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Received for review June 12, 1985. Accepted August 19, 1985. A portion of this research has been supported by Public Health Service Grant R01-GM-30735 from the National Institute of General Medical Science. The execution of this research was also assisted by Institutional Research Grants from the National Science Foundation for the purchase of a mass spectrometer and a Fourier transform NMR spectrometer.

Supplementary Material Available: Descriptions of the preparation and purification of each of the compounds listed in Table I (22 pages). Ordering information is given on any masthead page.

Preparation of New 9-Alkylthio-1,2,3,4-tetrahydroacridine Monomers and Dimers

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New compounds related to 1,2,3,4-tetrahydroacridine have been prepared and characterized. These monomeric as well as dimeric derivatives are of specific interest with respect to parasites.

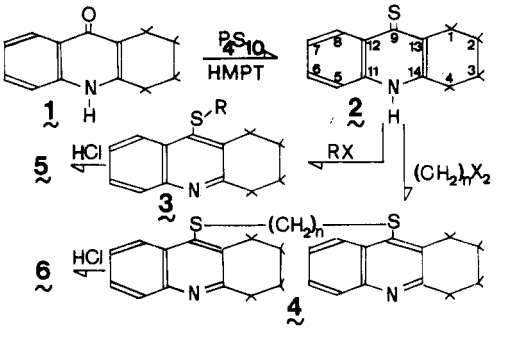
From a chemical point of view, there are no extensive studies about 1,2,3,4-tetrahydro-9-acridanones. Moreover, pharmacological properties of these compounds are not yet well-known, although antimalarials have been pointed out in this series (*1*). In addition, it must be emphasized that results concerning the 9-thio-substituted derivatives are the rarest among those of the compounds under discussion, despite the biological interest of the thio group.

That is why we were interested in the preparation of the following 9-thioalkyl-1,2,3,4-tetrahydroacridines, **3**, and 9,9′-dithio-1,2,3,4-tetrahydroacridinyl-α,ω-alkanes, **4**, within our researches into antiparasitics.

Results regarding **3** are gathered in Table I while results regarding **4** are collected in Table II. In addition ^{13}C NMR data concerning hydrochlorides are presented in Table III.

These compounds were prepared in good yield by using phase-transfer catalysis as previously done with other acridinics (*2–4*). Starting materials were either mono- or dihalogenoalkanes and 9-thio-1,2,3,4-tetrahydroacridanone (**2**). The latter has been prepared from 1,2,3,4-tetrahydro-9-acridanone (**1**) by means of phosphorus pentasulfide thiation (*5*) (Scheme I). The synthetic pathway proposed herein is a very convenient one for the preparation of antiamoebic or trypanocidal drugs (*6*).

Scheme I



General Procedure

A stirred mixture of 9-thio-1,2,3,4-tetrahydroacridanone (**2**) (10 mmol), alkylating agents (5 mmol in the case of **4**; 25 mmol in the case of **3**), triethylbenzylammonium chloride (3 mmol),

0021-9568/86/1731-0127$01.50/0

Table I. 9-Thioalkoxy-1,2,3,4-tetrahydroacridine Bases, 3, and Hydrochlorides, 5

compd	R	yield, %	mp, °C	mol formula[a]	^{1}H NMR ($CDCl_3$/Me_4Si_{int})[b] δ, ppm
3a	CH_3	68	65	$C_{14}H_{15}NS$ (229.4)	8.7 (m, 1 H); 8.4 (m, 1 H); 7.7 (m, 2 H); 3.7 (m, 2 H); 3.2 (m, 2 H); 2.6 (s, 3 H); 2.0 (m, 4 H)
3e	CH_2–C_6H_5	82	97	$C_{20}H_{19}NS$ (305.4)	8.5 (d, 1 H); 8.0 (d, 1 H); 7.6 (m, 2 H); 7.2 (*c*, 3 H); 7.0 (s, 2 H); 3.9 (s, 2 H); 3.1 (*c*, 2 H); 2.8 (*c*, 2 H); 1.9 (*c*, 2 H); 1.7 (*c*, 2 H)
3f	CH_2–(Cl-2′)–C_6H_4	79	86	$C_{20}H_{18}ClNS$ (339.9)	8.45 (d, 1 H); 8.0 (d, 1 H); 7.6–6.4 (m, 6 H); 4.0 (s, 2 H); 3.1 (t, 2 H); 2.85 (t, 2 H); 1.9–1.6 (m, 4 H)
3g	CH_2–(Cl-3′)–C_6H_4	76	90	$C_{20}H_{18}ClNS$ (339.9)	8.4 (d, 1 H); 8.0 (d, 1 H); 7.6 (m, 2 H); 7.2–6.6 (m, 4 H); 3.85 (s, 2 H); 3.15 (t, 2 H); 2.85 (t, 2 H); 1.9 (m, 2 H); 1.7 (m, 2 H)
3h	CH_2–(Cl-4′)–C_6H_4	77	110	$C_{20}H_{18}ClNS$ (339.9)	8.4 (d, 1 H); 8.0 (d, 1 H); 7.6 (m, 2 H); 6.9 (d, 2 H); 6.6 (d, 2 H); 3.85 (s, 2 H); 3.1 (t, 2 H); 2.8 (t, 2 H); 2.0–1.6 (m, 4 H)
5a	CH_3	60	212	$C_{14}H_{16}ClNS$ (265.8)	8.95 (d, 1 H); 8.5 (d, 1 H); 8.0–7.7 (m, 2 H); 3.7 (s, 2 H); 3.2 (s, 2 H); 2.6 (s, 3 H); 2.0 (s, 4 H)
5b	C_5H_{11}	66	158	$C_{18}H_{24}ClNS$ (321.9)	9.0 (d, 1 H); 8.6 (d, 1 H); 8.0–7.7 (m, 2 H); 3.7 (*c*, 2 H); 3.2 (*c*, 2 H); 3.0 (t, 2 H); 2.0 (c, 4 H); 1.6 (m, 2 H); 1.4 (m, 4 H); 0.9 (t, 3 H)
5c	C_8H_{17}	53	138	$C_{21}H_{30}ClNS$ (363.9)	9.0 (d, 1 H); 8.6 (d, 1 H); 8.0–7.7 (m, 2 H); 3.7 (*c*, 2 H); 3.2 (*c*, 2 H); 3.0 (t, 2 H); 2.0 (*c*, 4 H); 1.6 (m, 2 H); 1.4–1.1 (m, 10 H); 0.9 (t, 3 H)
5d	$C_{10}H_{21}$	77	127	$C_{23}H_{34}ClNS$ (392.0)	9.0 (d, 1 H); 8.6 (d, 1 H); 8.0–7.7 (m, 2 H); 3.7 (*c*, 2 H); 3.2 (*c*, 2 H); 3.0 (t, 2 H); 2.0 (*c*, 4 H); 1.6 (m, 2 H); 1.4–1.1 (m, 14 H); 0.9 (t, 3 H)
5e	CH_2–C_6H_5	65	180	$C_{20}H_{20}ClNS$ (341.9)	8.95 (d, 1 H); 8.55 (d, 1 H); 8.0–7.75 (m, 2 H); 7.2–6.7 (m, 5 H); 4.2 (s, 2 H); 3.6 (t, 2 H); 2.95 (t, 2 H); 1.8 (m, 4 H)
5f	CH_2–(Cl-2′)–C_6H_4	69	186	$C_{20}H_{19}Cl_2NS$ (376.3)	8.9 (d, 1 H); 8.55 (d, 1 H); 8.0–7.75 (m, 2 H); 7.4–7.0 (m, 3 H); 6.7 (d, 1 H); 4.2 (s, 2 H); 3.65 (t, 2 H); 2.0–1.7 (m, 4 H)
5g	CH_2–(Cl-3′)–C_6H_4	66	182	$C_{20}H_{19}Cl_2NS$ (376.3)	9.0 (d, 1 H); 8.6 (d, 1 H); 8.0–7.8 (m, 2 H); 7.2–7.0 (m, 3 H); 6.6 (d, 1 H); 4.1 (s, 2 H); 3.65 (t, 2 H); 3.0 (t, 2 H); 1.9 (m, 4 H)
5h	CH_2–(Cl-4′)–C_6H_4	65	197	$C_{20}H_{19}Cl_2NS$ (376.3)	9.0 (d, 1 H); 8.45 (d, 1 H); 8.0–7.8 (m, 2 H); 7.2 (d, 2 H); 6.85 (d, 2 H); 4.15 (s, 2 H); 3.6 (t, 2 H); 2.0–1.8 (m, 4 H)
5i	CH_2–(CF_3-3′)–C_6H_4	68	184	$C_{21}H_{19}F_3ClNS$ (409.9)	8.9 (d, 1 H); 8.5 (d, 1 H); 8.0–7.7 (m, 2 H); 7.5–7.0 (m, 4 H); 4.2 (s, 2 H); 3.6 (t, 2 H); 3.0 (t, 2 H); 2.0–1.7 (m, 4 H)
5j	$(CH_2)_2$–$N(CH_3)_2$	72	250	$C_{17}H_{24}Cl_2N_2S$ (359.4)	8.6 (m, 1 H); 8.4 (m, 1 H); 7.8 (7, 2 H); 3.7 (m, 2 H); 3.5–3.3 (m, 6 H); 2.8 (s, 6 H); 2.0 (m, 4 H)
5k	$(CH_2)_3$–$N(CH_3)_2$	60	213	$C_{18}H_{26}Cl_2N_2S$ (373.4)	8.8 (d, 1 H); 8.6 (d, 1 H); 7.8 (m, 2 H); 3.6 (m, 2 H); 3.2 (m, 6 H); 2.8 (s, 6 H); 2.2 (m, 2 H); 2.0 (m, 4 H)
5l	$(CH_2)_2$–$N(C_2H_5)_2$	64	220	$C_{19}H_{28}Cl_2N_2S$ (387.4)	8.4 (d, 1 H); 8.2 (d, 1 H); 7.8 (m, 2 H); 3.4 (m, 2 H); 3.2 (m, 4 H); 3.0 (m, 6 H); 2.0 (m, 4 H); 1.2 (t, 6 H)
5m	$(CH_2)_2$–N [$CH(CH_3)_2$]$_2$	61	215	$C_{21}H_{32}Cl_2N_2S$ (415.4)	8.6 (m, 2 H); 7.8 (m, 2 H); 3.9 (m, 2 H); 3.6 (m, 4 H); 3.3 (m, 2 H); 3.1 (m, 2 H); 2.0 (m, 4 H); 1.2 (dd, 12 H)

[a] The microanalyses, submitted for review, are in satisfactory agreement with the calculated values. [b] Recorded with a Bruker AM 200 spectrometer. [c] Unresolved signal.

Table II. α,ω-Bis(9-thio-1,2,3,4-tetrahydroacridinyl)alkane Bases, 4, and Hydrochlorides, 6

compd	*n*	yield, %	mp, °C	mol formula[a]	^{1}H NMR ($CDCl_3$/Me_4Si_{int})[b] δ, ppm
4b	4	69	169	$C_{30}H_{32}N_2S_2$ (484.7)	8.4 (d, 2 H); 8.0 (d, 2 H); 7.7–7.4 (m, 4 H); 3.1 (m, 8 H); 2.7 (m, 4 H); 1.9 (m, 8 H); 1.6 (q, 4 H)
4c	5	72	127	$C_{31}H_{34}N_2S_2$ (498.7)	8.5 (d, 2 H); 7.7 (d, 2 H); 7.5–7.3 (m, 4 H); 3.1 (m, 8 H); 2.9 (*c*, 4 H); 2.0–1.8 (m, 8 H); 1.4 (*c*, 6 H)
4d	6	78	124	$C_{32}H_{36}N_2S_2$ (512.7)	8.5 (d, 2 H); 7.9 (d, 2 H); 7.6–7.4 (m, 4 H); 3.1 (m, 8 H); 2.8 (m, 4 H); 2.0 (m, 8 H); 1.4 (m, 8 H)
6a	3	66	226	$C_{29}H_{32}Cl_2N_2S_2$ (543.6)	8.85 (d, 2 H); 8.4 (d, 2 H); 8.0–7.7 (m, 4 H); 3.6 (t, 4 H); 3.1 (m, 8 H); 2.0 (m, 8 H); 1.8 (q, 2 H)
6b	4	58	230	$C_{30}H_{34}Cl_2N_2S_2$ (557.6)	8.85 (d, 2 H); 8.5 (d, 2 H); 8.0–7.7 (m, 4 H); 3.7 (m, 4 H); 3.2 (*c*, 4 H); 2.95 (*c*, 4 H); 1.9 (m, 8 H); 1.6 (*c*, 4 H)
6c	5	64	150	$C_{31}H_{36}Cl_2N_2S_2$ (571.6)	8.9 (d, 2 H); 8.5 (d, 2 H); 8.0–7.75 (m, 4 H); 3.7 (*c*, 4 H); 3.2 (*c*, 4 H); 3.0 (m, 4 H); 2.0 (m, 8 H); 1.6 (m, 6 H)
6d	6	70	187	$C_{32}H_{38}Cl_2N_2S_2$ (585.6)	9.0 (d, 2 H); 8.55 (d, 2 H); 7.7 (m, 4 H); 3.7 (*c*, 4 H); 3.2 (*c*, 4 H); 3.0 (m, 4 H); 2.0 (*c*, 8 H); 1.5–1.3 (m, 8 H)
6e	7	66	172	$C_{33}H_{40}Cl_2N_2S_2$ (599.7)	8.95 (d, 2 H); 8.55 (d, 2 H); 7.9 (m, 4 H); 3.7 (*c*, 4 H); 3.2 (*c*, 4 H); 3.05 (m, 4 H); 2.0 (m, 8 H); 1.6–1.3 (m, 10 H)
6f	8	63	162	$C_{34}H_{42}Cl_2N_2S_2$ (613.7)	8.95 (d, 2 H); 8.6 (d, 2 H); 7.9 (m, 4 H); 3.7 (*c*, 4 H); 3.25 (*c*, 4 H); 3.0 (m, 4 H); 2.0 (m, 8 H); 1.6–1.25 (m, 12 H)
6g	10	57	160	$C_{36}H_{46}Cl_2N_2S_2$ (641.7)	8.9 (d, 2 H); 8.5 (d, 2 H); 8.0–7.7 (m, 4 H); 3.7 (m, 4 H); 3.2 (m, 4 H); 3.0 (m, 4 H); 2.0 (m, 8 H); 1.6–1.0 (m, 16 H)
6h	12	48	150	$C_{38}H_{50}Cl_2N_2S_2$ (669.8)	8.9 (d, 2 H); 8.55 (d, 2 H)); 8.0–7.7 (m, 4 H); 3.7 (m, 4 H); 3.2 (m, 4 H); 3.0 (m, 4 H); 2.0 (m, 8 H); 1.6–1.0 (m, 20 H)

[a] The microanalyses, submitted for review, are in satisfactory agreement with the calculated values. [b] Recorded with a Bruker AM 200 spectrometer. [c] Unresolved signal.

aqueous 50% potassium hydroxide (50 mL), and toluene (100 mL) is refluxed for 2 h. The toluene layer is separated, washed 5 times with water (50 mL every time), dried with sodium sulfate, and evaporated in vacuo. The residual oil is washed with ether and dissolved in a small amount of ethanol. Concentrated hydrochloric acid is dropped until it is a fully acidic medium.

Table III. ^{13}C NMR Data

compd	chemical shifts[a] ($CDCl_3/Me_4Si_{int}$), ppm
5a	29.1 (C-1); 20.6 (C-2); 21.9[b] (C-3); 28.4 (C-4); 121.6 (C-5); 133.1 (C-6); 129.2 (C-7); 126.4 (C-8); 156.8 (C-9); 136.4_5 (C-11); 128.3 (C-12); 135.7_5 (C-13); 155.2 (C-14)
5c	29.1 (C-1); 20.7[c] (C-2); 22.0[c] (C-3); 28.6 (C-4); 122.2 (C-5); 133.2 (C-6); 129.2 (C-7); 126.5_5 (C-8); 155.7 (C-9); 136.3 (C-11); 129.1 (C-12); 136.8 (C-13); 155.4 (C-14); 37.5 (CH_2-1′); 30.4 (CH_2-2′); 29.0_5[d] (CH_2-3′); 29.0[d] (CH_2-4′); 28.6[d] (CH_2-5′); 31.7 (CH_2-6′); 22.6 (CH_2-7′); 14.0 (CH_3)
5d	29.1_5 (C-1); 20.8[e] (C-2); 22.1[e] (C-3); 28.7 (C-4); 122.1 (C-5); 133.2 (C-6); 129.2 (C-7); 126.6 (C-8); 155.7 (C-9); 136.4 (C-11); 129.2 (C-12); 136.8 (C-13); 155.4 (C-14); 37.5 (CH_2-1′); 30.4 (CH_2-2′); 28.6[f] (CH_2-3′); 28.6[f] (CH_2-4′); 29.4[f] (CH_2-5′); 29.0[f] (CH_2-6′); 29.1_5[f] (CH_2-7′); 31.9 (CH_2-8′); 22.6_5 (CH_2-9′); 14.0_5 (CH_3)
5e	29.1 (C-1); 20.4_5[g] (C-2); 21.7[g] (C-3); 28.4 (C-4); 121.7 (C-5); 133.1 (C-6); 129.5 (C-7); 126.6 (C-8); 155.7 (C-9); 136.5 (C-11); 129.3 (C-12); 137.9 (C-13); 155.7 (C-14); 41.4 (CH_2-1′); 136.2 (C_{arom}1″); 128.5 (C_{arom}2″); 128.5 (C_{arom}3″); 127.9 (C_{arom}4″)
5j	28.9 (C-1); 20.0_5[h] (C-2); 21.3[h] (C-3); 28.1 (C-4); 120.9 (C-5); 132.8 (C-6); 12..1 (C-7); 126.5_5 (C-8); 151.9 (C-9); 136.3 (C-11); 128.3 (C-12); 137.1 (C-13); 156.3 (C-14); 33.2_5 (CH_2-1′); 24.5 (CH_2-2′); 55.0 (CH_2-3′); 41.9 (CH_3)
5k	29.1 (C-1); 20.2[i] (C-2); 21.4[i] (C-3); 28.2 (C-4); 121.6 (C-5); 132.7 (C-6); 129.1 (C-7); 126.4 (C-8); 149.2 (C-9); 137.2 (C-11); 128.7 (C-12); 137.7 (C-13); 156.8 (C-14); 29.4 (CH_2-1′); 55.3 (CH_2-2′); 41.8 (CH_3)
6a	29.4_5 (C-1); 20.7[j] (C-2); 22.0[j] (C-3); 28.7 (C-4); 122.6 (C-5); 133.0 (C-6); 129.3 (C-7); 126.1 (C-8); 153.0 (C-9); 136.7 (C-11); 129.0 (C-12); 137.4 (C-13); 156.1 (C-14); 35.3_5 (CH_2-α,α'); 30.9 (CH_2-β,β')
6b	29.2 (C-1); 20.7[k] (C-2); 22.0[k] (C-3); 28.7 (C-4); 122.4 (C-5); 133.3 (C-6); 129.4 (C-7); 126.2 (C-8); 154.0 (C-9); 136.6 (C-11); 129.0 (C-12); 1368 (C-13); 155.7_5 (C-14); 36.4 (CH_2-α,α'); 2995 (CH_2-β,β')
6c	29.2_5 (C-1); 20.7[l] (C-2); 22.0[l] (C-3); 28.7 (C-4); 122.2 (C-5); 133.3 (C-6); 129.3 (C-7); 126.4 (C-8); 155.0 (C-9); 136.5 (C-11); 129.0_5 (C-12); 136.8 (C-13); 155.6 (C-14); 37.0 (CH_2-α,α'); 29.9 (CH_2-β,β'); 27.7_5 (CH_2-γ,γ')
6d	29.1 (C-1); 20.7[m] (C-2); 22.0[m] (C-3); 28.7 (C-4); 122.1_5 (C-5); 133.3 (C-6); 129.3 (C-7); 126.5 (C-8); 155.3 (C-9); 136.4 (C-11); 129.1 (C-12); 136.8 (C-13); 155.5 (C-14); 37.1_5 (CH_2-α,α'); 30.2_5 (CH_2-β,β'); 28.2 (CH_2-γ,γ')

[a] Recorded with a Bruker AM 200 spectrometer. [b-m] These attributions may be commuted.

Hydrochloride is precipitated by addition of ether in a wide quantity. The salt is recrystallized from either an ethanol–ether mixture or an ethanol–acetone mixture.

Acknowledgment

The authors thank J. C. Gastaud for the technical assistance.

Registry No. **2**, 82791-68-2; **3a**, 99053-30-2; **3e**, 99053-52-8; **3f**, 99053-53-9; **3g**, 99053-54-0; **3h**, 99053-55-1; **4b**, 99053-56-2; **4c**, 99053-57-3; **4d**, 99053-58-4; **5a**, 99053-31-3; **5b**, 99053-32-4; **5c**, 99053-33-5; **5d**, 99053-34-6; **5e**, 99053-35-7; **5f**, 99053-36-8; **5g**, 99053-37-9; **5h**, 99053-38-0; **5i**, 99053-39-1; **5j**, 99053-40-4; **5k**, 99053-41-5; **5l**, 99053-42-6; **5m**, 99053-43-7; **6a**, 99053-44-8; **6b**, 99053-45-9; **6c**, 99053-46-0; **6d**, 99053-47-1; **6e**, 99053-48-2; **6f**, 99053-49-3; **6g**, 99053-50-6; **6h**, 99053-51-7; CH_3Br, 74-83-9; $C_5H_{11}Br$, 110-53-2; $C_8H_{17}Br$, 111-83-1; $C_{10}H_{21}Br$, 112-29-8; $BrCH_2C_6H_5$, 100-39-0; 2-$BrCH_2C_6H_4Cl$, 611-17-6; 3-$BrCH_2C_6H_4Cl$, 766-80-3; 4-$BrCH_2C_6H_4Cl$, 622-95-7; 3-$BrCH_2C_6H_4CF_3$, 402-23-3; $Br(CH_2)_2N(CH_3)_2$, 5459-68-7; $Br(CH_2)_3N(CH_3)_2$, 53929-74-1; $Br(CH_2)_2N(CH_2CH_3)_2$, 5392-81-4; $Br(CH_2)_2N(CH(CH_3)_2)_2$, 90221-88-8; $Br(CH_2)_3Br$, 109-64-8; $Br(CH_2)_4Br$, 110-52-1; $Br(CH_2)_5Br$, 111-24-0; $Br(CH_2)_6Br$, 629-03-8; $Br(CH_2)_7Br$, 4549-31-9; $Br(CH_2)_8Br$, 4549-32-0; $Br(CH_2)_{10}Br$, 4101-68-2; $Br(CH_2)_{12}Br$, 3344-70-5.

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Received for review May 29, 1985. Accepted July 19, 1985. This work was partially supported by a grant of the C.N.R.S. (PIRMED program 06931-1051).

Picrates of Some Ring-Substituted 2-Amino- and 3-Aminopyridines

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The preparation of the picrates of nine ring-substituted 2-amino- and 3-aminopyridines is described. Melting points and methods of purification are also presented.

In past years we have prepared various ring-substituted 2-amino- and 3-aminopyridines as synthetic intermediates. Since picrates are one of the better qualitative analytical derivatives for amines, and since the picrate derivatives for the aforementioned aminopyridines have never been reported, we now wish to report the preparation and melting points of these picrates.

Elemental analyses (C, H, N) in agreement with theoretical values, and which confirm 1:1 stoichiometry for the picrate salts, were obtained and submitted for review. Experimental data for the picrates are reported in Table I.

Experimental Section

Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Melting points were taken on a Mel-Temp apparatus and are uncorrected.

Picrate Formation—General Procedure. The appropriate aminopyridine (0.005 mol) was dissolved in absolute ethanol (35

0021-9568/86/1731-0129$01.50/0