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While the reaction of the cyclopropane ester **1** with hydrazine hydrate or phenylhydrazine led to the formation of diazabicycloheptenones, its reaction with several *para*-substituted phenylhydrazines gave the corresponding hydrazones. With hydroxylamine, either oxime or 1,2-oxazinone is formed.

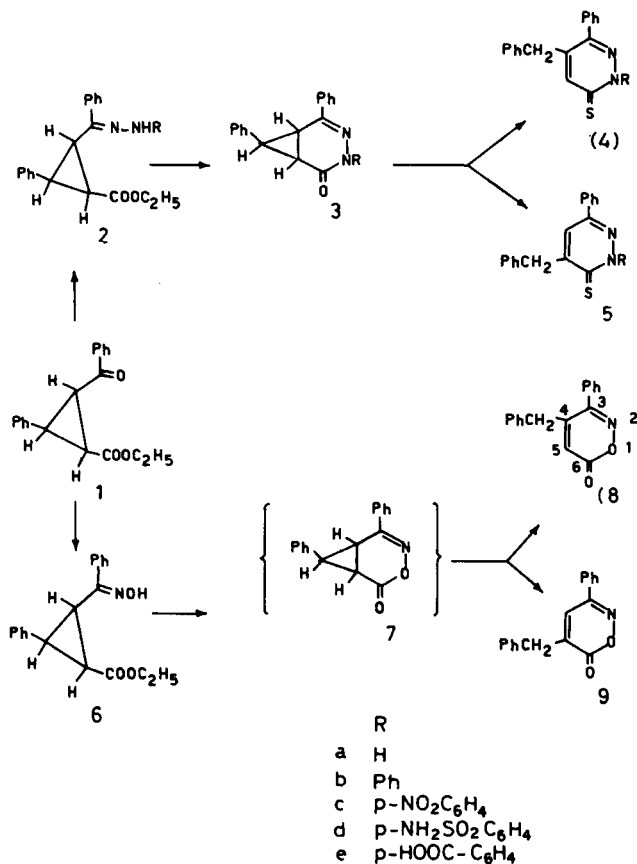
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Most of the methods adopted for the synthesis of pyridazinones usually involve cyclization of γ -keto acids or esters with hydrazine derivatives (1). In an attempt to prepare pyridazinone derivatives with fused cyclopropane ring which are of special interest in their relation to the diazanorcaradiene ring system (2), ethyl 2-benzoyl-3-phenylcyclopropanecarboxylate (**1**) was prepared and its reactions with several hydrazine derivatives were investigated. The cyclopropane ester **1** was obtained as a major product in the thermal decomposition of ethyl 4-phenyl-3-benzoyl-2-pyrazoline-5-carboxylate. 4,6-Diphenyl-2*H*-pyran-2-one was also isolated from the pyrolysis products (3).

In an earlier publication (3) we reported that 5,7-diphenyl-3,4-diazabicyclo[4.1.0]hept-4-en-2-one (**3a**) was formed from the reaction of the γ -keto ester **1** with hydrazine hydrate. No intermediate hydrazone (or hydrazide) was isolated in the above reaction. However, in the present study, in the reaction of **1** with phenylhydrazine, the hydrazone **2b** could be isolated and was further converted into 3,5,7-triphenyl-3,4-diazabicyclo[4.1.0]hept-4-en-2-one (**3b**) on boiling its ethanolic solution. The infrared spectra of the pyridazinones **3a,b** showed a cyclic carbonyl absorption in the region 1676-1700 cm^{-1} . Their ^1H nmr spectra exhibited the three cyclopropane ring protons as a complex multiplet at δ 2.2-3.2, while the NH proton appeared as an exchangeable broad signal at δ 11.03.

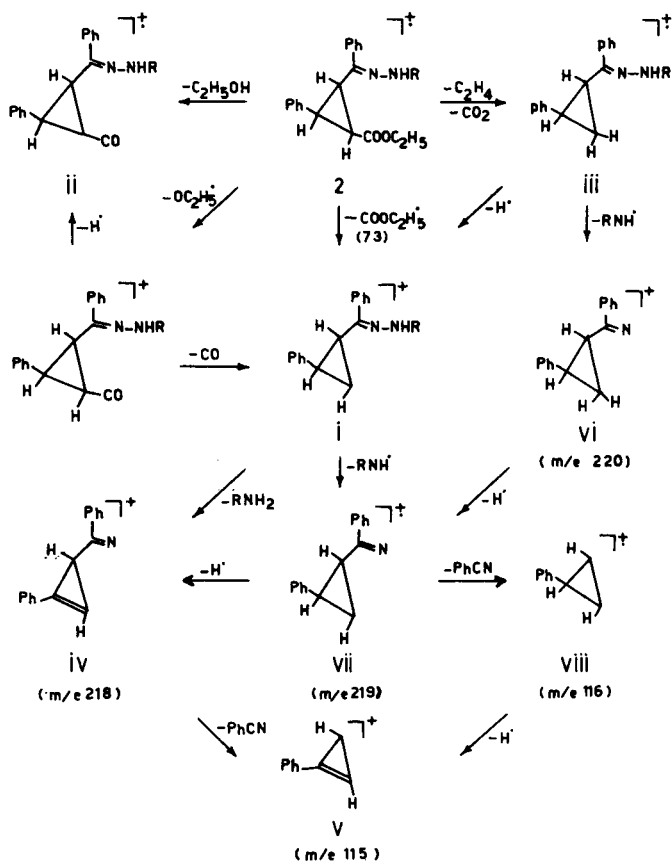
The mass spectrum of the pyridazinone **3a** showed the molecular ion peak as the base peak while for **3b** the base peak was the M-CO species and the molecular ion was only 3% abundant. The fragmentation pattern of these diazabicycloheptenones suggest that under electron impact, the pyridazinone ring is more easily cleaved than the cyclopropane. Such conclusion is evident from the existence of intense peaks at *m/e* 116 and 115 corresponding to the species *viii* and *v*, respectively (Scheme II).

The reaction of pyridazinones with phosphorus pentasulfide usually leads to the formation of the corresponding thio-analogues (4). However, the reaction of the diazabicycloheptenones **3a,b** with phosphorus pentasulfide



Scheme I

afforded the 3-thiopyridazinones **4** or **5a,b**. The infrared spectra of these thiopyridazinones exhibited a thiocarbonyl absorption at 1140 cm^{-1} . Their ^1H nmr spectra (deuteriochloroform or DMSO-*d*₆) showed a sharp singlet at δ 3.3-4.3 (2H) for the methylene protons. No separate signal could be assigned for the H-4 (structure **4**) or H-5 (structure **5**) proton which is most probably overlapped by the complex aromatic protons multiplet. The formation of these thiopyridazinones from the corresponding diazabicycloheptenones **3** is assumed to take place *via* isomerization involving fission of the cyclopropane ring.



Contrary to hydrazine or phenylhydrazine, the reaction of **1** with *p*-nitrophenylhydrazine, *p*-sulfamylphenylhydrazine or phenylhydrazine-*p*-carboxylic acid led to the formation of the corresponding hydrazones **2c-e**, respectively, which could not be further cyclized. The open chain structure of these hydrazones was established by the presence of a strong ester carbonyl absorption in the region 1700-1710 cm^{-1} as well as an NH band in the range 3330-3350 cm^{-1} in their infrared spectra. Furthermore, the presence of an ethyl ester signals in their ^1H nmr spectra confirms this assignment.

The structure of these hydrazones was further confirmed from their mass spectral data. The probable structure of the common prominent peaks as well as their fragmentation pathways are shown in Scheme II. They gave a strong molecular ion peaks while the base peaks are the $\text{M}-\text{COOC}_2\text{H}_5$ ions *i* formed by a successive loss of OC_2H_5 radical and CO molecule. Elimination of ethyl alcohol molecule from the molecular ion gave the species *ii* while the loss of CO_2 and ethylene molecules gave the radical ion *iii*. The moderately intense peak at m/e 218 can be formulated as the cation *iv* assumed to be formed from the base peak *i* via fission of the N-N bond and subsequent loss of an aromatic amine molecule, which is usually observed in the mass spectra of phenylhydrazones (5) and aroylhydrazones (6). Subsequent elimination of benzonitrile molecule from *iv* leads to the intense peak at m/e 115 formulated as the cation *v*. The latter can be also formed from *iii* via elimination of an amine radical giving the intense peak at m/e 220 *vi* which loses proton giving the radical ion *vii*. Successive loss of benzonitrile and proton leads to the cation *v*.

1,2-Oxazinones are usually formed in the reaction of γ -keto acids or esters with hydroxylamine (7). In the present study, the reaction of the cyclopropane ester **1** with hydroxylamine in ethanol afforded the oxime **6** whose infrared spectrum exhibited an ester carbonyl at 1700 cm^{-1} as well as an OH absorption at 3450 cm^{-1} . However, when the above reaction was carried out in pyridine 3-phenyl-4- (or 5)benzyl-6*H*-1,2-oxazin-6-one (**8** or **9**) was separated which is assumed to be formed *via* the oxime **6**, elimination of ethanol leading to the bicyclic lactone **7** and subsequent fission of the cyclopropane ring. The infrared spectrum of this product exhibited a lactone carbonyl absorption at 1750 cm^{-1} . Its ^1H nmr spectrum showed a sharp singlet at δ 3.23 (2H) which can be assigned to the methylene protons and a multiplet at δ 7.3 for the aromatic and H-4 (or H-5) ring proton. It is worthy to mention that while elemental analysis and infrared spectrum do not exclude the isomeric bicyclic lactone structure **7** for this product,

Table I
Analytical Data

Compound	M.p. °C	Formula	Calcd. %				Found %			
			C	H	N	S	C	H	N	S
2b	150	$\text{C}_{25}\text{H}_{24}\text{N}_2\text{O}_2$	78.1	6.3	7.3		78.4	6.3	7.0	
2c	208	$\text{C}_{25}\text{H}_{23}\text{N}_3\text{O}_4$	69.9	5.4	9.8		69.7	5.4	9.5	
2d	265	$\text{C}_{25}\text{H}_{25}\text{N}_3\text{O}_4\text{S}$	64.8	5.4	9.1	6.9	64.6	5.7	8.8	7.1
2e	204	$\text{C}_{25}\text{H}_{24}\text{N}_3\text{O}_4$	72.9	5.7	6.5		72.7	5.7	6.3	
3b	162	$\text{C}_{23}\text{H}_{18}\text{N}_2\text{O}$	81.6	5.4	8.3		81.7	5.3	8.5	
4 or 5a	195	$\text{C}_{17}\text{H}_{14}\text{N}_2\text{S}$	73.4	5.1	10.1	11.5	73.6	5.4	10.1	11.4
4 or 5b	160	$\text{C}_{25}\text{H}_{18}\text{N}_2\text{S}$	77.9	5.1	7.9	9.1	78.1	5.5	8.3	9.1
6	176	$\text{C}_{17}\text{H}_{19}\text{NO}_3$	73.8	6.2	4.5		73.5	5.9	4.9	
8 or 9	182	$\text{C}_{17}\text{H}_{13}\text{NO}_2$	77.5	5.0	5.3		77.8	4.6	5.3	

Table II
Infrared and Electronic Spectral Data

Compound	C=O (ester)	Ir (cm ⁻¹)		Uv λ max, nm, (ϵ)		
		C=S	NH			
2b	1700		3400	223 (1808)	237* (1506)	328 (1808)
2c (a)	1710		3350	222 (2636)	287 (764)	395 (3095)
2d	1705		3300, 3400	239 (2629)	261 (2525)	305 (1349)
2e (b)	1700		3330	229 (2238)	272 (671)	342 (3837)
3a (c)	1676 (d)		3070, 3120	220 (23840)	268 (13110)	294 (14100)
3b	1700 (d)				246 (1457)	303 (985)
4 or 5a		1140	3250	230* (975)	267 (755)	315 (1706)
4 or 5b		1135		234 (1943)		345 (1686)
6 (e)	1700			225 (1310)		
8 or 9	1750 (f)			240* (988)		

*Shoulder. (a) This compound showed two bands at 1350 and 1520 cm⁻¹ for the nitro group. (b) The C=O of the carboxylic group appeared at 1670 cm⁻¹. (c) Data taken from reference (3). (d) This band is due to the pyridazinone carbonyl. (e) The oxime OH appeared as a broad absorption at 3450 cm⁻¹. (f) This band is due to the 1,2-oxazinone carbonyl.

Table III
¹H Nmr Spectral Data

Compound	Solvent	¹ H Nmr Chemical Shifts (δ /ppm)					
		CH ₃ (t)	CH ₂ (q) (ester)	CH ₂ (s)	Cyclopropane protons(m)	ArH (m)	Others (s)
1	Deuteriochloroform	1.13	4.10		2.5-3.5	7.1	
2b	Deuteriochloroform	1.00	3.89		2.3-3.1	7.4	
2c	Deuteriochloroform	1.00	3.80		2.3-3.0	7.6	
2e	DMSO-d ₆	0.93	3.83		2.2-2.9	7.5	9.94 (1H, COOH)
3a	DMSO-d ₆				2.2-3.2	7.3	11.03 (1H, NH)
3b	Deuteriochloroform				2.4-3.1	7.5	
4 or 5a	Deuteriochloroform			4.30		7.5	
4 or 5a	DMSO-d ₆			4.05		7.5	14.7 (1H, NH)
4 or 5b	DMSO-d ₆			3.33		7.6	
8 or 9	DMSO-d ₆			3.23		7.3	

t: Triplet (J = 7.0 Hz), q: quartet (J = 7.0 Hz), s: singlet and m: multiplet.

the absence of the three cyclopropane ring protons which usually resonate in the region δ 2.3-3.5 in its ¹H nmr spectrum confirms the 1,2-oxazinone structure (**8** or **9**).

The mass spectrum of the oxime **6** lacked the molecular ion peak, while the base peak was observed at *m/e* 247 corresponding to M-OH-OC₂H₅ species. However, the fragmentation pattern was quite similar to that observed for the hydrazones **2** (Scheme II).

EXPERIMENTAL

Microanalyses were performed by Microanalysis Unit, Cairo University, Cairo. Infrared spectra were measured with a Unicam SP200 spectrophotometer for potassium bromide pellets or in Nujol and electronic spectra were measured for methanolic solutions with a Unicam SP800 spectrophotometer. The ¹H nmr spectra were recorded on Varian T-60 and Jeol 100 spectrometers with TMS as an internal standard. Mass spectra were recorded on an LKB 9000 instrument.

Ethyl 3-Benzoyl-2-phenylcyclopropanecarboxylate (**1**) (Table III).

This compound, m.p. 103° (ethanol) was prepared by pyrolysis of ethyl 4-phenyl-3-benzoyl-2-pyrazoline-5-carboxylate (**3**); ms: *m/e* (relative abundance) M^+ 294 (5), 249 (11), 222 (29), 221 (100) ($M-COOC_2H_5$), 203 (8), 189 (16), 116 (7), 115 (31), 105 (67), 91 (5), 77 (31).

Cyclopropane Schiff Bases **2b-e** (Tables I, II, III).

A solution of ethyl 3-benzoyl-2-phenylcyclopropanecarboxylate (0.5 g., 0.0017 mole) in ethanol (20 ml.) was refluxed with the arylhydrazine (0.003 mole) for 5-8 hours. The Schiff bases were separated (55-65% yield) after concentration and crystallized from ethanol in needles; ms: *m/e* (relative abundance); **2b**: M^+ 384 (42), 339 (5), 338 (7), 312 (25), 311 (100), 292 (5), 220 (17), 219 (44), 218 (34), 208 (13), 206 (5), 181 (9), 180 (9), 116 (13), 115 (26), 105 (8), 104 (10), 103 (9), 92 (23), 91 (17), 77 (22); **2c**: M^+ 429 (53), 403 (16), 384 (13), 383 (16), 357 (26), 356 (100), 292 (8), 291 (8), 257 (8), 226 (11), 225 (11), 221 (11), 220 (42), 219 (95), 218 (26), 217 (11), 206 (11), 204 (11), 203 (11), 202 (11), 193 (11), 191 (11), 189 (8), 178 (11), 165 (16), 152 (8), 131 (11), 130 (8), 117 (16), 116 (37), 115 (74), 105 (16), 104 (21), 103 (26), 102 (11), 91 (26), 89 (16), 77 (37), 65 (16).

3,5,7-Triphenyl-3,4-diazabicyclo[4.1.0]hept-4-en-2-one (**3b**) (Tables I, I, III).

A solution of **1** (0.5 g., 0.0017 mole) in ethanol (20 ml.) was refluxed with phenylhydrazine (0.5 g., 0.004 mole) for 9 hours. The pyridazinone **3b** (65% yield) which separated after concentration crystallized from ethanol in needles. It was also prepared (60% yield) by refluxing the phenylhydrazone **2b** in ethanol for 5 hours; ms: *m/e* (relative abundance); **3a**: M^+ 262 (100), 261 (67), 247 (7), 246 (7), 245 (13), 234 (3), 233 (10), 218 (17), 217 (13), 205 (10), 204 (10), 203 (13), 202 (13), 130 (23), 129 (10), 128 (13), 127 (13), 116 (57), 115 (70), 105 (10), 104 (13), 103 (17), 102 (13), 101 (10), 91 (13), 89 (17), 77 (57); **3b**: M^+ 338 (3), 314 (5), 312 (26), 310 (100), 294 (5), 292 (5), 222 (8), 221 (36), 220 (59), 219 (35), 218 (8), 208 (14), 181 (11), 180 (11), 116 (18), 115 (45), 105 (12), 104 (15), 103 (15), 93 (12), 92 (35), 91 (26), 77 (42).

4-(or 5)-Benzyl-6-phenyl-3-thiopyridazines (**4** or **5a,b**) (Tables I, II, III).

A solution of the bicycloheptenones **3a,b** (0.5 g., 0.0019 mole) in dry benzene (20 ml.) was refluxed with phosphorus pentasulfide (1.5 g.,

0.0067 mole) for 7 hours. The benzene solution was then washed with 10% ammonium sulfide solution, water, dried (sodium sulfate) and evaporated. The residue afforded the thiopyridazine **4** or **5a,b** (65% yield) after treating with petroleum ether (b.p. 60-80°) which crystallized from benzene-ethanol in yellow needles.

Ethyl 3-Benzoyl-2-phenylcyclopropanecarboxylate Oxime (**5**) (Tables I, II).

A solution of **1** (0.5 g., 0.0017 mole) in ethanol (20 ml.) was refluxed with hydroxylamine hydrochloride (0.5 g., 0.015 mole) and sodium acetate (0.5 g., 0.005 mole) for 4 hours. The oxime (60% yield) which separated after dilution with water crystallized from ethanol in needles; ms: *m/e* (relative abundance): 264 (2), 263 (8), 248 (20), 247 (100), 246 (18), 236 (9), 235 (4), 228 (5), 220 (2), 219 (93), 218 (34), 217 (17), 205 (30), 204 (10), 203 (13), 202 (12), 191 (9), 165 (6), 144 (11), 131 (10), 129 (10), 116 (56), 115 (95), 105 (10), 104 (18), 103 (21), 102 (9), 101 (9), 91 (10), 89 (18), 77 (30).

3-Phenyl-4-(or 5)-benzyl-6H-oxazin-2-one (**8** or **9**) (Tables I, II, III).

A solution of **1** (1 g., 0.0034 mole) in pyridine (10 ml.) was refluxed with hydroxylamine hydrochloride (0.5 g., 0.0015 mole) for 8 hours. The oxazinone (**8** or **9**) (50% yield) separated on dilution with water and crystallized from methanol in needles.

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