Compound **4c** was obtained in 18% yield: mp 229–230 °C (ether–chloroform); ^{1}H NMR ($CDCl_3$) δ 2.20 (s, 6 H, 2 CH_3), 2.36 (s, 3 H, CH_3), 2.94 (s, 3 H, CH_3SO_2), 7.0–8.2 (3 m, 9 aromatic H); mass spectrum, *m/e* (rel intensity) 435 (62, $M^{+\cdot}$), 371 (11, $M^{+\cdot} - SO_2$), 356 (7, $M^{+\cdot} - CH_3SO_2$), 294 (4, $M^{+\cdot} - PhSO_2$), 292 (100, $M^{+\cdot} - CH_3SO_2 - SO_2$), 173 (57), 133 (8.5, $CH_3C_6H_4NCO^{+\cdot}$). Anal. Calcd for $C_{19}H_{21}N_3O_5S_2$ (mol wt 435): C, 52.41; H, 4.83; N, 9.66. Found: C, 52.37; H, 4.85; N, 9.62.

In order to determine the product distribution under various conditions (Table I), we used the same procedure, and the reaction mixture was analyzed by ^{1}H NMR.

Reaction of 1 with Carbethoxy Isothiocyanate. A solution of **1** (0.002 mol) and a tenfold excess of carbethoxy isothiocyanate in 5 mL of dry chloroform was stirred at room temperature for 16 h. After removal of the solvent and the excess of isothiocyanate in vacuo, the residue was triturated with 20 mL of ether–hexane to give **7a** in 78% yield: mp 122–123 °C (ether–hexane); ^{1}H NMR ($CDCl_3$) δ 1.42 (t, 3 H, CH_3), 2.12 (s, 6 H, 2 CH_3), 2.42 (s, 3 H, CH_3), 2.92 (s, 3 H, CH_3SO_2), 4.44 (q, 2 H, CH_2), 7.04 and 7.28 (2 d, 4 aromatic H); mass spectrum, *m/e* (rel intensity) 383 (100, $M^{+\cdot}$), 310 (4, $M^{+\cdot} - EtCO_2$), 234 (2, $M^{+\cdot} - CH_3C_6H_4NCS$), 173 (5), 149 (5, $CH_3C_6H_4NCS^{+\cdot}$). Anal. Calcd for $C_{16}H_{21}N_3O_4S_2$ (mol wt 383): C, 50.13; H, 5.48; N, 10.97. Found: C, 50.02; H, 5.48; N, 10.95.

Reaction of 1 with Phenylsulfonyl Isothiocyanate. Equimolar amounts (0.002 mol) of **1** and phenylsulfonyl isothiocyanate were stirred in 5 mL of chloroform at room temperature for 1 day. The solvent was then removed under reduced pressure, and the white residue was crystallized from carbon tetrachloride–chloroform to give **7b** in 94% yield: mp 262–263 °C; ^{1}H NMR (Me_2SO-d_6, HMDS) δ 2.28 (s, 9 H, 3 CH_3), 2.88 (s, 3 H, CH_3SO_2), 7.0–8.2 (3 m, 9 aromatic H); mass spectrum, *m/e* (rel intensity) 451 (0.2, $M^{+\cdot}$), 387 (52, $M^{+\cdot} - SO_2$), 372 (6, $M^{+\cdot} - CH_3SO_2$), 310 (6, $M^{+\cdot} - PhSO_2$), 308 (100, $M^{+\cdot} - SO_2 - CH_3SO_2$), 173 (55), 149 (8, $CH_3C_6H_4NCS^{+\cdot}$), 131 (14, $CH_3C_6H_4NCN^{+}$). Anal. Calcd for $C_{19}H_{21}N_3O_4S_3$ (mol wt 451): C, 50.55; H, 4.66; N, 9.31. Found: C, 50.48; H, 4.59; N, 9.30.

Reaction of 1 with *tert*-Butylcyanoketene. *tert*-Butylcyanoketene was generated by thermolysis of 2,5-di-*tert*-butyl-3,6-diazidobenzoquinone (0.75 mmol) in 10 mL of dry benzene for 1 h.[8] After the mixture was cooled to room temperature, **1** (1.5 mmol) was added, and the solution was stirred at room temperature for 1 day. The ^{1}H NMR spectrum of the reaction mixture showed the presence of **8a** and **5** in a ratio of 3:1. Purification of the reaction residue by column chromatography on silica gel with ether–hexane as the eluent furnished pure **8a** in 70% yield: mp 215.5–216.5 °C (chloroform–ether); ^{1}H NMR ($CDCl_3$) δ 1.26 (s, 9 H, *t*-Bu), 1.98 (s, 6 H, 2 CH_3), 2.44 (s, 3 H, CH_3), 2.88 (s, 3 H, CH_3SO_2), 7.0–7.4 (2 d, 4 aromatic H); mass spectrum, *m/e* (rel intensity) 375 (37, $M^{+\cdot}$), 360 (100, $M^{+\cdot} - CH_3$), 252 (13, $M^{+\cdot}$ – *t*-Bu(CN)C=C=O), 173 (11), 107 (20, *t*-Bu(CN)C=$C^{+\cdot}$). Anal. Calcd for $C_{19}H_{25}N_3O_3S$ (mol wt 375): C, 60.80; H, 6.67; N, 11.20. Found: C, 60.69; H, 6.73; N, 11.20.

Reaction of 1 with Diphenylketene. A solution of **1** (0.002 mol) and a threefold excess of diphenylketene in 5 mL of dry chloroform was stirred at room temperature for 7 h. After removal of the solvent the residue was chromatographed on silica gel with ether–hexane as the eluent to give **8b** in 98% yield: mp 151–152 °C (ether–hexane); ^{1}H NMR ($CDCl_3$) δ 2.00 (s, 6 H, 2 CH_3), 2.18 (s, 3 H, CH_3), 2.84 (s, 3 H, CH_3SO_2), 6.6–7.4 (2 m, 14 aromatic H); mass spectrum, *m/e* (rel intensity) 446 (98, $M^{+\cdot}$), 252 (100, $M^{+\cdot} - Ph_2CCO$), 194 (14, $Ph_2CCO^{+\cdot}$), 173 (55), 166 (17, $Ph_2C^{+\cdot}$). Anal. Calcd for $C_{26}H_{26}N_2O_3S$ (mol wt 446): C, 69.96; H, 5.83; N, 6.28. Found: C, 70.01; H, 5.89; N, 6.20.

Acknowledgment. The authors are indebted to the University for a postdoctoral fellowship to C.-C.Y. Financial support from the Ministry of National Education is gratefully acknowledged.

Registry No. 1, 66255-50-3; **3a**, 62962-34-9; **3b**, 71436-55-0; **3c**, 71436-56-1; **4a**, 71436-57-2; **4c**, 71436-58-3; **5**, 62962-31-6; **6**, 62962-36-1; **7a**, 71436-59-4; **7b**, 71436-60-7; **8a**, 71436-61-8; **8b**, 71436-62-9; phenylsulfonyl isocyanate, 2845-62-7; phenyl isocyanate, 103-71-9; benzoyl isocyanate, 4461-33-0; benzamide, 55-21-0; carbethoxy isothiocyanate, 16182-04-0; phenylsulfonyl isothiocyanate, 1424-53-9; *tert*-butylcyanoketene, 29342-22-1; 2,5-di-*tert*-butyl-3,6-diazidobenzoquinone, 29342-21-0; diphenylketene, 525-06-4.

(8) H. W. Moore and W. Weyler, *J. Am. Chem. Soc.*, **92**, 4132 (1970); **93**, 2812 (1971).

Facile Entry into the Thiazolo[3,2-*a*]indol-3(2*H*)-one System via an Unusual Reaction with Thionyl Chloride[1a]

H. D. Hollis Showalter,*[1b] Mohammed T. Shipchandler, and Lester A. Mitscher

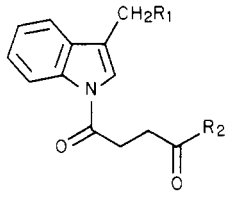
Division of Natural Products Chemistry, The Ohio State University, Columbus, Ohio 43210

Edward W. Hagaman

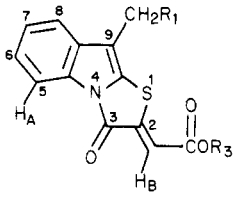
Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

Received May 14, 1979

During the course of our synthetic investigations into the canthin-6-one series[2] we treated γ-oxo-3-[(methoxycarbonyl)methyl]-1*H*-indole-1-butanoic acid (**1a**) with oxalyl chloride to give the acid chloride **1b** which was used without isolation in a Friedel–Crafts intramolecular cyclization. However, similar reaction of **1a** with refluxing thionyl chloride followed by methanol treatment did not give the expected methyl ester **1c** but instead gave orange fibrous needles of **2a** in 20% yield. This represents only



1a, $R_1 = CO_2CH_3$; $R_2 = OH$
b, $R_1 = CO_2CH_3$; $R_2 = Cl$
c, $R_1 = CO_2CH_3$; $R_2 = OCH_3$
d, $R_1 = H$; $R_2 = OH$



2a, $R_1 = CO_2CH_3$; $R_3 = CH_3$
b, $R_1 = H$; $R_3 = CH_3$
c, $R_1 = H$; $R_3 = CH_2C(CH_3)_3$

the second documented entry into this class of tricyclic heterocycles and serves as a convenient synthetic alternative to the procedure of Ficken and Kendall[3] into this relatively inaccessible ring system. The corresponding reaction of γ-oxo-3-methyl-1*H*-indole-1-butanoic acid (**1d**) with thionyl chloride followed by quenchings with methanol or neopentyl alcohol led respectively to **2b** (62%) and **2c** (63%).

The unequivocal structural proof of **2** rests on its ^{1}H and ^{13}C NMR data along with comparison to **3** whose

(1) (a) Research sponsored in part by the Division of Chemical Sciences, U.S. Department of Energy, under Contract W-7405-eng-26 with the Union Carbide Corp. (b) Warner-Lambert/Parke-Davis Pharmaceutical Research Division, Ann Arbor, MI 48106.

(2) L. A. Mitscher, M. Shipchandler, H. D. H. Showalter, and M. S. Bathala, *Heterocycles*, **3**, 7 (1975).

(3) G. E. Ficken and J. D. Kendall, British Patent 874 809 (1961).

0022-3263/79/1944-3994$01.00/0

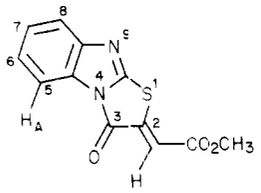
Table I. Chemical Shifts and Selected Long-Range Coupling Constants of 2 and 3[a]

carbon	2b ($^{n>1}J_{CH}$)	2c ($^{n>1}J_{CH}$)	$\Delta\delta$ [b]	3 ($^{n>1}J_{CH}$)
C(2)	146.9 (1.8)	146.5 (2.0)	+0.4	145.0
C(3)	158.4 (5.1)	158.4 (5.2)		157.4 (5.6)
C(4a)	133.0[c]	132.9[c]		130.1
C(5)	113.3	113.3		112.8
C(6)	125.0[c]	124.9[c]		126.4[c]
C(7)	124.2[c]	124.2[c]		124.9[c]
C(8)	118.5[c]	118.4[c]		120.0[c]
C(8a)	128.8	128.8		148.9
C(9)	112.3	112.2		
C(9a)	135.6[c]	135.5[c]		154.9
CH_3	8.3	8.4		
C(2)=CH	116.1	116.5	−0.4	121.4
ester C=O	166.2 (3.9)	165.9	+0.3	165.6 (3.9)
OCH_3	52.3			53.0
OCH_2		74.7		
$(CH_3)_3C$		26.3, 31.2		

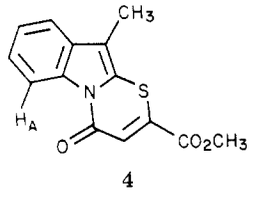
[a] Spectra determined in $CDCl_3$ solution. Chemical shifts are expressed on the Me_4Si scale: $\delta^{Me_4Si} = \delta^{CDCl_3} + 76.9$ ppm. [b] $\Delta\delta = \delta(2b) - \delta(2c)$. [c] Assignments in any vertical column may be interchanged.

synthesis[4-6] and structure elucidation by X-ray[5] and ^{13}C NMR spectroscopy[6] have been recently reported.[7]

In the ^1H NMR spectrum of **2b** the two methyl groups appear as singlets at δ 2.20 and 3.86. In addition, a one-proton sharp singlet (H_B) is present at δ 6.95. The presence of four aromatic protons, one of which appears as a downfield multiplet at δ 8.0 (H_A) and is close to the corresponding value (δ 7.9) for **3**, suggests structure **2b**, (*Z*)-methyl (9-methyl-3-oxothiazolo[3,2-*a*]indol-2(3*H*)-ylidene)acetate, as opposed to isomeric structure **4** whose



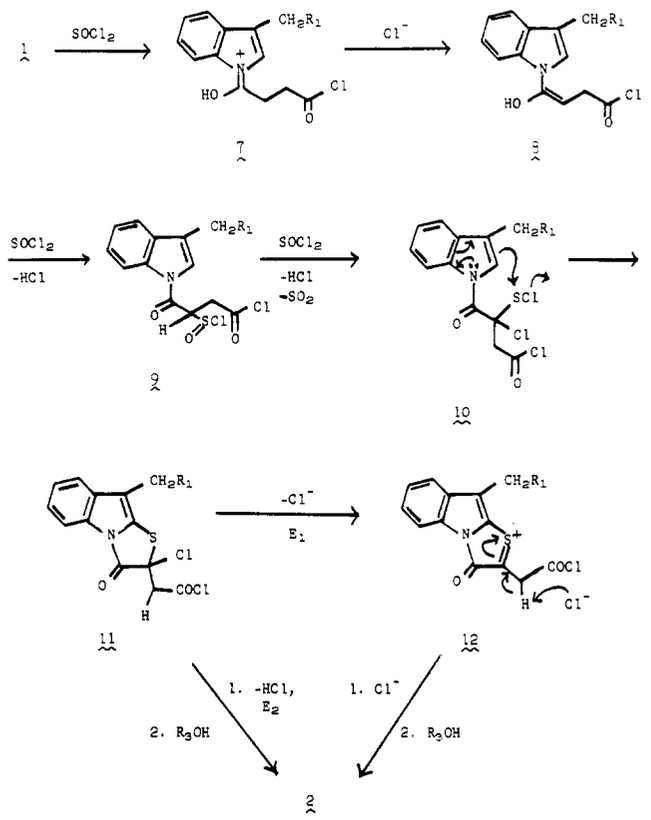
3



4

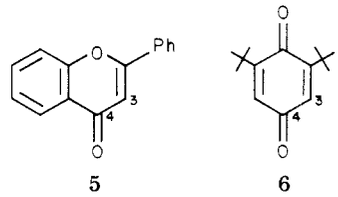
δ_{H_A} by analogy is predicted to be at lower field.[4,6] Further support for the assigned structure is provided by corroborative ^{13}C NMR data of **2b**, **2c**, and **3**, whose assignments are detailed in Table I. The assignment of structure **2** as opposed to isomeric **4** is based on the magnitude of the long-range C–H coupling constants in the unsaturated 1,4-dicarbonyl moiety. The ester and amide carbonyl resonances appear at lowest field in the spectra. The differentiation of these signals relies on the small, reproducible chemical shift perturbation of the ester carbonyl between **2b** and **2c** and is confirmed by the observation of a quartet ($^3J_{CH}$ = 3.9 Hz) and poorly resolved triplet ($\gamma_{1/2}$ = 7.5 Hz) for the ester carbonyl in **2b** and **2c**, respectively, in the coupled spectra.

Scheme I



The carbon resonances of the olefinic linkages also experience a small shift alteration between **2b** and **2c** which allows their direct assignment. In the coupled spectra the olefinic methine resonance is the only sharp one-bond doublet, indicating the absence of hydrogens two and three bonds removed from this site. The nonprotonated olefinic carbon appears as a well-resolved doublet ($^2J_{CH}$ = 1.8 Hz).

In **2b** and **2c** the amide carbonyl displays a single long-range coupling of 5 Hz. This value is in the range of three-bond C–H coupling constants and larger than normally observed for two-bond interactions.[8] For comparison, the two-bond coupling $^2J_{C(4)C(3)}$ in **5**[8] is 1.8 Hz and that in **6** is not resolved. $^3J_{C(1)H(3)}$ in **6** is 8.0 Hz and is typical of ^3J transmitted through a trans trigonal carbon path. Hence, the 5-Hz coupling constant of the amide carbonyl of **2** and the absence of additional resolved coupling to the ester carbonyl are compatible only with ring system **2**.



5 6

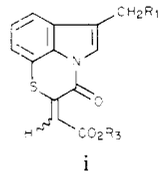
The coupled ^{13}C NMR spectrum of **3** reveals a 5.6-Hz coupling constant between the amide carbonyl and the

(4) L. V. Zav'yalova, N. K. Rozhkova, and K. L. Seitanidi, *Khim. Geterotsikl. Soedin.*, 11, 47 (1975); *Chem. Abstr.*, **83**, 9941 (1975).

(5) A. McKillop, G. C. A. Bellinger, P. N. Preston, A. Davidson, and T. J. King. *Tetrahedron Lett.*, 2621 (1978). Following submission of this manuscript, an article relating to McKillop's findings appeared in the literature. See J. J. Wade, *J. Org. Chem.*, **44**, 1816 (1979).

(6) K. Nagarajan, M. D. Nair, and J. A. Desai, *Tetrahedron Lett.*, 53 (1979).

(7) The possibility of substitution occurring at C-7 in the benzenoid ring of **1a** and **1d** is remote as C-2 is the most reactive position; thus structure i is ruled out.



i

Further substantiation is provided by unambiguous chemical shift and multiplicity data from the ^1H and ^{13}C NMR spectra.

(8) C.-J. Chang, *Lloydia*, **41**, 17 (1978).

olefinic proton. Since the orientation of the carbomethoxy substituent is known to be trans to the amide carbonyl,[6] the similar $^3J_{CH}$ values in **2** and **3** strongly suggest the former incorporates the fumarate geometry (*Z* isomer).

The unexpected generation of the tricyclic thiazoloindole system is representative of a number of recently reported cases in which thionyl chloride mediated chemistry has led to unanticipated results.[9-11] Literature reports of anomalous reactions of indole and 1-acylindole substrates with thionyl chloride are sparse.[12] Szmuszkovicz[13] reported the generation of indolyl sulfinyl chlorides, sulfides, and disulfides. Ohki and Nagasaka[14] found that thionyl chloride treatment of *N*-phthaloyl-7-acetyltryptophan followed by methanol led to the corresponding methyl ester, albeit in poor yield. Possible products resulting from sulfur incorporation were not reported.

Mechanistically, we postulate that the formation of **2** occurs by an oxidative mechanism, shown in Scheme I, that has substantial documentation, initially by Krubsack and Higa[15-17] and later by Ohoka.[18] Thionyl chloride treatment of **1** would lead to preferential iminium species **7**, the putative intermediate in the facile acid hydrolysis of *N*-acylindoles. Its isomerization to species **8** would lead to rapid electrophilic addition of thionyl chloride to give sulfinyl chloride **9**. Further addition of thionyl chloride followed by Pummerer-type rearrangement would lend the α-chlorosulfenyl chloride **10** whose subsequent ring closure and loss of HCl, by either an E_1- or an E_2-type mechanism, followed by ester formation would give the observed product. The question of stereospecific formation of the *Z* isomer must await further investigation.

Compounds **1a**, **1d**, **2a**, and **2b** showed no significant in vitro antibacterial activity when tested in an agar-dilution streak assay.[19]

Experimental Section

Melting points are uncorrected. Microanalyses were performed by Midwest Microlaboratories, Indianapolis, IN. IR spectra were recorded on a Perkin-Elmer Model 257 or Digilab FTS-14 instrument. UV spectra were taken on a Cary Model 15 or 118 recording spectrophotometer. Mass spectra were obtained from an AEI MS-9, Dupont 21-491, or Finnigan 1015 instrument operating at 70 eV. ^{1}H NMR spectra were recorded with a Varian A-60A or Bruker WH-90 (for compounds **2b** and **2c**) spectrometer. Chemical shifts are reported in δ units relative to tetramethylsilane. ^{13}C NMR spectra were obtained on a Varian FT-80 spectrometer operating at 18.8 kG and were recorded for 4000-Hz spectral widths. Proton–carbon coupling constants were determined by using the gated-decoupling technique[20] and possess ±0.6-Hz digital resolution in the frequency domain spectra.

γ-Oxo-3-[(methoxycarbonyl)methyl]-1*H*-indole-1-butanoic Acid (1a). To a stirred DMF suspension (50 mL) of NaH (1.30 g, 54.2 mmol) at 25 °C was added dropwise methyl 3-indolylacetate[21] (10.0 g, 52.9 mmol) in 75 mL of DMF. After stirring for 1 h at 25 °C, succinic anhydride (5.83 g, 58.3 mmol) in 75 mL of DMF was added dropwise and stirring continued for 24 h. The mixture was poured into 300 mL of H_2O and extracted with EtOAc (2 × 150 mL) to remove unreacted starting materials and organic impurities. The aqueous layer was adjusted to pH 2 with concentrated HCl and extracted with EtOAc (4 × 150 mL). The combined organic phases were washed with H_2O (4 × 300 mL) and brine (300 mL), dried over anhydrous $MgSO_4$, and evaporated in vacuo at 40 °C to leave 9.53 g of a solid residue which crystallized from 95% EtOH as white needles (8.86 g, 62%): mp 151–153 °C; UV (MeOH) λ_{max} 298 nm (log ϵ 3.85), 291 (3.80), 238 (4.26); IR (KBr) 3300–2500 (br), 1740, 1708, 1692 cm^{-1}; ^{1}H NMR (Me_2SO-d_6) δ 2.70 (m, 2 H), 3.20 (m, 2 H), 3.65 (s, 3 H), 3.80 (s, 3 H), 7.20–7.70 (m, 3 H), 7.83 (s, 1 H), 8.20–8.42 (m, 1 H); mass spectrum, *m/e* (rel intensity) 290 (3), 289 (M$^+$, 14), 189 (42), 131 (10), 130 (100), 101 (6).

Anal. Calcd for $C_{15}H_{15}NO_5$: C, 62.29; H, 5.22; N, 4.88. Found: C, 61.79; H, 5.16; N, 4.84.

γ-Oxo-3-methyl-1*H*-indole-1-butanoic acid (1d) was obtained from skatole by the same procedure described above in 56% yield (crystallization from EtOAc as white needles): mp 148–149 °C; UV (MeOH) λ_{max} 301 nm (log ϵ 3.91), 292 (3.87), 239 (4.33); IR (KBr) 3250–2400 (br), 1710, 1682 cm^{-1}; ^{1}H NMR (Me_2SO-d_6) δ 2.25 (s, 3 H), 2.73 (m, 2 H), 3.20 (m, 2 H), 6.90–7.80 (m, 4 H), 8.10–8.40 (m, 1 H); mass spectrum, *m/e* (rel intensity) 232 (4), 231 (M$^+$, 25), 131 (100), 130 (60).

Anal. Calcd for $C_{13}H_{13}NO_3$: C, 67.52; H, 5.67; N, 6.06. Found: C, 67.35; H, 5.63; N, 5.90.

(*Z*)-Methyl 2,3-Dihydro-2-(2-methoxy-2-oxoethylidene)-3-oxothiazolo[3,2-*a*]indole-9-acetate (2a). Acid **1a** (500 mg, 1.73 mmol) and $SOCl_2$ (10 mL) were refluxed for 5 h. After removal of excess $SOCl_2$ in vacuo, dry CH_3OH (50 mL) was added to the red residue and the mixture heated over a steam bath for 10 min. Evaporation of excess CH_3OH followed by silica gel column chromatography (elution with benzene) afforded 136 mg of a major component crystallized from EtOAc as orange fibers (116 mg, 20%): mp 164–165 °C; UV ($CHCl_3$) λ_{max} 433 nm (log ϵ 3.72), 284 (4.35); IR (KBr) 1740, 1728, 1685 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.66 (s, 2 H), 3.78 (s, 3 H), 3.90 (s, 3 H), 7.05 (s, 1 H), 7.20–7.50 (m, 3 H), 8.00–8.20 (m, 1 H); mass spectrum, *m/e* (rel intensity) 333 (6), 332 (8), 331 (M$^+$, 41), 273 (19), 272 (100), 244 (28), 212 (10).

Anal. Calcd for $C_{16}H_{13}NO_5S$: C, 57.99; H, 3.95; N, 4.22. Found: C, 57.57; H, 4.24; N, 4.25.

(*Z*)-Methyl (9-methyl-3-oxothiazolo[3,2-*a*]indol-2(3*H*)-ylidene)acetate (2b) was obtained from **1d** by the same procedure described above in 62% yield: mp 197–198 °C; UV ($CHCl_3$) λ_{max} 436 nm (log ϵ 3.85), 287 (4.41); IR (KBr) 1730, 1695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.20 (s, 3 H), 3.86 (s, 3 H), 6.95 (s, 1 H), 7.15–7.50 (m, 3 H), 7.89–8.13 (m, 1 H); mass spectrum, *m/e* (rel intensity) 275 (6), 274 (14), 273 (M$^+$, 100), 242 (8), 214 (7).

Anal. Calcd for $C_{14}H_{11}NO_3S$: C, 61.53; H, 4.06; N, 5.12. Found: C, 61.40; H, 4.10; N, 5.01.

(*Z*)-2,2-Dimethylpropyl (9-methyl-3-oxothiazolo[3,2-*a*]-indol-2(3*H*)-ylidene)acetate (2c) was obtained from **1d** by the same procedure described above, with quenching by excess neopentyl alcohol in 1,2-dichloroethane, in 63% yield (crystallization from hexanes–EtOAc): mp 178–179 °C; UV ($CHCl_3$) λ_{max} 435 (log ϵ 3.84), 287 (4.42); IR (KBr) 1720, 1685 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.00 (s, 9 H), 2.20 (s, 3 H), 3.96 (s, 2 H), 6.99 (s, 1 H), 7.08–7.48 (m, 3 H), 7.89–8.13 (m, 1 H); mass spectrum, *m/e* (rel intensity) 331 (8), 329 (M$^+$, 97), 259 (100), 242 (26), 214 (11), 186 (25).

Anal. Calcd for $C_{18}H_{19}NO_3S$: C, 65.63; H, 5.81; N, 4.25. Found: C, 65.25; H, 5.92; N, 4.02.

Acknowledgment. We thank Professor A. McKillop for kindly providing an authentic sample of **3**. Financial support by the National Institutes of Health, Grant AI-13155, and an S. B. Penick Fellowship to HDHS, administered by the American Foundation for Pharmaceutical Education, is gratefully acknowledged.

Registry No. 1a, 55854-69-8; **1d**, 71382-21-3; **2a**, 71382-22-4; **2b**, 71382-23-5; **2c**, 71382-24-6; methyl 3-indolylacetate, 1912-33-0; succinic anhydride, 108-30-5; 3-methyl-1*H*-indole, 83-34-1; thionyl chloride, 7719-09-7; neopentyl alcohol, 75-84-3.

(9) K. Oka and S. Hara, *Tetrahedron Lett.*, 3059 (1977), and references therein.
(10) M. Cushman and L. Cheng, *J. Org. Chem.*, **43**, 3781 (1978).
(11) B. A. Dreikorn, A. F. Elsasser, and G. P. Jordan, *J. Org. Chem.*, **44**, 877 (1979).
(12) W. A. Remers in "Indoles", Part I, W. J. Houlihan, Ed., Wiley-Interscience, New York, 1972, p 87.
(13) J. Szmuszkovicz, *J. Org. Chem.*, **29**, 178 (1964).
(14) S. Ohki and T. Nagasaka, *Chem. Pharm. Bull.*, **19**, 545 (1971).
(15) A. J. Krubsack and T. Higa, *Tetrahedron Lett.*, 5149 (1968).
(16) T. Higa and A. J. Krubsack, *J. Org. Chem.*, **40**, 3037 (1975).
(17) T. Higa and A. J. Krubsack, *J. Org. Chem.*, **41**, 3399 (1976).
(18) M. Ohoka, T. Kojitani, S. Yanagida, M. Okahara, and S. Komori, *J. Org. Chem.*, **40**, 3540 (1975).
(19) L. A. Mitscher, R.-P. Leu, M. S. Bathala, W.-N. Wu, J. L. Beal, and R. White, *Lloydia*, **35**, 157 (1972).
(20) R. Freeman, *J. Chem. Phys.*, **53**, 457 (1970).
(21) R. Stauffer, *Helv. Chim. Acta*, **49**, 1199 (1965).