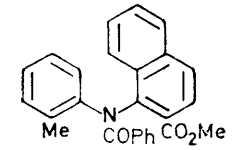
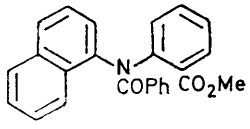
The gross fragmentation patterns under electron impact of some aryl *N*-arylbenzimidates. *N*-benzoyldiarylamines, and acridones are examined and compared with their thermal reactions. Evidence is adduced for a reverse Chapman rearrangement in the molecular ion of some *N*-benzoyldiarylamines.

THE Chapman rearrangement [1-4] of appropriately substituted benzimidates can be used to prepare *N*-benzoyldiphenylaminocarboxylic acids and acridones.[5-7] The preparation by this method of the naphthylamines (I)—(III) is now reported. *N*-2-Methylphenylbenzimidoyl chloride reacts instantaneously with the sodio-derivative of methyl 1-hydroxy-2-naphthoate to form the benzimidate (IV); (V) and (VI) are prepared from *N*-1-naphthylbenzimidoyl chloride. On heating these benzimidates undergo rearrangement exothermically to form (I)—(III) respectively.



(I)



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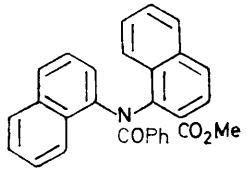
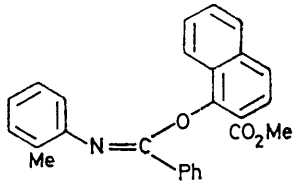
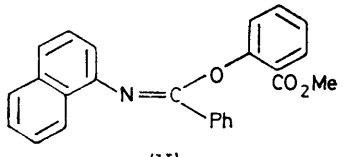


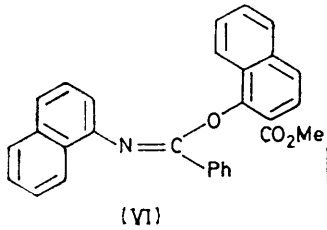
(III)



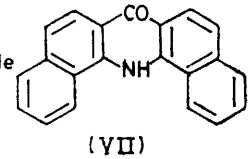
(IV)



(V)



(VI)



(VII)

The benzimidate (VI) undergoes rearrangement particularly vigorously: when it was heated to 284° the temperature rose spontaneously to 310° and the acridone (VII) was obtained; [7] however, when the temperature was kept just below 280°, the ester (III) was formed in excellent yield. Whereas esters (I) and (II) could, by controlled hydrolysis,[5] be converted into the corresponding acids, the only product isolated from similar treatment of (III) was the acridone (on acidification of the alkaline hydrolysis solution, even at 0°, the yellow colour of the acridone appeared). The other two acids form acridones when heated above their m.p.s.

The acridones have high m.p.s and are stable to heat.

This is then a group of four related types of compound, of which the thermal behaviour is known, and it becomes interesting to make a parallel study of the gross fragmentation patterns of their mass spectra. The Table shows a selection of each of the chemical types, with the relative abundances of salient peaks classified in columns with a selected stoicheiometry.

In the mass spectrum of a typical benzimidate, $Ar^1N{=}CPh(OAr^2)$, the peak corresponding to the molecular ion $M^{+\cdot}$ is small; $(M - 31)^+$ (for loss of OMe) and $(M - 59)^+$ (for loss of CO_2Me) are very weak. Each spectrum is dominated by a base peak corresponding to the composition $Ar^1\overset{+}{N}{\equiv}CPh$; the fragment OAr^{2+} does not appear except as a trace in one example. The general pattern fits the process $Ar^1N{=}CPh(OAr^2)^{+\cdot} \longrightarrow Ar^1\overset{+}{N}{\equiv}CPh + OAr^{2\cdot}$; a peak at *m/e* 105, probably $PhCO^+$, occurs in all the spectra, although normally in small abundance. It occurs, however, to the extent of 41% in 2-methoxycarbonyl-1-naphthyl *N*-(1-naphthyl)benzimidate (Table) and may reflect some significant thermal rearrangement to amide in this compound before splitting. A metastable peak at 56·5, which is commonly present ($PhCO^+ \longrightarrow Ph^+ + CO$), confirms this interpretation. Accurate mass measurements were made for peaks at 259, 230, 194, and 105 of compound (iv); the empirical formulae assigned to 194 and 105 are confirmed; structures assigned to *m/e* 259 and 230 are described under the *N*-benzoyldiarylamine (ix). Peaks for $(M - PhCO_2Me)^+$, which could represent acridones, are missing or very slight; a trace of 295 in (v) could be due to acridone; the compound is reported to form acridone very easily on heating,[7] but on electron impact loss of the methylsalicoyloxyl radical dominates its

[1] A. W. Chapman, *J. Chem. Soc.*, 1925, 1992.
[2] A. W. Chapman, *J. Chem. Soc.*, 1929, 569.
[3] R. Roger and D. G. Neilson, *Chem. Rev.*, 1961, 179.
[4] J. W. Schulenberg and S. Archer, *Organic Reactions*, 1965, **14**, 1.
[5] M. M. Jamison and E. E. Turner, *J. Chem. Soc.*, 1937, 1954.
[6] M. M. Harris, W. G. Potter, and E. E. Turner, *J. Chem. Soc.*, 1955, 145.
[7] J. Cymerman-Craig and J. W. Loder, *J. Chem. Soc.*, 1955, 4309.

spectrum. Figures for the chloro-compounds (vi) and (vii) demonstrate that chlorine is lost more easily from the 2- than from the 4-position, in accord with previous findings.[8-10]

The *N*-benzoyldiarylamino-2-carboxylates, $Ar^1N(COPh)\cdot Ar^2$, rearrangement products of methoxycarbonylbenzimidates, all have *m/e* 105 (presumably $PhCO^+$) Such reverse rearrangements, thermally brought about, have never been observed;[4] Chapman[11] himself considered that the thermal rearrangement of aryl *N*-arylbenzimidates should be reversible, but did not succeed in isolating any benzimidates from heated *N*-benzoyldiphenylamines. The Chapman rearrangement is known to be intramolecular[1,12] and, following a suggestion of

Relative abundances of main peaks in mass spectra [*m/e* (intensity; s = <5%, w = very weak)]

Aryl *N*-arylbenzimidates $Ar^1N{=}CPh(OAr^2)$ where Ar^1 carries 2-CO_2Me

	Ar^1	Ar^2	*M*	$M - OAr^2$	$M - OAr^1$	PhCO	Ph	Ar^1	Acridone
i	Ph	2-$CO_2MeC_6H_4$	331(8)	180(100)	238(s)	105(8)	77 (35)	77	
ii	2-MeC_6H_4	2-CO_2Me-6-MeC_6H_3	359(s)	194(100)	252(s)	105(s)	77(5)	91(21)	
iii	1-$C_{10}H_7$	2-$CO_2MeC_6H_4$	381(6)	230(100)	238(5)	105(9)	77(9)	127(34)	
iv	2-MeC_6H_4	2-COMe-1-$C_{10}H_6$	395(s)	194(100)	288(w)	105(s)	77(s)	91(27)	
v	1-$C_{10}H_7$	2-CO_2Me-1-$C_{10}H_6$	431(s)	230(100)	288(9)	105(41)	77(12)	127(26)	
vi	4-ClC_6H_4	2-$CO_2MeC_6H_4$	365(6)	214(100)	238(s)	105(24)	77(18)	111(20)	
vii	2-ClC_6H_4	2-CO_2Me-6-MeC_6H_3	379(s)	214(100)	252	105(10)	77(30)	111(24)	

Methyl *N*-benzoylarylaminoarenecarboxylates $Ar^1N(COPh)Ar^2$ where Ar^2 carries 2-CO_2Me

viii	1-$C_{10}H_7$	2-$CO_2MeC_6H_4$	381(7)	230(s)	238(51)	105(100)	77(29)	127(s)	245(s)
ix	2-MeC_6H_4	2-CO_2Me-1-$C_{10}H_6$	395(w)	194(91)	288(s)	105(100)	77(30)	91(s)	259(61)
x	1-$C_{10}H_7$	2-CO_2Me-1-$C_{10}H_6$	431(12)	230(51)	288(37)	105(100)	77(30)	127(s)	295(8)
xi	4-ClC_6H_4	2-$CO_2MeC_6H_4$	365(16)	214(5)	238(10)	105(100)	77(33)	111(s)	229(5)
xii	2-ClC_6H_4	2-CO_2Me-C_6H_4	365(s)	214(s)	238(s)	105(100)	77(48)	111(s)	229(s)

N-Benzoylarylaminoarenecarboxylic acids $Ar^1N(COPh)Ar^2$ where Ar^2 carries 2-CO_2H

xiii [a]	Ph	2-$CO_2HC_6H_4$	317(6)	180(s)	224(s)	105(71)	77 (40)	77	195(100)
xiv [b]	Ph	2-CO_2H-6-MeC_6H_3	331(7)	180(12)	238(w)	105(52)	77 (30)	77	209(100)
xv [c]	2-MeC_6H_4	2-CO_2H-6-MeC_6H_3	345(s)	194(12)	238(w)	105(100)	77(52)	91(s)	223(100)
xvi [d]	1-$C_{10}H_7$	2-$CO_2HC_6H_4$	367(s)	230(w)	224(s)	105(100)	77(55)	127(s)	245(60)
xvii [e]	2-MeC_6H_4	2-CO_2H-1-$C_{10}H_6$	381(6)	194(50)	274(w)	105(89)	77(39)	91(s)	259(100)
xviii [f]	4-ClC_6H_4	2-$CO_2HC_6H_4$	351(s)	214(w)	224	105(100)	77(58)	111(w)	229(52)
xix [g]	2-ClC_6H_4	2-CO_2H-6-MeC_6H_3	365(s)	214(w)	238(w)	105(100)	77(59)	111(w)	243(56)
xx [g]	2-FC_6H_4	2-CO_2H-6-MeC_6H_3	349(s)	198(16)	238	105(78)	77(56)	95(w)	227(100)

Acridones

		M	*M* − CO	*M* − CHO
xxi	Benz[*c*]acridin-7(12*H*)-one	245(100)	217(11)	216(17)
xxii	9-Methylbenz[*c*]acridin-7(12*H*)-one	259(100)	231(s)	230(15)
xxiii	Dibenz[*c*,*h*]acridin-7(14*H*)-one	295(100)	267(9)	266(11)

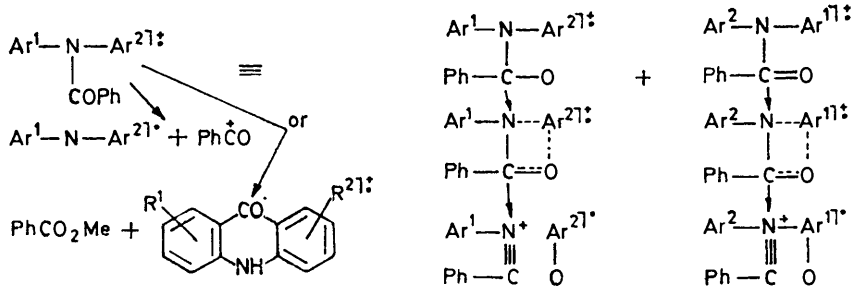
Intensity of $PhCO_2H$ peak: [a] s; [b] s; [c] 8; [d] 43; [e] 9; [f] 8; [g] 7; [h] s.

as their base peak. $M^{+\cdot}$ is again very slight: all show *m/e* 77 (Ph^+, 30—50%) and most a metastable peak at 56·5; all show *small* peaks corresponding to the acridone, a recognised thermal reaction product.[1] After these similarities, there are variations of quantities within common patterns. Particularly interesting is the occurrence of signals corresponding to $(M - OAr^1)^+$ *and* $(M - OAr^2)^+$. These could be fragments formed by what might be termed a ' reverse Chapman rearrangement ' (although it would not be necessary for the rearrangement to proceed beyond the formation of a transition complex for the fragmentation to be achieved). Bennett,[13] has been shown to involve a nucleophilic displacement of oxygen by nitrogen on an aromatic ring.[12] This requires a four-membered cyclic transition state.

Johnstone *et al.*[14] have studied the mass spectrum of the trifluoroacetyl derivative of *N*-methylaniline, and find that it can be explained if the normal loss of CF_3 and CO is accompanied by another reaction in which there is rearrangement of the molecular ion accompanied by loss of a phenoxyl radical; Bentley *et al.*[15] have classified this, along with some related processes, as a four-centre π system reaction. If the *N*-benzoyldiarylamines

[8] S. A. Benezra and M. M. Bursey, *J. Chem. Soc.* (*B*), 1971, 1515.
[9] M. A. Baldwin, A. G. Loudon, A. Maccoll, D. Smith, and A. Ribera, *Chem. Comm.*, 1967, 350.
[10] M. A. Baldwin and A. G. Loudon, *Org. Mass. Spectrometry*, 1969, **2**, 549.
[11] A. W. Chapman, *J. Chem. Soc.*, 1927, 1743.
[12] K. B. Wiberg and B. I. Rowland, *J. Amer. Chem. Soc.*, 1955, **77**, 2205.
[13] G. M. Bennett, *Ann. Report Chem. Soc.*, 1929, **26**, 123.
[14] R. A. W. Johnstone, D. W. Payling, and A. Prox, *Chem. Comm.*, 1967, 826.
[15] T. W. Bentley, R. A. W. Johnstone, and D. W. Payling, *Chem. Comm.*, 1968, 1154.

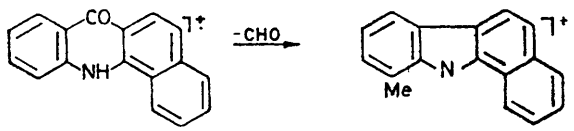
can be examples of this class, the four-centre π systems could exist in two conformations, of which one might be favoured. A rationalisation of the spectral peaks observed for *N*-benzoyldiarylamino-2-carboxylates is then given by Scheme 1.



SCHEME 1

The possibility that a benzoyldiarylaminocarboxylate might contain some of the unrearranged benzimidate has been given consideration; any pair have the same elementary analysis and the differences in their i.r. spectra (SP 200) are not striking. Fortunately the evidence against this possibility is conclusive. If the mass spectra of the pair (iii) and (viii) are compared, it is seen that (viii) has a substantial $(M - OAr)^+$ peak. This could not arise from the benzimidate, in which the group Ar^2, not Ar^1, is attached to oxygen.

Metastable peaks in the spectrum of (ix) correspond to $194^2/395$ and $230^2/259$; 230, which is small and not shown in the Table, probably reflects loss of CHO from the acridone (Scheme 2). Accurate mass measurements

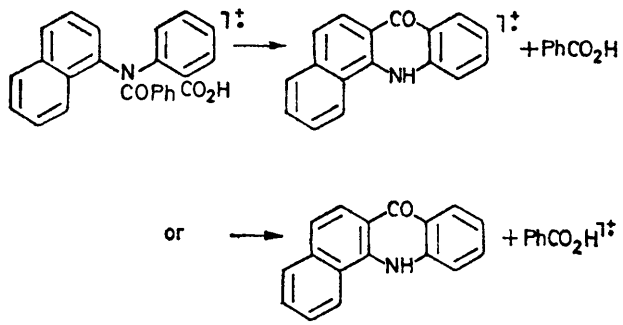


SCHEME 2

confirm that the empirical constitution of peaks at 288, 259, 230, 194, and 105 are consistent with Schemes 1 and 2. Once again chlorine is lost more readily from the 2-chloro- (xiii) than from the 4-chloro- (xii) compound.

In contrast with their methyl esters, the *N*-benzoyldiarylamino-carboxylic acids show a fragmentation with loss of $PhCO_2H$ which is at least comparable in intensity with the peak for $PhCO^+$ and may even surpass it. In the one case where the $(M - PhCO_2H)^+$ peak (? acridone) falls to 60% of the base peak (xvi) a peak at 122 ($PhCO_2H$) is raised to 43%, suggesting that acridone is still a major fragment but that it may not always be the electron-short fragment (Scheme 3). This easy loss of benzoic acid parallels the thermal reaction.[5] Accurate mass measurements for compound (xvii) confirm the stoicheiometry proposed for peaks at 259, 230, 194, and 105. Metastable peaks appear at $230^2/259$, $259^2/381$, and $194^2/381$; the first of these may represent loss of CHO from acridone. All the acids show peaks which could be formed by the four-centre route, but they are small in comparison with $(M - PhCO_2H)^+$ or $PhCO^+$.

Of the halogeno-acids (xviii)—(xx) the mass spectrum of the fluoro-compound does not show loss of fluorine atoms; the base peak in its spectrum is that of the corresponding acridone; however, the 2-chloro-acid shows a peak for $(M - Cl)^+$ and also one for (acridone — $Cl)^+$; the 4-chloro-acid apparently holds its chlorine



SCHEME 3

atom more tightly. Here again the loss of halogen is in line with previous work.[8-10]

The acridones are stable under electron impact; $(M)^{+\cdot}$ is by far the strongest peak. The only other peaks of any significance can be rationalised as $(M - CO)^+$ and $(M - CHO)^+$.

Bentley and Johnstone [16] have made a comprehensive critical appraisal of mechanistic studies in mass spectrometry and have directed attention to the pitfalls inherent in drawing comparisons between chemical processes, in chemically controlled conditions, and processes operative in mass spectroscopy; analogies should not necessarily be expected between the behaviour of a molecule and its counterpart with one electron less. The divergent behaviour of the diarylbenzimidates under the two treatments is a case in point; on heating (solvent unnecessary) they form *N*-benzoyldiarylamines in yields approaching the theoretical, while on electron impact they form stable carbonium ions of stoicheiometry corresponding to $Ar^1N{\equiv}C{-}Ph$. On the other hand, a knowledge of the Chapman rearrangement (thermal) has proved helpful for the interpretation of the mass spectra

[16] T. W. Bentley and R. A. W. Johnstone, *Adv. Phys. Org. Chem.*, 1970, **8**, 151.

of the *N*-benzoyldiphenylamines, even though it is a reverse process, not realised in practice, which is postulated.

EXPERIMENTAL

Mass Spectra.—Spectra were taken with an A.E.I. MS902 double-focusing mass spectrometer at 70 eV. The ion source temperatures were 120° (iii), 150° (vi) and (xi), 180° (i), (ii), (v), (vii), (viii), and (xvi), 200° (iv), (ix), (xii)—(xv), and (xvii)—(xx), 220° (xxiii), and 250° (xxi) and (xxii).

2-*Methoxycarbonyl*-1-*naphthyl* N-(2-*methylphenyl*)*benzimidate* (IV) was prepared in 79% yield by standard methods [3-5] from the sodio-derivative of methyl-1-hydroxy-2-naphthoate (this ester, prepared by a variety of standard methods, gave prisms on quick crystallisation from methanol and needles on slow crystallisation: polymorphism has been reported [17] and m.p.s varying from 53 [17] to >78° [7,17-19] have been noted; the highest m.p. observed in the present work was 84°) and *N*-(2-methylphenyl)benzimidoyl chloride.[20] It crystallised from ethanol, m.p. 132—133° (Found: C, 79·0; H, 5·4; N, 3·6. $C_{26}H_{21}NO_3$ requires C, 79·0; H, 5·3; N, 3·5%), $M^{+\cdot}$ (mass spectrum) gave a signal which was too weak for accurate mass measurement.

Methyl 1-(N-*Benzoyl*-o-*toluidino*)-2-*naphthoate* (I).—The imidate (IV), heated to 180°, underwent rearrangement, the internal temperature rising to 230°. The *product* (90%) crystallised from ethanol, m.p. 172° [Found: C, 78·7; H, 5·45; N, 3·7; O, 12·2%; *M* (mass spectrum), 395·1492. $C_{26}H_{21}NO_3$ requires C, 79·0; H, 5·3; N, 3·5; O, 12·1%; *M*, 395·152, the $M^{+\cdot}$ signal was very weak].

1-(N-*Benzoyl*-o-*toluidino*)-2-*naphthoic Acid.*—Hydrolysis of the ester (I) under standard conditions [5] for 2 h gave the *acid* (90%) which crystallised from methanol with one molecule of solvent, m.p. 142° (decomp.) (Found: C, 75·4; H, 5·6; N, 3·4; O, 15·5%; *M*, 381·1363. $C_{26}H_{23}NO_4$ requires C, 75·5; H, 5·6; N, 3·4; O, 15·5%; *M*, 381·1365).

11-*Methylbenz*[c]*acridin*-7(12H)-*one.*—The above acid was heated at 160° for 10 min and the product (*ca.* 100%) was washed with hot water to remove benzoic acid and crystallised from ethanol. It formed yellow silky needles, m.p. 280—281° (lit.,[7] 274°) [Found: *M* (mass spectrum), 259·1004. Calc. for $C_{18}H_{13}NO$: 259·0997].

2-*Methoxycarbonylphenyl* N-(1-*naphthyl*)*benzimidate* (V) was prepared by condensing the sodio-derivative of methyl salicylate with *N*-1-naphthylbenzimidoyl chloride [21] under standard conditions.[3,4] It crystallised from cyclohexanone in needles (80%), m.p. 117—118° (Found: C, 78·55; H, 5·1; N, 3·8; O, 12·4%; *M*, 381·1369. $C_{25}H_{19}NO_3$ requires C, 78·7; H, 5·0; N, 3·7; O, 12·6%; *M*, 381·1365).

Methyl 2-(N-*Benzoyl*-1-*naphthylamino*)*benzoate.*[22]—Rearrangement of the above benzimidate took place exothermically at 220°, when the temperature within the reaction vessel rose to 242°. The *ester* (96%) crystallised from ethanol, m.p. 185° (Found: C, 78·6; H, 5·0; N, 3·8; O, 12·75%; *M*, 381·1365. $C_{25}H_{19}NO_3$ requires C, 78·7; H, 5·0; N, 3·7; O, 12·6%; *M*, 381·1365).

2-(N-*Benzoyl*-1-*naphthylamino*)*benzoic Acid.*[22]—Hydrolysis of the ester (II) under standard conditions [5] for 1 h gave the *acid* (90%) which crystallised from methanol with one molecule of solvent, m.p. 132° (decomp.) (Found: C, 74·95; H, 5·25; N, 3·7; O, 16·2%; *M*, 367·1209. $C_{25}H_{21}NO_4$ requires C, 75·2; H, 5·3; N, 3·5; O, 16·0%; *M*, 367·1208).

Methyl 1-(N-*Benzoyl*-1-*naphthylamine*)-2-*naphthoate.*—Careful heating of (2-methoxycarbonyl-1-naphthyl) *N*-(1-naphthyl)benzimidate,[7] m.p. 140—141°, just below 280° caused rearrangement to take place and avoided further reaction to the acridone. The *product* after crystallisation from methanol, had m.p. 158—159° (decomp.), and contained one molecule of solvent (Found: C, 77·7; H, 5·4; N, 3·1; O, 13·7%; *M*, 431·1527. $C_{30}H_{25}NO_4$ requires C, 77·7; H, 5·4; N, 3·0; O, 13·8%; *M*, 431·1521). Attempts were made to hydrolyse the methoxycarbonyl group to the acid; on all occasions, acidification of the alkaline hydrolysis solution gave dibenz[*c*,*h*]acridin-7(14*H*)-one, m.p. 336—338° (decomp.) (lit.,[7] 331—332°).

Benz[c]*acridin*-7(12H)-*one.*— 2-(*N*-benzoyl-1-naphthylamino)benzoic acid when heated at 160° for 10 min gave benzoic acid and benz[*c*]acridin-7(12*H*)-one (*ca.* 100%) which crystallised from pyridine as yellow needles, m.p. >350° [previously prepared by another route (lit.,[23] m.p. >350°)] [Found: *M* (mass spectrum), 245·0838. Calc. for $C_{17}H_{11}NO$: 245·0841].

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