Carbon-13 NMR and Mass Spectra of Some *N*-Arylmaleimides Substituted at the 2-Position

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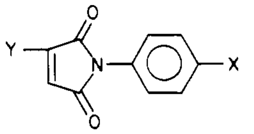
Carbon-13 NMR of several novel *N*-arylmaleimides substituted at 2-positions are presented. In addition, mass spectra of four of the imides substituted with chloro or cyclopropylamino groups are also reported. The data reveal the absence of trace isoimides in the prepared samples.

Introduction

N-substituted maleimides are known to polymerize producing useful polyimides of high thermal stability (*1*). In our laboratory the chemistry of substituted cyclic imides has received considerable attention in the preparation of new types of polyimides using the cyclopolymerization theory of Butler (*2–4*). Thus *N*-allylmaleimide (*5*), and *N*-allylcitraconimide (*6*) were synthesized and polymerized to low molecular weight polymers. However, attempts to polymerize *N*-aryl-2-(allylamino)maleimide or *N*-aryl-2-(cyclopropylamino)maleimide were not successful (*7*). Although structures of the new monomers were proved by H-1 NMR, IR, and elemental analysis, one may not yet be

Table I



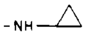
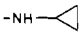
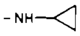
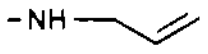
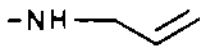
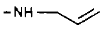
compd	X	Y	% yield
1a	H	H	85
2a	H	Cl	66
2b	$-CH_3$	Cl	83.5
2c	$-OCH_3$	Cl	71.2
3a	H		75
3b	$-CH_3$		80
3c	$-OCH_3$		65
4a	H		88
4b	$-CH_3$		80
4c	$-OCH_3$		80

Table II. Mass Spectral Data of *N*-Phenyl-2-(cyclopropylamino)maleimide[a,b]

m/e	type of peak[d]	% rel intens[c]	*m/e*	type of peak[d]	% rel intens[c]
39		35	93	r	58
40		10	94	i	8
41		56	104		16.5
51		14	107		8
52		15	108	r	100
53		22	109		35
54		19	135	d	16
55		1.5	136		10
56		4	172		11
57		2	173	i	2
64		10	183		6
65		9	187		4
68		53	199		12
77		30	200		25
78		7	201		20
80		62	202		2
81		67	228	P	95
82		5	229	P + 1	17

[a] Molecular weight: 228; molecular formula: $C_{13}H_{12}N_2O_2$. [b] Temperature of ionization chamber: 120 °C. [c] Relative to base peak. [d] r = rearranged ion, i = isotope peak, and d = doubly charged peak.

Table III. Mass Spectral Data of *N*-(*p*-Methoxyphenyl)-2-(cyclopropylamino)maleimide[a,b]

m/e	type of peak[d]	% rel intens[c]	*m/e*	type of peak[d]	% rel intens[c]
39		15	123		68
40		11	124	i	8
41		41	134		15
51	i	4	135	d	3
52		8.5	136		7
53		14	149	r	12
54		8	150	i	2
65	r	6	175		4
68		30	203		3
80		42	229		4
81		38	230		18
93	r	6	231		9
108	d, r	70	232	i	1.5
109	r	18	258	P	100
110	i	1	259	P + 1	16

[a] Molecular weight: 258; molecular formula: $C_{14}H_{14}N_2O_3$. [b] Temperature of ionization chamber: 100 °C. [c] Relative to base peak. [d] r = rearranged peak, i = isotope peak, and d = doubly charged peak.

Table IV. Mass Spectral Data of 2-Chloro-*N*-phenylmaleimide[a,b]

m/e	type of peak[d]	% rel intens[c]	*m/e*	type of peak[d]	% rel intens[c]
37		2.5	77		24
38		10	88		6
39		24.5	89		3
40		8	90		4
41		6	91		3.5
42	i	1	92		7
44		5	93	r	100
45		7	94		11
46	i	1	99		14
47		4.5	102		3.5
50		5	119	r	3
51		17	120		2
52		6	144		34
53		5	145		6
54		11.5	146	d	7
60		6.5	172		2.5
63		6	173		20
64		8	191		21.5
65		25	207	P	7
66		25	209	P + 1	2
67	i	3			

[a] Molecular weight: 207.5; molecular formula: $C_{10}H_6NO_2Cl$. [b] Temperature of ionization chamber: 120 °C. [c] Relative to base peak. [d] r = rearranged ion, i = isotope peak, and d = doubly charged peak.

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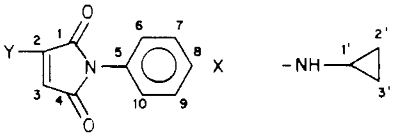
Table V. Mass Spectral Data of 2-Chloro-*N*-(*p*-methoxyphenyl)maleimide[a,b]

m/e	type of peak	% rel intens[c]	m/e	type of peak	% rel intens[c]	m/e	type of peak	% rel intens[c]	m/e	type of peak	% rel intens[c]
39		5	78		12	134		28	194		7
50		3	79	i	1.5	135		1.5	203		35
51		9	80		5	146		2	204	i	5
52		9	88		12	149	r	44	222		24
53		8	89		0.5	150		5	223		3
60		10	82		4	158		9	224		11
62		2	106		18	159		2	237	P	100
63		3	118		4	160		5	238		16
64		2.5	119		2	174		3	239	P + 2	33
77		2				188		11			

[a] Molecular weight: 237.5; molecular formula: $C_{11}H_8NO_3Cl$. [b] Temperature of ionization chamber: 70 °C. [c] Relative to base peak. [d] r = rearranged ion and i = isotope peak.

Table VI. Carbon-13 Chemical Shifts (ppm) of *N*-Arylmaleimides Substituted at the 2-Position



compd	carbon numbers in the compd										
	d1	d2	d3	d4	d5	d6, d10	d7, d9	d8	d1′	d2′	d3′
1a	167.21	127.95	127.95	167.21	131.34	127.04	129.08	128.29			
2a	167.04	139.64	127.85	164.05	131.33	126.89	128.41	128.1			
2b	167.21	139.53	127.75	164.25	137.65	126.67	129.33	129.33			
2c	167.37	139.56	127.70	165.23	123.89	128.35	114.15	158.91			
3a	170.50	151.23	89.81	165.82	132.39	126.41	128.91	128.75	25.78	6.05	6.05
3b	170.56	151.19	84.58	165.79	136.52	126.33	129.19	129.64	25.68	5.93	5.93
3c	170.84	151.24	84.54	166.00	124.92	128.02	114.05	158.32	25.70	5.82	5.82
4a	170.73	150.12	84.59	165.94	136.51	126.31	129.21	129.66	46.13	132.87	116.97
4b	170.58	150.09	83.58	165.77	132.23	126.37	128.64	128.95	46.05	132.81	116.97
4c	171.00	150.16	83.55	166.14	124.96	127.95	114.04	158.32	46.17	132.88	116.97

content, since the method employed for the preparation could produce some of the isoimides (*8–11*). Therefore, confirmation from C-13 NMR and mass spectrometry was desirable. With the exception of a paper by Relles and Schluenz (*12*) we could not locate other analytical data about substituted maleimides. It seems that C-13 NMR and mass spectrometry are good techniques to distinguish between imides and isoimides (*12*).

Experimental Section

Synthesis of N-Arylmaleimides Substituted at 2-Positions. Table I contains the structures and yields of all the maleimides that were prepared in this study. Compounds **1a** through **2c** were prepared according to literature (*13*). The rest of the substituted maleimides were synthesized following a procedure by Augustin and Kohler (*14*, *15*).

Mass Spectrometry. Four of the prepared compounds of Table I were of special interest to us, namely, *N*-phenyl-2-(cyclopropylamino)maleimide (**3a**), *N*-(*p*-methoxyphenyl)-2-(cyclopropylamino)maleimide (**3c**), *N*-phenyl-2-(allylamino)maleimide (**4a**), and *N*-(*p*-methoxyphenyl)-2-(allylamino)maleimide (**4c**). The mass spectra were recorded by Analytische Laboratorien, Elbach, West Germany.

Carbon-13 NMR Spectra. The C-13 spectra of all samples were recorded in 5-mm NMR sample tubes as 15% solution in Me_2SO-d_6. All compounds were referenced to internal Me_4Si. A Varian FT-80A spectrometer operating at 20 MHz was used, and the spectra were recorded at ambient probe temperature. Proton coupled and decoupled C-13 NMR spectra were run at a spectral width of 4 kHz, flip angle 45°, acquisition time 1 s, and delay time 3 s.

Results

Mass Spectrometry. Tables II–V contain results of mass spectral analysis of compounds **3a**, **3c**, **2a**, and **2c**, respectively. The data do not show metastable ions since the laboratory which performed the mass spectra (see Experimental Section) provided us only with a graphical presentation of the data and not the original spectra from which metastable ions could be determined. Interpretation and mechanistic discussion of the fragmentation pattern of the above compounds will be published elsewere.

Carbon-13 NMR. Proton coupled C-13 spectra yield one band coupling and were used in the assignment of the C-13 signals of the studied compounds. In compounds **4b**, C-1′(t) with $J_{C\text{-}1'\text{-}H}$ = 140.9 Hz, C-2′(d) with $J_{C\text{-}2'\text{-}H}$ = 180.0 Hz, C-3′(t) with $J_{C\text{-}3'\text{-}H}$ = 156.5 Hz; C-3(d) with $J_{C\text{-}3\text{-}H}$ = 156.5 Hz, and C-6(d) with $J_{C\text{-}6\text{-}H}$ = 162.6 Hz. Those values are close to those of similar compounds studied by others (*16*, *17*). The assignment of the proton decoupled C-13 spectra of the studied compounds was achieved by using the proton coupled spectra together with the available information on similar compounds (*18*, *19*).

Registry No. **1a**, 941-69-5; **2a**, 42595-16-4; **2b**, 53281-67-7; **2c**, 53281-68-8; **3a**, 89543-29-3; **3b**, 89543-30-6; **3c**, 89543-31-7; **4a**, 89543-32-8; **4b**, 89543-33-9; **4c**, 89543-34-0.

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A Synthetic Approach toward the Synthesis of Indolizines via 1,3-Dipolar Cycloaddition Reactions of Cycloimmonium Ylide

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Dehydrohalogenation of *N*-(2-aroylmethyl)-2-picolinium and -4-picolinium bromide, prepared by the quanternization of corresponding bromide salt with triethylamine, afforded a highly reactive cycloimmonium ylide. Its 1,3-dipolar cycloaddition reactions with various dipolarophiles have been investigated. These reactions ultimately result in the formation of novel heterocyclic compounds. The structural assignment of the products were made on the basis of elemental analyses and spectroscopic data.

Introduction

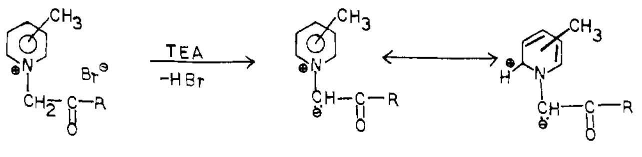
The chemistry of cycloimmonium ylide has engaged the attention of chemists because of their importance as useful intermediates in the synthesis of novel heterocyclics. Despite the wide applicability of cycloimmonium ylide (*1-11*) in synthetic studies, no information is available concerning the 1,3-dipolar cycloaddition reactions of methyl-substituted pyridinium ylide.

In the course of our investigations on the preparative utility of cycloimmonium ylide, we wish to report the syntheses and physical and spectral properties of indolizines having biological activities.

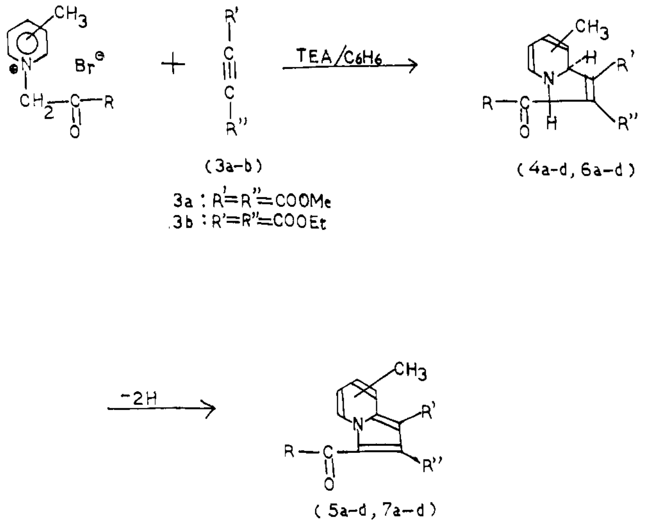
Results and Discussion

Treatment of ω-bromo ketones with picolines in anhydrous benzene at reflux temperature lead to the quarternization of picolines giving *N*-(2-aroylmethyl)picolinium bromides (Scheme I), in excellent yield. The bromide salts when treated with triethylamine in dry benzene immediately generated a dark red coloration due to the formation of corresponding ylide, which on subsequent reaction with various dipolarophiles (acetylenic esters) gave five-membered heterocyclic derivatives (**5a-d**, **7a-d**).

Scheme I



Scheme II



The reaction of picolinium ylides with the acetylenic triple bond of acetylenic ester such as dimethyl acetylenedicarboxylate and diethyl acetylenedicarboxylate appears to proceed by the nucleophilic attack of the carbanion similar to the first step of Michael type of addition. The stabilization of this zwitterion presumably takes place by internal nucleophilic attack of the carbanion on the α-position of the picoline ring

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