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Reaction of sulfene with *N,N*-disubstituted 3-aminomethylene-1-(methyl, methylphenyl, phenyl)-4-piperidones and 3-aminomethylene-2,3-dihydro-1-phenyl-4(1*H*)quinolones gave *N,N*-disubstituted 4-amino-3,4,5,6,7,8-hexahydro-6-(methyl, methylphenyl, phenyl)-1,2-oxathiino[5,6-*c*]pyridine 2,2-dioxides and 4-amino-6-phenyl-3,4,5,6-tetrahydro-1,2-oxathiino[5,6-*c*]quinoline 2,2-dioxides, respectively, whereas *N,N*-disubstituted 3-aminomethylene-2,3-dihydro-1-methyl-4(1*H*)quinolones did not react. Slow air oxidation in the cold of intermediates 2,3-dihydro-3-hydroxymethylene-1-(methyl, phenyl)-4(1*H*)quinolones gave the corresponding 1-substituted 1,4-dihydro-4-oxo-3-quinolinecarboxyaldehydes.

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In previous work we described the synthesis of 1,2-oxathiin derivatives condensed with an oxygen or sulfur heterocycle, by 1,4-cycloaddition of *N,N*-disubstituted 3-aminomethylene-4-chromanones, -2,3-dihydro-4-thiochromanones, and -2,3,5,6-tetrahydro-4-thiopyranones to sulfene (1,2). We wish to report now the synthesis of derivatives of 1,2-oxathiin condensed with a nitrogen heterocycle, namely 1,2-oxathiino[5,6-*c*]quinoline and 1,2-oxathiino[5,6-*c*]pyridine: few derivatives of the latter were described previously by us (3).

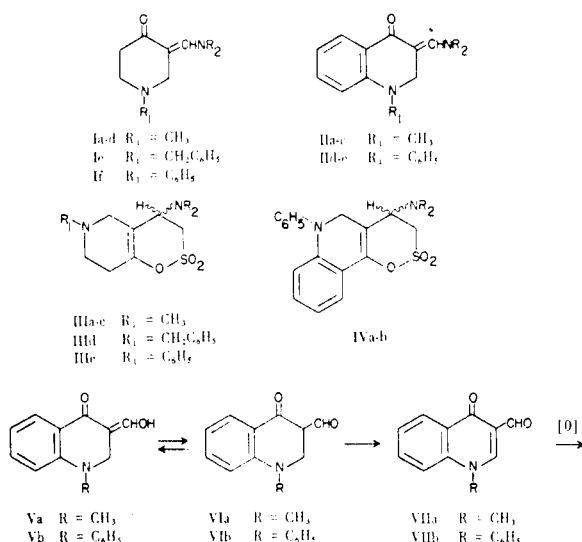
For this purpose we synthesized in low to fair yield a series of *N,N*-disubstituted 3-aminomethylene-1-(methyl, methylphenyl)-4-piperidones Ia-e (Tables I and II) following a procedure described in the early literature (4), namely from amine hydrochloride and sodium salt of α -hydroxymethylene-ketone. In the present circumstances it was indeed impossible to isolate the free α -hydroxymethylene-ketone by acidification of the aqueous solution

of its sodium salt owing to the fair basicity of ring nitrogen atom. On the other hand, *N,N*-disubstituted 3-aminomethylene-2,3-dihydro-1-(methyl, phenyl)-4(1*H*)quinolones IIa-e (Tables III and IV) could be prepared, generally in high yield, from secondary amines and the crude readily isolable α -hydroxymethyleneketones Va-b. Also enamine If could be obtained in low yield from unstable 3-hydroxymethylene-1-phenyl-4-piperidone and piperidine; other secondary amines gave no results.

Enaminoketones I and II are probably E-isomers, at least as can be seen from the strong upfield shift of NCH₂ protons (~ 0.4 -0.7 ppm) caused by the phenyl group in compounds Id and IIe (see Tables II and IV).

Reaction of enamines I and II with methanesulfonyl chloride and triethylamine (sulfene prepared *in situ*) gave in good yield *N,N*-disubstituted 4-amino-3,4,5,6,7,8-hexahydro-1,2-oxathiino[5,6-*c*]pyridine 2,2-dioxides IIIa-e (Table V) and 4-amino-3,4,5,6-tetrahydro-1,2-oxathiino[5,6-*c*]quinoline 2,2-dioxides IVa-b (Table VII), respectively, only when 1-substituent of the enamine was a phenyl group (enamines If and IId,e), but yields generally decreased or the reaction quite failed when 1-substituent was an alkyl group (enamines Ia,b,d and IIa,b,c). The adducts obtained showed ir and nmr spectra (Tables VI and VIII) in agreement with the proposed structure [compare (2)]. Therefore, when in enamines I and II, the 1-nitrogen is sufficiently nucleophilic, it appears that sulfene can interact with it instead of giving dipolar 1,4-cycloaddition.

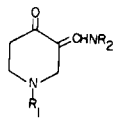
We had already noticed (3) that in the preparation of 2,3-dihydro-3-hydroxymethylene-1-(methyl, phenyl)-4(1*H*)quinolones Va-b two different by-products were obtained. One of these was also obtained in the present work as the main product in the reaction of enamines IIa,b with sulfene. The compounds have been now recognized as 1-substituted 1,4-dihydro-4-oxo-3-quinoline-



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Table I

N,N-Disubstituted 3-Aminomethylene-1-(methyl, methylphenyl, phenyl)-4-piperidones (1a-f)

Formula Number	R ₁	NR ₂	Yield %	B.p./mm Hg or M.p. °C	Molecular Formula	Analyses % C	% Calcd./Found H	N
1a	CH ₃	N(C ₂ H ₅) ₂	15	115-116/0.4	C ₁₁ H ₂₀ N ₂ O	67.31 67.56	10.27 10.41	14.27 14.25
1b	CH ₃		60	110-120/0.4	C ₁₁ H ₁₈ N ₂ O	68.01 67.63	9.34 9.66	14.42 14.32
1c	CH ₃		32	128-130/0.2	C ₁₂ H ₂₀ N ₂ O	69.19 69.40	9.68 9.58	13.45 13.15
1d	CH ₃	N(CH ₃)C ₆ H ₅	22	150-152/0.4	C ₁₄ H ₁₈ N ₂ O	73.01 72.85	7.88 8.16	12.16 11.90
1e	CH ₂ C ₆ H ₅	N(CH ₃)C ₆ H ₅	16	160-170/0.2	C ₂₀ H ₂₂ N ₂ O	78.40 78.08	7.24 7.54	9.14 9.18
1f	C ₆ H ₅		25	121 (a)	C ₁₇ H ₂₂ N ₂ O	75.52 75.24	8.20 7.94	10.36 10.50

(a) After chromatography on Florisil ® with diethyl ether.

Enamines 1a-e were prepared according to (3), and 1f according to (1).

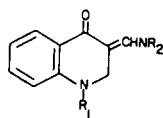
Table II

Uv, Ir and Nmr Spectral Data of Compounds 1a-f

Compound	Uv	Ir, cm ⁻¹ (tetrachloromethane)		Nmr, δ (tetrachloromethane)
	λ max nm (log ε)	C=O	C=C	
1a	328.5 (4.26)	1653	1532	1.24 (t, J = 7.3, 2CH ₃), 2.1-3.0 (m, CH ₂ -5 + CH ₂ -6), 2.34 (s, NCH ₃), 3.32 (q, J = 7.3, 2NCH ₂), 3.38 (near s, CH ₂ -2), 7.25 (m, =CHN)
1b	335 (4.29)	1660	1548	1.92 (m, 2CH ₂ pyr.), 2.05-2.75 (m, CH ₂ -5 + CH ₂ -6), 2.34 (s, NCH ₃), 3.58 (m, CH ₂ -2 + 2NCH ₂ pyr.), 7.45 (near s, =CHN)
1c	329 (4.23)	1656	1542	1.65 (m, 3CH ₂ pip.), 2.1-2.8 (m, CH ₂ -5 + CH ₂ -6), 2.34 (s, NCH ₃), 3.40 (m, CH ₂ -2 + 2NCH ₂ pip.), 7.16 (near s, =CHN)
1d	235 (3.61) 332 (4.14)	1683	1550	2.20 (s, NCH ₃), 2.15-2.75 (m, CH ₂ -5 + CH ₂ -6), 2.98 (m, CH ₂ -2), 3.41 (s, NCH ₃), 7.12 (m, C ₆ H ₅), 7.40 (m, =CHN)
1e	250 (4.13) 308 (3.69)	1667	1542	2.1-2.9 (m, CH ₂ -2 + CH ₂ -5 + CH ₂ -6), 3.33 (s, NCH ₃), 3.40 (s, NCH ₂ Ph), 6.2-7.4 (m, 2C ₆ H ₅), 7.38 (m, =CHN)
1f	251.5 (4.06) 330 (4.24)	1660	1548	1.68 (m, 3CH ₂ pip.), 2.56 (near t, J = 6, CH ₂ -5), 3.48 (m, 2NCH ₂ pip.), 3.58 (near t, J = 6, CH ₂ -6), 4.30 (near s, CH ₂ -2), 6.7-7.5 (m, C ₆ H ₅), 7.60 (m, =CHN) (a)

(a) In deuteriochloroform.

Table III

N,N-Disubstituted 3-Aminomethylene-1-(methyl, phenyl)-2,3-dihydro-4(1*H*)quinolones (IIa-e)

Formula Number	R ₁	NR ₂	Yield %	M.p. °C	Molecular Formula	Analyses % Calcd./Found		
						C	H	N
IIa	CH ₃	N(C ₂ H ₅) ₂	70	81 (a)	C ₁₅ H ₂₀ N ₂ O	73.74 73.45	8.25 8.44	11.47 11.52
IIb	CH ₃		82	111 (a)	C ₁₆ H ₂₀ N ₂ O	74.97 74.72	7.86 7.97	10.93 10.96
IIc	CH ₃	N(CH ₃)C ₆ H ₅	10	140 (b)	C ₁₈ H ₁₈ N ₂ O	77.67 77.30	6.52 6.65	10.06 10.36
IId	C ₆ H ₅		73	138 (c)	C ₂₁ H ₂₂ N ₂ O	79.21 79.45	6.96 7.20	8.80 8.50
IIe	C ₆ H ₅	N(CH ₃)C ₆ H ₅	67	99 (b)	C ₂₃ H ₂₀ N ₂ O	81.15 81.18	5.92 6.03	8.23 8.00

(a) From anhydrous diethyl ether. (b) From ethyl acetate. (c) From 95% ethanol.
Enamines IIa,b were prepared according to (1), and IIc,d,e according to (8).

Table IV

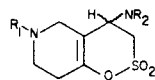
Uv, Ir and Nmr Spectral Data of Compounds IIa-e

Compound No.	UV λ max nm (log ϵ)	Ir, cm ⁻¹		Nmr, δ (deuteriochloroform)
		C=O	C=C	
IIa	248.5 (4.44) 274 sh (3.86) 345 (4.15) 407 (3.97)	1653	1546 (a)	1.22 (t, J = 7.5, 2CH ₃), 2.83 (s, NCH ₃), 3.26 (q, J = 7.5, 2NCH ₂), 4.12 (m, CH ₂ -2), 6.35-7.65 (m, H-6 + H-7 + H-8), 7.36 (m, =CHN), 7.7-7.9 (m, H-5) (a)
IIb	250 (4.41) 274 sh (3.92) 347 (4.16)	1640	1527 (b)	1.64 (m, 3CH ₂ pip.), 2.90 (s, NCH ₃), 3.40 (m, 2NCH ₂ pip.), 4.25 (m, CH ₂ -2), 6.4-7.5 (m, H-6 + H-7 + H-8), 7.58 (near s, =CHN), 7.85-8.05 (m, H-5)
IIc	250.5 (4.60) 293 (3.78) 330 (4.07) 341.5 (4.05)	1635	1556 (a)	3.00 (s, NCH ₃), 3.65 (s, NCH ₃), 4.46 (near s, CH ₂ -2), 6.4-7.7 (m, 8H ar. + =CHN), 8.30-8.55 (m, H-5)
IId	241.5 (4.34) 302 (4.08) 339 (4.12) 415 (3.84)	1640	1528 (b)	1.62 (m, 3CH ₂ pip.), 3.40 (m, 2NCH ₂ pip.), 4.73 (s, CH ₂ -2), 6.5-7.8 (m, 8H ar.), 7.60 (s, =CHN), 7.95 and 8.08 (2d, J ~ 2, H-5)
IIe	240 (4.31) 294.5 (4.13) 361 (4.21) 424 (3.94)	1643	1533 (b)	3.45 (s, NCH ₃), 4.02 (m, CH ₂ -2), 6.50-7.55 (m, 13H ar.), 7.73 (m, =CHN), 7.96 and 8.09 (2d, J ~ 2, H-5)

(a) In tetrachloromethane. (b) In chloroform.

Table V

N,N-Disubstituted 4-Amino-3,4,5,6,7,8-hexahydro-6-(methyl, methylphenyl, phenyl)-1,2-oxathiino[5,6-*c*]pyridine 2,2-Dioxides (IIIa-c)



Formula Number	R ₁	NR ₂	Yield %	M.p. °C	Molecular Formula	Analyses % C	% Calcd./Found H	N
IIIa	CH ₃	N(C ₂ H ₅) ₂	37	56 (a)	C ₁₂ H ₂₂ N ₂ O ₃ S	52.53 52.23	8.08 8.38	10.21 10.32
IIIb	CH ₃		27	116 (b)	C ₁₂ H ₂₀ N ₂ O ₃ S	52.92 53.28	7.40 7.39	10.29 10.57
IIIc	CH ₃		56	120 (b)	C ₁₃ H ₂₂ N ₂ O ₃ S	54.52 54.45	7.74 7.91	9.78 9.50
IIId	CH ₂ C ₆ H ₅	N(CH ₃)C ₆ H ₅	40	152 (c)	C ₂₁ H ₂₄ N ₂ O ₃ S	65.60 65.52	6.29 6.25	7.29 7.61
IIIe	C ₆ H ₅		55	117 (b)	C ₁₈ H ₂₄ N ₂ O ₃ S	62.04 62.00	6.94 6.96	8.04 8.15

(a) After chromatography on Florisil ® with diethyl ether. (b) From anhydrous diethyl ether. (c) From 95% ethanol. All compounds were prepared according to (1), using anhydrous tetrahydrofuran as solvent.

Table VI

Ir and Nmr Spectral Data of Compounds IIIa-e

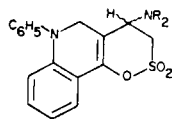
Compound	Ir, cm ⁻¹ (tetrachloromethane)			Nmr, δ (tetrachloromethane)
	C=C	O=S=O		
IIIa	1678	1383	1187	1.10 (t, J = 7.2, 2CH ₃), 2.35 (s, NCH ₃), 2.45 (q, J = 7.2, 2NCH ₂), 2.90 (m, CH ₂ -5), 2.03-3.05 (m, CH ₂ -7 + CH ₂ -8), 3.05-4.30 (m, CH ₂ -3 + CH-4).
IIIb	1705	1383	1185	1.78 (m, 2CH ₂ pyr.), 2.33 (s, NCH ₃), 2.63 (m, 2NCH ₂ pyr. + CH ₂ -7 + CH ₂ -8), 2.93 (m, CH ₂ -5), 3.1-4.3 (m, CH ₂ -3 + CH-4).
IIIc	1692	1382	1186	1.53 (m, 3CH ₂ pip.), 2.33 (s, NCH ₃), 2.48 (m, 2NCH ₂ pip. + CH ₂ -7 + CH ₂ -8), 2.89 (m, CH ₂ -5), 3.1-4.2 (m, CH ₂ -3 + CH-4).
IIId	1705	1382	1182 (a)	2.1-2.9 (m, CH ₂ -7 + CH ₂ -8), 2.76 (s, NCH ₃), 3.02 (m, CH ₂ -5), 3.2-3.7 (m, CH ₂ -3 + NCH ₂ Ph), 4.90 (m, CH-4), 6.65-7.60 (m, 2C ₆ H ₅) (b)
IIIe	1703	1387	1188	1.53 (m, 3CH ₂ pip.), 2.42 (m, 2NCH ₂ pip. + CH ₂ -8), 2.85-4.20 (m, 3CH ₂ + CH-4), 6.5-7.4 (m, C ₆ H ₅).

(a) In chloroform. (b) In deuteriochloroform.

carboxaldehydes VIIa-b on the following basis. Compound VIIa was already known and showed m.p. and uv spectrum in agreement with those described (5,6); moreover its structure, as well as that of VIIb, was confirmed by ir, nmr and ms data (see Experimental). Compounds VIIa-b could arise from a facile air oxidation of the tautomeric

forms VIa-b originating from α-hydroxymethyleneketones Va-b; actually, VIIa-b could be obtained from Va-b in fair to good yield by slow air oxidation in the cold during about two months. Finally, we tried also the dipolar 1,4-cycloaddition of enamines I and II with dichloroketene [prepared *in situ* from dichloroacetyl chloride and tri-

Table VII

N,N-Disubstituted 4-Amino-6-phenyl-3,4,5,6-tetrahydro-1,2-oxathiino[5,6-*c*]quinoline 2,2-Dioxides (IVa-b)

Formula Number	NR ₂	Yield %	M.p. °C	Molecular Formula	Analyses %	Calcd./Found	
					C	H	N
IVa		84	178 (a)	C ₂₂ H ₂₄ N ₂ O ₃ S	66.64 66.65	6.10 6.14	7.07 6.78
IVb	N(CH ₃)C ₆ H ₅	80	145 (a)	C ₂₄ H ₂₂ N ₂ O ₃ S	68.88 68.57	5.30 5.53	6.69 6.58

(a) From ethyl acetate.

All compounds were prepared according to (1), using anhydrous tetrahydrofuran as solvent.

Table VIII

Ir and Nmr Spectral Data of Compound IVa-b

Compound No.	Ir, cm ⁻¹ (chloroform)			Nmr, δ (deuteriochloroform)
	C=C	O=S=O		
IVa	1675	1380	1188	1.45 (m, 3CH ₂ pip.), 2.44 (m, 2NCH ₂ pip.), 3.55 (m, CH ₂ -3), 3.7-4.3 (m, CH-4), 4.47 (m, CH ₂ -5), 6.55-7.75 (m, 9H ar.).
IVb	1675	1384	1182	2.84 (s, NCH ₃), 3.58 (m, CH ₂ -3), 4.43 (m, CH ₂ -5), 4.75-5.35 (m, CH-4), 6.50-7.75 (m, 2NC ₆ H ₅ + 4 H ar.).

ethylamine, compare (7)], but in any case we were unable to isolate the adduct even if in a few cases (enamines Ia, IIe) its formation and/or that of dehydrochlorinated products could be inferred from ir absorptions of the reaction mixture.

EXPERIMENTAL

Uv spectra were measured in 95% ethanol with a Hitachi-Perkin-Elmer Model EPS-3T spectrophotometer. Ir spectra were taken on a Perkin-Elmer Model 257 spectrometer and nmr spectra were recorded on a Perkin-Elmer Model R12 instrument (60 MHz; TMS as internal standard; J in Hz). Mass spectra were obtained with a GC/MS Varian Mat 111 spectrometer. Melting points were determined with a Fisher-Johns apparatus.

3-Hydroxymethylene-1-phenyl-4-piperidone was prepared (1) from 1-phenyl-4-piperidone (0.02 mole), ethyl formate (0.04 mole) and sodium methoxide (0.04 mole) in anhydrous benzene. The very unstable crude compound obtained by acidification at pH 5 (yield 97%) was used immediately without any purification; ir (tetrachloromethane): ν max 1710 (broad), 1633, 1587 cm⁻¹.

Compound VIIa.

A solution of Va (3) (7.56 g., 0.04 mole) in diethyl ether (80 ml.) was kept in a refrigerator in a loosely stoppered flask.

Every five days the precipitate which formed was filtered and the solution was concentrated, total yield after 55 days, 5.23 g. (70%); m.p. 210° from 95% ethanol [lit. (5) 217-218°]; uv: λ max nm (log ϵ), 217 (4.43), 233.5 (4.37), 265 (3.91), 324 (4.21) [lit. (6), 233 (4.35), 264 sh (3.90), 325 (4.17)]; ir (chloroform): ν max 3020, 3005, 2850, 1681, 1633, 1612, 1553, 1503 cm⁻¹; nmr (deuteriochloroform): δ 3.95 (s, NCH₃), 7.58 (mc, CH-6 + CH-7 + CH-8), 8.30 (s, CH-2), 8.4-8.7 (m, CH-5), 14.53 (s, CHO); ms: m/e 187 (M⁺, 11%), 160 (11), 159 (100), 131 (23), 130 (29), 77 (18), 57 (16), 55 (11), 45 (18), 44 (30), 40 (18), 31 (34), 29 (11).

Anal. Calcd. for C₁₁H₉NO₂: C, 70.58; H, 4.85; N, 7.48. Found: C, 70.30; H, 4.94; N, 7.36.

The same compound was also obtained as the main product (58-72%) in the reaction of enamines IIa,b with sulfene.

Compound VIIb.

Starting from Vb (3) (2.51 g., 0.01 mole) and following the above procedure, 0.78 g. (31%) of VIIb was obtained, m.p. 187° from 95% ethanol; uv: λ max nm (log ϵ), 216 (4.41), 232.5 (4.44), 264 sh (3.89), 318 sh (4.23), 3.27.5 (4.25); ir (chloroform): ν max, 3030, 3000, 2855, 1675, 1627, 1592, 1545 cm⁻¹; nmr (deuteriochloroform): δ 7.57 (mc, NC₆H₅ + 3H ar.), 8.30 (s, CH-2), 8.4-8.75 (m, CH-5), 14.3 (s, CHO); ms: m/e 249 (M⁺, 6%), 222 (14), 221 (100), 220 (28), 204 (14), 193 (16), 192 (8), 191 (10), 165 (10), 110 (6), 89 (7), 77 (13), 57 (8), 55 (6), 51 (13).

Anal. Calcd. for C₁₆H₁₁NO₂: C, 77.09; H, 4.45; N, 5.62.

Found: C, 76.81; H, 4.57; N, 5.57.

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