istered by the American Chemical Society, and by the University of Wisconsin–Eau Claire University Research Fund.

Registry No. 1-CH_2OTs, 75421-01-1; 2-CH_2OTs, 75444-03-0; 3-CH_2OTs, 13866-80-3; 4-CH_2OTs, 80360-28-7; 5-CH_2OTs, 2346-03-4; 7-CO_2CH_3, 97234-98-5; 7-CO_2H, 97234-99-6; 7-CH_2OH, 97235-01-3; 7-CH_2OTs, 97235-00-2; 8-CH_2OCH_3, 97235-04-6; 8-CH_2OH, 97276-76-1; 8-CH_2OTs, 97276-77-2; 9-CO_2Et, 97235-05-7; 9-CH_2OH, 97235-06-8; 9-CH_2OTs, 97235-07-9; 12, 75421-03-3; 13-CH_2OCH_3, 97235-03-5; 14, 61855-77-4; 15, 97235-02-4; 16, 80360-30-1.

Syntheses of a New Thioaldehyde Precursor and Bis(trichloromethyl)pyrimidines

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Received February 19, 1985

In a preceding paper[1] we reported syntheses of 2*H*-1,4-thiazine-2,6-dicarboxylates and pyrrole-3,4-dicarboxylates from the reactions of S_2Cl_2 or SCl_2 with 3-aminoacrylates substituted with an aryl or a perfluoroalkyl group at the 3-position. In an effort to determine the scope and limitations of this methodology, we also studied the reaction of SCl_2 with ethyl 3-amino-4,4,4-trichlorocrotonate (1) under similar conditions.

Surprisingly, reaction of 1 with SCl_2 at 50–55 °C gave, instead of the expected 2*H*-1,4-thiazine and pyrrole, the pyrimidinone 2 as the major product (40%), together with the 4-ethoxypyrimidine 3 (5%) and the diazathiabicyclooctene 4 (12%). See Scheme I. The yield of 4 could be improved by conducting the reaction at room temperature. In this manner 2 and 4 were isolated in 33% and 34% yields, respectively. The structures of 2 and 3 were determined by spectral methods and elemental analyses. The 4-ethoxypyrimidine 3 was obtained also by alkylation of 2 with ethyl iodide.

The structural assignment of 4 was confirmed by single-crystal X-ray crystallography.[2] An ORTEP drawing of the crystal structure is shown in Figure 1. The structure in Figure 1 is established relative to other possible structures by the shorter double bonds between N_1–C_2 = 1.269 Å and C_4–O_3 = 1.213 Å. In contrast to the N_1–C_2 double bond length, the C_1–N_1 single bond is 1.478 Å.

It was apparent that 2 could be derived from 4 by a retro-Diels–Alder reaction. We confirmed this by isolating 2 (80% yield) from a solution of 4 heated in chlorobenzene at 80 °C (Scheme II). Although the byproduct ethyl thioxoacetate (5) was known[3] to be unstable and to dimerize or polymerize readily, we were able to trap it with conjugated dienes to provide adducts 6 and 7 in moderate yields (85% and 48%, respectively).

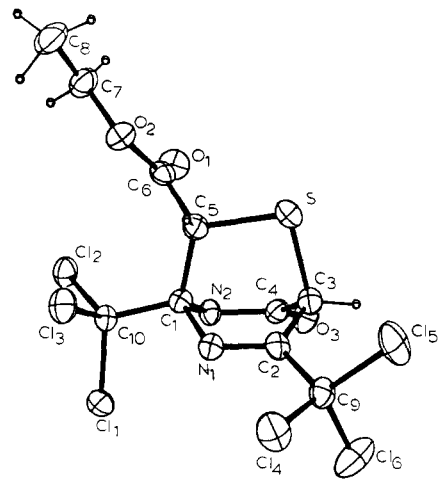
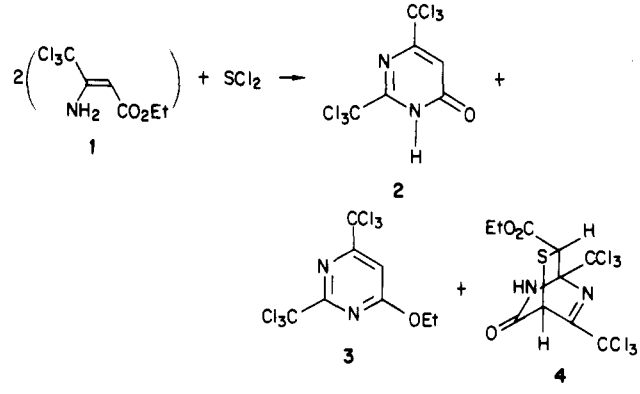
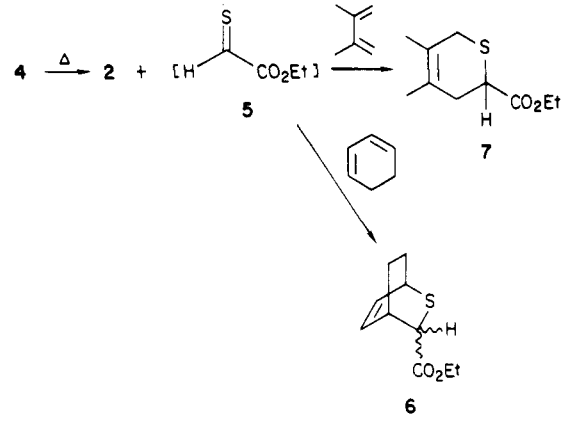


Figure 1. ORTEP drawing for 4.

Scheme I



Scheme II



Either of the two mechanistic pathways shown in Scheme III may explain the formation of 4 from 1. Pathway A is similar to that proposed[1] for the formation of 3,5-bis(perfluoroalkyl)-2*H*-1,4-thiazine-2,6-dicarboxylates from 3-amino-3-(perfluoroalkyl)acrylates; however, instead of loss of ammonia to provide 2*H*-1,4-thiazine product, the intermediate 9 isomerizes to 10, which then cyclizes to give 4. In pathway B the intermediate 8 cyclizes to 11 through an intramolecular attack of the amino group on the ester carboxyl first; 11 then cyclizes to 4 by an intramolecular Michael addition of the imino nitrogen to the vinyl carbon of the α,β-unsaturated ester.

The reasons are not clear at this time for the different course of reaction observed for 1 on one hand and the 3-(perfluoroalkyl)- and aryl-3-aminoacrylates on the other hand.

(1) Lee, L. F.; Howe, R. K. *J. Org. Chem.* **1984**, *49*, 4780.

(2) A small irregular-shaped crystal of 4 (~0.25 mm on an edge) was found to be triclinic (space group $P\bar{1}$) having a = 8.584 (3) Å, b = 9.343 (4) Å, c = 11.957 (4) Å, α = 107.86 (3)°, β = 109.45 (2)°, γ = 97.381 (3)°, and V = 831.8 (5) Å^3. X-ray data were collected on a Syntex $P2_1$ Autodiffractometer using Mo Kα radiation. 1981 reflections having $2\theta \leq 45°$ (of 2187 unique data) were used in the final full-matrix least-squares refinement to give residuals R_1 = 2.74% and R_2 = 4.68%. The final refinement included all non-hydrogen atoms with anisotropic thermal parameters and the hydrogens with isotropic temperature parameters. A final difference Fourier map showed no features of structural significance.

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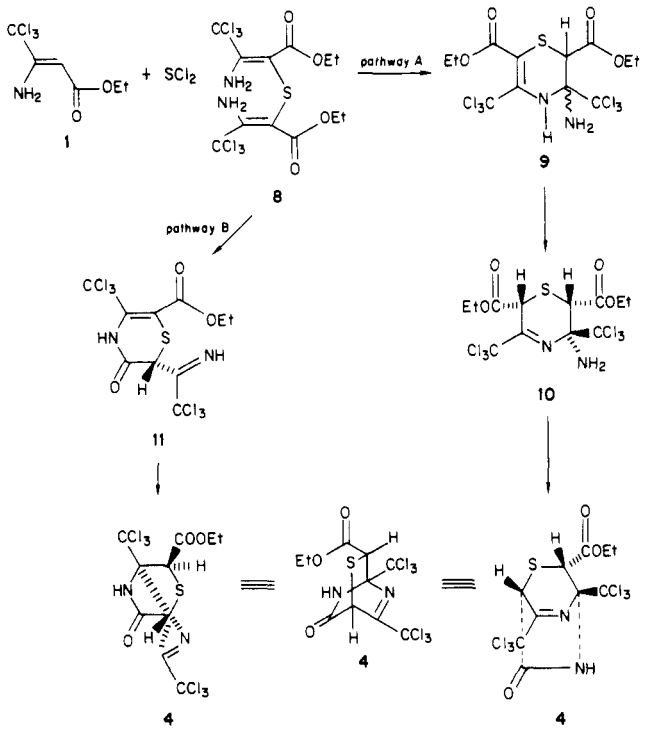
Scheme III



Since **2** can be isolated readily due to its insolubility in chlorobenzene, our method constitutes a convenient synthesis of **2**. Our method of generating and trapping electron-deficient thioaldehyde **5** complements several elegant methods recently developed by others[3-5] and has the advantages of neutral and nonphotolytic conditions.

Experimental Section

Melting points were determined with a Laboratory Devices Mel-Temp apparatus and are uncorrected. ^{1}H NMR spectra were recorded on Varian T-60 (60 MHz) and Varian EM-360L (60 MHz) spectrometers. ^{13}C NMR spectra were measured at 25.05 MHz with a JEOL FX-100 spectrometer. ^{1}H NMR and ^{13}C NMR Spectra were recorded in $CDCl_3$ unless otherwise noted and are expressed in parts per million (ppm) downfield from Me_4Si; couplings are in hertz. Mass spectra were dtermined with a Varian Mat 311A instrument operating on either electron-impact (EI) or field-ionization (FI) mode. IR spectra were recorded on a Perkin-Elmer 727B spectrometer. Column chromatography (CC) was performed with 60–200-μm silica gel 60 (EM Reagents). High-performance liquid chromatography (HPLC was performed on a Waters Auto 500 preparative LC using a Prep-pak 500 silica cartridge. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, GA. Unless otherwise noted, the organic layers were dried over $MgSO_4$ and concentrated in vacuo with a Buchi rotary evaporator. The flash distillations were performed with a Kugelrohr distillation apparatus, and the recorded temperature for a specific fraction was the temperature of the Kugelrohr pot.

Reaction of 1 with SCl_2: Isolation of 2,6-Bis(trichloromethyl)-4(3*H*)-pyrimidinone (2), 2,4-Bis(trichloromethyl)-6-ethoxypyrimidine (3), and Ethyl 1,3-Bis(trichloromethyl)-5-thia-2,7-diaza-8-oxobicyclo[2.2.2]oct-2-ene-6-carboxylate (4). A. Reaction at 50–55 °C. To a cold (3 °C) solution of 10.4 g (0.1 mol) of SCl_2 in 50 mL of chlorobenzene was added a solution of 46.5 g (0.2 mol) of 1[6] in 50 mL of chlorobenzene in 1 h. The reaction mixture was stirred at 50–55 °C for 64 h and filtered. The insoluble solid was washed successively with ether, chloroform, and water to give 11.2 g (34%) of **2**: mp 258–264 °C dec; ^{1}H NMR (Me_2SO-d_6) δ 11.6 (br s, 1 H), 7.33 (s, 1 H); ^{13}C NMR (Me_2SO-d_6) δ 171.5, 165.2, 163.6, 103.3, 95.4, 94.3; MS, *m/e* (relative intensity) 334 (2), 332 (4), 330 (5), 328 (M^+, 3), 299 (12), 297 (59), 295 (91), 293 (44), 260 (7), 258 (6), 234 (9), 233 (5), 232 (21), 231 (11), 230 (13), 229 (6), 125 (15), 123 (40), 121 (19), 119 (27), 117 (36), 114 (15), 113 (11), 112 (10), 111 (35), 110 (25), 109 (100), 108 (47), 107 (92).

Anal. Calcd for $C_6H_2Cl_6N_2O$: C, 21.77; H, 0.61; N, 8.47; Cl, 64.31. Found: C, 21.76; H, 0.64; N, 8.48; Cl, 64.18.

The ether and chloroform washes were combined and concentrated. The residue was stirred with acetone and filtered to give additional 1.2 g (4%) of **2**, mp 257–264 °C dec. The original chlorobenzene mother liquor was concentrated. The residue (32.9 g) was stirred with hexane and filtered, and the solid was washed with ethanol to give 5.5 g (12%) of **4**, as prisms: mp 214–233 °C dec; ^{1}H NMR (Me_2SO-d_6) δ 10.32 (s, 1 H, NH), 5.19 (s, 1 H), 4.38 (s, 1 H), 4.16 (q, J = 7, 2 H), 1.25 (t, J = 7, 3 H); ^{13}C NMR (Me_2SO-d_6) δ 170.9, 166.1, 164.9, 98.3, 92.0, 86.3, 62.1, 51.9, 39.6, 13.3; IR ($CHCl_3$) 3380, 1720, 1640 cm^{-1}; MS (FI), *m/e* (relative intensity) 452 (42), 450 (100), 448 (80), 446 (M^+, 58), 330 (76), 131 (22), 118 (25).

Anal. Calcd for $C_{10}H_8Cl_6N_2O_3S$: C, 26.74; H, 1.80; N, 6.24; Cl, 47.38; S, 7.14. Found: C, 26.78; H, 1.84; N, 6.24; Cl, 47.34; S, 7.21.

The combined hexane and ethanol filtrates were concentrated, and the residue was stirred with hexane and chloroform. The insoluble material (1.0 g) was filtered and recrystalled from chloroform to give additional 0.8 g (2%) of **2**. The hexane–chloroform mother liquor was concentrated. The residual oil (26.1 g) was chromatographed [CC, 5:1 petroleum ether (30–75 °C)–EtOAc]. The earlier fraction (8.8 g) was rechromatographed to give 1.6 g (5%) of **3**: mp 25.5–26.5 °C; ^{1}H NMR δ 7.3 (s, 1 H), 4.62 (q, J = 7, 2 H), 1.47 (t, J = 7, 3 H); ^{13}C NMR δ 171.4, 166.7, 165.0, 103.7, 95.9, 94.7, 64.7, 14.1; IR ($CHCl_3$) 1580, 1560 cm^{-1}; MS (FI), *m/e* (relative intensity) 362 (100), 360 (39), 358 (81), 356 (M^+, 39).

Anal. Calcd for $C_8H_6Cl_6N_2O$: C, 26.77; H, 1.71; N, 7.77; Cl, 59.30. Found: C, 26.77; H, 1.69; N, 7.81; Cl, 59.28.

B. Reaction at Room Temperature. To a 0 °C solution of 10.4 g (0.10 mol) of SCl_2 in 50 mL of chlorobenzene was added dropwise a solution of 46.5 g (0.20 mol) of 1 in 50 mL of chlorobenzene over a period of 1 h. The reaction mixture was stirred at room temperature for 3 days, and the resulting precipitate was filtered and washed with chlorobenzene to give 11.9 g (36%) of **2**. The filtrate was concentrated, and the residual brown oil was triturated with ethanol–cyclohexane (7:3). The resulting white solid was filtered and washed with 10 mL of cold ethanol–cyclohexane, affording 14.9 g (33%) of **4**.

Conversion of 4 to 2. A mixture of 0.80 g (1.78 mmol) of **4** and 30 mL of chlorobenzene was heated at 80 °C for 16 h. The insoluble solid was filtered to give 0.47 g (80%) of **2**, mp 258–262 °C dec.

Preparation of 3 from 2. A mixture of 3.1 g (0.01 mol) of **2**, 1.38 g (0.01 mol) of K_2CO_3, 10.0 g (0.064 mol) of ethyl iodide, and 20 mL of DMF was stirred for 3 days and poured into 200 mL of water. The mixture was extracted with 100 mL of ether twice. The combined ether extracts were washed twice with water, dried, and concentrated to give 2.9 g of residue. This residue was chromatographed (HPLC, 9:1 hexane–EtOAc). The first fraction (1.5 g) was further chromatographed (HPLC, cyclohexane) to give 0.9 g (25%) of a low-melting solid, which was identical with **3** by ^{1}H NMR.

Ethyl 2-Thiabicyclo[2.2.2]oct-5-ene-3-carboxylate (6).[3] A slurry of 12.0 g (0.15 mol) of 1,3-cyclohexadiene and 4.5 g (0.01 mol) of **4** was stirred at reflux under N_2 for 15 h. The reaction mixture was cooled and filtered. The filtrate was concentrated, and the residue was flash distilled [105 °C (1 torr)] to afford 1.69 g (85%) of a colorless oil: ^{1}H NMR δ 6.60 (br t, 1 H), 6.20 (br t, 1 H), 4.10 (q, J = 7, 2 H), 3.98 (d, J = 3, 1 H), 3.66–3.13 (m, 2 H), 2.38–1.08 (m, 4 H), 1.23 (t, J = 7, 3 H).

(3) Bladon, C. M.; Ferguson, I. E. G.; Kirby, G. W; Lochead, A. W.; McDougall, D. C. *J. Chem. Soc., Chem. Commun.* **1983**, 423.

(4) Vedejs, E.; Eberkin, T. Hh.; Varie, D. L. *J. Am. Chem. Soc.* **1982**, *104*, 1445.

(5) (a) Baldwin, J. E.; Lopez, R. C. G. *Tetrahedron* **1983**, *39*, 1487 and references cited therein. (b) Baldwin, J. E.; Lopez, R. C. G. *J. Chem. Soc., Chem. Commun.* **1982**, 1029.

(6) (a) Bodnarchuk, N. D.; Gavrilenko, B. R.; Derkach, G. I. *J. Org. Chem. USSR (Engl. Transl.)* **1968**, *4*, 1645. (b) Coenen, M.; Faust, J.; Ringel, C.; Mayer, R. *J. Prakt. Chem.* **1965**, *27*, 239.

Anal. Calcd for $C_{10}H_{14}O_2S$: C, 60.57; H, 7.12. Found: C, 60.73; H, 7.15.

Ethyl 3,4-Dimethyl-5,6-dihydro-2*H*-thiine-6-carboxylate (7).[3] A slurry of 11.5 g (0.140 mol) of 2,3-dimethyl-1,3-butadiene and 4.5 g (0.010 mol) of **4** was stirred at reflux under N_2 for 16 h. The reaction mixture was cooled to room temperature and filtered. The filtrate was concentrated, and the residue was flash distilled at 0.25 torr to give 0.95 g (48%) of a colorless liquid: bp 86–88 °C [lit.[3] bp 110–120 °C (3 torr)]; ^{1}H NMR δ 4.17 (q, J = 7, 2 H), 3.59 (t, J = 7, 1 H), 3.06 (m, 2 H), 2.43 (m, 2 H), 1.70 (s, 6 H), 1.26 (t, J = 7, 3 H).

Anal. Calcd for $C_{10}H_{16}O_2S$: C, 59.97; H, 8.05. Found: C, 59.46; H, 8.03.

Registry No. **1**, 41404-93-7; **2**, 97171-53-4; **3**, 97171-54-5; **4**, 97171-55-6; **6**, 87258-39-7; **7**, 87258-36-4; SCl_2, 10545-99-0; CH_2=$C(CH_3)C(CH_3)$=CH_2, 513-81-5; 1,3-cyclohexadiene, 592-57-4.

Supplementary Material Available: Additional X-ray crystallographic data for compound **4** and tables of positional and thermal parameters and bond distances and angles (9 pages). Ordering information is given on any current masthead page.

Reaction of Benzylchlorocarbene with Hydrogen Chloride

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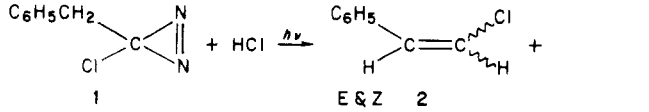
The reaction of benzylchlorocarbene generated from 0.02 M solutions of 3-benzyl-3-chlorodiazirine in benzene with methanol has been found to be termolecular and gives rise to three products, (*E*)- and (*Z*)-chlorostyrene, HCl, and phenylacetaldehyde dimethyl acetal.[1] However, when the diazirine concentration is increased to 0.08 M, a fourth product is formed in a significant amount. Product analysis reveals that this product is 1-phenyl-2,2-dichloroethane. As diazirine concentration is increased, the amount of HCl in the reaction mixtures builds up. Since the reactions of benzylchlorocarbene toward HCl and methanol are competitive processes,[2] the formation of the dichloroethane suppresses the formation of the acetal. This observation led us to examine the reaction of HCl with the chlorocarbene since very little is known about the reaction of acid with carbene despite the wealth of information available on the carbene reaction with alcohols and olefins.[3] We report herein our findings on the kinetics and mechanism of the chlorocarbene–HCl reaction in ether solution.

Solutions of 3-chloro-3-benzyldiazirine (**1**) (0.01 M) in



1 E & Z 2

$C_6H_5CH_2CHCl_2$

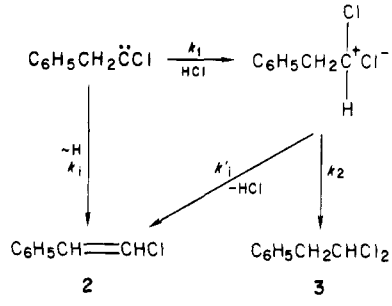
3

dried ether were photolyzed in the presence of various concentrations of HCl from 1 to 22 °C such that the concentrations of HCl were always in excess. The products were (*E*)- and (*Z*)-chlorostyrene (**2**) and 1-phenyl-2,2-dichloroethane (**3**).

Table I. Distribution of Products from the Photolysis of 1 as a Function of [HCl] and Temperature

[HCl], M	1.0 °C		14.4 °C		22.0 °C	
	3/2	(*Z*)-/(*E*)-2	3/2	(*Z*)-/(*E*)-2	3/2	(*Z*)-/(*E*)-2
0.10	0.614	0.29	0.616	0.31	0.666	0.31
0.21	0.963	0.36	0.995	0.38	0.964	0.39
0.31	1.21	0.41	1.21	0.43	1.24	0.44
0.42	1.29	0.45	1.40	0.47	1.49	0.48
0.62	1.69	0.51	1.66	0.53	1.91	0.52
1.20	1.93	0.60	1.85	0.62	1.95	0.62
1.30	2.03	0.61	2.06	0.64	2.08	0.63

Scheme I



The product **2** could result from an intramolecular 1,2-H shift in the photochemically generated benzylchlorocarbene, and product **3** could arise from its reaction with HCl. Temperature does not appear to have an effect on the product distribution as can be seen in Table I. Control experiments confirm that **2** and **3** maintain their identity under reaction conditions and that **3** does not revert to **2**.

A plot of **3**/**2** vs. [HCl] shows pronounced curvature (Figure 1); this could be due to the formation of an intermediate prior to product formation.

The kinetic results can be accommodated by Scheme I in which the carbene can rearrange to **2** by a 1,2-H shift to react with HCl giving an intermediate which subsequently collapses to **3**. This intermediate is likely an ion pair since the solvent used is of low polarity.[4] As well, the ion pair can undergo elimination of HCl leading to **2**. The possible rearrangement of this ion pair to a phenonium ion can be excluded since no product other than **2** and **3** was detected.

Since the formation of the ion pair is a bimolecular reaction, an increase in HCl concentration leads to a higher concentration of **3**. However, the high concentration of HCl has two effects on the formation of **2**. The yields of chlorostyrene increase in the k_i' step and decrease in the k_i step. It is possible that the trend toward higher Z/E ratio of **2** with higher HCl concentration may be accounted

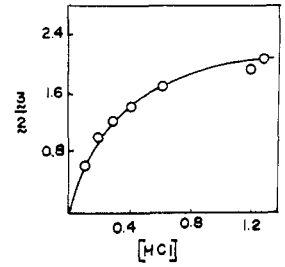


Figure 1. Plot of **3**/**2** vs. [HCl] at 14.4 °C.

(1) Liu, M. T. H.; Subramanian, R. *J. Chem. Soc., Chem. Commun.* **1984**, 1062.

(2) Relative rate studies at 20 °C have shown that the reaction of benzylchlorocarbene with HCl is 10 times faster than with MeOH.

(3) Kirmse, W. "Carbene Chemistry", 2nd ed.; Academic Press: New York, 1971. Moss, R. A.; Jones, M., Jr. "Carbenes"; Vols. 1 and 2, Wiley: New York, 1973, 1975; Vols. 1, 2.

(4) Cocivera, M.; Winstein, S. *J. Am. Chem. Soc.* **1963**, *85*, 1702.

0022-3263/85/1950-3218$01.50/0