Conjugated Schiff's Bases

16—Substituent Effect on Electron Impact Fragmentation of Some 1-Oxa-4-azabutadienes[1]

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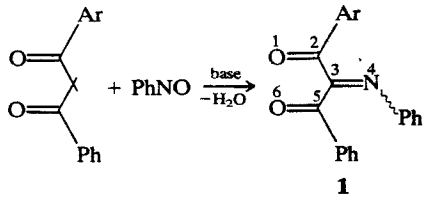
The electron impact fragmentation patterns of some 1-oxa-4-azabutadienes have been determined and supported by the corresponding metastables. The effect of substituents on this fragmentation has been investigated. Satisfactory correlation of intensity ratios of the peaks characterizing the primary fragmentation versus the Brown and Okamoto σ^+ substituent parameters has been found. The relationship between the substituent parameters and the dissociation energy $E_{D,C(3)-C(5)}$, estimated with the help of appearance energies has been considered.

INTRODUCTION

Substituent effects on electron impact induced fragmentation and the various LFER-type correlations have been fairly widely studied during recent years.[2–4] These investigations, however, have been mainly concerned with direct substituent influence. The question has arisen as to whether such effects could be transmitted by a long, partly crossed π electron system and to what degree. To answer this question we have investigated selectively substituted 1-oxa-4-azabutadienes chosen as model compounds. These compounds fragmented following very simple patterns and were relatively easily obtainable via a base-promoted condensation of 1,3-diaryl 1,3-diketones, selectively substituted in one of their aryl rings, with nitrosobenzene (Scheme 1).[5,6] The 2-aryl-3-benzoyl-4-phenyl-1-oxa-4-azabutadienes (**1**) were isolated and purified as an



1

1	Ar	**1**	Ar
a	Phenyl	**f**	4′-Bromophenyl
b	4′-Methoxyphenyl	**g**	3′-Chlorophenyl
c	4′-Methylphenyl	**h**	2′,4′,6′-Trimethylphenyl
d	4′-Phenylophenyl	**i**	1′-Naphthyl
e	4′-Chlorophenyl	**j**	4′-Nitrophenyl

Scheme 1

almost equivalent mixture of the *E* and *Z* geometric isomers (*syn* and *anti*). Nevertheless, this mixture was successfully used for investigation of the substituent effect regarding the negligible role of geometric isomerism on electron impact fragmentation.[7]

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RESULTS AND DISCUSSION

As was mentioned above, the molecular ions of the chosen model compounds **1** followed simple fragmentation patterns based on the C(2)–C(3) and C(3)–C(5) carbon–carbon bond cleavages. Loss of either aroyl or benzoyl radicals produced complementary 1-oxa-4-azabutadiene ions (m^*) which were responsible for the peaks at mass m/z 208 (and (131 + Ar) (Ar designates the appropriate aryl ring). Detachment of the aroyl or/and benzoyl fragments bearing charge gave prominent peaks at m/z (28 + Ar) and 105, respectively. This pathway was only partly supported by metastables. The origin of the peaks at m/z (Ar + 28) and 105 was also connected with the secondary fragmentation process, i.e. decomposition of the (131 + Ar) and 208 1-oxa-4-azabutadiene ions (m^*). Formation of the complementary phenyl isocyanide radical ions was only shown by very low intensity peaks at m/z 103 (see experimental section). The main fragmentation pathways of the molecular ions $[\mathbf{1}]^{+\cdot}$ are shown in Scheme 2. Decomposition of the aroyl ions was connected with decarbonylation (m^*)[8] yielding the aryl ions from which the prominent peaks m/z 77 and Ar originated. The aryl ions fragmented after well-known pathways.[9,10]

The molecular ions $[\mathbf{1}]^{+\cdot}$ also showed a slight resemblance to the parent vicinal triketones which are capable of reducing the carbon skeleton by ejecting the central carbonyl group as the neutral carbon monoxide molecule.[11] However, in the case of the molecular ions $[\mathbf{1}]^{+\cdot}$ the phenyl isocyanide molecule should be eliminated. Such a process was marked by very low intensity peaks only at mass m/z (133 + Ar), but was fully supported by the corresponding metastables and exact mass determination. It is probable that a cyclic-type transition state facilitates phenyl isocyanide ejection (Scheme 3).[12]

The effect of substituents on the primary fragmentation, i.e. detachment of the aroyl-type fragments from

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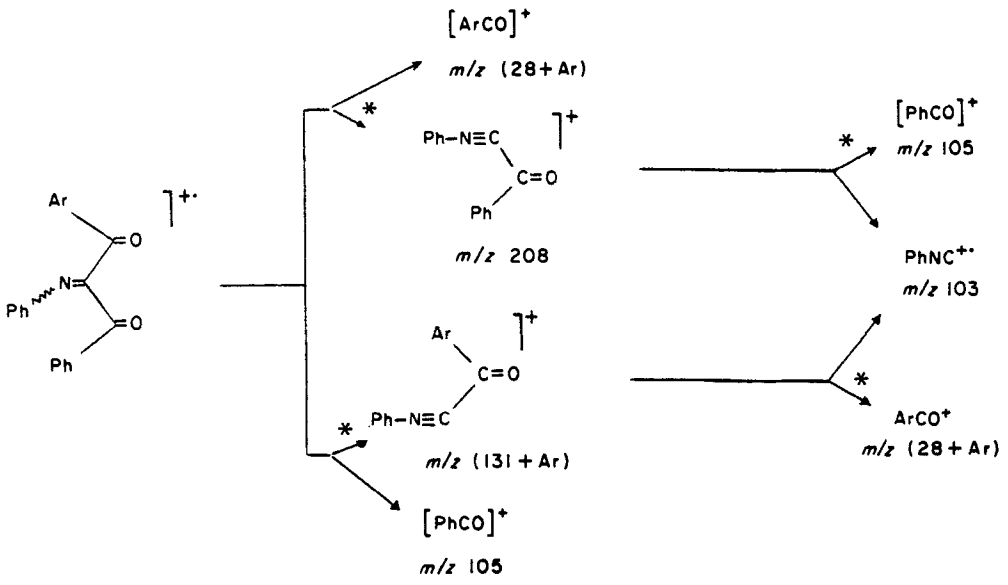
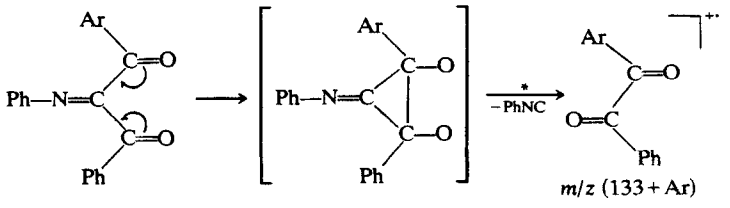
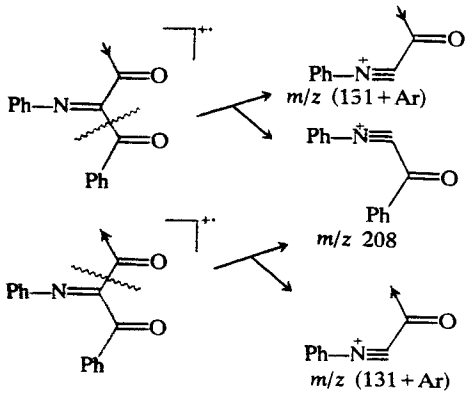


Scheme 2



Scheme 3

$[\mathbf{1}]^{+\cdot}$, was marked. When the aryl ring contained electron-releasing groups elimination of the benzoyl radical predominated and peaks at m/z (131+Ar) were more intense than those at m/z 208. On the other hand, electron-withdrawing substituents in the aryl ring caused favourable loss of the aroyl radical. In this case the intensity of the peaks at m/z 208 was higher than those at m/z (131+Ar) (Scheme 4).



Scheme 4

The observed facts can be expressed using the Hammett-type relationship[13] and the linear dependence was found by plotting the logarithm of the intensity ratios ($I_{208}/I_{(131+Ar)}$) versus the Brown and Okamoto σ^+ substituent parameters (Fig. 1).[14] Figure 1 shows the ρ value equal to 1.091 which is somewhat greater than similar data reported for the substituent effect on electron impact induced fragmentation of some disubstituted benzene derivatives.[21] As expected steric congestion affected fragmentation to a distinct degree.[18] Displacement of the substituent position from *para*, *meta* to *ortho* and increase of its size (mesityl and 1-naphthyl) caused predominance of C(2)–C(3)

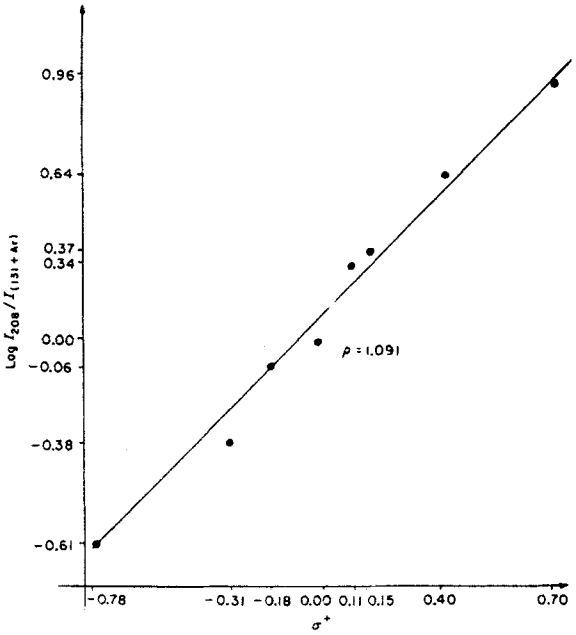


Figure 1. Diagram of the log ($I_{208}/I_{(131+Ar)}$) intensity ratios versus σ^+ substituent parameters. Correlation coefficient, $r = 0.979$.

bond cleavage and loss of the bulkier aroyl radical. Hence intensity ratios $I_{208}/I_{(131+Ar)}$ did not fit the regular dependence with the σ^+ parameters mentioned above. The ratios were equal to 1.25 and 2.46 for mesityl and 1-naphthyl, respectively.

The relative abundances of the aroyl and aryl ions did not fulfil any reasonable correlation, probably due to overlapping of the primary, secondary and tertiary fragmentation processes producing the same type of ions. Appearance energies were also considered as possible factors useful for determination of the substituent effects on dissociation energy of both C(2)–C(3) and C(3)–C(5) carbon–carbon bonds. Defining appearance energy as an approximate sum of a dissociation energy and an ionization energy of a radical formed[15] it could be pointed out that appearance energies of the ions m/z 208 reflect variations of the dissociation energy of the C(2)–C(3) bond:

$$AP^{H}_{208} - AP^{X}_{208} = E^{H}_{D,C(2)-C(3)} - E^{X}_{D,C(2)-C(3)}$$

where AP^{H}_{208} designates the appearance potential of the non-substituted compound and AP^{X}_{208} the appearance energy of the ion m/z 208 of the substituted compound **1** by a group X, and assuming that the ionization energy of the radical m/z 208 has a constant value. Appearance energies of the chosen ions derived from the molecular ions of **1** were evaluated with the help of the EVD method[16,17] using argon as a standard gas (IP = 15.755 eV[17]). The values given have been averaged from at least three independent measurements. The experimental error of the EVD method was estimated to be within the range of 0.7 eV. This sometimes made it difficult to differentiate the IEs and AEs due to the great structural resemblance of both the molecular and parent diketone ions.

The accuracy of this method seemed to be sufficient for our investigation and was calibrated by using the appearance potential of the phenyl ion. The obtained value of 15.65∓0.12 eV reproduced sufficiently the reported data, 15.58+0.1 eV.[17] Relative abundances and appearance and ionization energies for the main ions derived from the compounds **1**, are listed in Table 1.

As was expected the values of $(AP^{H} - AP^{X})$ of the ion 208 correlated with the σ^+ parameters. Figure 2 shows the strong deflection along with the change in electronic behaviour of the substituents. The ρ values changed from −4.169 to +5.364, respectively. This fitted well the displacement of the fragmentation mechanism from C(2)–C(3) to C(3)–C(5) bond cleavage. A similar correlation was found for ionization energies (Fig. 3)[19,21] The ρ values were 0.504 and −0.973 for electron-releasing and electron-withdrawing groups, respectively. Correlation coefficients were equal to 0.668 and 0.999. However, elimination of the methyl group from the correlation improved the r value to 0.996. This correlation showed participation of substituents in the stabilization of the molecular ions. Its similarity to the dependence of the APs and σ^+ substituent parameters showed great structural resemblance of the molecular and parent 208 and (131+Ar) diketone ions. It was predicted that introduction of a substituent would decrease the

Table 1. Relative abundances and appearance and ionization energies for the main ions from compounds 1

No.	m/z	Rel. abund.	AE(IE) (eV)
1a	313	35.1	8.01±0.05
1b	343	25.4	4.85±0.10[a]
1c	327	36.7	7.42±0.06[a]
1d	389	13.0	7.20±0.06
1e	346/348	35.2/14.6	7.12±0.10
1f	391/393	9.6/9.6	6.89±0.20
1g	346/348	7.3/2.7	4.89±0.20
1a	208	94.3	8.42±0.10
1b	208	2.4	4.81±0.35[a]
1c	208	14.0	7.28±0.06[a]
1d	208	4.6	7.52±0.18
1e	208	96.8	7.70±0.12
1f	208	45.1	7.66±0.14
1g	208	25.0	6.16±0.20
1b	238	10.4	4.81±0.30[a]
1c	222	33.7	7.46±0.08
1d	284	5.3	7.02±0.06
1e	242/244	30.5/13.2	7.52±0.15
1f	286/288	9.6/9.6	7.64±0.07
1g	242/244	4.1/1.6	5.06±0.12
1a	105	100	9.84±0.05
1b	105	81.8	8.44±0.04
1c	105	75.0	9.53±0.12
1d	105	74.9	9.12±0.05
1e	105	100	9.33±0.05
1f	105	100	9.51±0.35
1b	135	100	7.93±0.13
1c	119	100	9.11±0.04
1d	181	100	8.42±0.11
1e	139/141	86.3/28.5	9.82±0.06
1f	183/185	82.8/86.7	9.82±0.09

[a] Values which were not differentiated within the error of the EVD method.

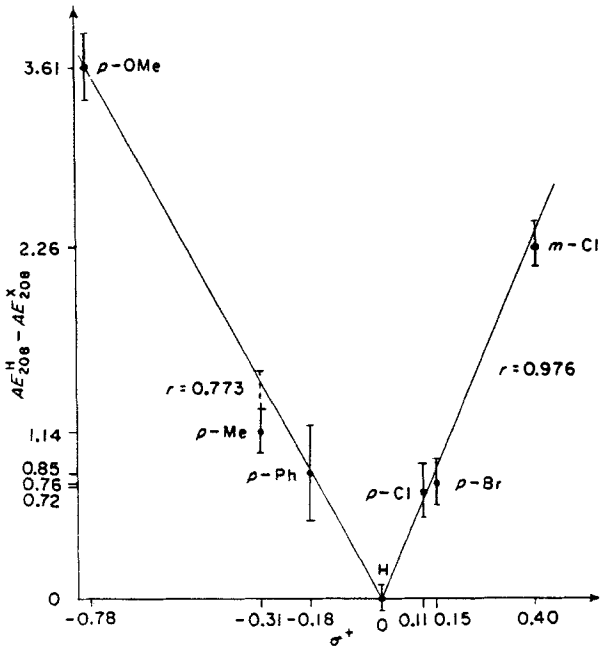


Figure 2. Diagram of the AE_{208} values versus σ^+ substituent parameters.

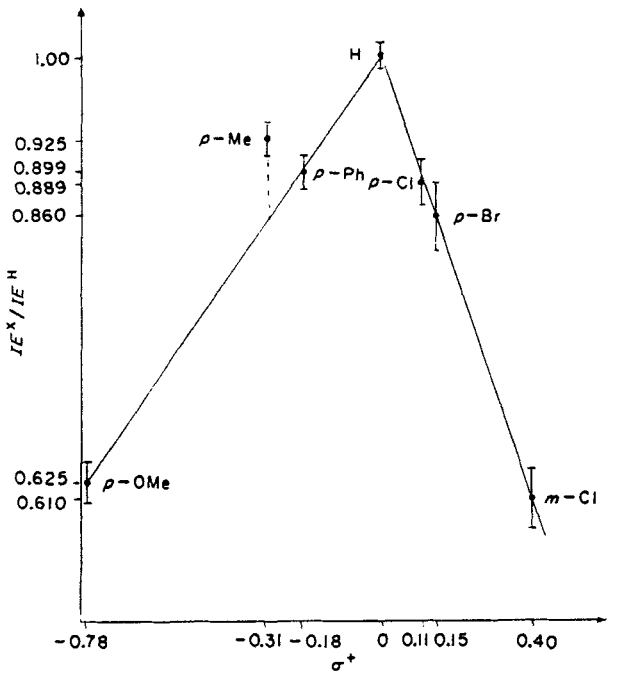


Figure 3. Diagram of the IE^X/IE^H ionization energy ratio versus σ^+ substituent parameters.

molecular ion stability affecting either the C(2)–C(3) or the C(3)–C(5) bonds. Maximum deviations were observed in the case of the methyl group attached to the aryl ring. This seemed to be connected with the entirely different electronic character of the methyl substituent compared with the others examined which contained π electrons (Ph, NO_2), or at least unshared electrons (OMe, Cl, Br). The effect of the methyl group proved to be distinctly smaller than that predicted by the relationship. Generally, however, it can be concluded that substituents are capable of regularly affecting the electron impact induced fragmentation via a long, partly crossed π electron system. *AE*s and *IE*s can be useful for exposing such substituent effects.

CONCLUSIONS

(i) The substituent effect is proved to be transmitted by the long, crossed π electron system of 1-oxa-4-azabutadienes.

(ii) The relative abundances of the peaks originating from the primary fragmentation followed correctly the Hammett dependence versus σ^+ parameters.

(iii) Steric congestion (*ortho* effect) strongly affected the fragmentation, making loss of the bulkier fragment predominant.

(iv) A correct relationship was found between the σ^+ parameters and the appearance energy differences ($AE^H_{208} - AE^X_{208}$) and ionization energy ratio (IE^X/IE^H).

EXPERIMENTAL

1-Oxa-4-azabutadienes (**1**) were synthesized using the base-promoted condensation of 1,3-diarylpropan-1,3-diones with nitrosobenzene.[20] Yields were 40–80%.

2,4-Diphenyl-3-benzoyl-1-oxa-4-azabutadiene (1a).[20] M.p.: 82–84 °C. ^{1}H NMR (ppm): 8.22–8.00, m, 4H; 7.70–6.70, m, 11H. Additional mass data (*m/z*, % of the base peak): $(133+Ar)^+$, 210, 0.3; $[PhNC]^{+\cdot}$, 103, 2.8; $[Ph]^+$, 77, 62.1.

2-(4′-Methoxyphenyl)-3-benzoyl-4-phenyl-1-oxa-4-azabutadiene (1b). Oil (see below); $C_{22}H_{17}O_3N$; mol. wt, 343.13. Calc.: %C, 76.93; H, 4.99; N, 4.08. Found: %C, 76.62; H, 4.97; N, 4.10. IR (cm^{-1}): 3060, 3040, w, CH aliph.; 2830, w, OCH_3; 1680, s, CO; 1670, s, CO; 1635, m, C=N; 1440, 1365, s, CH_3 def.; 845, 770, 700, s, ring subst. ^{1}H NMR (ppm): 8.30–8.05, m, 4H; 7.80–6.95, m, 10H; 3.68, *syn*, 3.60, *anti*, s, 3H. Additional mass data (*m/z*, %): $[133+Ar]^+$, 240, 1.3; $[PhNC]^{+\cdot}$, 103, 2.9; $[Ar]^+$, 107, 15.8; 92, 25.4; $[Ph]^+$, 77, 84.3.

2-(4′-Methylphenyl)-3-benzoyl-4-phenyl-1-oxa-4-azabutadiene (1c).[20] M.p.: 79–80 °C. ^{1}H NMR (ppm): 8.30–8.05, m, 4H; 7.80–6.95, m, 10H; 2.42, *syn*, 2.31, *anti*, s, 3H; Additional mass data (*m/z*, %): $[133+Ar]^+$, 224, 3.7; $[PhNC]^{+\cdot}$, 103, 3.7; $[Ar]^+$, 91, 98.4; $[Ph]^+$, 77, 90.7.

2-(4′-Phenylophenyl)-3-benzoyl-4-phenyl-1-oxa-4-azabutadiene (1d). M.p.: 108–109 °C. $C_{27}H_{19}O_2N$; mol. wt, 389.15. Calc.: %C, 83.26; H, 4.92; N 3.60. Found: %C, 83.06; H, 4.86; N, 3.60. IR (cm^{-1}): 3060, 3020, w, CH aliph.; 1670, s, CO; 1640, m, C=N; 833, 770, 700, s, ring subst. ^{1}H NMR (ppm): 8.40–8.15, m, 4H; 7.90–7.00, m, 20H. Additional mass data (*m/z*, %): $[133+Ar]^+$, 286, 1.6; $[PhNC]^{+\cdot}$, 103, 2.6; $[PhPh]^+$, 153, 28.5; 152, 42.2, 151, 11.3; $[Ph]^+$, 77, 41.2.

2-(4′-Chlorophenyl)-3-benzoyl-4-phenyl-1-oxa-4-azabutadiene (1e).[20] M.p.: 76–78 °C. ^{1}H NMR (ppm): 8.32–8.05, m, 4H; 7.95–6.90, m, 10H. Additional mass data (*m/z*, %): $[133+Ar]^+$, 244/246, 3.9/1.3; $[PhNC]^{+\cdot}$, 103, 5.8; $[Ar]^+$, 111/113, 74.7/26.6; $[Ph]^+$, 77, 98.1.

2-(4′-Bromophenyl)-3-benzoyl-4-phenyl-1-oxa-4-azabutadiene (1f).[20] M.p.: 85–86 °C. ^{1}H NMR (ppm): 8.40–8.10, m, 4H; 8.00–6.90, m, 10H. Additional mass data (*m/z*, %): $[133+Ar]^+$, 286/288, 1.3/1.3; $[PhNC]^{+\cdot}$, 103, 4.5; $[Ar]^+$, 155/157, 20.1/18.6; $[Ph]^+$, 77, 88.1.

2-(3′-Chlorophenyl)-3-benzoyl-4-phenyl-1-oxa-5-azabutadiene (1g).[20] M.p.: 74–76 °C. ^{1}H NMR (ppm): 8.35–8.00, m, 4H; 7.70–6.85, m, 10H. Additional mass data (*m/z*, %): $[133+Ar]^+$, 244/246, 2.9/0.3; $[Ar+28]^+$, 139/141, 51.1/17.2; $[PhCO]^+$, 105, 100; $[Ar]^+$, 111/113, 14.9/5.3; $[Ph]^+$, 77, 37.5.

2-(2′,4′,6′-Trimethylphenyl)-3-benzoyl-4-phenyl-1-oxa-4-azabutadiene (1h). M.p.: 126–127 °C. $C_{24}H_{21}O_2N$; mol. wt, 355.17, Calc.: %C, 81.09; H, 5.96; N, 3.94. Found: %C, 80.87; H, 5.98; N, 3.94. IR (cm^{-1}): 3050, 3020, w, CH aliph.; 2950, 2920, s, m, CH_3; 1680, s, CO; 1665, s, CO; 1650, m, C=N; 1450, 1375, s, CH_3, def.; 875, 772, 700, s, ring subst. ^{1}H NMR (ppm): 7.80–6.85, m, 12H; 2.38, s, 6H; 2.29, s, 3H. Mass data (*m/z*, %): $[M]^{+\cdot}$, 355, 13.3; $[M+1]^+$, 356, 4.3; $[131+Ar]^+$, 250, 2.0; $[133+Ar]^+$, 252, —; 208, 2.5;

$[Ar+28]^+$, 147, 100; $[Ar]^+$, 119, 30.4; 104, 5.2; $[PhCO]^+$, 105, 45.8; $[PhNO]^{+\cdot}$, 103; 6.1; 91, 16.1; $[Ph]^+$, 77, 26.8.

2-(1'-Naphthyl)-3-benzoyl-4-phenyl-1-oxa-4-azabutadiene (1i). M.p.: 91–92 °C. $C_{25}H_{17}O_2N$; mol. wt, 363.14. Calc.: %C, 82.61; H, 4.72; N, 3.86. Found: %C, 82.27; H, 4.62; N, 3.83. IR (cm^{-1}): 3080, 3060, 3020, CH ar., w; 1660, s, CO; 1640, s, CO; 1630, m, C=N; 770, 700, s, ring subst. ^1H NMR (ppm): 8.95–6.75, m, 17H. Mass data (*m/z*, %): $[M]^{+\cdot}$, 363, 30.8; $[M+1]^+$, 364, 8.8; $[131+Ar]^+$, 258, 6.1; $[133+Ar]^+$, 260, 3.0; 208, 15.0; $[ArCO]^+$, 155, 100; $[Ar]^+$, 127, 99.2; 126, 11.5; 101, 5.7; $[PhCO]^+$, 105, 99.8; $[Ph]^+$, 77, 62.2.

2-(4'-Nitrophenyl)-3-benzoyl-4-phenyl-1-oxa-1-azabutadiene (1j). Oil (see below), $C_{21}H_{14}O_4N_2$; mol. wt, 358.11. Calc.: %C, 70.37; H, 3.94; N, 7.82. Found: %C, 70.11; H, 3.90; N, 7.79. IR (cm^{-1}): 3110, 3090, 3060, w, CH ar.; 1715, s, CO; 1670, s, CO; 1640, m, C=N; 1596, 1525, s, NO_2; 850, 725, 695, s, ring subst. ^1H NMR (ppm): 8.30–6.80, m, 14H. Mass data (*m/z*, %): $[M]^{+\cdot}$, 358, 3.4; $[M+1]^+$, 359, 0.8; $[131+Ar]^+$, 253, 2.2; $[133+Ar]^+$, 255, 1.8; 208, 19.5; $[ArCO]^+$, 150, 27.5; 134, 1.6; $[PhCO]^+$, 105, 100; $[Ar]^+$, 122, 0.5; 106, 8.0; 92, 2.7; $[Ph]^+$, 77, 28.8.

Both the oily compounds (**1b** and **1j**) were purified on a column filled with Al_2O_3 (Brockmann 90, II/III activity) using dichloromethane/*n*-pentane 1:2 mixture as an eluent. Attempts to distil off the oils even in high vaccum (0.002 mm Hg) failed because of thermal decomposition.

^1H NMR spectra were determined on a Hitachi–Perkin–Elmer R-24B spectrometer, in $CDCl_3$ using TMS as internal standard.

Mass spectra were recorded on an LKB-9000S spectrometer under the following conditions: voltage, 70 eV; acc. voltage, 3.5 kV; I.S. temp., 250°C; D.I. temp., 70–120 °C.

IR spectra were made on a Perkin–Elmer 257 spectrophotometer using KBr pills or as a film (**1b** and **1j**).

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