Table I. Characterization Data of 7-Substituted 9,10-Dimethyldibenz[*b*,*e*]indolizine-8,11-diones

compd[a,b]	AMC used	yield, %	mp, °C	^{1}H NMR δ[c]
I	CH_3NO_2	11	>300 decomp	2.2 (d, 6 H), 7.75 (m, 7 H)
II	$C_2H_5NO_2$	19	290 decomp	2.0 (d, 6 H), 2.85 (s, 3 H), 7.5 (m, 5 H), 8.9 (d, 1 H)
III	$CH_3COCH_2COCH_3$	56	286	2.1 (d, 6 H), 2.9 (s, 3 H), 7.5 (m, 4 H), 8.4 (m, 1 H), 9.0 (d, 1 H)
IV	$CH_3COCH_2CO_2C_2H_5$	68	>300 decomp	1.65 (t, 3 H), 2.2 (s, 6 H), 4.8 (q, 2 H), 7.7 (m, 4 H), 8.45 (m, 1 H), 9.3 (d, 1 H)
V	CH_3COCH_2COPh	39	>280 decomp	2.25 (d, 6 H), 7.75 (m, 10 H), 9.35 (d, 1 H)
VI	$NCCH_2CO_2C_2H_5$	40	>320 decomp	2.3 (s, 6 H), 7.8 (m, 5 H), 9.35 (d, 1 H)

[a] Compounds I to V were obtained as deep-red crystals and compound VI as an orange powder. [b] The IR spectra of I to VI exhibited ν(C=O) at 1630–1700 cm^{-1} besides the characteristic peaks. Compound VI also exhibited ν(C≡N) at 2215 cm^{-1}. [c] The ^{1}H NMR spectra were all recorded in CF_3COOH.

Experimental Section

Melting points were determined by using a Gallenkamp heated block apparatus.

IR spectra were recorded on a Perkin-Elmer 337 spectrometer using KBr disks.

PMR were recorded on a Jeol C-60 HL high-resolution NMR spectrometer using Me_4Si as internal standard.

Microanalyses were carried out by the Analytical Department at the Iraqi National Oil Co. Elemental analyses (C, H, N) were obtained and submitted for review and were within ∓0.4% of the theoretical value (Table I).

Synthesis of 7-Substituted 9,10-Dimethyldibenz[*b*,*e*]indolizine-8,11-diones

General Method. A mixture of 2,3-dibromo-5,6-dimethylbenzo-1,4-quinone (0.0017 mol) which was prepared following the method of Smith and Austin (*4*), excess quinoline (6 cm^3), and the active methylene compound (AMC) (3.5 cm^3) was heated under reflux in ethanol (25 cm^3) for 3 h. The reaction mixture was cooled and the dark precipitate filtered off, washed well with ethanol, dried, and then crystallized from acetone.

Registry No. I, 108594-48-5; II, 108562-24-9; III, 108562-25-0; IV, 108562-26-1; V, 108562-27-2; VI, 108562-28-3; $MeNO_2$, 75-52-5; $EtNO_2$, 79-24-3; $CH_3C(O)CH_2C(O)CH_3$, 123-54-6; $CH_3C(O)CH_2C(O)OEt$, 141-97-9; $CH_3C(O)CH_2C(O)Ph$, 93-91-4; $NCCH_2C(O)OEt$, 105-56-6; 2,3-dibromo-5,6-dimethyl-2,5-cyclohexadiene-1,4-dione, 38969-08-3; quinoline, 91-22-5.

Literature Cited

(1) Al-Sammerrai, D. A.; Ralph, J. T.; West, D. E. *J. Heterocycl. Chem.* **1980**, *17*, 1705.
(2) Al-Sammerrai, D. A.; Salih, Z. S. *Indian J. Chem.*, in press.
(3) Luckenbaugh, R. W. Ph.D. Thesis, University of Maryland, 1952.
(4) Smith, L. I.; Austin, P. L. *J. Am. Chem. Soc.* **1942**, *64*, 528.

Received for review October 7, 1986. Revised manuscript received March 16, 1987. Accepted April 24, 1987.

Synthesis and Spectroscopic Properties of Some New Substituted Saccharin Anils

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Fourteen new substituted saccharin anils have been synthesized by the reaction of pseudosaccharin chloride with various substituted anilines. The IR, proton NMR, and carbon-13 NMR spectral properties are presented and discussed.

Introduction

A large number of saccharin derivatives were synthesized (*1–5*) and were reported to show antibacterial activity (*6–12*). On the other hand only saccharin aniline (*13*) was reported in the literature. In this work 14 new saccharin derivative anils are prepared (Table I). The compounds were prepared by the reaction of chlorosaccharin with various substituted aromatic amines. The structures and physical properties of these compounds are given in Tables I and II. The IR, ^{1}H NMR, and carbon-13 NMR spectral data are presented in Tables II and III.

Scheme I

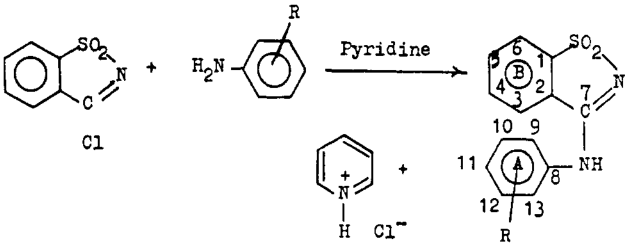

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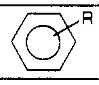
Table I. Physical Properties of Substituted Saccharin Anils

compd no.	R	molecular formula	mp, °C	yield, %
1	H	$C_{13}H_{10}N_2O_2S$	317	78.0
2	*p*-CH_3	$C_{14}H_{12}N_2O_2S$	318–319	85.0
3	*p*-OCH_3	$C_{14}H_{12}N_2O_3S$	287	70.0
4	*p*-$COCH_3$	$C_{15}H_{12}N_2O_3S$	330	67.0
5	*p*-Cl	$C_{13}H_9ClN_2O_2S$	320–321	76.0
6	*p*-NO_2	$C_{13}H_9N_3O_4S$	355	86.0
7	*m*-CH_3	$C_{14}H_{12}N_2O_2S$	306–307	69.0
8	*m*-Cl	$C_{13}H_9ClN_2O_2S$	313–314	62.0
9	*m*-NO_2	$C_{13}H_9N_3O_4S$	335	71.0
10	*o*-CH_3	$C_{14}H_{12}N_2O_2S$	276	77.0
11	*o*-OCH_3	$C_{14}H_{12}N_2O_3S$	295	84.0
12	*o*-$COCH_3$	$C_{15}H_{12}N_2O_3S$	290	84.0
13	*o*-Cl	$C_{13}H_9ClN_2O_2S$	265–267	69.0
14	*o*-NO_2	$C_{13}H_9N_3O_4S$	312–313	79.0

Table II. Proton Chemical Shift (ppm) for Substituted Saccharin Anil

compd no.	δ_{H_6}	δ_{H_3}, δ_{H_4}, δ_{H_5}		δ_{NH}[a]
1	8.43 (m)	7.87 (m)	7.37 (m)	10.78
2	8.43 (m)	7.87 (m)	7.50 (m)	10.75
5	8.43 (m)	7.93 (m)	7.68 (m)	10.87
6	8.37 (m)	8.18 (m)	7.93 (m)	11.12
7	8.43 (m)	7.87 (m)	7.37 (m)	10.68
8	7.06 (m)	6.62 (m)	6.18 (m)	9.43
9	8.75 (m)	8.37 (m)	7.87 (m)	11.12
10	8.31 (m)	7.87 (m)	7.31 (m)	10.75
13	8.31 (m)	7.93 (m)	7.50 (m)	11.00
14	8.25 (m)	7.93 (m)	7.68 (m)	11.31

[a] Broad band assigned to NH protons (*16*).

Experimental Section

Saccharin (30 g, 0.163 mol) was mixed with phosphorous pentachloride (50 g, 0.163 mol) and left to react at 175–180 °C for 1.5 h (*14*). The mixture was left to cool; phosphorous oxychloride was distilled under vacuum and the pseudosaccharin chloride crystals were recrystallized from benzene (p 141–144 °C), (Scheme I). Pseudosaccharin chloride was mixed with the proper aromatic amine (1 to 1) and then 5–10 mL of dried pyridine was added to the mixture. After the reaction was complete (exothermic), cold water was added and the precipitate was recrystallized from pyridine in the presence of charcoal. The physical properties are given in Tables I and II. Melting points were determined on a Thomas Hoover Model 6427-F10. Elemental analyses were performed by Alfred Bernhardt Laboratories, Ruhr, Germany; IR absorption spectra were recorded on a Perkin Elmer 137 A spectrometer as KBr wafers.

Proton NMR spectra were measured for solutions in Me_2SO-d_6 with Me_4Si as internal reference. Carbon-13 spectra were measured for solutions in Me_2SO-d_6 with Me_4Si as internal reference. Proton coupled and decoupled carbon-13 NMR spectra were run at a spectral width of 4 kHz, flip angle 45°, acquisition time 1 s, and delay time 3 s. All NMR measurements were made on a Varian FT 80 A machine operated at 80 MHz for proton and 20 MHz for carbon-13.

The IR spectra of substituted saccharin anils exhibited a C=N stretching at 1560 cm^{-1} and the sulfone group asymmetric vibration showed variation in position from 1280 to 1320 cm^{-1}, whereas the symmetric vibration absorbed at 1160 cm^{-1} (*15*). The secondary NH vibration appears at 3300–3310 cm^{-1}; other vibrations are ν_{C-NH} at 1120 cm^{-1} and $\nu_{C=C}$ at 1450 and 1615 cm^{-1}.

Elemental analyses (C, H, N) for compounds **1–14** in agreement with theoretical values were obtained and submitted for review.

Registry No. **1**, 7668-23-7; **2**, 108666-41-7; **3**, 107920-31-0; **4**, 108666-42-8; **5**, 108666-43-9; **6**, 108666-44-0; **7**, 108675-05-4; **8**, 108666-45-1; **9**, 108666-46-2; **10**, 108666-47-3; **11**, 107922-15-6; **12**, 108666-48-4; **13**, 108666-49-5; **14**, 108666-50-8; $C_6H_5NH_2$, 62-53-3; 4-$H_3CC_6H_4NH_2$, 106-49-0; 4-$H_3COC_6H_4NH_2$, 104-94-9; 4-$H_3CCOC_6H_4NH_2$, 99-92-3; 4-$ClC_6H_4NH_2$, 106-47-8; 4-$O_2NC_6H_4NH_2$, 100-01-6; 3-$H_3CC_6H_4NH_2$, 108-44-1; 3-$ClC_6H_4NH_2$, 108-42-9; 3-$O_2NC_6H_4NH_2$, 99-09-2; 2-$H_3CC_6H_4NH_2$, 95-53-4; 2-$H_3COC_6H_4NH_2$, 90-04-0; 2-$H_3CCOC_6H_4NH_2$, 551-93-9; 2-$ClC_6H_4NH_2$, 95-51-2; 2-$O_2NC_6H_4NH_2$, 88-74-4; saccharin, 81-07-2; pseudosaccharin chloride, 567-19-1.

Table III. Carbon-13 Chemical Shift (ppm) of Substituted Saccharin Anils[a]

compd no.	δ_1	δ_2	δ_3	δ_4	δ_5	δ_6	δ_7	δ_8	δ_9	δ_{10}	δ_{11}	δ_{12}	δ_{13}	δ_{CH_3}
1	140.88	128.29	123.56	133.68	121.43	133.26	156.84	137.47	122.15	129.01	125.70	129.01	122.15	
2	140.92	128.32	123.47	133.57	121.37	133.19	156.60	135.01	122.02	129.39	135.01	129.39	122.02	20.52
4	140.62	128.20	123.91	134.09	121.73	133.62	157.12	141.77	121.55	129.53	134.09	129.53	121.55	
5	140.73	128.78	123.39	133.78	121.47	133.32	156.84	136.48	123.59	128.95	133.06	128.95	123.59	
6	140.58	128.12	124.19	134.48	122.01	133.94	157.55	143.71	122.23	125.17	144.17	125.17	122.23	
7	140.84	128.32	123.55	133.69	121.46	133.31	156.73	137.42	122.50	138.42	126.42	128.89	119.31	21.14
8	140.63	128.04	123.62	133.86	121.42	133.41	156.98	138.97	121.51	133.22	125.32	130.72	120.42	
9	140.54	128.00	123.72	134.03	121.66	133.53	157.53	138.77	116.23	148.03	119.93	130.58	127.78	
10	142.00	127.76	123.29	133.73	121.34	133.26	158.k9	135.13	134.11	130.78	126.78	127.76	126.53	17.62
11	141.87	127.95	123.51	133.87	121.58	133.44	158.66	125.12	153.26	114.61	126.70	121.31	123.15	55.97[b]
12														
13	141.99	127.46	123.42	133.97	121.51	133.47	159.16	133.84	128.35	129.41	127.0	127.11	123.45	
14	141.78	127.38	123.57	134.57	121.93	133.96	158.95	130.07	144.31	128.51	128.64	134.80	125.79	
3	141.01	128.39	123.48	133.69	121.49	133.32	156.57	130.22	123.78	114.29	157.11	114.29	123.78	55.44[b]

[a] The assignments were made by using C-13 chemical shifts of similar compounds (*17*) and by using the additivity rule (*18*). [b] δ_{OCH_3}.

J. Chem. Eng. Data **1987**, *32*, 393–394 **393**

Literature Cited

(1) Jesurum, J. A. *Ber*. **1893**, *26*, 2287.
(2) Meadoe, J. R.; Reid, E. E. *J. Am. Chem. Soc*. **1843**, *65*, 457.
(3) Seki, I.; Matsuno, T. *Chem. Abstr*. **1970**, *73*, 45499*t*.
(4) Wataya, M.; Yamaguchi, M.; Onodeta, N. *Chem. Abstr*. **1975**, *83* (17), 147470*a*.
(5) Chiyomaru, I.; Kawada, S.; Takita, K. *Chem. Abstr*. **1973**, *78*, 155417*a*.
(6) Chien-Pen, Lo, *Chem. Abstr*. **1962**, *56*, 1806*c*.
(7) Chiyomatu, I.; Yoshinaga, E.; Takita, K. *Chem. Abstr*. **1974**, *80*, 67412*f*.
(8) Tsuchiya, S.; Kawada, S.; Chiyomatu, I.; Takita, K. *Chem. Abstr*. **1973**, *79*, 74939*t*.
(9) Staehle, H.; Koeppe, H.; Kummer, W.; Zeile, K. *Chem. Abstr*. **1972**, *77*, 164669*r*.
(10) Wade, P. C.; Vogt, B. R. *Chem. Abstr*. **1979**, *91*(11–12), 91636*e*.
(11) Wade, P. C.; Vogt, B. R. *Chem. Abstr*. **1980**, *92*(13), 110999*q*.
(12) Wade, P. C.; Kissick, T. P. *Chem. Abstr*. **1980**, *92*(21), 181165*a*.
(13) Hettler, H. *Z. Anal. Chem*. **1966**, *9*, 220.
(14) Vogel, A. I. *Practical Organic Chemistry*, 3rd ed; Longman: London, 1974; p 978.
(15) Conley, R. T. *Infrared Spectroscopy*; Allyn and Bacon: Boston, 1966.
(16) Jackman, L. M.; Sternhell, S. *Application of NMR in Organic Chemistry*, 2nd ed.; Pergamon: New York, 1969.
(17) Ewing, D. F. *Org. Magn. Reson*. **1979**, *12*, 499.
(18) Levy, G. C.; Lichter, L. R.; Nelson, G. L. *Carbon-13 NMR Spectroscopy*, 2nd ed.; Wiley: New York, 1980; p 111.

Received for review October 6, 1986. Revised manuscript received March 2, 1987. Accepted April 24, 1987.

5-(Substituted benzamido)-2-chloro-3-methylpyridines

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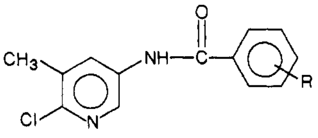
The preparation of 10 5-(substituted benzamido)-2-chloro-3-methylpyridines is described. These compounds were synthesized by the Schotten–Baumann reaction of 5-amino-2-chloro-3-methylpyridine with the appropriately substituted benzoyl chloride. Experimental and spectral data for the 10 compounds are presented.

5-Benzamido-2-chloro-3methylpyridine (1) has recently been shown to possess low level herbicidal properties toward certain types of barnyard grasses. In an effort to induce more significant activity, we have prepared a series of derivatives with a variety of substituents on the benzene ring.



Experimental Section

Elemental analyses (C, H, N) in agreement with theoretical values were obtained by Galbraith Laboratories, Knoxville, TN, and were submitted for review. Melting points were taken on a Mel-Temp apparatus and are uncorrected (Table I). Infrared spectra were obtained on a Perkin-Elmer 337 spectrophotometer with samples prepared as KBr disks. Proton nuclear magnetic resonance spectra were obtained in either deuteriochloroform or acetone-d_6 on a Varian Em-360 instrument with tetramethylsilane as internal standard.

***Benzamido Derivative Formation*: *General Procedure*.** A mixture of 5-amino-2-chloro-3-methylpyridine (2) (0.5 g, 0.0035 mol), the appropriately ring-substituted benzoyl chloride (1.0 mL), and 10% sodium hydroxide (10 mL) in a 25-mL glass-stoppered flask was agitated vigorously on a mechanical shaker for 15 min. In some cases it was necessary to stop the shaker intermittently in order to pulverize the oily solid with a spatula.

Table I. Experimental and Spectral Data[a] for 5-(Substituted benzamido)-2-chloro-3-methylpyridines

compd	R	yield, %	mp, °C	IR, ν, cm^{-1}
I	*m*-Br	61	146–147	3300, 1658, 1582, 1527, 1460, 1299, 1205, 1147, 1053, 877.2, 799.4, 720.5
II	*o*-Cl	86	133–134	3236, 1658, 1587, 1506, 1385, 1302, 1044, 867.3, 736.4, 718.9
III	*p*-Cl	87	193–194	3300, 1675, 3268, 1648, 1592, 1524, 1486, 1272, 1053, 990.1, 873.4 839.6, 741.8, 716.9
IV	*m*-Cl	86	144–146	3268, 1648, 1527, 1412, 1311, 1269, 1054, 881.1, 805.2, 778.2, 711.7
V	*p*-F	97	193–194	3290, 1653, 1603, 1582, 1531, 1506, 1235, 1224, 1136, 1050, 873.4, 847.5, 719.4
VI	*o*-F	88	116–117	3378, 1664, 1580, 1520, 1481, 1449, 1294, 1224, 1149, 1071, 1048, 892.9, 871, 809.7, 765.5, 740.7, 714.8
VII	*m*-NO_2	78	224–226	3290, 1661, 1531, 1462, 1403, 1350, 1319, 1284, 1148, 1052, 897.7, 848.9, 807, 717.9
VIII	*m*-F	86	144–145	3322, 1650, 1592, 1522, 1290, 1182, 1058, 829.9, 827.8, 793.7, 718.9
IX	*p*-CF_3	87	207–209	3311, 1658, 1605, 1585, 1534, 1464, 1414, 1332, 1138, 1100, 1080, 1000, 874.9, 849.6, 832.6, 764.5, 722
X	*p*-Br	75	188–190	3290, 1648, 1592, 1524, 1401, 1309, 1151, 1053, 996, 873.4, 829.2, 740.7, 720.5

[a] Proton NMR spectra for all compounds revealed a 3 H singlet for the methyl protons in the range δ 2.30 to 2.50 and the aromatic and amido protons as a composite 7 H multiplet in the range δ 7.00 to 8.90.

0021-9568/87/1732-0393$01.50/0