Mass Spectra of 5-Styryl and 5-Acylpyrazoles

Hassan El Khadem,

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

Rodger L. Foltz,

Organic Chemistry Section, Battelle Columbus Laboratories,
Columbus, Ohio 43201

and

Derek Horton

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

Received February 1, 1974

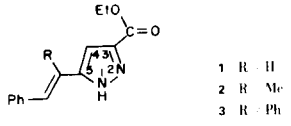
High-resolution, electron-impact, mass-spectrometric measurements have been made on three types of pyrazoles. Type I comprised ethyl 5-styrylpyrazole-3-carboxylates having in the α-position of the styryl group either a hydrogen atom, a methyl, or a phenyl group. Type II were 1,3,5-trisubstituted pyrazoles having phenyl (or *p*-substituted phenyl) groups in position 1, amide or carboxylate groups in position 3, and styryl (or α-substituted styryl) groups in position 5. Type III differed from type II in possessing a readily cleaved acyl or aroyl group instead of the styryl group. The compounds containing styryl groups gave significant ions corresponding to the formation of polycyclic heteroaromatic rings, in addition to various other fragments derived from such rings. Intensities and accurate mass-measurements are given for all ions having intensities exceeding 5% of the base peak.

The mass spectra of substituted pyrazoles have been extensively studied and the mode of fragmentation of this heterocycle is now well understood (1-5). Reported in the present paper is a high-resolution mass spectrometric investigation of the significant ions produced by electron bombardment of polysubstituted pyrazoles, especially those having styryl groups attached to the α-position to one of the ring nitrogen atoms. Such styryl pyrazoles should be capable of forming stable condensed-ring heteroarmatic fragments analogous to the phenanthrene formed during electron bombardment of such styryl arenes as stilbene (6). To confirm this and to investigate the effect of an *N*-phenyl group on the formation of such fragments, we investigated the mass spectra of 5-styrylpyrazole-3-carboxylates and -3-carboxamides having either a hydrogen atom or an aryl group attached to *N*-1 or the pyrazole ring. Further, to differentiate between the aryl substituent attached to *N*-1 and the phenyl ring of the styryl group, the former was labeled with a *p*-substituent such as a methyl group or a halogen atom. Also studied for comparison were the spectra of trisubstituted pyrazoles having 5-acyl or 5-aroyl groups instead of the 5-styryl group, since they would be incapable of forming condensed rings like the previous compounds.

The exact assignments made possible by correlating the high resolution mass spectra of twenty-four trisubstituted pyrazoles constitute valuable reference material for subsequent work on this important class of heterocycles.

Further, they demonstrate in an unambiguous manner the formation of polycyclic heteroatomic ring ions from the molecular ions of 5-styryl pyrazoles and not from the 5-aryl or 5-aroyl derivatives.

Three types of pyrazoles were investigated (see Table I). The first type (compounds **1-3**) included ethyl 5-styrylpyrazole-3-carboxylates having in the α-position of the styryl group either a hydrogen atom (**1**), a methyl group (**2**), or a phenyl group (**3**). (See also Figure 1.)



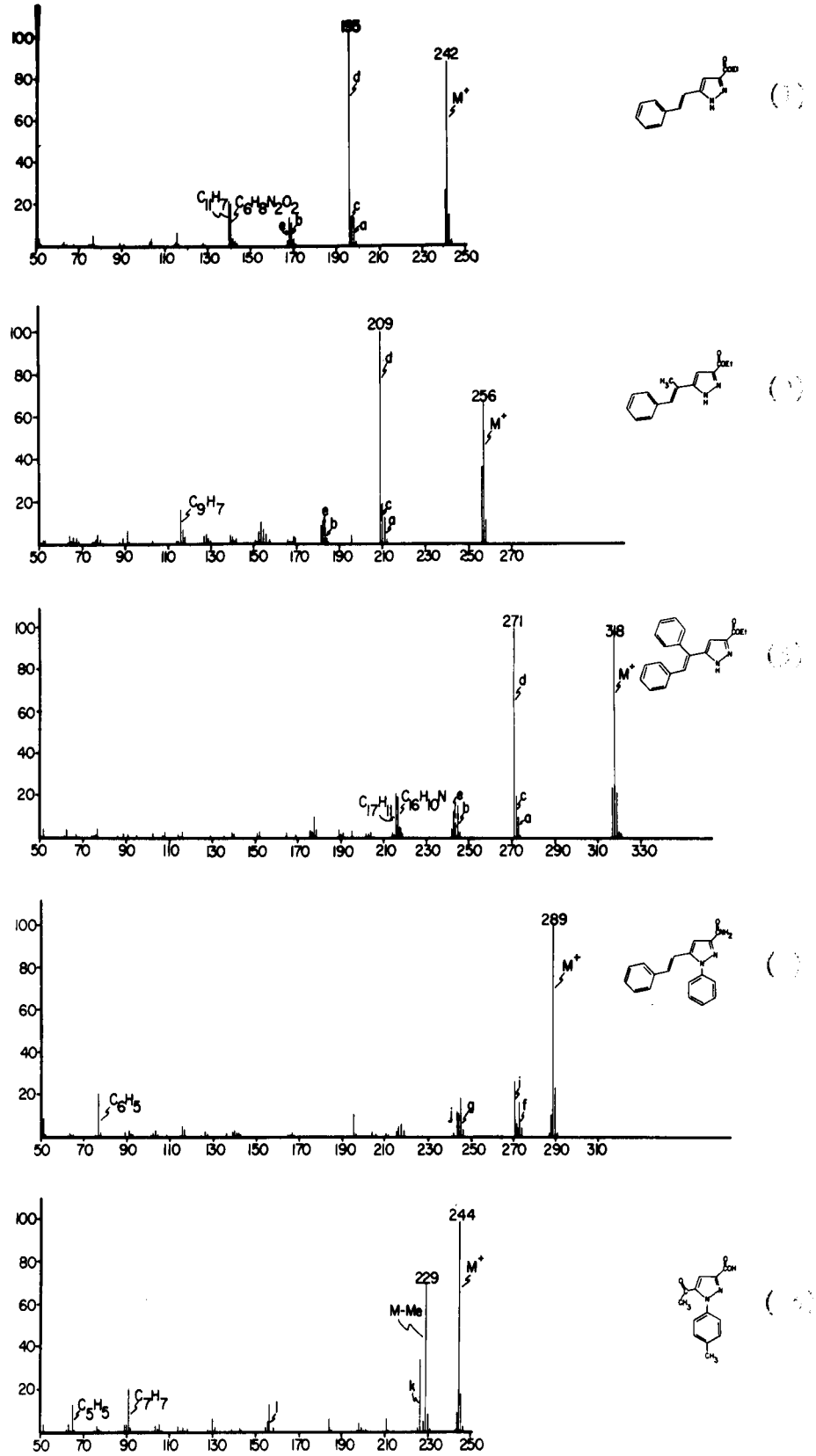


Figure 1. Mass Spectra of Compounds **1**, **2**, **3**, **4**, and **13**.

TABLE (1)

Mass-Spectral Data for Pyrazole Derivatives (*a*)

Mass Measured	Mass Calcd.	Intens.	Formula	Assignment (*b*)
Ethyl 5-Styrylpyrazole-3-carboxylate (1)				
243.1113	243.1089	15	$C_{13}{}^{13}CH_{14}N_2O_2$	
242.1069	242.1055	86	$C_{14}H_{14}N_2O_2$	M^+
241.0973	241.0977	26	$C_{14}H_{13}N_2O_2$	M^+-H
197.0721	197.0715	14	$C_{12}H_9N_2O$	*a*
196.0614	196.0637	15	$C_{12}H_8N_2O$	*c*
195.0568	195.0558	100	$C_{12}H_7N_2O$	*d*
169.0751	169.0766	12	$C_{11}H_9N_2$	*b*
168.0685	168.0687	14	$C_{11}H_8N_2$	*e*
140.0578	140.0568	20	$C_6H_8N_2O_2$	
139.0539	139.0548	21	$C_{11}H_7$	
115.0552	115.0548	7	C_9H_7	
77.0413	77.0391	5	C_6H_5	
Ethyl 5-(α-Methylstyryl)pyrazole-3-carboxylate (2)				
257.1246	257.1245	12	$C_{14}{}^{13}CH_{16}N_2O_2$	
256.1209	256.1212	66	$C_{15}H_{16}N_2O_2$	M^+
255.1091	255.1133	37	$C_{15}H_{15}N_2O_2$	M^+-H
211.0855	211.0871	13	$C_{13}H_{11}N_2O$	*a*
210.0752	210.0793	19	$C_{13}H_{10}N_2O$	*c*
209.0719	209.0715	100	$C_{13}H_9N_2O$	*d*
183.0914	183.0922	10	$C_{12}H_{11}N_2$	*b*
182.0838	182.0844	12	$C_{12}H_{10}N_2$	*e*
181.0741	181.0766	9	$C_{12}H_9N_2$	*e*-H
154.0672	154.0657	7	$C_{11}H_8N$	
153.0693	153.0704	11	$C_{12}H_9$	
152.0613	152.0626	5	$C_{12}H_8$	
116.0603	116.0626	6	C_9H_8	
115.0553	115.0548	17	C_9H_7	
91.0542	91.0548	7	C_7H_7	
Ethyl 5-(α-Phenylstyryl)pyrazole-3-carboxylate (3)				
319.1412	319.1402	23	$C_{19}{}^{13}CH_{18}N_2O_2$	
318.1374	318.1368	97	$C_{20}H_{18}N_2O_2$	M^+
317.1233	317.1290	24	$C_{20}H_{17}N_2O_2$	M^+-H
5-Styryl-1-*p*-tolylpyrazole-3-carboxamide (5)				
304.1383	304.1405	26	$C_{18}{}^{13}CH_{17}N_3O$	
303.1368	303.1372	100	$C_{19}H_{17}N_3O$	M^+
288.1181	288.1137	17	$C_{18}H_{14}N_3O$	M^+-Me
287.1214	287.1184	15	$C_{19}H_{15}N_2O$	*f*
285.1056	285.1028	22	$C_{19}H_{13}N_2O$	H
271.0870	271.0871	27	$C_{18}H_{11}N_2O$	*i*
259.1252	259.1235	16	$C_{18}H_{15}N_2$	*g*
258.1152	258.1157	9	$C_{18}H_{14}N_2$	*g*-H
257.1062	257.1079	9	$C_{18}H_{13}N_2$	
243.0948	243.0922	7	$C_{17}H_{11}N_2$	*j*
209.0711	209.0715	13	$C_{13}H_9N_2O$	
155.0546	115.0548	7	C_9H_7	
91.0558	91.0548	14	C_7H_7	
77.0397	77.0391	5	C_6H_5	
65.0394	65.0391	8	C_5H_5	
Ethyl 5-(α-Methylstyryl)-1-phenylpyrazole-3-carboxylate (6)				
333.1554	333.1558	27	$C_{20}{}^{13}CH_{20}N_2O_2$	
332.1530	332.1525	100	$C_{21}H_{20}N_2O_2$	M^+
331.1436	331.1446	12	$C_{21}H_{19}N_2O_2$	M^+-H
287.1239	287.1184	22	$C_{19}H_{15}N_2O$	*f*
285.1078	285.1028	10	$C_{19}H_{13}N_2O$	*i*
272.0928	272.0950	13	$C_{18}H_{12}N_2O$	*f*-Me
271.0894	271.0871	60	$C_{18}H_{11}N_2O$	
260.1282	260.1313	6	$C_{18}H_{16}N_2$	
259.1234	259.1235	20	$C_{18}H_{15}N_2$	*g*
209.0713	209.0715	23	$C_{13}H_9N_2O$	
115.0543	115.0548	8	C_9H_7	
77.0407	77.0391	14	C_6H_5	
51.0205	51.0235	6	C_4H_3	
Ethyl 1-*p*-Chlorophenyl-5-(α-methylstyryl)pyrazole-3-carboxylate (7)				
368.1118	368.1105	30	$C_{21}H_{19}N_2O_2{}^{37}Cl$	
367.1173	367.1169	32	$C_{20}{}^{13}CH_{19}N_2O_2Cl$	
366.1123	366.1135	10	$C_{21}H_{19}N_2O_2Cl$	M^+

(a) Peaks having intensities >5% of the base peak are listed. (b) Letters correspond to fragments discussed in the text.

TABLE (1)
(Continued)

Mass Measured	Mass Calcd.	Intens.	Formula	Assignment (*b*)
273.1006	273.1028	11	$C_{18}H_{13}N_2O$	*a*
272.0912	272.0950	20	$C_{18}H_{12}N_2O$	*c*
271.0875	271.0871	100	$C_{18}H_{11}N_2O$	*d*
245.1079	245.1079	16	$C_{17}H_{13}N_2$	*b*
244.0985	244.1000	7	$C_{17}H_{12}N_2$	*e*
243.0915	243.0922	13	$C_{17}H_{11}N_2$	*e*-H
242.0837	242.0844	5	$C_{17}H_{10}N_2$	
218.0943	218.0970	5	$C_{16}H_{12}N$	
217.0859	217.0891	9	$C_{16}H_{11}N$	
216.0811	216.0813	19	$C_{16}H_{10}N$	
215.0844	215.0861	21	$C_{17}H_{11}$	
178.0771	178.0782	11	$C_{14}H_{10}$	
51.0297	51.0235	5	C_4H_3	
1-Phenyl-5-Styrylpyrazole-3-carboxamide (4)				
290.1256	290.1249	23	$C_{17}{}^{13}CH_{15}N_3O$	
289.1231	289.1215	100	$C_{18}H_{15}N_3O$	M^+
288.1139	288.1137	12	$C_{18}H_{14}N_3O$	M^+-H
273.1051	273.1028	17	$C_{18}H_{13}N_2O$	*f*
272.0938	272.0950	7	$C_{18}H_{12}N_2O$	
271.0900	271.0871	27	$C_{18}H_{11}N_2O$	*i*
245.1081	245.1079	18	$C_{17}H_{13}N_2$	*g*
244.1001	244.1000	12	$C_{17}H_{12}N_2$	*g*-H
243.0919	243.0922	13	$C_{17}H_{11}N_2$	*j*
218.0954	218.0970	6	$C_{16}H_{12}N$	
217.0845	217.0891	5	$C_{16}H_{11}N$	
195.0571	195.0558	12	$C_{12}H_7N_2O$	
115.0539	115.0548	6	C_9H_7	
77.0424	77.0391	20	C_6H_5	
51.0240	51.0235	8	C_4H_3	

Mass Measured	Mass Calcd.	Intens.	Formula	Assignment
331.1447	331.1446	20	$C_{21}H_{19}N_2O_2$	M^+-Cl
323.0742	323.0765	12	$C_{19}H_{14}N_2O^{37}Cl$	
322.0784	322.0760	8	$C_{20}H_{15}O_2Cl$	
321.0748	321.0795	35	$C_{19}H_{14}N_2OCl$	
319.0622	319.0638	8	$C_{19}H_{12}N_2OCl$	*f*
307.0425	307.0452	9	$C_{18}H_{10}N_2O^{37}Cl$	H
306.0471	306.0560	6	$C_{18}H_1N_2OCl$	
305.0444	305.0482	29	$C_{18}H_{10}N_2OCl$	
295.0792	295.0816	8	$C_{18}H_{14}N_2{}^{37}Cl$	
294.0841	294.0923	6	$C_{18}H_{15}N_2Cl$	
293.0789	293.0845	23	$C_{18}H_{14}N_2Cl$	*g*
286.1033	286.1106	20	$C_{19}H_{14}N_2O$	
285.1009	285.1028	91	$C_{19}H_{13}N_2O$	*i*
259.1201	259.1235	5	$C_{18}H_{15}N_2$	
258.1131	258.1157	7	$C_{18}H_{14}N_2$	*g*-Cl
257.1044	257.1079	8	$C_{18}H_{13}N_2$	*j*
243.0324	243.0325	9	$C_{13}H_8N_2OCl$	
242.0838	242.0844	5	$C_{17}H_{10}N_2$	
168.0783	168.0791	6	$C_6H_{15}NO_2Cl$	
129.0692	129.0704	6	$C_{10}H_9$	
115.0547	115.0548	25	C_9H_7	
91.0544	91.0548	12	C_7H_7	
75.0231	75.0235	12	C_6H_3	

(*a*) Peaks having intensities >5% of the base peak are listed.
(*b*) Letters correspond to fragments discussed in the text.

Mass Measured	Mass Calcd.	Intens.	Formula	Assignment
Ethyl 1-*p*-Bromophenyl-5-(α-methylstyryl)				
412.0607	412.0609	58	$C_{21}H_{19}N_2O_2{}^{81}Br$	
411.0640	411.0663	16	$C_{20}{}^{13}CH_{19}N_2O_2Br$	

Mass Measured	Mass Calcd.	Intens.	Formula	Assignment
Ethyl 1-*p*-Bromophenyl-5-(α-phenylstyryl)pyrazole-3-carboxylate (11)				
474.0736	474.0766	89	$C_{26}H_{21}N_2O_2{}^{81}Br$	
473.0799	473.0820	24	$C_{25}{}^{13}CH_{21}N_2O_2Br$	

TABLE (1)
(Continued)

Mass Measured	Mass Calcd.	Intens.	Formula	Assignment
410.0614	410.0630	57	$C_{21}H_{19}N_2O_2Br$	M^+
367.0210	367.0270	16	$C_{19}H_{14}N_2O^{81}Br$	
365.0219	365.0289	20	$C_{19}H_{14}N_2OBr$	*f*
339.0295	339.0321	8	$C_{18}H_{14}N_2{}^{81}Br$	
337.0304	337.0340	10	$C_{18}H_{14}N_2Br$	*g*
331.1434	331.1446	13	$C_{21}H_{19}N_2O_2$	M-Br
316.1187	316.1212	15	$C_{20}H_{16}N_2O_2$	M-(Br+Me)
286.1024	286.1106	21	$C_{19}H_{14}N_2O$	*f*-Br
285.0996	285.1028	100	$C_{19}H_{13}N_2O$	*i*
259.1216	259.1235	7	$C_{18}H_{15}N_2$	
258.1141	258.1157	8	$C_{18}H_{14}N_2$	*g*-Br
257.1067	257.1079	10	$C_{18}H_{13}N_2$	*j*
244.0987	244.1000	11	$C_{17}H_{12}N_2$	
243.0892	243.0922	6	$C_{17}H_{11}N_2$	
242.0831	242.0844	7	$C_{17}H_{10}N_2$	*j*-Me
230.0933	230.0970	6	$C_{17}H_{12}N$	
128.0583	128.0586	6	$C_5H_8N_2O_2$	
115.0536	115.0548	22	C_9H_7	
91.0538	91.0548	10	C_7H_7	
77.0377	77.0391	6	C_6H_5	
76.0296	76.0313	10	C_6H_4	
75.0222	75.0235	7	C_6H_3	
51.0239	51.0235	6	C_4H_3	

Ethyl 5-(α-Phenylstyryl)-1-*p*-tolylpyrazole-3-carboxylate (9)

409.1877	409.1871	34	$C_{26}{}^{13}CH_{24}N_2O_2$	
408.1825	408.1838	100	$C_{27}H_{24}N_2O_2$	M^+
393.1522	393.1603	11	$C_{26}H_{21}N_2O_2$	M^+-Me
363.1566	363.1497	10	$C_{25}H_{19}N_2O$	*f*
361.1419	361.1341	5	$C_{25}H_{17}N_2O$	H
347.1268	347.1184	13	$C_{24}H_{15}N_2O$	*i*
335.1626	335.1548	10	$C_{24}H_{19}N_2$	*g*
331.1506	331.1446	6	$C_{21}H_{19}N_2O_2$	
286.1097	286.1106	7	$C_{19}H_{14}N_2O$	*f*-Ph
285.1057	285.1028	13	$C_{19}H_{13}N_2O$	
178.0767	178.0782	6	$C_{14}H_{10}$	
91.0557	91.0548	6	C_7H_7	

Mass Measured	Mass Calcd.	Intens.	Formula	Assignment
472.0756	472.0786	86	$C_{26}H_{21}N_2O_2Br$	M
429.0379	429.0426	13	$C_{24}H_{16}N_2O^{81}Br$	
427.0390	427.0446	14	$C_{24}H_{16}N_2OBr$	*f*
401.0442	401.0477	11	$C_{23}H_{16}N_2{}^{81}Br$	
399.0450	399.0497	12	$C_{23}H_{16}N_2Br$	*g*
398.0385	398.0418	6	$C_{23}H_{15}N_2Br$	*j*Br
393.1581	393.1603	11	$C_{26}H_{21}N_2O_2$	M-Br
348.1205	348.1263	26	$C_{24}H_{16}N_2O$	
347.1178	347.1184	100	$C_{24}H_{15}N_2O$	*i*
321.1379	321.1392	7	$C_{23}H_{17}N_2$	
320.1311	320.1313	10	$C_{23}H_{16}N_2$	*j*H
319.1239	319.1235	11	$C_{23}H_{15}N_2$	*j*
293.1162	293.1204	6	$C_{22}H_{15}N$	
292.1104	292.1126	11	$C_{22}H_{14}N$	
242.0821	242.0844	6	$C_{17}H_{10}N_2$	*j*-Ph
217.0888	217.0891	6	$C_{16}H_{11}N$	
216.0825	216.0813	8	$C_{16}H_{10}N$	
180.0920	180.0939	12	$C_{14}H_{12}$	
179.0838	179.0861	14	$C_{14}H_{11}$	
178.0762	178.0782	25	$C_{14}H_{10}$	
77.0380	77.0391	12	C_6H_5	
76.0305	76.0313	10	C_6H_4	
75.0222	75.0235	7	C_6H_3	
51.0240	51.0235	9	C_4H_3	

Ethyl 1-*p*-Iodophenyl-5-(α-phenylstyryl)pyrazole-3-carboxylate (12)

521.0664	521.0681	31	$C_{25}{}^{13}CH_{21}N_2O_2I$	
520.0632	520.0648	100	$C_{26}H_{21}N_2O_2I$	M
475.0253	475.0307	12	$C_{24}H_{16}N_2OI$	*f*
447.0442	447.0358	7	$C_{23}H_{16}N_2I$	*g*
393.1619	393.1603	6	$C_{26}H_{21}N_2O_2$	M-I
348.1209	348.1263	24	$C_{24}H_{16}N_2O$	*f*-I
347.1153	347.1184	85	$C_{24}H_{15}N_2O$	*i*
321.1364	321.1392	7	$C_{23}H_{17}N_2$	
320.1303	320.1313	9	$C_{23}H_{16}N_2$	*g*-I
319.1200	318.1235	12	$C_{23}H_{15}N_2$	*j*
293.1180	293.1204	5	$C_{22}H_{15}N$	
292.1119	292.1126	12	$C_{22}H_{14}N$	

TABLE (1)
(Continued)

Mass Measured	Mass Calcd.	Intens.	Formula	Assignment
Ethyl 1-*p*-Chlorophenyl-5-(α-phenylstyryl)pyrazole-3-carboxylate (10)				
430.1265	430.1262	38	$C_{26}H_{21}N_2O_2{}^{37}Cl$	
429.1308	429.1325	37	$C_{25}{}^{13}CH_{21}N_2O_2Cl$	
428.1280	428.1291	100	$C_{26}H_{21}N_2O_2Cl$	M
393.1574	393.1603	9	$C_{26}H_{21}N_2O_2$	M-Cl
385.0872	385.0921	5	$C_{24}H_{16}N_2O{}^{37}Cl$	
383.0882	383.0951	16	$C_{24}H_{16}N_2OCl$	*f*
355.0976	355.1002	12	$C_{23}H_{16}N_2Cl$	*g*
348.1193	348.1262	11	$C_{24}H_{16}N_2O$	*f*-Cl
347.1163	347.1184	47	$C_{24}H_{15}N_2O$	*i*
319.1183	319.1235	5	$C_{23}H_{15}N_2$	*j*
305.0450	305.0482	8	$C_{18}H_{10}N_2OCl$	
178.0769	178.0782	11	$C_{14}H_{10}$	
111.0000	111.0001	5	C_6H_4Cl	
75.0229	75.0235	5	C_6H_3	
5-Acetyl-1-*p*-tolylpyrazole-3-carboxylic Acid (13)				
245.0911	245.0881	18	$C_{12}{}^{13}CH_{12}N_2O_3$	
244.0871	244.0848	100	$C_{13}H_{12}N_2O_3$	M^+
243.0780	243.0770	9	$C_{13}H_{11}N_2O_3$	M-H
230.0671	230.0691	10	$C_{12}H_{10}N_2O_3$	
229.0636	229.0613	69	$C_{12}H_9N_2O_3$	M-Me
227.0831	227.0820	33	$C_{13}H_{11}N_2O_2$	*k*
211.0513	211.0508	6	$C_{12}H_7N_2O_2$	*k*-CH_4
183.0572	183.0558	7	$C_{11}H_7N_2O$	*k*-CO-CH_4
157.0759	157.0766	14	$C_{10}H_9N_2$	*l*
156.0676	156.0687	5	$C_{10}H_8N_2$	*l*-H
130.0657	130.0657	6	C_9H_8N	
91.0547	91.0548	20	C_7H_7	
65.0411	65.0391	13	C_5H_5	
5-Acetyl-1-*p*-tolylpyrazole-3-carboxamide (14)				
244.1059	244.1041	20	$C_{12}{}^{13}CH_{13}N_3O_2$	
243.1016	243.1008	100	$C_{13}H_{13}N_3O_2$	M^+
242.0914	242.0929	5	$C_{13}H_{12}N_3O_2$	M-H
229.0779	229.0851	7	$C_{12}H_{11}N_3O_2$	
228.0782	228.0773	52	$C_{12}H_{10}N_3O_2$	M-Me
227.0824	227.0820	29	$C_{13}H_{11}N_2O_2$	*k*H
243.0905	243.0922	7	$C_{17}H_{11}N_2$	
242.0832	242.0844	6	$C_{17}H_{10}N_2$	*j*-Ph
179.0828	179.0861	5	$C_{14}H_{11}$	
178.0766	178.0782	16	$C_{14}H_{10}$	
77.0387	77.0391	12	C_6H_5	
76.0311	76.0313	19	C_6H_4	
63.0259	63.0235	6	C_5H_3	
51.0246	51.0235	8	C_4H_3	
50.0150	50.0156	8	C_4H_2	
Ethyl 5-Acetyl-1-*p*-bromophenylpyrazole-3-carboxylate (16)				
339.0107	339.0123	24	$C_{13}{}^{13}CH_{13}N_2O_3{}^{81}Br$	
338.0067	338.0089	97	$C_{14}H_{13}N_2O_3{}^{81}Br$	
337.0129	337.0143	24	$C_{13}{}^{13}CH_{13}N_2O_3Br$	
336.0092	336.0109	100	$C_{14}H_{13}N_2O_3Br$	M^+
214.0363	214.0378	12	$C_{11}H_6N_2O_3$	
197.0039	197.035	7	$C_{11}H_5N_2O_2$	*k*-Br-Me
170.0463	170.0480	8	$C_{10}H_6N_2O$	
142.0514	142.0531	14	$C_9H_6N_2$	*l*-Br
115.0412	115.0422	7	C_8H_5N	
76.0302	76.0313	26	C_6H_4	
75.0232	75.0235	25	C_6H_3	
63.0312	63.0235	6	C_5H_3	
50.0156	50.0156	18	C_4H_2	
43.0163	43.0184	88	C_2H_3O	
29.0391	29.0391	45	C_2H_5	
27.0235	27.0235	17	C_2H_3	
5-Benzoyl-1-*p*-tolylpyrazole-3-carboxamide (17)				
306.1201	306.1198	24	$C_{17}{}^{13}CH_{15}N_3O_2$	
305.1158	305.1164	100	$C_{18}H_{15}N_3O_2$	M^+
304.1074	304.1086	12	$C_{18}H_{14}N_3O_2$	M-H
290.0985	290.0929	19	$C_{17}H_{12}N_3O_2$	M-Me
289.1029	289.0977	23	$C_{18}H_{13}N_2O_2$	*k*
288.1152	288.1137	10	$C_{18}H_{14}N_3O$	M-OH
259.0885	259.0871	13	$C_{17}H_{11}N_2O$	
228.0778	228.0773	8	$C_{12}H_{10}N_3O_2$	M-Ph
157.0763	157.0766	31	$C_{10}H_9N_2$	*l*
144.0453	144.0449	7	C_9H_6NO	

TABLE (1)
(Continued)

Mass Measured	Mass Calcd.	Intens.	Formula	Assignment
226.0970	226.0980	6	$C_{13}H_{12}N_3O$	M-OH
158.0790	158.0844	6	$C_{10}H_{10}N_2$	
157.0769	157.0766	38	$C_{10}H_9N_2$	*l*H
130.0658	130.0657	7	C_9H_8N	
91.0538	91.0548	23	C_7H_7	
Ethyl 5-Acetyl-1-*p*-chlorophenylpyrazole-3-carboxylate (15)				
295.0658	295.0619	23	$C_{13}{}^{13}CH_{13}N_2O_3{}^{37}Cl$	
294.0632	294.0585	43	$C_{14}H_{13}N_2O_3{}^{37}Cl$	
293.0693	293.0648	64	$C_{13}{}^{13}CH_{13}N_2O_3Cl$	
292.0625	292.0615	100	$C_{14}H_{13}N_2O_3Cl$	M^+
277.0403	277.0380	13	$C_{13}H_{10}N_2O_3Cl$	M-Me
249.0174	249.0245	29	$C_{12}H_8N_2O_2{}^{37}Cl$	
248.0256	248.0352	10	$C_{12}H_9N_2O_2Cl$	*k*H
247.0223	247.0274	73	$C_{12}H_8N_2O_2Cl$	*k*
179.0195	179.0198	8	$C_9H_6N_2{}^{37}Cl$	
177.0228	177.0219	27	$C_9H_6N_2Cl$	*l*
111.0011	111.0001	8	C_6H_4Cl	
75.0235	75.0235	6	C_6H_3	
43.0171	43.0184	22	C_2H_3O	
29.0392	29.0391	11	C_2H_5	
Ethyl 5-Benzoyl-1-*p*-bromophenylpyrazole-3-carboxylate (19)				
401.0249	401.0279	23	$C_{18}{}^{13}CH_{15}N_2O_3{}^{81}Br$	
400.0208	400.0246	83	$C_{19}H_{15}N_2O_3{}^{81}Br$	
399.0240	399.0299	24	$C_{18}{}^{13}CH_{15}N_2O_3Br$	
398.0217	398.0266	84	$C_{19}H_{15}N_2O_3Br$	M
106.0359	106.0418	7	C_7H_6O	
105.0329	105.0340	100	C_7H_5O	Bz
78.0447	78.0469	6	C_6H_6	
77.0399	77.0391	85	C_6H_5	Ph
76.0317	76.0313	21	C_6H_4	
75.0238	75.0235	15	C_6H_3	
51.0237	51.0235	23	C_4H_3	
50.0158	50.0156	13	C_4H_2	

Mass Measured	Mass Calcd.	Intens.	Formula	Assignment
105.0344	105.0340	63	C_7H_5O	
91.0549	91.0548	23	C_7H_7	
77.0394	77.0391	36	C_6H_5	
65.0410	65.0391	11	C_5H_5	
51.0236	51.0235	9	C_4H_3	
5-Benzoyl-1-*p*-chlorophenylpyrazole-3-carboxylic acid (18)				
329.0444	329.0462	6	$C_{16}{}^{13}CH_{11}N_2O_3{}^{37}Cl$	
328.0409	328.0428	33	$C_{17}H_{11}N_2O_3{}^{37}Cl$	
327.0449	327.0492	25	$C_{16}{}^{13}CH_{11}N_2O_3Cl$	
326.0433	326.0458	91	$C_{17}H_{11}N_2O_3Cl$	M^+
325.3333	325.0380	10	$C_{17}H_{10}N_2O_3Cl$	M-H
311.0429	311.0401	10	$C_{17}H_{10}N_2O_2{}^{37}Cl$	
310.0501	310.0509	7	$C_{17}H_{11}N_2O_2Cl$	
309.0463	309.0431	31	$C_{17}H_{10}N_2O_2Cl$	*k*
281.0413	281.0373	10	$C_{16}H_8N_2O{}^{37}Cl$	
279.0368	279.0325	16	$C_{16}H_8N_2O_2Cl$	
249.0038	249.0067	15	$C_{11}H_6N_2O_3Cl$	
177.0209	177.0219	5	$C_9H_6N_2Cl$	*l*
154.0185	154.0167	5	$C_9H_2N_2O$	
106.0374	106.0418	8	C_7H_6O	
105.0336	105.0340	100	C_7H_5O	
78.0451	78.0469	8	C_6H_6	
77.0398	77.0391	70	C_6H_5	
75.0242	75.0235	14	C_6H_3	
Ethyl 5-Carbamoyl 1-*p*-chlorophenylpyrazole-3-carboxylate (22)				
296.0621	296.0616	8	$C_{12}{}^{13}CH_{12}N_3O_3{}^{37}Cl$	
295.0587	295.0538	37	$C_{13}H_{12}N_3O_3{}^{37}Cl$	
294.0653	294.0600	25	$C_{12}{}^{13}CH_{12}N_3O_3Cl$	
293.0597	293.0567	100	$C_{13}H_{12}N_3O_3Cl$	M
277.0406	277.0380	6	$C_{13}H_{10}N_2O_3Cl$	M-NH_2
265.0200	265.0254	6	$C_{11}H_8N_3O_3Cl$	M-C_2H_4
250.0203	250.0197	26	$C_{11}H_7N_3O_2{}^{37}Cl$	
249.0198	249.0193	15	$C_{11}H_8N_3O_2Cl$	*k*H

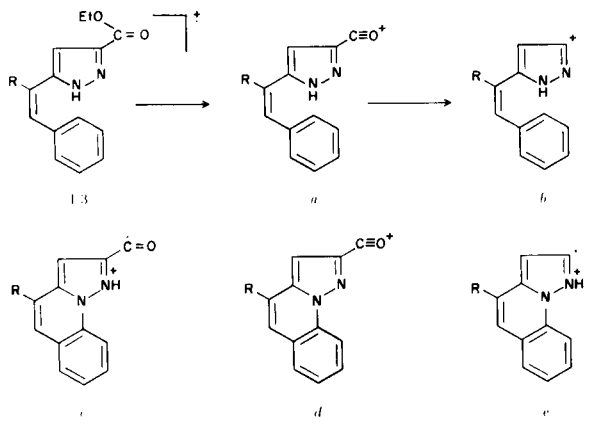
TABLE (1)
(Continued)

Mass Measured	Mass Calcd.	Intens.	Formula	Assignment
29.0390	29.0391	35	C_2H_5	
27.0230	27.0235	11	C_2H_3	
18.0106	18.0106	81	H_2O	
Ethyl 5-Benzoyl-1-*p*-iodophenylpyrazole-3-carboxylate (20)				
447.0130	447.0161	27	$C_{18}{}^{13}CH_{15}N_2O_3I$	
446.0084	446.0127	100	$C_{19}H_{15}N_2O_3I$	M
142.0508	142.0531	5	$C_9H_6N_2$	*l*-I
105.0332	105.0340	50	C_7H_5O	Bz
77.0389	77.0391	44	C_6H_5	Ph
76.0305	76.0313	21	C_6H_4	
51.0246	51.0235	11	C_4H_3	
50.0162	50.0156	10	C_4H_2	
29.0386	29.0391	16	C_2H_5	
1-*p*-Chlorophenylpyrazole-3,5-dicarboxamide (21)				
267.0442	267.0418	6	$C_{10}{}^{13}CH_9N_4O_2{}^{37}Cl$	
266.0406	266.0384	33	$C_{11}H_9N_4O_2{}^{37}Cl$	
265.0464	265.0448	22	$C_{10}{}^{13}CH_9N_4O_2Cl$	
264.0433	264.0414	100	$C_{11}H_9N_4O_2Cl$	M
250.0222	250.0197	15	$C_{11}H_7N_3O_2{}^{37}Cl$	
249.0314	249.0305	10	$C_{11}H_8N_3O_2Cl$	M-NH
248.0264	248.0227	43	$C_{11}H_7N_3O_2Cl$	*k*
247.0393	247.0387	7	$C_{11}H_8N_4OCl$	
179.0186	179.0189	10	$C_9H_6N_2{}^{37}Cl$	
178.0209	178.0181	6	$C_9H_5N_2{}^{37}Cl$	
177.0211	177.0219	32	$C_9H_6N_2Cl$	*l*
176.0087	176.0141	8	$C_9H_5N_2Cl$	*l*-H
150.0123	150.0110	5	C_8H_5NCl	
129.0163	129.0159	6	$C_6H_6N{}^{37}Cl$	
127.0194	127.0189	17	C_6H_6NCl	
110.9994	111.0001	20	C_6H_4Cl	PhCl
75.0241	75.0235	13	C_6H_3	
248.0232	248.0227	76	$C_{11}H_7N_3O_2Cl$	*k*
221.0337	221.0356	10	$C_{10}H_8N_3OCl$	
179.0191	179.0189	20	$C_9H_6N_2{}^{37}Cl$	
177.0211	177.0219	65	$C_9H_6N_2Cl$	*l*
176.0120	176.0141	14	$C_9H_5N_2Cl$	*l*-H
150.0115	150.0110	6	C_8H_5NCl	
142.0531	142.0531	6	$C_9H_6N_2$	*l*-Cl
127.0180	127.0189	15	C_6H_6NCl	
112.9962	112.9981	7	$C_6H_4{}^{37}Cl$	
110.9994	111.0001	21	C_6H_4Cl	PhCl
75.0243	75.0235	15	C_6H_3	
43.9993	44.0011	11	N_2O	
29.0392	29.0391	23	C_2H_5	
18.0106	18.0106	19	H_2O	
1-*p*-Bromophenylpyrazole-3,5-dicarboxamide (23)				
310.9952	310.9922	20	$C_{10}{}^{13}CH_9N_4O_2{}^{81}Br$	
309.9917	309.9889	96	$C_{11}H_9N_4O_2{}^{81}Br$	
308.9949	308.9942	25	$C_{10}{}^{13}CH_9N_4O_2Br$	
307.9940	307.9909	100	$C_{11}H_9N_4O_2Br$	M
293.9772	293.9701	32	$C_{11}H_7N_3O_2{}^{81}Br$	
292.9851	292.9800	9	$C_{11}H_8N_3O_2Br$	M-NH
291.9771	291.9721	36	$C_{11}H_7N_3O_2Br$	*k*
290.9908	290.9881	6	$C_{11}H_8N_4OBr$	M-OH
222.9685	222.9694	22	$C_9H_6N_2{}^{81}Br$	
221.9644	221.9616	7	$C_9H_5N_2{}^{81}Br$	
220.9706	220.9714	21	$C_9H_6N_2Br$	*l*
219.9637	219.9636	5	$C_9H_5N_2Br$	*l*-H
213.0530	213.0538	5	$C_{11}H_7N_3O_2$	*k*-Br
172.9651	172.9663	13	$C_6H_6N{}^{81}Br$	
170.9685	170.9683	14	C_6H_6NBr	
156.0471	156.9476	13	$C_6H_4{}^{81}Br$	
154.9494	154.9496	13	C_6H_4Br	PhBr
142. 0519	142.0531	8	$C_9H_6N_2$	
76.0327	76.0313	14	C_6H_4	
75.0254	75.0235	13	C_6H_3	
50.0164	50.0156	6	C_4H_2	

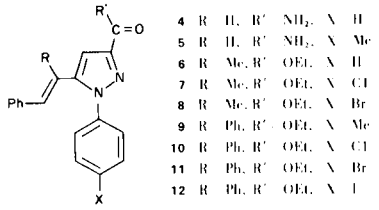
TABLE (1)
(Continued)

Measured	Mass Calcd.	Intens.	Formula	Assignment
1-*p*-Iodophenylpyrazole-3,5-dicarboxamide (24)				
356.9858	356.9804	22	$C_{10}{}^{13}CH_9N_4O_2I$	
355.9815	355.9770	100	$C_{11}H_9N_4O_2I$	M
339.9647	339.9583	24	$C_{11}H_7N_3O_2I$	*k*
338.9795	338.9743	6	$C_{11}H_8N_2OI$	M-OH
268.9596	268.9576	15	$C_9H_6N_2I$	*l*
218.9525	218.9545	10	C_6H_6NI	
202.9331	202.9358	7	C_6H_4I	PhI
142.0526	142.0531	7	$C_9H_6N_2$	
76.0324	76.0313	12	C_6H_4	
57.0693	57.0704	5	C_4H_9	

Compounds **1-3** showed significant molecular-ion peaks that are the second-largest peaks in the spectra. They are followed by small (< 5%) M-Et peaks, more-important M-OEt peaks (*a*), and M-CO_2Et peaks (*b*). Alternatively, compound **1** lost the styryl side-chain and yielded a fragment $C_6H_8N_2O_2$; this fragment is insignificant in the α-substituted styryl derivatives **2** and **3**. The most important ion (base peak) in the spectra of compounds **1-3** is a fragment that corresponds to the loss of ·OEt and two hydrogen atoms. In the case of ethyl 5-styrylpyrazole-3-carboxylate (**1**), this fragment has the formula $C_{12}H_7N_2O$, and the loss of the two hydrogen atoms might be attributed to the conversion of the styryl side-chain into a phenylacetylenic one. However, since this intense peak is present in the spectra of the α-substituted styryl derivatives, and compound **2** yielded an ion $C_{13}H_9N_2O$ and compound **3** the corresponding ion $C_{18}H_{11}N_2O$, it is logical to suggest a fused, tricyclic, nitrogen-heterocyclic structure such as *d* to these fragments. The protonated forms of *d* have intensities of 15% for compound **1**, 19% and 20% for **2** and **3** respectively. These fragments, formulated *c*, are thought to arise by a McLafferty type of rearrangement involving *N*-2 of the pyrazole ring and the CH_2 group of the ethyl ester. Subsequent loss of CO from fragments *c* and *d* yields smaller fragments *e* and *e*-H. Hydrocarbons resulting from the loss of the two nitrogen atoms and the CO_2Et group from the parent compounds are quite significant. Thus, a hydrocarbon $C_{11}H_7$ produced in the spectrum of compound **1** had an amplitude 21% of the base peak, and the corresponding $C_{12}H_9$ and $C_{17}H_{11}$ ions in compound **2** and **3** had amplitudes of 11 and 21%, respectively.



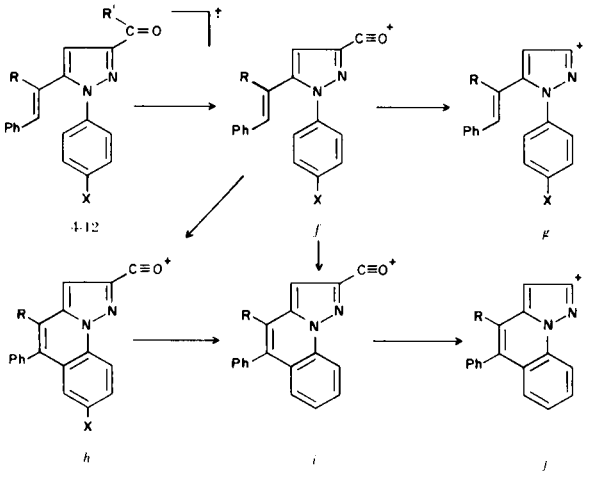
The next group of compounds investigated (see Table I and Fig. 1) comprised trisubstituted pyrazoles (4-12) having phenyl or *p*-substituted phenyl groups in position 1, amide or carboxylate ester groups in position 3, and a styryl or α-substituted styryl group in position 5.



4	R	H,	R′	NH_2,	X H
5	R	H,	R′	NH_2,	X Me
6	R	Me,	R′	OEt,	X H
7	R	Me,	R′	OEt,	X Cl
8	R	Me,	R′	OEt,	X Br
9	R	Ph,	R′	OEt,	X Me
10	R	Ph,	R′	OEt,	X Cl
11	R	Ph,	R′	OEt,	X Br
12	R	Ph,	R′	OEt,	X I

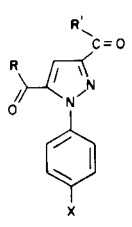
Whether the compound is an amide (R′ = NH_2) or an ester (R′ = OEt), the molecular-ion peak is generally either the most significant or the second most significant peak in the spectra. The molecular ion readily loses the R′ group (·NH_2 in amides and ·OEt in esters) to give a fragment *f*, and a ·COR′ group to give a fragment *g*. As in the previous group of compounds (**1-3**), peak *f* is followed by a peak corresponding to the loss of two hydrogen atoms, attributable to the formation of tricycles of the type *i*, which are simple phenyl-substituted forms of *d*.

Interestingly, if *p*-substituted phenyl groups are attached to *N*-1 of the pyrazole ring, these peaks (*i*) usually correspond to the loss of ·OEt, the *p*-substituent, and a hydrogen atom. Accordingly, fragment *i* has the formula $C_{18}H_{11}N_2O$ in the case of the 1-aryl-5-styrylpyrazoles (**4** and **5**), $C_{19}H_{13}N_2O$ in the α-methylstyryl compounds (**6-8**), and



$C_{24}H_{15}N_2O$ in the α-phenylstyryl derivatives (**9-12**), irrespective of the substituent in the *p*-position of the 1-phenyl group. Fragment *i* is either the base peak or the second largest peak in the spectrum, and even in compounds **4** and **5** it probably does not arise significantly from the formation of the 5-substituted arylacetylene because the α-substituted styryl derivatives (**6-12**) as readily generate the same intense peak. It is possible that, during cyclization, the hydrogen atom attached to position 2 of the phenyl ring is displaced to the *para* position vacated by loss of the *p*-substituent. Further fragmentation of this major tricyclic intermediate (*i*) leads to a variety of minor fragments through loss of the α-substituent of the styryl group, the loss of a CO group (*j*), and other pathways.

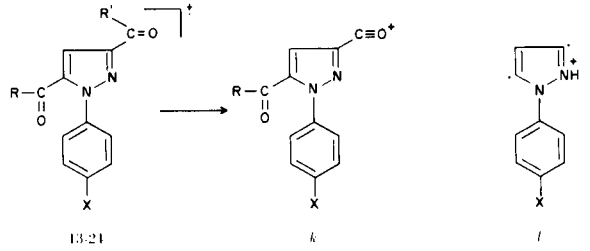
It is evident from the foregoing discussion that the 3-styrylpyrazoles of series I and II (compounds **1-12**) tend to form ions assigned as the tricyclic ring-systems of the types *d* and *i*. Furthermore, the same compounds (**1-12**) give rise to hydrocarbon fragments arising from the styryl side-chain and one carbon atom (probably C-5) of the pyrazole ring. Thus styryl pyrazoles (compounds **1, 4, 5**) give rise to an indenyl ion C_9H_7. The α-methylstyryl derivatives (compounds **2, 6-8**) give rise to the corresponding $C_{10}H_9$ ion, and α-phenylstyryl pyrazoles (compounds **3, 9-12**) to the $C_{15}H_{11}$ fragment. They may also give peaks corresponding to the formation of disubstituted acetylenes (7); methylphenylacetylene (C_9H_8) in the case of the α-methylstyryl derivatives and diphenylacetylene ($C_{14}H_{10}$) from the α-phenylstyryl derivatives.



13	R	Me,	R'	OH,	X	Me
14	R	Me,	R'	NH_2,	X	Me
15	R	Me,	R'	OEt,	X	Cl
16	R	Me,	R'	OEt,	X	Br
17	R	Ph,	R'	NH_2,	X	Me
18	R	Ph,	R'	OH,	X	Cl
19	R	Ph,	R'	OEt,	X	Br
20	R	Ph,	R'	OEt,	X	I
21	R	NH_2,	R'	NH_2,	X	Cl
22	R	NH_2,	R'	OEt,	X	Cl
23	R	NH_2,	R'	NH_2,	X	Br
24	R	NH_2,	R'	NH_2,	X	I

The third group of pyrazoles investigated (compounds **13-24**) were 1,3,5-trisubstituted pyrazoles having aryl groups in position 1, ester, amide, or carboxylic acid groups in position 3, and acyl or aroyl groups in position 5.

These compounds do not undergo the type of cyclization described for styryl derivatives of the two previous groups, since the 5-acyl or aroyl radicals are readily split off due to their greater stability. The molecular-ion peak in these compounds is usually the base peak and is followed by the second-largest peak in the spectrum (*k*), corresponding to the loss of the substituent R' (NH_2, OEt, or OH) to give a pyrazole derivative having a $C\equiv O^+$ group in position 3. Removal of the *p*-substituent from the phenyl ring, especially Br and I, is quite facile. In this group of compounds, the most firmly bound substituent to the pyrazole ring is the phenyl group attached to position 1 of the pyrazole. Accordingly, an important peak in these compounds is a protonated 1-phenylpyrazole lacking the substituents in positions 3 and 5 (*l*). This is much stronger than the nonprotonated fragment M-(COR' + RCO).



The synthesis of the compounds needed for this study was achieved by condensation of 2,4-dioxo-6-phenylhex-5-enoates and various hydrazines by a method described earlier (7,8).

EXPERIMENTAL

The electron-impact mass spectra were obtained by using an AEI MS-902 mass spectrometer operated at an effective resolving power of approximately 15,000. The samples were introduced into the ion source by means of a direct-insertion probe while simultaneously bleeding in the reference compound, perfluorotributylamine. Repetitive scans were made at a scan rate of 40 seconds per mass decade while the sample probe was heated from room temperature to about 200°. The signal output from the mass spectrometer was digitized and recorded on magnetic tape for subsequent computer processing.

The MS-902 is equipped with an SRIC CIS-2 ion source which can be operated in either the electron-impact or chemical-ionization mode. At the time these mass spectra were obtained, a significantly higher sensitivity could be achieved by operating the ion source at 500-eV ionizing voltage. Since 500-eV mass spectra show essentially the same relative ion intensities as the more commonly used 70-eV, the higher ionization voltage was used.

The ion source temperature was maintained at 150°.

The pyrazoles used in these experiments were analytically pure, and were obtained by the methods cited in the literature (8,9).

REFERENCES

(1) H. Budzikiewicz, C, Djerassi, A. H. Jackson, G. W. Kenner, D. J. Newman, and J. M. Wilson, *J. Chem. Soc.*, 1949 (1964).

(2) R. A. Khmelnitskii, A. P. Krasnoshchek, and V. I. Vysotskii, *Izv. Timiryazev. Selskokhox. Akad.*, **6**, 178 (1969).

(3) B. K. Simons, R. K. M. R. Kallury and J. H. Bowie, *Org. Mass Spectrom.*, **2**, 739 (1969).

(4) J. van Thuijl, K. J. Klebe, and J. J. van Houte, *Org. Mass Spectrom.*, **3**, 1549 (1970); **5**, 1101 (1971); **7**, 1165 (1973).

(5) J. van Thuijl, K. J. Klebe, and J. J. van Houte, *J. Heterocyclic Chem.*, **8**, 311 (1971).

(6) R. A. W. Johnstone and S. D. Ward, *J. Chem. Soc. (C)*, 1805 (1968).

(7) Q. N. Porter and J. Baldas, Mass Spectrometry of Heterocyclic Compounds, Wiley-Interscience, New York, 1971, p. 326-351.

(8) H. El Khadem, Z. El-Shafei, L. Rateb, and H. Mokhtar, *J. Heterocyclic Chem.*, **10**, 15 (1973).

(9) H. El Khadem, L. Rateb, and H. Mokhtar, *J. Chem. Soc. (C)*, 1845 (1968).