Deoxygenation and X-Ray Photoelectron Studies on some Quinoxalines and their *N*-Oxides

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Deoxygenation results of some quinoxaline dioxides with phosphorous trichloride are presented and compared with previous deoxygenations with other reagents. Differentiation between isomeric quinoxaline oxides using X-ray photoelectron spectroscopy is also discussed.

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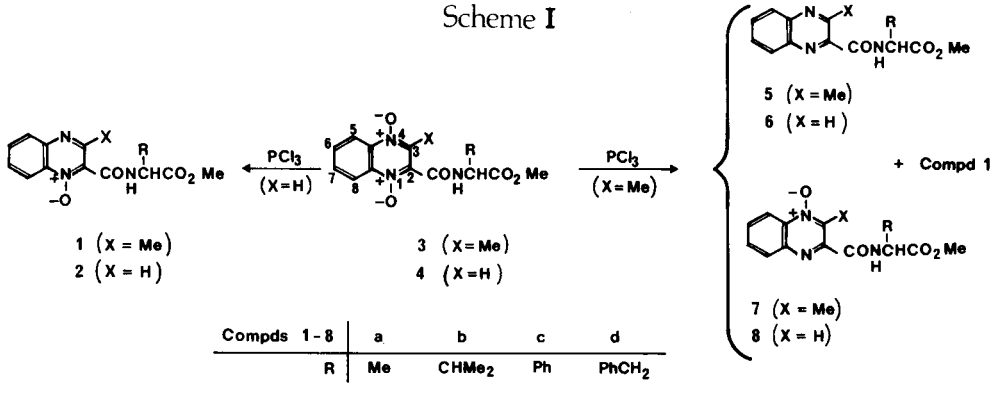
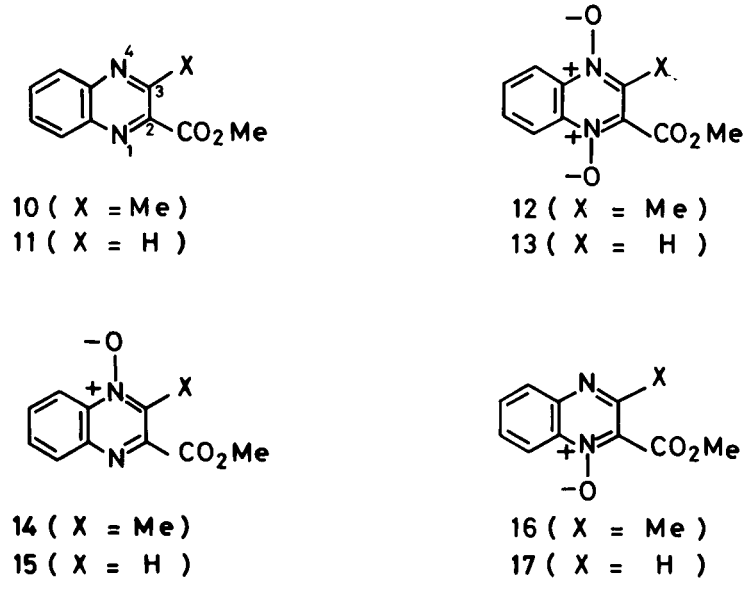
Introduction.

In a recent study (1), we have investigated the deoxygenation of *N*-(2-quinoxaloyl)-L-α-amino ester dioxides (**4a-d**) and their C_3-methyl analogues **3a-d** (Scheme 1). Each of the two reagents used exhibited a certain selectivity. Trimethyl phosphite was found to remove either the *N*-1-oxygen (series **3a-d**) or the *N*-4-oxygen (series **4a-d**). Alkaline sodium dithionite, however, removed the *N*-1-oxygen in both series. These results were supported by ms, pmr and uv spectral data (1).

Scheme I



Scheme II



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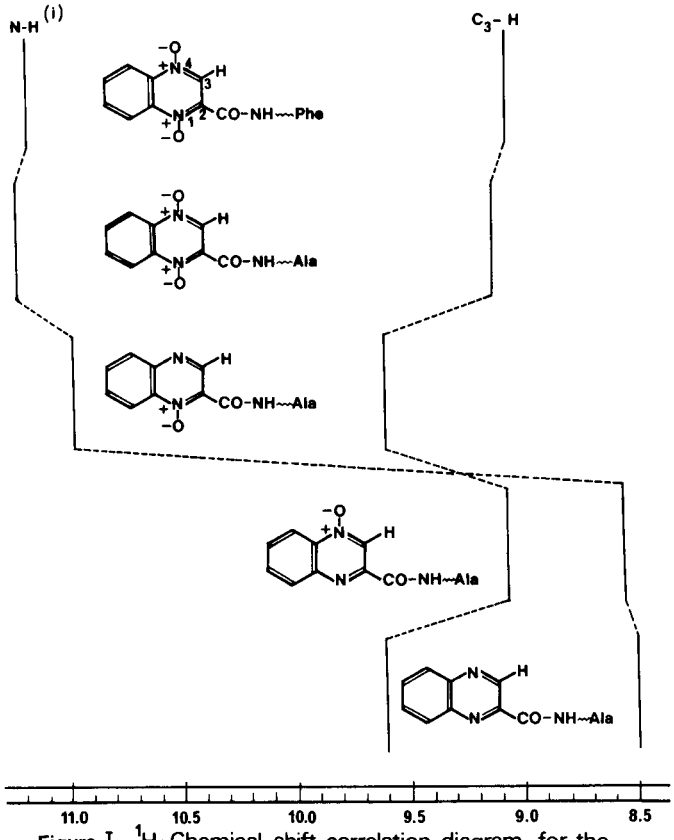

Figure I. ^{1}H-Chemical shift correlation diagram for the C_3-H, and the amide N-H protons of compounds **2** **4a**, **4d**, **6a** and **8a**. i Center of doublet.

Ala = Alanine residue ; Phe = Phenylalanine residue.

In the present study, we report the results of deoxygenation of either series of compounds **3a-d** and **4a-d** by phosphorus trichloride [a powerful deoxygenation agent that found wide applicatins in synthetic work involving similar systems (2,3)], comparing them with those of trimethyl phosphite. We also report X-ray photoelectron spectral results that support previous *N*-oxide assignments for some compounds **1a-8a** and the related parent analogues **10-17** (Schemes I and II).

Results and Discussion.

Deoxygenation with Phosphorus Trichloride.

Phosphorus trichloride is found to be highly selective for compounds **4a-d** and removed the *N*-4-oxygen. It is, however, less selective for **3a-d** where the corresponding *N*-1-oxides **1a-d**, the isomeric *N*-4-oxides **7a-d**, and the quinoxalines **5a-d** were obtained. The ratios of these in the mixture, 60:25:15, where estimated from the integrated peak areas of the C_3-methyl protons' signal at about 2.73, 2.95 and 3.02 ppm, respectively (Table II and Figure II). Under the same reaction conditions, monoxide **1a** gave the corresponding quinoxaline **5a** in 65% yield, the rest being **1a**, recovered unchanged. Monoxide **2a** under identical conditions, was recovered unchanged. It should be mentioned that the selectivity of phosphorus trichloride in the case of **4a-d** parallels that of trimethyl phosphite. Spectroscopic data indicate that the *N*-1 oxygen is involved in strong intrahydrogen bonding with the amid-NH (1). This situation singles out the *N*-4-oxygen as the preferred site of attack by both phosphorus reagents.

Table I

The Chemical Shifts (f), δ (ppm), for the Different Protons of Compounds **2a-d**, **8a-d** and **4a-d**

Compound No.	H_8 (m)	H_5 (m)	H_6,H_7 (s)	C_3-H (d)	N_{10}-H	C_{11}-H (s)	-OCH_3	R
2a	8.68	8.18	7.92	9.60	10.87, 11.00	4.82 (m)	3.82	CH_3: 1.55, 167 (d)
2b	8.67	8.17	7.95	9.63	10.87, 11.00	4.80 (m)	3.77	$CH(CH_3)_2$: 2.23 (m); 1.02, 1.15 (d)
2c	8.67	8.20	7.96	9.63	12.05, 12.17	5.73, 5.83 (d)	3.80	Ph: 7.47 (m) (k)
2d	8.65	8.20	7.90	9.58	10.84, 10.97	5.07 (m)	3.73	CH_2-Ph: 3.20, 3.23, 3.33 (2d); 7.22 (s)
8a	8.17	8.68	7.88	9.06	8.52 (g)	4.82 (m)	3.78	CH_3: 1.53, 1.63 (d)
8b	8.20	8.65	7.90	9.06	8.50 (g)	4.72 (m)	3.78	$CH(CH_3)_2$: 2.33 (m); 1.00, 1.10 (d)
8c	8.20	8.63	7.87	9.03	8.85, 8.98	5.72, 5.83 (d)	3.78	Ph: 7.43 (m)
8d	8.17	8.63	7.87	9.05	8.48 (g)	5.06 (m)	3.78	CH_2-Ph: 3.22, 3.32 (d); 7.25 (s)
	H_8,H_5 (m)							
4a	8.67		7.94	9.11	11.18, 11.26	4.80 (m) (h)	3.78	CH_3: 1.56, 1.62 (d)
4b	8.66		7.95	9.12	11.18, 11.27	4.76 (m)	3.78	$CH(CH_3)_2$: 2.33 (m); 1.03, 1.11 (d)
4c	8.67		7.94	9.08	11.69, 11.78	5.73 5.80 (d)	3.78	Ph: 7.41 (m) (k)
4d	8.60		7.90	9.04	11.11, 11.20	5.02 (m)	3.75	CH_2-Ph: 3.19, 3.22, 3.27, 3.29, (2d); 7.26 (s)

(f) (g) (k) See footnote (f), (g), (k) Table II; (h) Pseudopentet ($J_{CH\text{-}NH} = J_{CH\text{-}CH_3} = 7$ Hz).

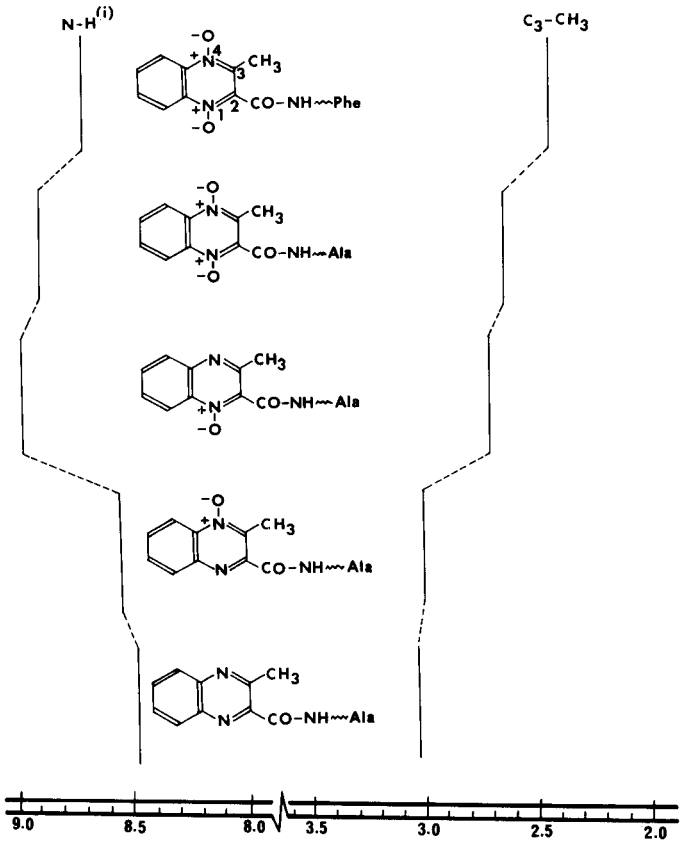

Figure II. H–Chemical shift correlation diagram for the C_3-CH_3 and the amide N–H protons of compounds 1a, 3a, 3d, 5a and 7a. (i) Center of doublet.

Ala = Alanine residue; Phe = Phenylalanine residue.

Whereas trimethyl phosphite is still selective towards series **3a-d**, the other phosphorus reagent is less so. An explanation of this difference may be found by considering that the dipolar *N*-oxide grouping can serve both as an electron-donor (4) or an electron-acceptor (5). The results of the present study seem to indicate that the *N*-oxide grouping acts as an electron-donor with phosphorus trichloride, but acts as an electron-acceptor with trimethyl phosphite. This is in part due to the difference in the electron density of the central phosphorus atom, that is itself determined by the nature of the substituents (4,6). In series **3a-d**, the *N*-1-oxygen is known to be involved in a relatively weak intrahydrogen bridging (compared to series **4a-d**) (1), and should, therefore, be a better electron donor. It is therefore capable of competing with the *N*-4-oxygen, hence the reduced selectivity. Where the *N*-1-oxide group is acting as an electron acceptor, this role is enhanced in compounds **3a-d** by the neighbouring electron-withdrawing carboxamido group. The nucleophilic phosphorus atom in trimethyl phosphite is able to approach this oxygen, to achieve its selective removal. In the absence of an electron-withdrawing group to enhance the electron-accepting power of the *N*-oxide group, the reaction fails (7).

The above explanation is not probably the whole picture, as the C_2/C_3-substituents may still exert steric influence onto the course of these deoxygenations. One literature report (8) described the selective removal of the *N*-4-oxygen with phosphorus trichloride in compound **9** in which this *N*-4-oxygen is practically free of the steric compression prevalent around the *N*-1-oxygen.

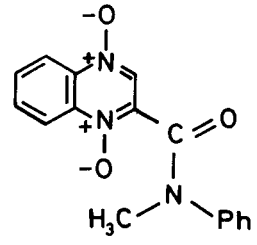

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Table II

The Chemical Shifts (f), δ (ppm), for the Different Protons of Compounds **1a-d** and **7a-d**

Compound No.	H_8 (m)	H_5,H_6,H_7 (m)	C_3-CH_3 (s)	$N_{10}-H$ (d)	$C_{11}-H$	$-OCH_3$ (s)	R
1a	8.37	7.75	2.70	8.95, 9.08	4.78 (m)	3.78	CH_3: 1.53, 1.65 (d) (k)
1b	8.38	7.77	2.73	8.88, 9.02	4.75 (m)	3.78	$CH(CH_3)_2$: 2.37 (m); 1.02, 1.05, 1.13, 1.17 (2d)
1c	8.47	7.85	2.76	9.63, 9.77	5.65, 5.76 (d)	3.75	Ph: 7.48 (m) (k)
1d	8.47	7.80	2.73	8.96, 9.10	5.12 (m)	3.75	CH_2-Ph: 3.20, 3.23, 3.33 (2d); 7.27 (s)
		H_5 (m) / H_6,H_7 (m)					
7a	8.16	8.60 / 7.88	3.02	8.56 (g)	4.75 (m)	3.78	CH_3: 1.53, 1.65 (d)
7b	8.15	8.60 / 7.83	3.03	8.55 (g)	4.72 (m)	3.80	$CH(CH_3)_2$: 2.28 (m); 1.00, 1.12 (d)
7c	8.13	8.54 / 7.83	3.03	8.87, 9.00	5.65, 5.76 (d)	3.80	Ph: 7.42 (m)
7d	8.00	8.52 / 7.78	3.00	8.47 (g)	5.06 (m)	3.77	CH_2-Ph: 3.22, 3.32 (d); 7.25 (s)

(f) Solvent: deuteriochloroform; signals described as (s): singlet, (d): doublet, (m): center of multiplet. (g) Hidden under the C_5-H multiplet. (k) Prochiral group and shows anisochrony.

Table III

Inner-Shell (1s) Binding Energies in (eV Units) of Nitrogen, Oxygen and Carbon Atoms in Some 2-Quinoxaline-Esters, -Amides and their *N*-Oxides

Compound No.	N (1s)			O (1s)			C (1s)		
1a	400.3	401	404	5.32.7	533.8	535.5	286.2	287	289.5
2a	400.9		404.7	532.8	534.4	535.5	285.9	287.2	289.6
3a		401.3	404.3	532.4	534.5		286.3	287.3	289.5
4a	400.8		403.9	532.4	533.5 (a)	534.6	286	287.2	289.6
5a	399.7	400.4			533.2	534.5	286		290
6a	400.3			532.5	533.6	534.5	285.5	286.5	289.7
7a	400.3		403.8	532.7	533.7	534.5	286.2	287.5	289.7
8a		401	404.6		533	534.5	286.4		290
10	400.2			532.5 (a)	533.7		286	286.7	290
11	400.4				533.3	534.3 (a)	286		290
12			403.8	532.8		534.5	286	287	290
13			403.5	532.1	533.9		285.6	286.9	298.8
14	399.6		403.7	532.5	533.5	534.8	285.5	286.7	289.8
15	400.5		404.8		533.5	534.7	286.3	287.5	290.5
16	400.4		~404	532.8			285.8		290
17	400.5		404.5		533.4	534.4	286.3		290.3

(a) Ill-defined inflexion.

As yet, there is no report on the selective removal of the *N*-4-oxygen in **3a-d** nor in **12**. However, the facile deoxygenation of the dioxides **3a-d** with phosphorus trichloride provides a convenient route for the preparation of the *N*-1-oxides **1a-d** (Scheme I) which were previously obtained in low yields by laborious methods (I).

2. Spectral Characterization.

(a) Pmr Spectra.

In a recent report (1), we have established that N-H, C_3-H and C_3-CH_3 proton chemical shifts can be used for differentiation of the isomeric quinoxaline monoxides. These principles are illustrated in Figures I and II. The full chemical shift data are presented in Tables I and II.

(b) X-Ray Photoelectron Spectra.

Previous X-ray photoelectron spectroscopic studies (XPS or ESCA) on some nitrogen containing compounds provided valuable structural information (9,10). It appears of interest to apply this recent technique to a series of quinoxalines and their mono- and dioxides. This is in order to measure the binding energies of the nitrogen (1s) orbitals and to detect the "interaction" between these orbitals and the adjacent groups. Such interaction (if present) would affect their binding energies and their intensities.

In the following discussion, the nitrogen (1s), oxygen (1s), and carbon (1s) orbitals will be dealt with separately in the individual series of compounds studied in this work.

Figures III, IV, V and VI represent the XPS spectra of quinoxaline-2-carboxylates, their C_3-methyl analogues, the quinoxaline-2-carboxamides and their C_3-methyl analogues respectively. Their N (1s), O (1s) and C (1s) binding energies (eV) are given in Table III.

The Nitrogen (1s) Orbital.

In the quinoxaline 2-carboxylate series (Figure III), each of compounds **11** and **13** shows almost one symmetrical nitrogen line at 400.4 eV and 403.5 eV, respectively. Compounds **15** shows two distinct nitrogen lines of roughly the same intensity at 400.5 eV and 404.8 eV. Of these, the line at 400.5 eV can be assigned to the unoxidized nitrogen (N-1), and the other line at 404.8 eV to the oxidized *N*-4-nitrogen. Compound **17** also shows two lines of different intensities at 400.5 eV and 404.5 eV. The stronger line at 400.4 eV is assigned to the unoxidized *N*-4-nitrogen, while the less intense line at 404.5 eV is assigned to the oxidized *N*-1-nitrogen. The substantial decrease in intensity of this line might be attributed to "interaction" between the *N*-1-oxide oxygen and the ester group. As expected, such interaction is not observed in the case of **15** where the two nitrogen lines are of similar intensity. A similar pattern is also observed in **14** and **16** (Figure IV). It is interesting to note that the energy separation between the (1s) orbitals of an unoxidized and an oxidized nitrogen (both present in compound **15** and **17**) is approximately 4 eV, while the difference for a reduced nitrogen in **11** and an oxidized nitrogen in **13** is approximately 3 eV. The decrease in the separation energy in the latter case may be attributed to an overall "interaction" between the two oxidized nitrogens in **13**. This conclusion is also true for the C_3-methyl analogues (Figure IV).

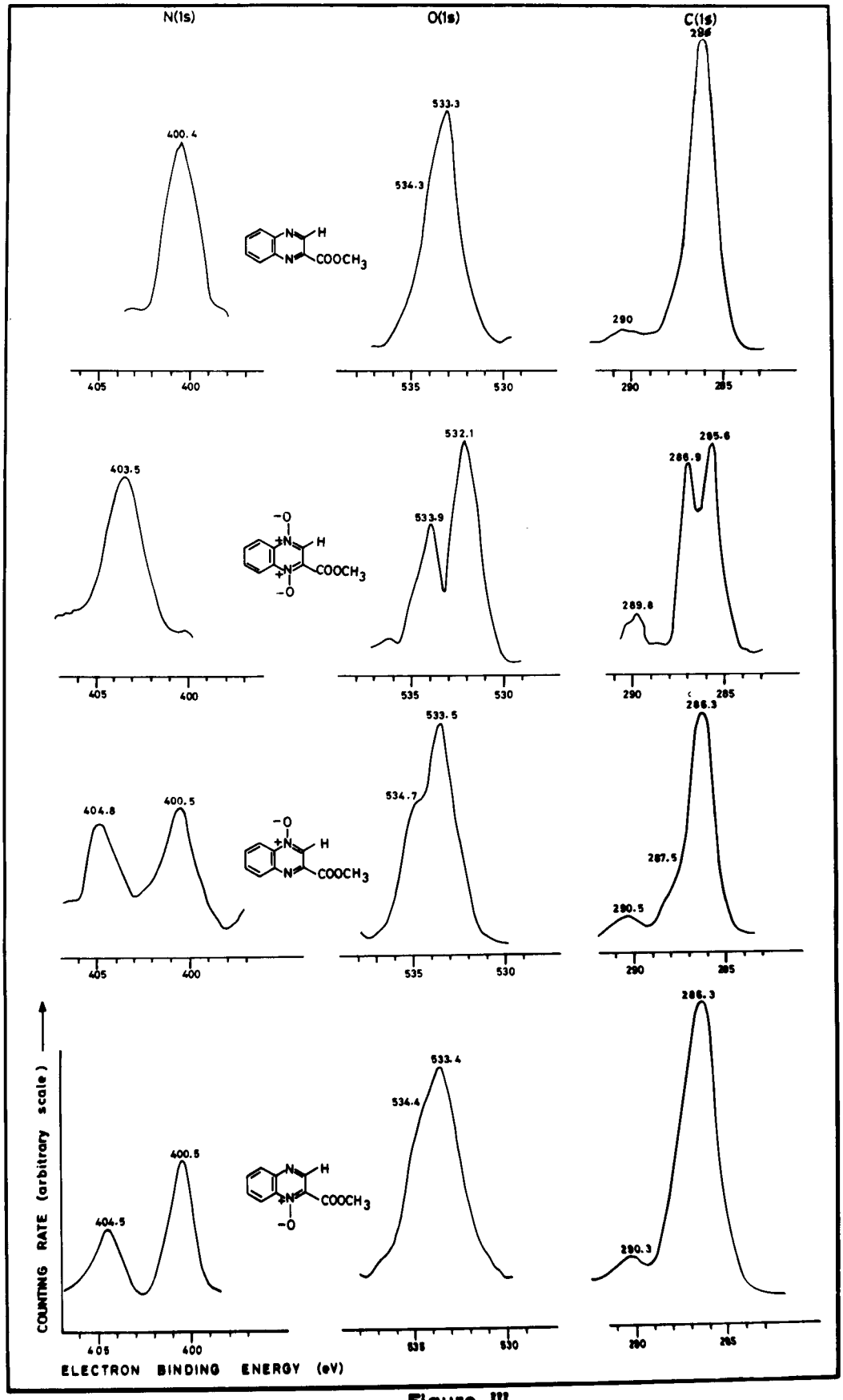

N(1s)
O(1s)
C(1s)
400.4
533.3
534.3
290
403.5
532.1
533.9
285.6
286.9
289.8
404.8
400.5
533.5
534.7
286.3
287.5
290.5
404.5
400.5
533.4
534.4
286.3
290.3
COOCH3
COUNTING RATE (arbitrary scale)
ELECTRON BINDING ENERGY (eV)

Figure III

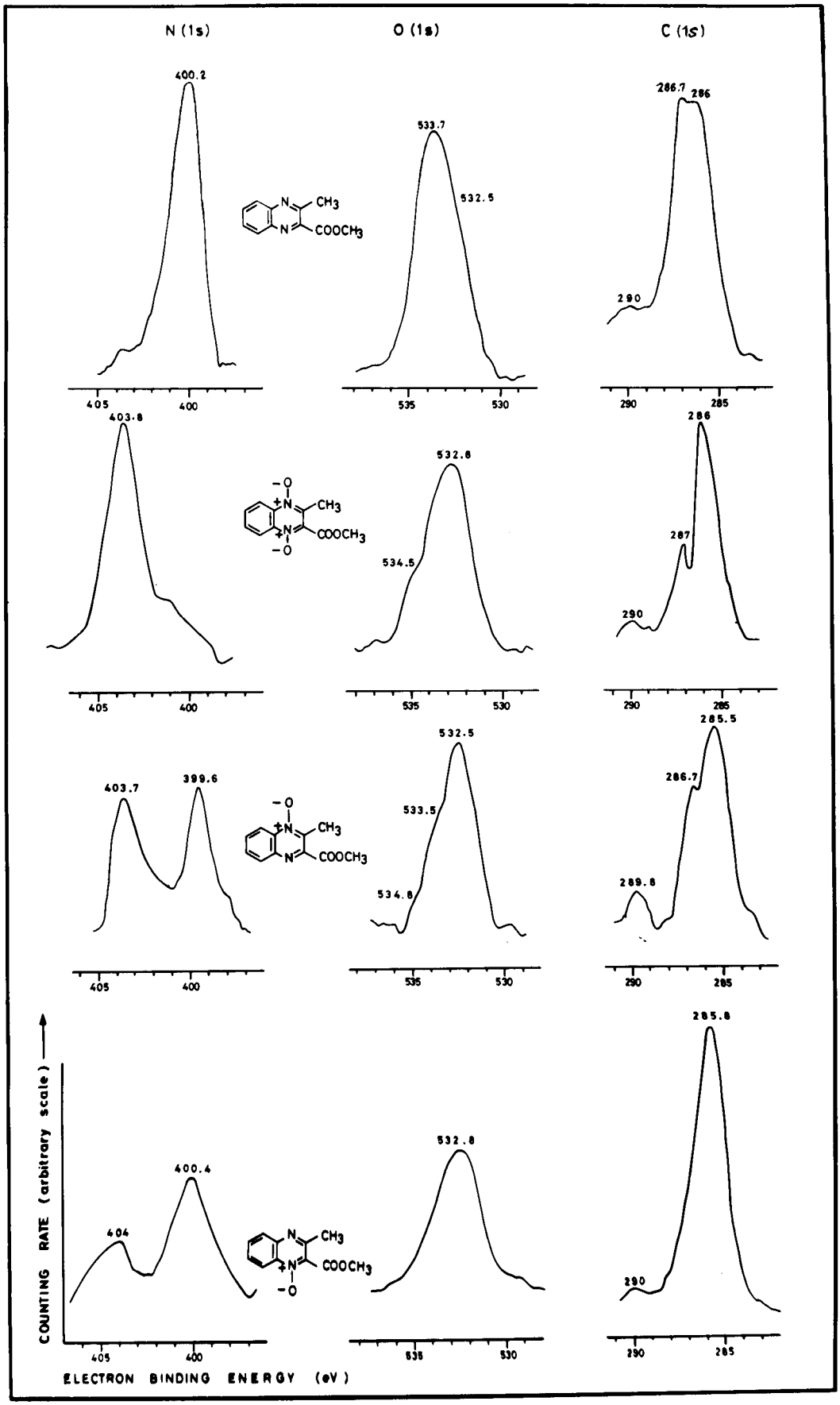

N (1s)
O (1s)
C (1s)
400.2
533.7
532.5
286.7
286
290
405
400
535
530
290
285
403.8
532.8
534.5
286
287
290
403.7
399.6
532.5
533.5
534.8
285.5
286.7
289.8
400.4
404
532.8
285.8
290
CH3
COOCH3
COUNTING RATE (arbitrary scale)
ELECTRON BINDING ENERGY (eV)

Figure IV

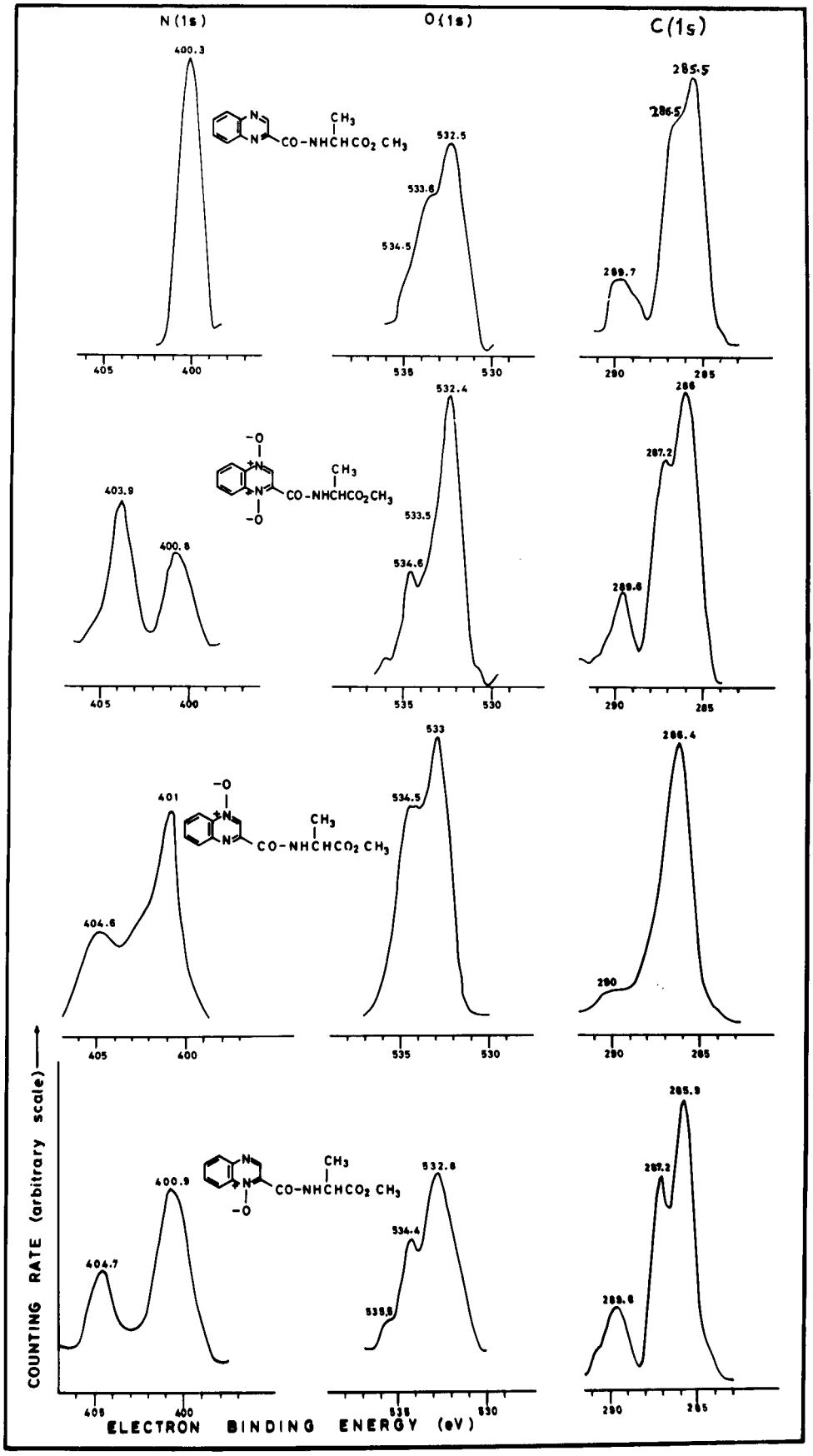
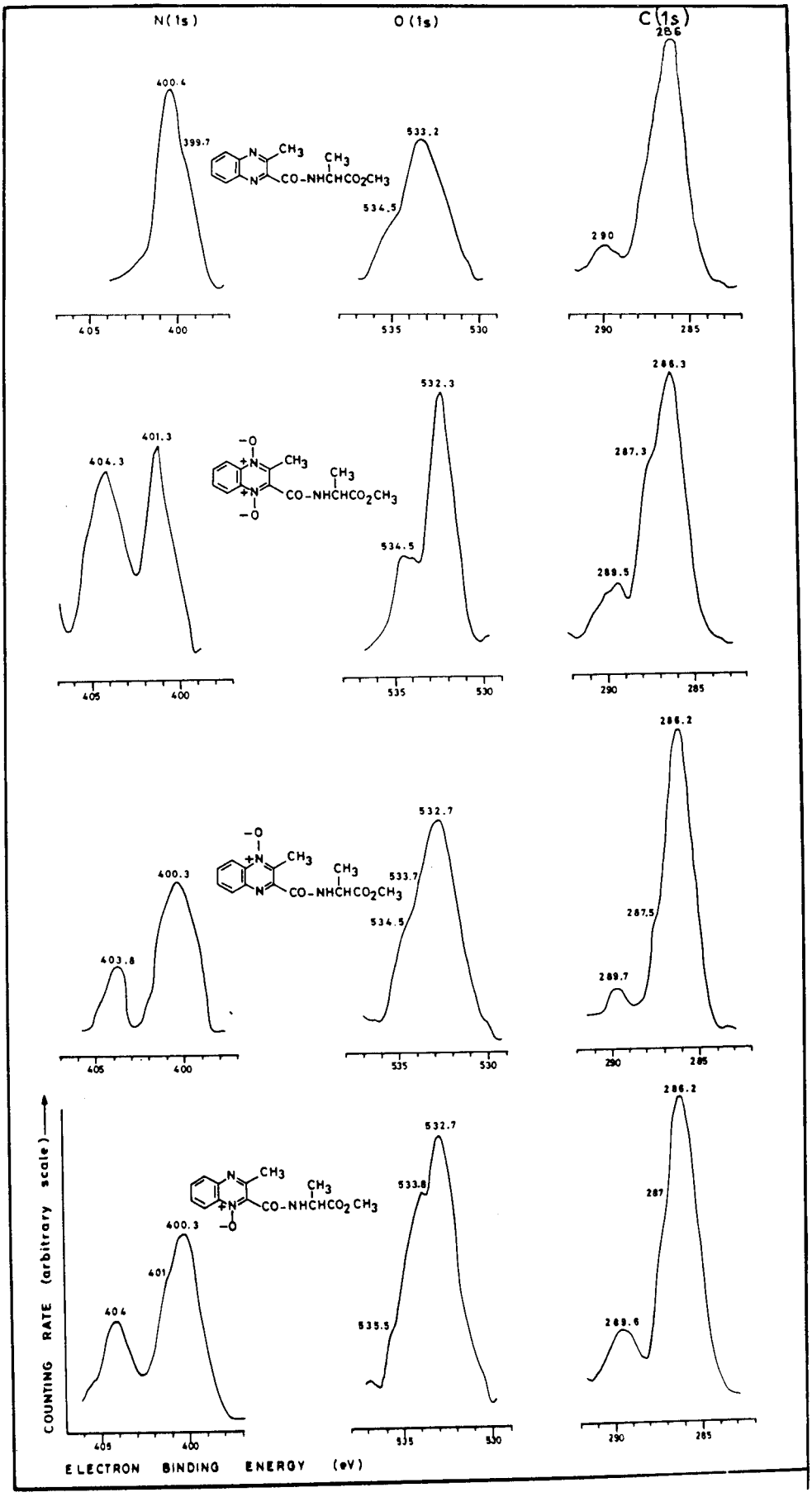

N(1s)
O(1s)
C(1s)
400.3
532.5
533.6
534.5
285.5
286.5
289.7
403.9
400.8
532.4
533.5
534.6
286
287.2
289.6
401
404.6
533
534.5
286.4
290
400.9
404.7
532.6
534.4
535.5
285.9
287.2
289.6
CO-NHCHCO2 CH3
CH3
COUNTING RATE (arbitrary scale)
ELECTRON BINDING ENERGY (eV)

Figure V


N(1s)
O(1s)
C(1s)
400.4
399.7
533.2
534.5
286
290
405
400
535
530
290
285
404.3
401.3
532.3
534.5
286.3
287.3
289.5
403.8
400.3
532.7
533.7
534.5
286.2
287.5
289.7
404
401
400.3
532.7
533.8
535.5
286.2
287
288.6
CH3
CH3
CO-NHCHCO2CH3
COUNTING RATE (arbitrary scale)
ELECTRON BINDING ENERGY (eV)

Due to electron release, the C_3-methyl group in **14** destabilizes the nitrogen (1s) orbital by about 1 eV. This leads to the observed decrease in the binding energy of the (1s) orbital (1 eV) in the oxidized nitrogen in **14** as compared to that in **15**.

In the case of 3-methyl quinoxaline 2-carboxamides, the analysis of the XPS spectra (Figure VI) becomes rather complicated due to the presence of the added nitrogen of the amide group. In compound **3a**, we observe the presence of two nitrogen (1s) lines at 401.3 eV and 404.3 eV, with approximately 1:2 intensities. The former line is assigned to the amide nitrogen. Its stabilization by about 1 eV, compared to its binding energy in **5a** (*Vide Infra*) is attributed to its intra-bridging to the *N*-1-oxide oxygen through hydrogen bonding. Also, in the case of **7a**, we observe two nitrogen (1s) lines of different intensity (2:1) at 400.3 eV and 403.8 eV respectively. The first line is assigned to the ring (N-1) nitrogen and to the amide nitrogen which both seem to have almost equal binding energies. The second line at 403.2 eV is assigned to the *N*-4-oxide nitrogen. In the case of **1a**, we observe two lines at 400.3 eV and 404 eV. The first intense line looks asymetrical with a slight shoulder at 401 eV attributed to the amide nitrogen (1s). The line at 404 eV is due to the oxidized *N*-1-nitrogen (1s). In the case of **5a**, we observe a broad unsymmetrical band in the nitrogen (1s) energy region at 400 eV. The shoulder of less intensity at 399.7 eV can be assigned to the *N*-4-nitrogen, while the more intense line at 400.4 eV is assigned to both the amide nitrogen and the ring *N*-1-nitrogen (Figure VI). Comparable trends are also observed in the corresponding series lacking the C_3-methyl groups (Figure V).

In conclusion XPS spectra of the different compounds studied are related to their structures in the following ways: (i) Each of the parent quinoxalines and the dioxides shows one symmetrical line for the N (1s) orbital. A difference of 3 eV differentiates the two series. (ii) A set of two lines appear for each of the isomeric monoxides. They are either of the same intensity (4-oxides) or of different intensities (1-oxides), and they can thus be differentiated. (iii) Each of the quinoxaline amide *N*-oxides shows two lines of different intensities. The more intense line appears either at higher energies (dioxides) or at lower energies (monoxides).

The Oxygen (1s) Orbital.

In the quinoxaline-2-carboxylate series (Figure III), the XPS spectrum of **11** shows almost one symmetrical line at 533.3 eV in the oxygen (1s) energy region. Obviously, this line corresponds to the two oxygens (1s) ester group. In the case of **15**, the band in Figure III shows one intense line at 533.5 eV and a weaker, but distinct shoulder at 534.7 eV. By analogy with **11**, the stronger line is assigned to the two oxygens (1s) ester group, while the shoulder is assigned to the *N*-4-oxygen (1s) orbital. The XPS spectrum of **17** shows a broad asymmetrical band in the oxygen (1s) region. It can be seen from Figure III that there is a maximum at 533.4 eV, and a not well defined shoulder at 534.4 eV. The stronger line is assigned to the two oxygens (1s) ester group, while the shoulder is assigned to the *N*-1-oxygen (1s) orbital. We attribute the overlap of these lines to the "interaction" of the *N*-1-oxygen with the vicinal ester group as was predicted previously on the basis of the nitrogen (1s) lines (*Vide Supra*). The spectra of **14** and **16** (Figure IV) can be rationalized on similar lines. As expected for the dioxide **12**, the very intense line at 532.8 eV (Figure IV) corresponds to the interacting ester oxygens and *N*-1-oxygen (1s) orbitals, while the shoulder at 534.5 eV corresponds to the *N*-4-oxygen (1s) orbital. Although not distinctly defined (as compared with **13**, Figure III), their intensities appear to be in a 3:1 ratio.

In the case of the quinoxaline-amino ester **5a** and its oxides **1a, 3a, 7a,** the side chain contains three oxygens. The XPS spectrum of **5a** (Figure VI) shows the presence of a strong line at 533.2 eV and a well distinct shoulder of less intensity at 534.5 eV. The stronger line is assigned to the two ester oxygens (1s) on the basis of previous assignments for the parent quinoxaline ester **10**. Consequently, the shoulder is assigned to the amide oxygen (1s) orbital.

In the case of **7a**, the oxygen (1s) band (Figure VI) seems to be more complicated than in previous cases. However, one can distinguish a strong lone at 532.7 eV, a distinct shoulder at 534.5 eV and a not well-defined shoulder at 533.7 eV. They belong to the two ester oxygens, the amide oxygen and the *N*-4-oxygen (1s) orbitals respectively. The last two are tentatively assigned on the assumption that the amide oxygen is not expected to interact with the *N*-4-oxygen. Its binding energy is then expected to be similar to that in **5a**. Peak assignments for the other two oxides, **1a** and **3a**, appear to be more complicated, possibly because of "interaction" between the *N*-1-oxygen and the adjacent amide grouping. The xps spectra of the corresponding quinoxaline amides, lacking the C_3-CH_3 group (**2a, 4a, 6a** and **8a**) seem to follow comparable trends (Figure V). On the whole, it can be concluded that the oxygen spectra are less useful than the nitrogen spectra for purposes of differentiation.

The Carbon (1s) Orbital.

The large number of carbon atoms in the above compounds makes it difficult to distinguish their individual binding energies. However, the carboxyl carbons of the ester and amide groups are expected to be at higher bind ing energies compared with the other carbons. The carbon (1s) energy region, in all of these compounds, shows a relatively small line at 289-290 eV which is assigned to the carboxylic carbons (1s) orbitals, while the strong line at 286 eV is attributed to the other carbons (1s) orbitals

(Figures III-VI). The spectra, however, are not very informative.

EXPERIMENTAL

Pmr Spectra were recorded on a Bruker WH-90 spectrometer equipped with Fourier transform facilities for solutions in deuteriochloroform with TMS as the internal reference.

A McPherson XPS-36 Spectrometer with MgK_{α} X-radiation source at 1253.6 eV was used. This instrument has a cryogenic pump to provide a pressure of less than 10^{-8} torr in the sample chamber. It also has an argon ion gun, with acceleration through 10 KV, for sample surface treatment. Samples were mounted on an Aluminium mesh. Sample temperatures were approximately 300 K.

Synthesis.

N-(2-Quinoxaloyll)-L-α-amino Ester 1-Oxides (**2a-d**) and their C_3-Methyl Analogues (**1a-d**).

The title compounds in this study are prepared by deoxygenation, using phosphorus trichloride, of the corresponding quinoxaline 1,4-dioxides. The latter were obtained following literature procedures (1,11).

General Procedure.

Phosphorus trichloride (Fluka, 15 ml.) was added to a solution of the particular quinoxaline 1,4-dioxide, **3a-d** or **4a-d**, (0.015 mole) in chloroform (50 ml.). The reaction mixture was stirred overnight at room temperature, poured into ice-water (80 ml.) and then treated with excess 1*N* aqueous sodium hydroxide (or saturated aqueous sodium carbonate). The chloroform layer was separated, and the aqueous layer was extracted with chloroform (2 × 300 ml.). The combined chloroform extracts were dried (magnesium sulfate) and evaporated to give yellow solids.

(i) *N*-(2-Quinoxaloyl)-L-α-amino Ester 1-Oxides (**2a-d**).

These monoxides were obtained in the pure form from the chloroform extract. Their identity was established by comparison with authentic samples obtained by deoxygenation with trimethyl phosphite (1).

(ii) *N*-(3-Methyl-2-quinoxaloyl)-L-α-amino Ester 1-Oxides (**1a-d**).

The evaporation of the chloroform extracts yielded the desired 1-oxides admixed with the isomeric 4-oxides and the corresponding quinoxalines. The contaminants were removed by successive washings of the crude products with diethyl ether. A final purification was achieved by preparative tlc, using Silica Gel (Merck, HF 254 + 366) and eluting with a chloroform-methanol solvent mixture (95:5 v/v). The quinoxaline 1-oxide derivative **2a** representing the series, was recovered unchanged after treatment with phosphorus trichloride in the above manner.

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