

Reaction of Dichloroketene and Sulfene with *N,N*-Disubstituted α -Aminomethyleneketones. Synthesis of Pyrano[2,3-*e*]indazole and 1,2-Oxathiino[6,5-*e*]indazole Derivatives

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The polar 1,4-cycloaddition of dichloroketene to *N,N*-disubstituted (*E*)-5-aminomethylene-1,5,6,7-tetrahydro-(1-methyl)(1-phenyl)-4*H*-indazol-4-ones V, prepared from 1,5,6,7-tetrahydro-(1-methyl)(1-phenyl)-4*H*-indazol-4-ones *via* the 5-hydroxymethylene derivatives, gave in good yield *N,N*-disubstituted 4-amino-3,3-dichloro-4,5,6,7-tetrahydro-(7-methyl)(7-phenyl)pyrano[2,3-*e*]indazol-2(3*H*)-ones VI, which are derivatives of the new heterocyclic system pyrano[2,3-*e*]indazole. Dehydrochlorination of VI with DBN afforded *N,N*-disubstituted 4-amino-3-chloro-6,7-dihydro(7-methyl)(7-phenyl)pyrano[2,3-*e*]indazol-2(5*H*)-ones VII generally in satisfactory yield. Full aromatization with DDQ of VII was tried only in the case of dimethylamino derivatives, giving a moderate yield of 3-chloro-4-dimethylamino(7-methyl)(7-phenyl)pyrano[2,3-*e*]indazol-2(7*H*)-ones. Cycloaddition of sulfene to V occurred only in the case of aliphatic *N*-substitution to give in moderate yield 4-dialkylamino-4,5,6,7-tetrahydro-(7-methyl)(7-phenyl)-3*H*-1,2-oxathiino[6,5-*e*]indazole 2,2-dioxides, which are derivatives of the new heterocyclic system 1,2-oxathiino[6,5-*e*]indazole.

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We recently described a convenient synthesis of a number of substituted 1,5,6,7-tetrahydro-4*H*-indazol-4-ones [1]. In pursuing our work on new heterocyclic systems having 2*H*-pyran and 1,2-oxathiin rings incorporated in potential pharmacologically active molecules [2,3], we have chosen 1-methyl and 1-phenyl-1,5,6,7-tetrahydro-4*H*-indazol-4-one I and II as synthons for the building up of two new heterocyclic systems, namely pyrano[2,3-*e*]indazole and 1,2-oxathiino[6,5-*e*]indazole.

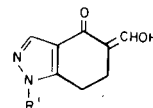
Reaction of indazolones I and II with ethyl formate and sodium gave in good yield the 5-hydroxymethylene derivatives III and IV, respectively (Table I). The starting enamines Va-h (Table II) were prepared in excellent yield from III, IV and secondary amines. They are probably *E* isomers, at least as can be seen from the upfield shifts of the CH₂-7 (0.6-0.9 ppm) and CH₂-6 (0.15-0.25 ppm) protons caused by the phenyl group(s) in compounds Vc,d,g,h in comparison with Va,b,e,f (Table III). By our method of cycloadding dichloroketene to *N,N*-disubstituted α -aminomethyleneketones [2], the reaction of Va-h with dichloroacetyl chloride and triethylamine (dichloroketene prepared *in situ*) occurred readily both in the case of aliphatic and aromatic *N*-substitution to give, generally in good yield, *N,N*-disubstituted 4-amino-3,3-dichloro-4,5,6,7-tetrahydro-(7-methyl)(7-phenyl)pyrano[2,3-*e*]indazol-2(3*H*)-ones VIa-h (Table IV), whose structure was confirmed by uv, ir and nmr spectral data (Table V). All these adducts were dehydrochlorinated with DBN according to [4] to afford *N,N*-disubstituted 4-amino-3-chloro-6,7-dihydro-(7-methyl)(7-phenyl)pyrano[2,3-*e*]indazol-2(5*H*)-ones VIIa-h generally in good yield (Tables VI and VII).

Compounds VIIa-h proved to be very resistant to a full

aromatization with DDQ in refluxing benzene [5,6]; therefore this reaction was tried only with VIIa,e to give, after a very long reflux time (about 12 days), 3-chloro-4-dimethylamino-(7-methyl)(7-phenyl)pyrano[2,3-*e*]indazol-2(7*H*)-ones

Table I

1,5,6,7-Tetrahydro-5-hydroxymethylene-(1-methyl)(1-phenyl)-4*H*-indazol-4-ones III and IV



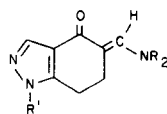
Formula Number	R'	Yield%	Mp °C [a]	Molecular Formula	Analyses %		
					Calcd./Found C	H	N
III	CH ₃	80	101	C ₉ H ₁₀ N ₂ O ₂	60.67 60.56	5.66 5.71	15.72 15.98
IV	C ₆ H ₅	73	105	C ₁₄ H ₁₂ N ₂ O ₂	69.99 70.07	5.03 4.97	11.66 11.91

UV, IR and NMR Spectral Data of Compounds III and IV

	UV, λ max nm (log ϵ)	IR, cm ⁻¹	NMR, δ
III	255 (3.91) 292 (4.05)	1723, 1642, 1590	2.74 and 2.82 (2 mc, CH ₂ -6 + CH ₂ -7), 3.81 and 3.94 (2 s, CH ₃ N), 7.38 (mc, =CH-O), 7.88 (s, CH-3), 8.00 (s, -CH=O), 11.90 (broad s, OH; disappears with deuterium oxide)
IV	228.5 (4.17) 257 (4.16) 294 (4.02)	1643, 1528	2.4-3.1 (m, CH ₂ -6 + CH ₂ -7), 7.54 (mc, C ₆ H ₅ + =CHOH), 8.13 (near s, CH-3)

[a] From anhydrous diethyl ether.

Table II

N,N-Disubstituted (*E*)-5-Aminomethylene-1,5,6,7-tetrahydro-(1-methyl)(1-phenyl)-4*H*-indazol-4-ones Va-h

Formula Number	R'	NR ₂	Yield %	Mp °C [a]	Molecular Formula	Analyses %		
						C	H	N
Va	CH ₃	N(CH ₃) ₂	78	164	C ₁₁ H ₁₃ N ₃ O	64.37	7.37	20.47
						64.34	7.28	20.50
Vb	CH ₃	Piperidino	74	130	C ₁₄ H ₁₉ N ₃ O	68.54	7.81	17.13
						68.50	7.80	17.15
Vc	CH ₃	N(CH ₃)C ₆ H ₅	74	183	C ₁₆ H ₁₇ N ₃ O	71.89	6.41	15.72
						71.90	6.38	15.70
Vd	CH ₃	N(C ₆ H ₅) ₂	79	194	C ₂₁ H ₁₉ N ₃ O	76.57	5.81	12.76
						76.55	5.79	12.80
Ve	C ₆ H ₅	N(CH ₃) ₂	81	172	C ₁₆ H ₁₇ N ₃ O	71.89	6.41	15.72
						72.18	6.63	15.51
Vf	C ₆ H ₅	Piperidino	83	151	C ₁₉ H ₂₁ N ₃ O	74.24	6.89	13.67
						74.49	6.82	13.50
Vg	C ₆ H ₅	N(CH ₃)C ₆ H ₅	90	167	C ₂₁ H ₁₉ N ₃ O	76.57	5.81	12.76
						76.55	5.80	12.76
Vh	C ₆ H ₅	N(C ₆ H ₅) ₂	88	236	C ₂₆ H ₂₁ N ₃ O	79.77	5.41	10.73
						79.86	5.41	10.66

[a] From ethyl acetate.

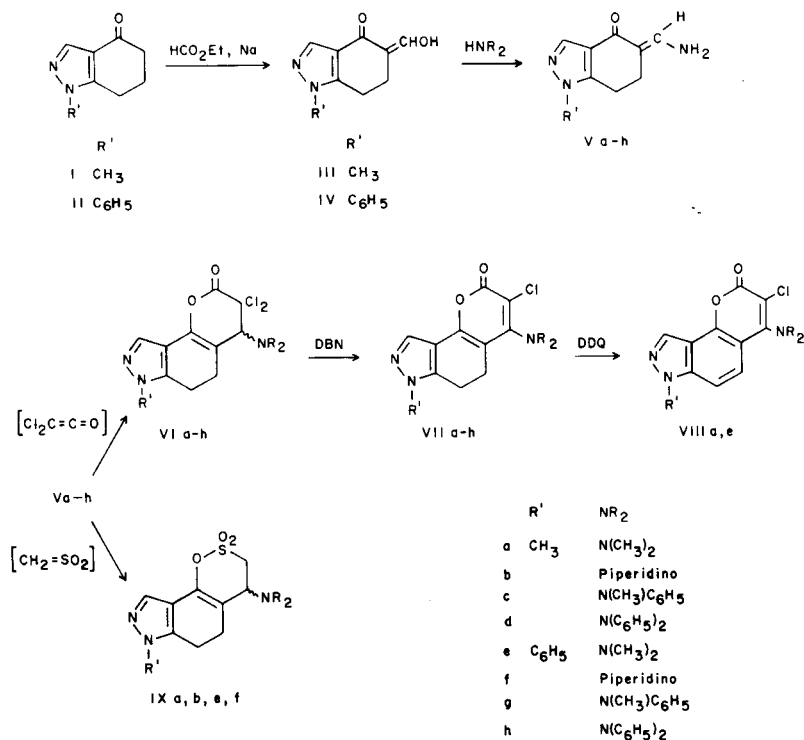


Table III

UV, IR and NMR Spectral Data of Compounds Va-h

Compound	UV, λ max nm (log ϵ)	IR, cm^{-1}		NMR, δ
		C=O	C=C	
Va	234 (3.96) 253 (3.97) 352 (4.38)	1642	1572	2.6-3.4 (m, CH_2 -6 + CH_2 -7), 3.12 [s, $(\text{CH}_3)_2\text{N}$], 3.81 (s, CH_3N -1), 7.53 (near s, =CHN), 7.90 (s, CH-3)
Vb	235 (3.94) 253 (3.95) 355 (4.39)	1637	1572	1.66 (mc, 3 CH_2 pip), 2.87 (mc, CH_2 -6 + CH_2 -7), 3.44 (mc, 2 CH_2N), 3.82 (s, CH_3N), 7.53 (near s, =CHN), 7.90 (s, CH-3)
Vc	237 sh (3.99) 255 (4.05) 364 (4.40)	1643	1568	2.15-2.90 (m, CH_2 -6 + CH_2 -7), 3.45 (s, CH_3NPh), 3.78 (s, CH_3N -1), 6.9-7.6 (m, $\text{C}_6\text{H}_5\text{N}$), 7.68 (near s, =CHN), 7.94 (s, CH-3)
Vd	243.5 (4.12) 277 (4.10) 372 (4.43)	1643	1566	2.13 (near t, J = 6.5, CH_2 - 7), 2.61 (near t, J = 6.5, CH_2 -6), 3.77 (s, CH_3N), 6.9- 7.6 (m, 2 $\text{C}_6\text{H}_5\text{N}$), 7.82 (near s, =CHN), 7.95 (s, CH-3)
Ve	228 (4.21) 258 (4.21) 355 (4.39)	1639	1569	2.97 (s, CH_2 -6 + CH_2 -7), 3.10 [s, $(\text{CH}_3)_2\text{N}$], 7.50 (mc, $\text{C}_6\text{H}_5\text{N}$ + =CHN), 8.12 (s, CH-3)
Vf	229 (4.19) 258 (4.19) 358 (4.43)	1638	1572	1.64 (mc, 3 CH_2 pip), 2.94 (s, CH_2 -6 + CH_2 -7), 3.40 (mc, 2 CH_2N), 7.51 (mc, $\text{C}_6\text{H}_5\text{N}$), 7.57 (near s, =CHN), 8.11 (near s, CH-3)
Vg	233 (4.24) 260 (4.18) 366 (4.41)	1645	1566	2.35 (mc, CH_2 -7), 2.81 (mc, CH_2 -6), 3.44 (s, CH_3N), 7.14 (mc, $\text{C}_6\text{H}_5\text{NMe}$), 7.46 (mc, $\text{C}_6\text{H}_5\text{N}$ -1), 7.70 (near s, =CHN), 8.13 (s, CH-3)
Vh	235 (4.32) 272 (4.26) 374.5 (4.43)	1650	1567	2.11 (near t, J = 6.6, CH_2 -7), 2.78 (near t, J = 6.6, CH_2 -6), 7.0-7.7 (m, 3 $\text{C}_6\text{H}_5\text{N}$), 7.90 (near s, =CHN), 8.16 (s, CH-3)

VIIIa,e (Table VIII) in good to moderate yield. The reaction of V with methanesulfonyl chloride and triethylamine (sulfene prepared *in situ*) occurred in moderate yield once more only in the case of aliphatic *N*-substitution to give 4-dialkylamino-4,5,6,7-tetrahydro-(7-methyl)(7-phenyl)-3*H*-1,2-oxathiino[6,5-*e*]indazole 2,2-dioxides IXa,b,e,f, whose structure was confirmed by uv, ir and nmr spectral data (Table IX).

EXPERIMENTAL

The uv spectra were measured in 95% ethanol with a Hitachi-Perkin-Elmer Model EPS-3T spectrophotometer. The ir spectra were taken in chloroform on a Perkin-Elmer Model 398 spectrophotometer; the nmr spectra were recorded in deuteriochloroform on a Perkin-Elmer Model R-600 instrument (60 MHz, TMS as internal standard, J in Hz). Melting points were determined with a Mettler FP1 apparatus.

1,5,6,7-Tetrahydro-5-hydroxymethylene-(1-methyl)(1-phenyl)-4*H*-indazol-4-ones III and IV.

A mixture of ketone I or II [1] (0.1 mole), ethyl formate (11.11 g, 0.15 mole) and sodium (2.53 g, 0.11 mole) in anhydrous toluene (650 ml) was kept at room temperature for 40 hours, starting the reaction by adding 0.5-1 ml of anhydrous ethanol. The mixture was treated with water (200 ml), the aqueous phase was extracted with ether and acidified with 6*M* hydrogen chloride (pH 3-4). The precipitate was extracted thoroughly with ether (III) or chloroform (IV), and the relative extracts were dried (magnesium sulfate) and evaporated under reduced pressure to give III or IV as white solids (Table I). About 10% of starting ketone was recovered from the ether extracts before acidification (see above).

General Procedure a) for Enaminones Va,b,e.

A solution of secondary amine (11 mmoles), hydroxymethyleneketone III or IV (10 mmoles) in anhydrous toluene (150 ml) was kept at room temperature for 24 hours. The toluene solution was decanted from the water which separated and evaporated under reduced pressure. The solid residue was purified by recrystallization from a suitable solvent (Table II).

General Procedure b) for Enaminones Vc,d,f,g,h.

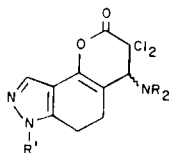
A solution of secondary amine (11 mmoles), hydroxymethyleneketone III or IV (10 mmoles) and *p*-toluenesulfonic acid (0.1 g) in anhydrous to-

Table V

UV, IR and NMR Spectral Data of Compounds VIa-h

Compound	UV, λ max nm (log ϵ)	IR, cm^{-1}		NMR, δ
		C=O	C=C	
VIa	255 sh (3.89) 279 (4.09)	1778	1678	2.52 [s, $(\text{CH}_3)_2\text{N}$], 2.79 (mc, CH_2 -5 + CH_2 -6), 3.72 (s, CH-4), 3.82 (s, CH_3N -7), 7.52 (s, CH-9)
VIb	255 sh (3.93) 279 (4.10)	1780	1680	1.47 (mc, 3 CH_2 pip), 2.78 (mc, 2 CH_2N + CH_2 -5 + CH_2 -6), 3.67 (s, CH-4), 3.82 (s, CH_3N), 7.51 (s, CH-9)
VIc	250.5 (4.27) 290 sh (3.82)	1784	1683	2.70 (s, CH_3NPh), 2.40-3.15 (m, CH_2 -5 + CH_2 -6), 3.80 (s, CH_3N -7), 4.94 (near s, CH-4), 6.70-7.45 (m, $\text{C}_6\text{H}_5\text{N}$), 7.55 (s, CH-9)
VI d	248 (4.23) 260 sh (4.20) 275 sh (4.11)	1784	1687	2.82 (s, CH_2 -5 + CH_2 -6), 3.78 (s, CH_3N), 5.26 (s, CH-4), 6.8- 7.5 (m, 2 $\text{C}_6\text{H}_5\text{N}$ + CH-9)
VIe	238 (4.18) 284 (4.19)	1779	1679	2.55 [s, $(\text{CH}_3)_2\text{N}$], 2.4-3.3 (m, CH_2 -5 + CH_2 -6), 3.77 (near s, CH-4), 7.50 (s, $\text{C}_6\text{H}_5\text{N}$), 7.76 (near s, CH-9)
VI f	237 (4.19) 283 (4.16)	1777	1677	1.48 (mc, 3 CH_2 pip), 2.4-3.3 (m, 2 CH_2N + CH_2 -5 + CH_2 - 6), 3.70 (s, CH-4), 7.51 (s, $\text{C}_6\text{H}_5\text{N}$), 7.76 (s, CH-9)
VI g	245 (4.40) 282 sh (4.10)	1783	1683	2.4-3.3 (m, CH_2 -5 + CH_2 -6), 2.73 (s, CH_3N), 4.97 (near s, CH-4), 6.8-7.4 (m, $\text{C}_6\text{H}_5\text{NMe}$), 7.49 (s, $\text{C}_6\text{H}_5\text{N}$ -7), 7.80 (s, CH-9)
VI h	225 (4.38) 241.5 (4.35) 265 sh (4.25) 280 sh (4.19)	1785	1683	2.5-3.2 (m, CH_2 -5 + CH_2 -6), 5.31 (near s, CH-4), 6.85-7.45 (m, 2 $\text{C}_6\text{H}_5\text{N}$), 7.50 (s, $\text{C}_6\text{H}_5\text{N}$ - 7), 7.59 (s, CH-9)

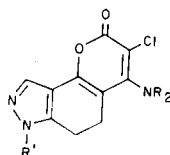
Table IV

N,N-Disubstituted 4-Amino-3,3-dichloro-4,5,6,7-tetrahydro-(7-methyl)(7-phenyl)pyrano[2,3-*e*]indazol-2(3*H*)-ones VIa-h [a]

Formula Number	R'	NR ₂	Yield %	Mp °C	Molecular Formula	Analyses %		
						Calcd./Found	C	H
VIa	CH ₃	N(CH ₃) ₂	89	185 [b]	C ₁₃ H ₁₅ Cl ₂ N ₃ O ₂	49.38	4.78	13.29
						49.17	4.55	13.30
VIb	CH ₃	Piperidino	49	140 [b]	C ₁₆ H ₁₉ Cl ₂ N ₃ O ₂	53.94	5.38	11.79
						53.80	5.32	11.80
VIc	CH ₃	N(CH ₃)C ₆ H ₅	78	147 [b]	C ₁₈ H ₁₇ Cl ₂ N ₃ O ₂	57.16	4.53	11.11
						57.24	4.51	11.13
VIId	CH ₃	N(C ₆ H ₅) ₂	83	159 [c]	C ₂₃ H ₁₉ Cl ₂ N ₃ O ₂	62.74	4.35	9.54
						62.88	4.35	9.50
VIe	C ₆ H ₅	N(CH ₃) ₂	67	127 [d]	C ₁₈ H ₁₇ Cl ₂ N ₃ O ₂	57.16	4.53	11.11
						56.91	4.51	11.35
VIIf	C ₆ H ₅	Piperidino	51	136 [d]	C ₂₁ H ₂₁ Cl ₂ N ₃ O ₂	60.30	5.06	10.04
						60.28	5.00	9.96
VIg	C ₆ H ₅	N(CH ₃)C ₆ H ₅	90	146 [b]	C ₂₃ H ₁₉ Cl ₂ N ₃ O ₂	62.74	4.35	9.54
						62.61	4.52	9.80
VIh	C ₆ H ₅	N(C ₆ H ₅) ₂	86	146 [c]	C ₂₈ H ₂₁ Cl ₂ N ₃ O ₂	66.94	4.21	8.36
						66.91	4.28	8.35

[a] All compounds were prepared according to the literature [6]; solvent, anhydrous toluene; reaction time, 4 hours at room temperature, with the exception of VIg (2 hours at 70°) and VIh (4 hours at 70°). [b] From ethyl acetate. [c] From 95% ethanol. [d] From anhydrous diethyl ether.

Table VI

N,N-Disubstituted 4-Amino-3-chloro-6,7-dihydro-(7-methyl)(7-phenyl)pyrano[2,3-*e*]indazol-2(5*H*)-ones VIIa-h [a]

Formula Number	R'	NR ₂	Yield %	Mp °C	Molecular Formula	Analyses %		
						Calcd./Found	C	H
VIIa	CH ₃	N(CH ₃) ₂	48	241 [b]	C ₁₃ H ₁₄ ClN ₃ O ₂	55.82	5.04	15.02
						55.66	5.01	14.98
VIIb	CH ₃	Piperidino	58	275 [b]	C ₁₆ H ₁₈ ClN ₃ O ₂	60.09	5.67	13.14
						59.90	5.62	13.00
VIIc	CH ₃	N(CH ₃)C ₆ H ₅	84	252 [b]	C ₁₈ H ₁₆ ClN ₃ O ₂	63.25	4.72	12.29
						63.06	4.55	12.28
VIId	CH ₃	N(C ₆ H ₅) ₂	84	290 [b]	C ₂₃ H ₁₈ ClN ₃ O ₂	68.40	4.49	10.40
						68.40	4.45	10.30
VIIe	C ₆ H ₅	N(CH ₃) ₂	37	229 [c]	C ₁₈ H ₁₆ ClN ₃ O ₂	63.25	4.72	12.29
						63.50	4.74	12.15
VIIf	C ₆ H ₅	Piperidino	79	232 [b]	C ₂₁ H ₂₀ ClN ₃ O ₂	66.05	5.28	11.00
						65.87	5.14	10.87
VIIfg	C ₆ H ₅	N(CH ₃)C ₆ H ₅	86	213 [b]	C ₂₃ H ₁₈ ClN ₃ O ₂	68.40	4.49	10.40
						68.31	4.27	10.60
VIIh	C ₆ H ₅	N(C ₆ H ₅) ₂	94	295 [c]	C ₂₈ H ₂₀ ClN ₃ O ₂	72.18	4.33	9.02
						72.25	4.44	9.05

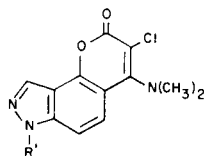
[a] All compounds were prepared from the corresponding VI by dehydrochlorination with DBN according to the literature [4]; solvent, anhydrous toluene; reflux time, 30 minutes. [b] From 95% ethanol. [c] From toluene.

Table VII
UV, IR and NMR Spectral Data of Compounds VIIa-h

Compound	UV, λ max nm (log ϵ)	IR, cm^{-1}		NMR, δ
		C=O	C=C	
VIIa	230 (3.94) 256 (3.99) 355 sh (4.17) 358 (4.19)	1693	1607 1568	2.86 (s, CH ₂ -5 + CH ₂ -6), 3.02 [s, (CH ₃) ₂ N], 3.81 (s, CH ₃ N-7), 7.68 (s, CH-9)
VIIb	230 (3.92) 257 (3.95) 339 (4.17) 360 sh (4.17)	1690	1610 1572	1.70 (mc, 3 CH ₂ pip), 2.90 (s, CH ₂ -5 + CH ₂ - 6), 3.29 (mc, 2 CH ₂ N), 3.83 (s, CH ₃ N), 7.66 (s, CH-9)
VIIc	238 (4.23) 265 sh (3.88) 376 (4.32)	1713	1610 1566	2.45-2.80 (m, CH ₂ -5 + CH ₂ -6), 3.34 (s, CH ₃ N- Ph), 3.77 (s, CH ₃ N-7), 6.80 (mc, 3 H aryl), 7.31 (mc, 2 H aryl), 7.75 (s, CH-9)
VIIId	235 (4.17) 275.5 (4.29) 380 (4.35)	1708	1610 1568	2.35-2.75 (m, CH ₂ -5 + CH ₂ -6), 3.74 (s, CH ₃ - N), 6.9-7.6 (m, 2 C ₆ H ₅ N), 7.76 (near s, CH-9)
VIIe	228 (4.23) 255.5 (4.13) 335 sh (4.23) 355 (4.25)	1698	1612 1568	3.03 (mc, 2 CH ₃ N + CH ₂ -5 + CH ₂ -6), 7.50 (s, C ₆ H ₅ N), 7.94 (s, CH-9)
VIIIf	228 (4.25) 257 (4.12) 345 (4.26)	1690	1611 1568	1.68 (mc, 3 CH ₂ pip), 2.97 (near t, J ~ 5, CH ₂ -5 + CH ₂ -6), 3.30 (mc, 2 CH ₂ N), 7.51 (s, C ₆ H ₅ N), 7.92 (s, CH-9)
VIIg	233.5 (4.34) 375 (4.38)	1712	1612 1563	2.49 (mc, CH ₂ -5), 2.87 (mc, CH ₂ -6), 3.35 (s, CH ₃ N), 6.60-7.45 (m, C ₆ H ₅ NMe), 7.47 (near s, C ₆ H ₅ N-7), 7.99 (near s, CH-9)
VIIh	223 sh (4.34) 257 sh (4.25) 271 (4.28) 379 (4.37)	1709	1613 1567	2.41 (mc, CH ₂ -5), 2.85 (mc, CH ₂ -6), 6.90-7.55 (m, 2 C ₆ H ₅ N), 7.44 (s, C ₆ H ₅ N-7), 8.00 (near s, CH-9)

Table VIII

3-Chloro-4-dimethylamino-(7-methyl)(7-phenyl)pyrano[2,3-*e*]-
indazol-2(7*H*)-ones VIIIa,e [a]



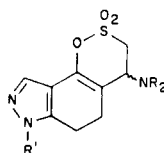
Formula Number	R'	Yield %	Mp °C	Molecular Formula	Analyses %		
					Calcd.	Found	
					C	H	N
VIIIa	CH ₃	40	228 [b]	C ₁₃ H ₁₂ ClN ₃ O ₂	56.22	4.35	15.13
					56.43	4.36	15.36
VIIIe	C ₆ H ₅	76	225 [c]	C ₁₈ H ₁₄ ClN ₃ O ₂	63.63	4.15	12.37
					63.48	3.92	12.35

UV, IR and NMR Spectral Data of Compounds VIIIa,e

	UV, λ max nm (log ε)	IR, cm ⁻¹	NMR, δ
VIIIa	219 (4.48) 258 (4.32) 299 (4.10) 329 (4.19)	1705, 1628, 1587, 1545, 1448	3.22 [s, (CH ₃) ₂ N], 4.10 (s, CH ₃ N-7), 7.27 and 7.66 (2 d, J = 9, CH-5 and CH-6), 8.24 (near s, CH-9)
VIIIe	215 sh (4.37) 241.5 (4.33) 260 (4.36) 304 sh (4.10) 333 (4.30)	1710, 1628, 1583, 1542, 1437	3.23 [s, (CH ₃) ₂ N], 7.20-7.95 (m, C ₆ H ₅ N + CH-5 + CH-6), 8.52 (near s, CH-9)

[a] All compounds were prepared according to the literature [5]; reflux time, 300 hours. [b] From 95% ethanol. [c] From toluene.

Table IX

4-Dialkylamino-4,5,6,7-tetrahydro-(7-methyl)(7-phenyl)-3*H*-1,2-oxathiino[6,5-*e*]indazole 2,2-Dioxides IXa,b,e,f [a]

Formula Number	R'	NR ₂	Yield %	Mp °C	Molecular Formula	Analyses %		
						Calcd./Found	C	H
IXa	CH ₃	N(CH ₃) ₂	44	157 [b]	C ₁₂ H ₁₇ N ₃ O ₃ S	50.87	6.05	14.83
						50.66	6.00	14.60
IXb	CH ₃	Piperidino	37	162 [c]	C ₁₅ H ₂₁ N ₃ O ₃ S	55.71	6.54	12.99
						55.82	6.48	13.11
IXe	C ₆ H ₅	N(CH ₃) ₂	50	197 [b]	C ₁₇ H ₁₉ N ₃ O ₃ S	59.11	5.54	12.16
						59.43	5.58	12.30
IXf	C ₆ H ₅	Piperidino	35	189 [b]	C ₂₀ H ₂₃ N ₃ O ₃ S	62.32	6.01	10.90
						62.06	5.93	10.93

UV, IR and NMR Spectral Data of Compounds IXa,b,e,f

	UV, λ max nm (log ε)	IR, cm ⁻¹		NMR, δ
		C=C	O=S=O	
IXa	250 (3.95) 255 (3.95) 267 sh (3.85)	1665	1377 1178	2.30 [s, (CH ₃) ₂ N], 2.73 (mc, CH ₂ -5 + CH ₂ -6), 3.1-3.6 (m, CH ₂ -3), 3.77 (s, CH ₂ -N-7), 3.7-4.2 (m, CH-4), 7.44 (near s, CH-9)
IXb	250 (3.96) 255 (3.97) 269 sh (3.82)	1666	1377 1183	1.54 (mc, 3 CH ₂ pip), 2.51 (mc, CH ₂ -5 + CH ₂ -6), 2.75 (mc, 2 CH ₂ N), 3.25-3.60 (m, CH ₂ -3), 3.78 (s, CH ₃ N), 3.7-4.2 (m, CH-4), 7.43 (s, CH-9)
IXe	224 (4.20) 251.5 (4.00) 261 (3.98) 276 (3.94)	1663	1378 1178	2.33 [s, (CH ₃) ₂ N], 2.55-3.20 (m, CH ₂ -5 + CH ₂ -6), 3.25-3.75 (m, CH ₂ -3), 3.80-4.25 (m, CH-4), 7.48 (s, C ₆ H ₅ N), 7.70 (near s, CH-9)
IXf	224 (4.22) 251 (4.03) 260.5 (4.00) 275.5 (3.95)	1663	1378 1184	1.53 (mc, 3 CH ₂ pip), 2.52 (mc, 2 CH ₂ N), 2.6-3.2 (m, CH ₂ -5 + CH ₂ -6), 3.53 (mc, CH ₂ -3), 3.7-4.3 (m, CH-4), 7.47 (s, C ₆ H ₅ N), 7.68 (near s, CH-9)

[a] All compounds were prepared according to the literature [7], using anhydrous THF as the solvent. [b] From 95% ethanol. [c] From ethyl acetate.

luene (200 ml) was refluxed for 4 hours in a Dean-Stark apparatus. After cooling, the solution was washed with 1*M* sodium hydroxide and water, dried (magnesium sulfate) and evaporated under reduced pressure. The solid residue was purified as above (Table II).

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