

Synthesis and Mass Spectra of *N*-Aryl-pyrroles and Their Chlorination Products

H. El Khadem and L. A. Kemler

Department of Chemistry and Chemical Engineering, Michigan Technological University, Houghton, Michigan 49931

and

Z. M. El-Shafei, M. M. A. Abdel Rahman and S. El Sadany

Department of Chemistry, Faculty of Science, Alexandria University, Alexandria, Egypt

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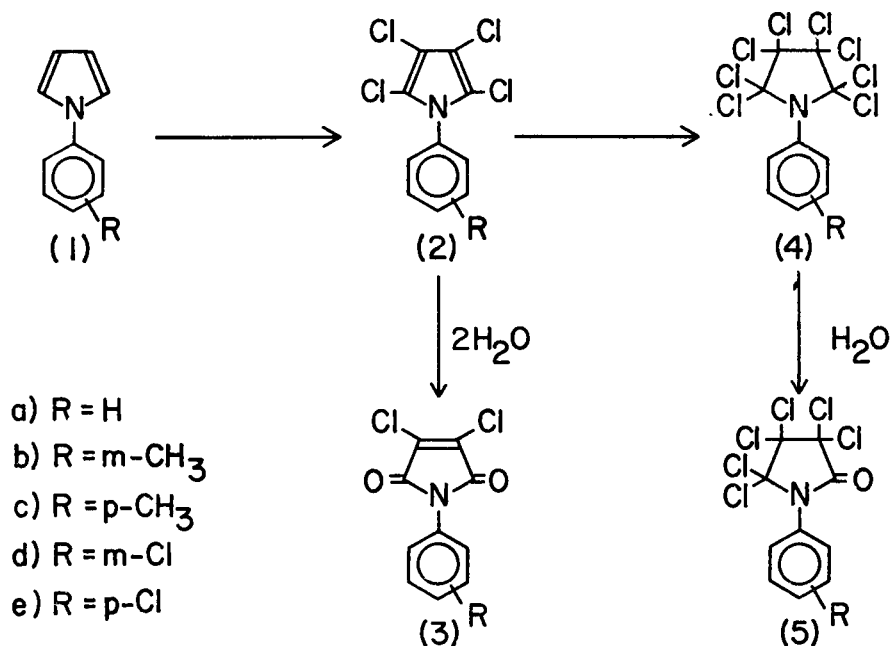
Chlorination of pyrrole with sulfuryl chloride is known (1) to give a pentachloro derivative which is readily hydrolyzed with boiling water to dichloromaleic imide. In the present work, we have prepared a number of *N*-arylpyrroles, subjected them to chlorination with chlorine gas in the presence of Lewis acids and hydrolyzed the products to *N*-aryldichloromaleic imides, and hexachloropyrrolidin-2-ones. A study was then made of the mass spectra of these different types of five-membered ring compounds, which are presently being screened for insecticidal activity (2).

The starting *N*-arylpyrroles were obtained in the usual manner by pyrolysis of the aromatic amine salts of galactaric acid (mucic acid) (3-5). A disadvantage of this synthetic method is that the yield of substituted pyrroles (see Table I) decreases considerably with increase of molecular weight; being less volatile, the higher molecular weight compounds tend to decompose before distilling.

In addition to the known *N*-phenyl, *N*-*m*- and *p*-tolyl (3-5) and *p*-chlorophenylpyrrole (6), two new *N*-arylpyrroles were prepared in this manner: *N*-*m*-chlorophenylpyrrole, and *N*-*p*-carbethoxyphenylpyrrole.

The mass spectra of *N*-arylpyrroles (see Figure 1), like those of alkyl pyrroles (7,8), are characterized by strong molecular ions which are base peaks. The second peak in intensity appears at m/e 115 irrespective of the substituent in the phenyl ring. This can either be due to the phenyl azirium ion radical or an indolium ion radical having lost the substituent in the benzene ring. The parent ion retaining the substituent appears as a relatively strong peak at 129 for the tolyl-pyrroles and 149 for the chlorophenylpyrroles. Other strong peaks in the spectra appeared at 104 (Ph NCH^+) and at 89 for $\text{C}_5\text{H}_5\text{N}^+$.

When *N*-phenylpyrrole (1a); *N*-*m*- and *p*-tolylpyrrole (1b; 1c) and *N*-*m*- and *p*-chlorophenylpyrrole (1d; 1e)



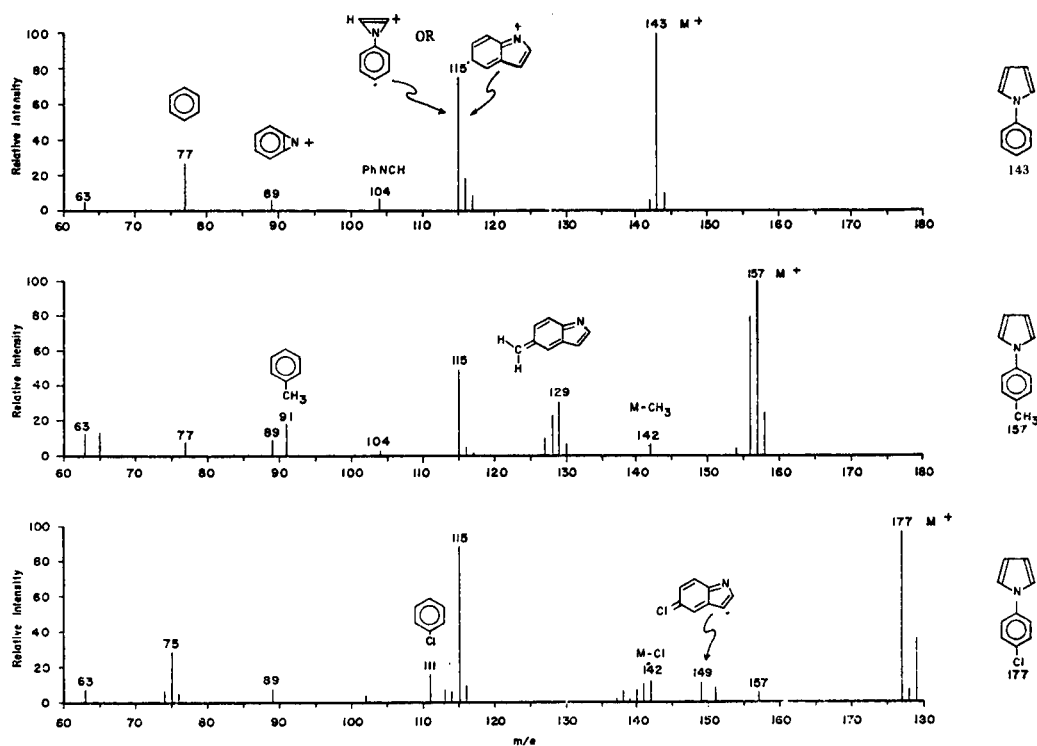
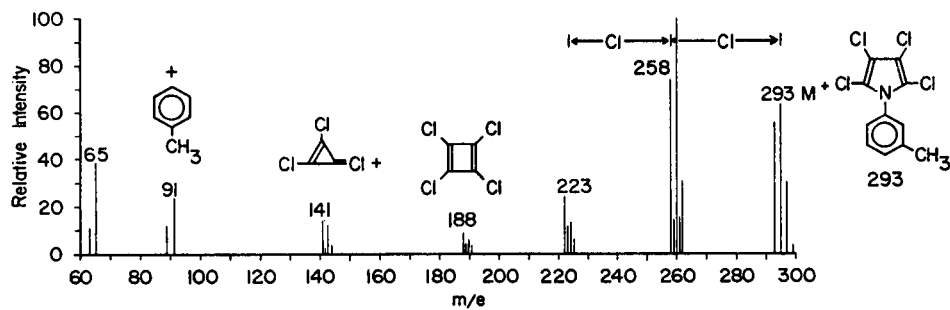
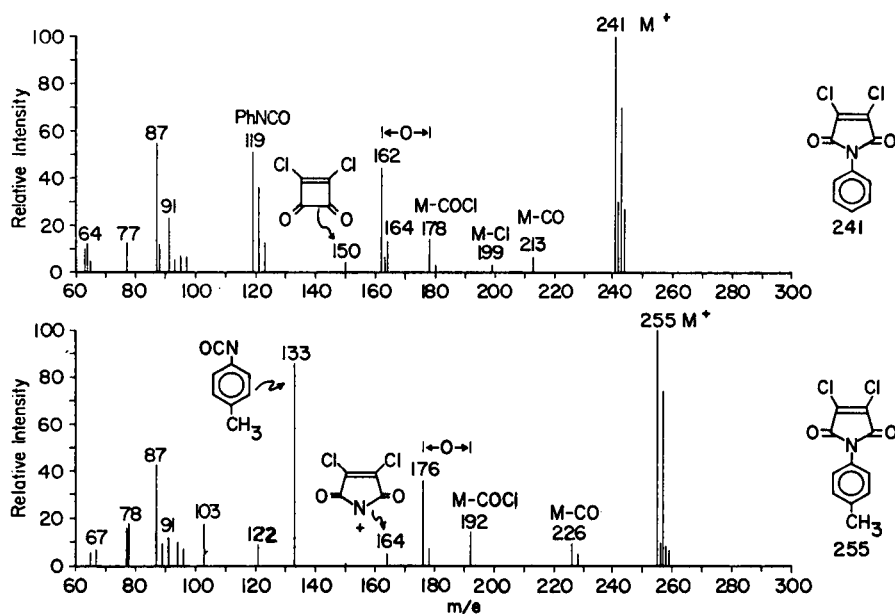
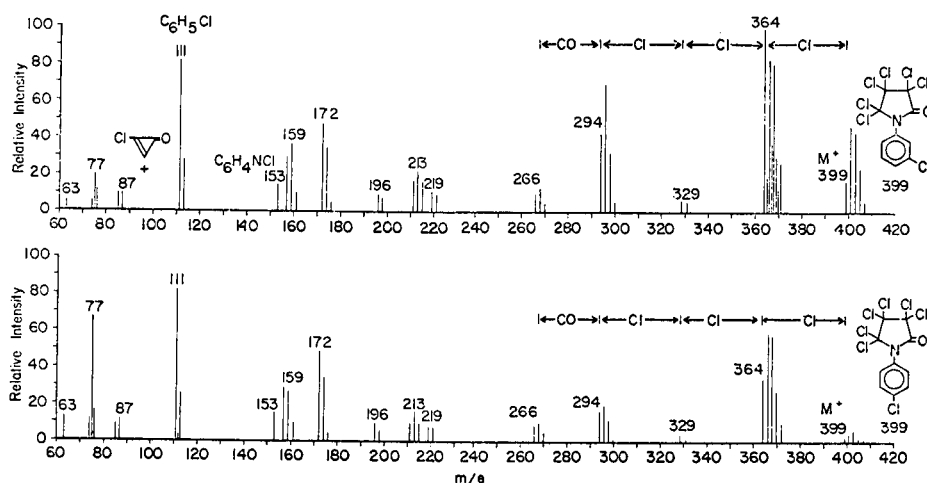
Figure 1. Mass Spectra of *N*-arylpyrroles.Figure 2. Mass Spectrum of *N*-*m*-Tolyltetrachloropyrrole.

TABLE I

N-Aryl-Pyrroles (1)

Substituent (R)	m.p.	Yield %	Formula	C	H	N	C	H	N	Ref.
H	57-60°	18	C ₁₀ H ₉ N	83.9	6.3	9.8	83.9	6.2	10.2	4
<i>p</i> -Me	82°	17	C ₁₁ H ₁₁ N	84.0	7.0	8.9	84.1	7.2	9.0	3
<i>m</i> -Me	b.p. 80° (5 mm)	16	C ₁₁ H ₁₁ N	84.0	7.0	8.9	83.9	7.1	8.8	
<i>p</i> -Cl	90°; 88° (a)	17	C ₁₀ H ₈ NCl	67.6	4.5	7.9	67.5	4.8	8.0	6
<i>m</i> -Cl	51°	9	C ₁₀ H ₈ NCl	67.6	4.5	7.9	67.3	4.5	7.9	
<i>p</i> -CO ₂ Et	89°	2	C ₁₃ H ₁₃ NO ₂	72.4	6.0	6.5	72.3	6.1	6.6	

(a) Prepared by ring contraction from the oxazine.

Figure 3. Mass Spectra of *N*-Aryldichloromaleic Imides.Figure 4. Mass Spectra of *N*-Chlorophenylpyrrolidin-2-ones.

were subjected to chlorination for different periods, electrophilic substitution occurred in the pyrrole ring before the phenyl ring was attacked. This is not surprising owing to the great susceptibility of pyrroles to electrophilic substitution and in view of the fact that the phenyl ring is deactivated by the electron attracting pyrrole ring. Chlorination was carried out by bubbling chloring gas in carbon tetrachloride in the presence of aluminum and ferric chloride for 5 or 10 hours. Only *N*-*m*-tolyltetrachloropyrrole (**2b**) was obtained in a crystalline form from this reaction. Its combustion analysis agreed with the

assigned structure and its ir spectrum showed no carbonyl band. The mass spectrum of this compound (see Figure 2) showed a strong molecular peak at m/e 293 and consecutive peaks 35 and 37 units apart due to the consecutive loss of chlorine³⁵ and chlorine³⁷ atoms. In addition to these, a relatively strong peak at m/e 188 was assigned to tetrachlorocyclobutadiene and a 141 peak assigned to trichlorocyclopropene.

When *N*-phenylpyrrole (**1a**) and *N*-*p*-tolylpyrrole (**1c**) were chlorinated for 5 hours under the same conditions, they yielded no crystalline product, but boiling the reac-

tion mixture with water afforded the crystalline dichloro-*N*-arylmaleic imides (**3a** and **3c**). The structure of these compounds was established by acid hydrolysis to aniline and *p*-toluidine, respectively, which were characterized as their *N*-acetyl derivatives. The ir spectra of the maleic imides showed carbonyl bands at 1720 cm^{-1} and their mass spectra (see Figure 3) were quite different from those of the *N*-arylpyrroles. They showed strong molecular peaks followed by M - CO peaks and M - (CO + Cl) peaks as well as important peaks corresponding to M - (CO + Cl + O). Breakage of the *N*-aryl bond was apparent in some peaks not influenced by substitution in the benzene ring, such as a peak at *m/e* 164 corresponding to the dichloro maleic imide, a 150 peak corresponding to dichlorobutenedione and a 122 peak corresponding to dichlorocyclopropanone.

Chlorination of *N*-*m*-chlorophenylpyrrole (**1d**) and *N*-*p*-chlorophenylpyrrole (**1e**) likewise yielded no crystalline chlorination products after 5 and 10 hours reaction time. However, the latter products, when subjected to mild hydrolysis, gave crystalline hexachloropyrrolidin-2-one. It seems that prolonged chlorination led to additional reactions and formation of the octachloro-derivatives (**4d** and **4e**); these upon hydrolysis, yielded the hexachloropyrrolidin-2-one (**5d** and **5e**). These compounds showed carbonyl bands at $\nu\ 1730\text{ cm}^{-1}$ and their mass spectra (see Figure 4) showed strong molecular peaks which subsequently gave peaks at 35 and 37 mass unit intervals corresponding to consecutive loss of Cl^{35} and Cl^{37} isotopes. After the loss of 3 chlorine atoms, a loss of CO (28) was apparent in the spectrum.

It seems that chlorination of the readily available *N*-aryl-pyrroles constitutes an easy route for the preparation of the dichloro-*N*-phenylmaleic imides and *N*-phenylpyrrolidin-2-one in good yields, and that mass spectroscopy does offer a valuable tool for recognizing the different types of heterocyclic chlorination products.

EXPERIMENTAL

Melting points were measured on a Kofler block and are uncorrected; ir spectra were recorded for potassium bromide discs with a Unicam SP200 spectrophotometer; mass spectra were recorded and measured by Mr. M. P. Gilles, Department of Chemistry and Chemical Engineering, Michigan Technological University, on a Varian M-66 instrument.

N-Arylpyrroles (**1**).

Galactaric acid (mucic acid) (21 g., 0.1 mole) was thoroughly mixed with 0.1 mole of the aromatic amine and the mixture heated in a distillation flask. The distillate was acidified with 2-*N*-hydrochloric acid and steam distilled, and the *N*-arylpyrroles obtained (see Table I) were purified either by distillation under reduced pressure for the liquid or crystallization from dilute

ethanol for solids.

N-Phenyldichloromaleic Imide (**3a**).

Chlorine was bubbled through a solution of *N*-phenylpyrrole (**4**) (0.5 g.) in carbon tetrachloride (50 ml.) containing aluminum chloride (0.2 g.) and ferric chloride (0.2 g.) for 5 hours. The solution was filtered from the catalyst, evaporated to dryness and then boiled with 5 ml. of water for 2 minutes. Upon cooling, *N*-phenyldichloromaleic imide (yield 0.7 g.) separated in colorless crystals, m.p. $209\text{--}210^\circ$ and was recrystallized from ethanol; $\nu\ \text{max}$ (potassium bromide) $1720\text{ (C=O)}\text{ cm}^{-1}$.

Anal. Calcd. for $\text{C}_{10}\text{H}_5\text{Cl}_2\text{NO}_2$: C, 49.6; H, 2.1; N, 5.8. Found: C, 50.1; H, 2.4; N, 5.8.

Hydrolysis of this compound with 2-*N*-hydrochloric acid for 1 hour at 100° followed by addition of excess sodium hydroxide and extraction with ether afforded aniline identified as acetanilide, m.p. and mixed m.p. 114° .

N-*p*-Tolyldichloromaleic Imide (**3c**).

Chlorine was bubbled through a solution of *N*-*p*-tolylpyrrole (**3**) (0.5 g.) in carbon tetrachloride (50 ml.) containing aluminum chloride and ferric chloride (0.2 g. each) for 5 hours. The filtrate when treated as above, yielded 0.75 g. of *N*-*p*-tolyl-dichloromaleic imide, m.p. 185° ; $\nu\ \text{max}$ (potassium bromide) $1720\text{ (C=O)}\text{ cm}^{-1}$.

Anal. Calcd. for $\text{C}_{11}\text{H}_7\text{Cl}_2\text{NO}_2$: C, 51.6; H, 2.7; N, 5.5. Found: C, 50.9; H, 2.9; N, 5.8.

Hydrolysis of this compound by refluxing with 2-*N*-hydrochloric acid for 1 hour, and adding excess sodium hydroxide followed by extraction with ether afforded *p*-toluidine identified as the *N*-acetyl derivative, m.p. and mixed m.p. 154° .

N-*m*-Tolyltetrachloropyrrole (**2b**).

Chlorine was bubbled for 5 hours through a solution of *N*-*m*-tolylpyrrole (0.5 g.) in carbon tetrachloride (50 ml.) containing a mixture of aluminum chloride and ferric chloride (0.2 g. each). The catalyst was filtered off and the residue recrystallized from ethanol in colorless plates, m.p. 96° (yield 0.3 g.); $\nu\ \text{max}$ (potassium bromide) $1605\text{ (C=N)}\text{ cm}^{-1}$.

Anal. Calcd. for $\text{C}_{11}\text{H}_7\text{Cl}_4\text{N}$: C, 44.5; H, 2.4; N, 4.8. Found: C, 44.9; H, 2.4; N, 4.6.

N-*p*-Chlorophenylhexachloro-3-pyrrolidin-2-one (**5e**).

To a solution of *p*-chlorophenylpyrrole (**6**) (0.5 g.) in carbon tetrachloride (50 ml.) a mixture of aluminum chloride and ferric chloride (0.2 g. each) was added and chlorine gas bubbled for 10 hours. The chlorinated mixture was filtered, evaporated to dryness and the residue boiled with 5 ml. of water for 2 minutes. On cooling, the title compound (yield 0.2 g.) separated and was crystallized from dilute ethanol in needles, m.p. 145° ; $\nu\ \text{max}$ (potassium bromide) $1720\text{ (C=O)}\text{ cm}^{-1}$.

Anal. Calcd. for $\text{C}_{10}\text{H}_4\text{NCl}_7\text{O}$: C, 29.8; H, 1.0; N, 3.5. Found: C, 30.1; H, 1.2; N, 3.3.

N-*m*-Chlorophenylhexachloro-3-pyrrolidin-2-one (**5d**).

Chlorine gas was bubbled for 10 hours through a solution of *N*-*m*-chlorophenylpyrrole (0.5 g.) as above. The title compound separated (yield 0.8 g.) and was crystallized from ethanol in plates, m.p. 95° ; $\nu\ \text{max}$ (potassium bromide) $1720\text{ (C=O)}\text{ cm}^{-1}$.

Anal. Calcd. for $\text{C}_{10}\text{H}_4\text{NCl}_7\text{O}$: C, 29.8; H, 1.0; N, 3.5. Found: C, 29.9; H, 1.1; N, 3.6.

REFERENCES

- (1) G. Muzzari, *Gazz. Chim. Ital.*, **32**, 28 (1920).
- (2) H. El Khadem, A. M. Kolkaila and M. H. Meshreki, *J. Chem. Soc.*, 3631 (1963).
- (3) L. Lichtenstein, *Ber.*, **14**, 933 (1881).
- (4) A. Pictet, *ibid.*, **37**, 2792 (1904).
- (5) H. Adkins and H. L. Coonradt, *J. Am. Chem. Soc.*, **63**, 1563 (1941).
- (6) J. Firl and G. Kresze, *Chem. Ber.*, **99**, 3695 (1966).
- (7) A. Kamal, Y. Heifer and A. A. Qureshi, *Pakistan J. Sci. Ind. Res.*, **14**, 184 (1971).
- (8) V. J. Vysotskii, R. A. Khmel'nitskii, J. J. Grandberg and G. V. Fridlyanskii, *Izv. Timiryazev. Sel'skokhoz. Akad.*, 227 (1971).