the catalytic hydrogenation, and Dr. George Lenz for the helpful discussions and assistance with the photochemical reactions described.

Registry No.—**1a**, 41034-52-0; **1b**, 41143-95-7; **2**, 53957-21-4; **3**, 53927-32-5; **4**, 53927-33-6; **5**, 13326-60-8; **6a**, 53927-34-7; **6b**, 53927-35-8; **7a**, 53927-36-9; **7b**, 53927-37-0; **7c**, 53927-38-1; **7d**, 53927-39-2; **8**, 53957-18-9; **9a**, 53927-40-5; β-(3,4-dimethoxyphenyl)ethylamine, 120-20-7; glyoxylic acid, 298-12-4; dimethyl acetylenedicarboxylate, 762-42-5; phenylacetylene, 536-74-3; α-bromopropiophenone, 2114-00-3; 1-methyl-3,4-dihydroisoquinoline, 2412-58-0; o-nitrophenylacetylene, 16433-96-8.

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Synthesis of Substituted 2*H*-1,3-Oxazine-2,6-diones by Reaction of Trimethylsilyl Azide with Maleic Anhydrides[1]

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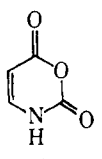
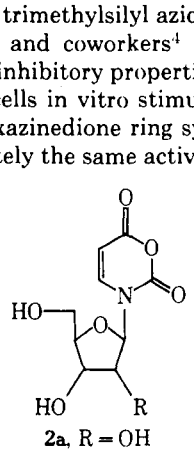
Received October 23, 1974

The synthesis of 4-bromo-, 4-chloro-, 4,5-dichloro-, 4-fluoro-, and 4-methyl-2*H*-1,3(3*H*)-oxazine-2,6-dione, as well as an improved synthesis of 2*H*-1,3(3*H*)-oxazine-2,6-dione, by reaction of trimethylsilyl azide with the corresponding maleic anhydride is described. This route is superior to other methods for preparation of 4-substituted oxaziniones. N-Methylation of the oxazinedione ring may be readily accomplished with dimethyl sulfate buffered by sodium bicarbonate.

The heterocycle derived from uracil by isosteric replacement of the imidic nitrogen, 2*H*-1,3(3*H*)-oxazine-2,6-dione or oxauracil (**1a**), was first prepared by Rinkes[2] in 1927 by sodium hypochlorite oxidation of maleimide. In 1972 this laboratory reported an alternate preparation of **1a** by reaction of maleic anhydride with trimethylsilyl azide.[3] Shortly thereafter, reports by Škoda and coworkers[4] and Bobek and coworkers[5] of the growth inhibitory properties of **1a** vs. *E. coli* and L1210 leukemia cells in vitro stimulated a renaissance of interest in the oxazinedione ring system. The *N*-riboside **2a** had approximately the same activity as **1a** in



1a

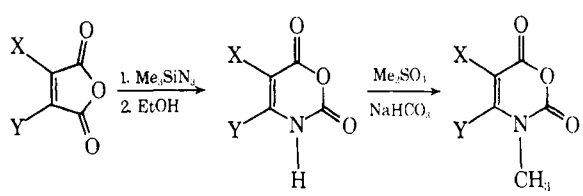


2a, R = OH
3a, R = H

inhibiting growth of L5178Y cells in culture,[6] while oxathymine **1i** was less inhibitory in microbial and tumor cell systems, and the deoxyriboside **3a** was about 1000 times more potent than **1a** in inhibiting *S. faecium* growth.[5] 5-Fluorooxauracil (**1h**) is active vs. the L1210 cell line, but toxic.[5b] The Škoda group has recently reported on the mechanism of inhibition of *E. coli* growth by **1a**, and detailed conditions of the hydrolytic fission of the oxazinedione ring.[7]

Our interest in the regioselective synthesis of alkyl- and halooxaziniones as agents against neoplastic and protozoan disease, particularly malaria, leads us to detail improved synthetic pathways to these heterocycles.

Synthesis. Oxauracil (**1a**) was first prepared by Rinkes by oxidation of maleimide[2] with basic aqueous sodium hypochlorite. Similar oxidation of citraconimide to 5-methyl-2*H*-1,3(3*H*)-oxazine-2,6-dione (oxathymine) has been reported.[5] Other syntheses of the ring system in **1** involve cyclization of the appropriate β-(ethoxycarbonylamino)-acrylic acid to the oxazinedione[5] or lead tetraacetate oxidation of maleic acid monoamide.[7] In a preliminary report[3] we synthesized **1a** by reaction of trimethylsilyl azide with maleic anhydride in benzene solvent.



1 **4**

The original trimethylsilyl azide–maleic anhydride reaction has been exteded to methyl- and halooxaziniones and appears to be the method of choice. Since the oxazinedione ring undergoes facile thermal decarboxylative polymerization to yield polyamides[8] and suffers hydrolytic ring fission at 25° in either acidic or basic media yielding formylacetic acid,[7] any synthetic procedure must be carried out at moderate temperature under essentially neutral conditions. In our hands, the Rinkes hypochlorite oxidation of either maleimide[2] or citrazonimide[5a] did not yield the corresponding oxazinedione even after several attempts in which the pH was carefully controlled.

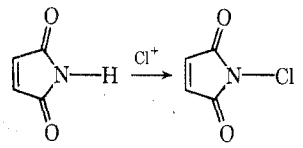
Table I
Methyl- and Halo-Substituted 2*H*-1,3(3*H*)-Oxazine-2,6-diones from Trimethylsilyl Azide and Substituted Maleic Anhydrides

Compd	X	Y	Yield, %	Procedure[a]	Reaction time, hr	δ, ppm C_4-H	δ, ppm C_5-H
1a	H	H	69	A	1.5	7.52	5.59
1b	H	CH_3	33	A	3.0		5.38
1c	CH_3	CH_3	0	B			
1d	H	Br	30	B	6.0		5.87
1e	H	Cl	57[b]	B	4.0		5.84
1f	Cl	Cl	38	A	6.0		
1g	H	F	10	A	0.75		5.36
1h	F	H		*c*			
1i	CH_3	H		*d*		7.57	
4a	H	H	71	C	20	7.75	5.65
4b	H	CH_3	64	C	22		5.60

[a] Procedure A, $CHCl_3$ solution (see Experimental Section); procedure B, neat (see Experimental Section); procedure C, dimethyl sulfate–sodium bicarbonate in acetone (see Experimental Section). [b] Commercially available 70% azeotrope of chloromaleic anhydride–maleic anhydride was employed. [c] See ref 5b. [d] See ref 5a.

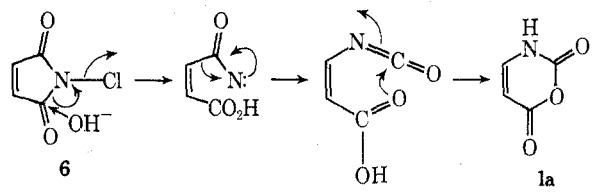
The synthetic utility of our procedure is that it permits a one-step regioselective synthesis of 4-substituted oxazinediones **1** in acceptable yields from commercially available maleic anhydrides (see Table I).

The Rinkes hypohalite oxazinedione procedure probably proceeds via the intermediacy of *N*-chloromaleimide (**6**), which then suffers hydrolytic fission and rearrangement to **1a**. We have isolated **6** by treatment of maleimide with ei-



6

ther sodium or calcium hypochlorite in aqueous acetic acid. Indeed, **6** does rearrange to **1a** in aqueous sodium bicarbonate solution. We have not maximized the yield for this procedure; however, it has merit as a possible route to 5-substituted oxazinediones, as Bobek[5] has converted citraconimide into oxathymine by hypochlorite oxidation.

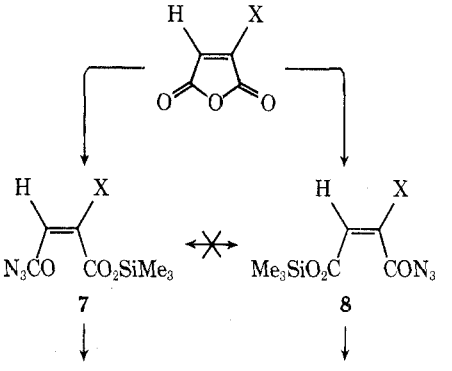


6 **1a**

Spectral Analysis. The oxazinedione ring system can readily be identified by ir or ^{1}H NMR spectral analysis. A characteristic ir spectrum has two strong sharp carbonyl stretching absorptions at 1815–1780 cm^{-1} (C_6 carbonyl) and at 1755–1710 (C_2 carbonyl) together with a strong absorption at 1670–1602 cm^{-1} (C_4–C_5 alkene stretch). A broad absorption in the 3400–3100 cm^{-1} range for the N–H stretch was also visible. The characteristic ^{1}H NMR resonances for the C_5 proton were in the 5.38–5.87 ppm region while the C_4 proton (β to the C_6 carbonyl) resonated at 7.52 ppm in **1** and at 7.57 ppm in 5-methyl-2*H*-1,3(3*H*)-oxazine-2,6-dione (oxathymine).[4] Data are summarized in Table I above. Dominant features of the mass spectra are a moderate to strong molecular ion together with a prominent M − 44 peak corresponding to extrusion of carbon dioxide from the molecular ion.

N-Methylation of 1a,b. Introduction of functionalities at nitrogen in the oxazinedione ring system has proved quite difficult due to the previously described instability of the ring to hydrolysis in acidic or basic media. Attempts to N-methylate the ring failed with methyl iodide and methyl fluorosulfonate, apparently due to generation of acidic hydrogen iodide and fluorosulfonic acid as the reactions proceeded. However, Fieser[9] describes the mild alkylating system acetone–dimethyl sulfate–potassium carbonate for methylation of plant phenols. We found that a modified procedure employing the mild buffe sodium bicarbonate resulted in N-methylated oxazinediones in 65–70% yields. The chemical shift of the methyl singlet was consistent with N- rather than O-alkylation, as was the infrared spectrum where both characteristic oxazinedione carbonyl-stretching frequencies at 1780 and 1720 cm^{-1} were still present.

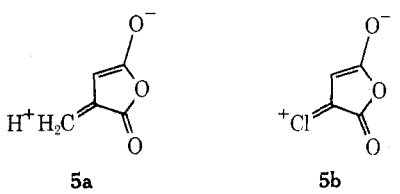
Orientation of Nitrogen Insertion into the Substituted Maleic Anhydrides. Examination of the product distribution given in Table I indicates that 4-substituted products are produced preferentially over 5-substituted oxazinediones. While the exact mechanism for these transformations is not certain, it seems highly probable that the initial nucleophilic attack of azide at an anhydride carbonyl determines the regiochemistry of product oxazinedione;[10] i.e., **7** and **8** do not interconvert.[11]



7 **8**

5-substituted product 4-substituted product

Obviously, steric interference by the substituent is not product determining since the more hindered carbonyl is preferentially attacked, even in the case of the bulky bromine group. Electronic factors must be rate determining for these systems. Although little substantive information is available concerning regioselectivity of nucleophilic attack at substituted maleic anhydrides, the azide should attack the most electropositive carbonyl, i.e., the carbonyl α to the substituent. For the halo substituents simple inductive electron withdrawal from the proximate carbonyl by the electronegative halogens could be invoked. However, this rationalization breaks down for the methyl substituent since inductively this electron-releasing group should make the α-carbonyl less electropositive. It appears that a conjugative interaction between the substituent and the double bond must be invoked, involving canonical resonance forms such as **5**. This resonance interaction feeds electron density



5a **5b**

to the carbonyl β to the substituent carbonyl making it less susceptible to nucleophilic attack. For the methyl group a hyperconjugative type interaction **5a** could be involved.

This effect is analogous to the similar orientation effects observed for methyl- and halo-substituted aromatic rings. The nonreactivity of dimethylmaleic anhydride under our reaction conditions is also consistent with such an interaction. For this compound both carbonyls would possess added electron density, making nucleophilic attack by an azide a higher activation energy process. Electron supply via **5b** must, in the case of dichloromaleic anhydride (**1f**), be overridden by inductive electron withdrawal, since **1f** reacts smoothly.

Further mechanistic study of this synthetic procedure will be the subject of another communication.

Experimental Section[12]

General Comments. Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 727 infrared spectrophotometer. Proton magnetic resonance spectra were obtained with a Varian XL-100-15 spectrometer using an internal tetramethylsilane standard. Elemental analyses were pformed by Galbraith Laboratories, Knoxville, Tenn. All solvents were reagent grade and dried over Linde 4A molecular sieves before use. The fluoromaleic anhydride was synthesized according to the literature procedure.[13] Trimethylsilyl azide was purchased from Petrarch Systems Inc., Levittown, Pa.

Synthesis of 2*H*-1,3(3*H*)-Oxazine-2,6-diones. Method A. Chloroform Procedure. A solution of the appropriately substituted maleic anhydride in chloroform was refluxed with a slight excess of trimethylsilyl azide until gas evolution slowed. Cooling of the solution of 0° and hydrolysis with absolute ethanol gave the desired product which was washed with chloroform. Purifications were effected by recrystallization from boiling ethyl acetate or by sublimation.

The following oxaziniediones were synthesized, with slight modification, by the above procedure.

2*H*-1,3(3*H*)-Oxazine-2,6-dione (1a). Maleic anhydride (4.8 g, 49 mmol) in deuteriochloroform (15 ml) was refluxed with trimethylsilyl azide (6.0 g, 52 mmol) for 1 hr resulting in evolution of 900 ml of gas. ^{1}H NMR (CH_3CN internal standard) showed resonances consistent with a silylated oxazinedione intermediate at δ 0.43 [s, 9, $(CH_3)_3Si$-], 5.59 (d, 1, J = 7.5 Hz, C_5-H), and 7.29 (d, 1, J = 7.5 Hz, C_4-H). Dilution with 20 ml of benzene and hydrolysis with ethanol gave 3.81 g (69%) of off-white powder: mp 158–158.5° (lit.[3] mp 158–159° dec; ir (mull) 3300 (m), 3150 (m), 3120 (m), 1790 (s), 1710 (vs), 1635 (s), 1200 (s), 1105 (s), 1055 (m), 980 (s) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 5.56 (d, 1, J = 7.5 Hz, C_5-H), 7.52 (d, 1, J = 7.5 Hz, C_4-H), 10.75 (broad, 1, NH); MS (70 eV) *m/e* (rel intensity) 113 M^+ (58), 69 M − CO_2 (100), 43 $HNCO^+$ (52), and 44 $CO_2{\cdot}^+$ (52).

4-Methyl-2*H*-1,3(3*H*)-oxazine-2,6-dione (1b). Citraconic anhydride (56.0 g, 0.5 mol) was refluxed with trimethylsilyl azide (61.0 g, 0.53 mol) in 75 ml of chloroform for 5 hr. Work-up as described in procedure A above gave 21.0 g (33%) of microcrystalline white powder, mp 140–5° dec. Crystallization from ethyl acetate gave 10.6 g of **1b**: mp 176.5°; ir (mull) 3300 (m), 3125 (m), 1790 (s), 1710 (s), 1640 (s), 1040 (m), 970 (m) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 2.08 (s, 3, C_4-methyl), 5.38 (s, 1, C_5-H), 11–12 (broad, 1, N-H); MS (70 eV) *m/e* (rel intensity) 127 M^+ (57.2), 83 M − CO_2 (46), 68 M − $HNCO_2$ (46), 44 $CO_2{\cdot}^+$ (41.3), 42 (100).

Anal. Calcd for $C_5H_5NO_3$: C, 47.25; H, 3.96; N, 11.02. Found: C, 47.37; H, 3.98; N, 11.16.

4-Fluoro-2*H*-1,3(3*H*)-oxazine-2,6-dione (1g). Fluoromaleic anhydride (2.9 g, 25 mmol) in 10 ml of chloroform was stirred with trimethylsilyl azide (3.45 g, 30 mmol) for 10 min and then refluxed for 0.5 hr. Cooling to room temperature and hydrolysis with 1.5 ml of absolute ethanol gave 0.34 g (10−) of off-white powder: mp 113–114° dec; ir (mull) 3200 (m), 1800 (s), 1750 (s), 1670 (s), 1060 (m), 990 (m), 810 (m) cm^{-1}; ^{1}H NMR (acetone-d_6) δ 5.36 (d, 1, J = 7 Hz, C_5-H), 8.5 (broad, 1, NH).

Sublimation [75° (0.02 mmHg)] gave an analytical sample, mp 104–105.5° dec.

Anal. Calcd for $C_4H_2FNO_3$: C, 36.67; H, 1.54; F, 15.00; N, 10.69. Found: C, 36.37; H, 1.62; F, 15.04; N, 10.65.

4,5-Dichloro-2*H*-1,3(3*H*)-oxazine-2,6-dione (1f). Dichloromaleic anhydride (8.35 g, 50 mmol) in 20 ml of *p*-dioxane was refluxed with trimethylsilyl azide (5.8 g, 50 mmol) for 5 hr; 1.05 l. of gas were evolved. The solution was cooled to room temperature, filtered, treated with 3.5 ml of absolute ethanol, and diluted with 50 ml of chloroform. Cooling to −20° gave 3.74 g (38%) of off-white crystals, mp 209–210° dec. Recrystallization from 1:1 ethyl acetate–hexane gave 2.2 g of light yellow crystals: mp 204–206° dec; ir (mull) 3100 (w), 1815 (s), 1755 (s), 1605 (m), 995 (m), 895 (m) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 9.9 (broad, NH).

Anal. Calcd for $C_4HCl_2NO_3$: C, 26.40; H, 0.56; Cl, 38.97; N, 7.70; O, 26.37. Found: C, 26.48; H, 0.57; Cl, 39.07; N, 7.61; O, 26.28.

Method B. Neat Procedure. Chloro- and bromomaleic anhydrides were found to react sluggishly when treated with trimethylsilyl azide by procedure A above; therefore they were treated without solvent with a sizable excess of trimethylsilyl azide. The procedure consists of gently heating the reactants until a moderate gas evolution occurs. The pot is cooled when necessary to moderate the reaction. A nitrogen evolution rate of approximately 1 l./hr is preferable. Overheating the solution must be avoided as a vigorous and uncontrollable reaction will ensue resulting in intractable tars. After approximately the stoichiometric amount of nitrogen has been evolved, the reaction is cooled to room temperature, diluted with benzene, and hydrolyzed with a stoichiometric amount of absolute ethanol and the product purified by vacuum sublimation or recrystallization.

4-Chloro-2*H*-1,3(3*H*)-oxazine-2,6-dione (1e). Chloromaleic anhydride (6.0 g, 70% by weight, 32 mmol) and trimethylsilyl azide (11.0 g, 95 mmol) were heated cautiously to 70–90° for 1 hr. Dilution with 40 ml of benzene and work-up as described above gave 2.7 g of tan powder, mp 133.5–134.5° dec. Sublimation at 100° (0.02 mmHg) afforded 1.43 g (29%) of white powder, mp 135–137° dec. Crystallization from ethyl acetate gave white needles, 0.40 g: mp 139–140° dec; ir (mull) 3120 (m), 1790 (s), 1725 (s), 1615 (s), 1120 (m), 980 (m) cm^{-1}; ^{1}H NMR (acetone-d_6) δ 5.84 (s, C_5-H), 11.0 (broad, NH).

Anal. Calcd for $C_4H_2ClNO_3$: C, 32.57; H, 1.37; N, 9.49; Cl, 24.03. Found: C, 32.66; H, 1.42; N, 9.56; Cl, 24.11.

4-Bromo-2*H*-1,3(3*H*)-oxazine-2,6-dione (1d). Bromomaleic anhydride (8.85 g, 50 mmol) and trimethylsilyl azide (8.9 g, 77 mmol) reacted at 70–90° for 1 hr as described above. Work-up as described above followed by cooling to 0° gave 3.0 g (30%) of tan powder containing approximately 10% of the isomeric 5-bromo isomer. Pure material may be obtained by repeated recrystallization from hot ethyl acetate: mp 149–151° dec; ir (mull) 3175 (m), 1780 (s), 1602 (s) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 5.87 (s, 1, C_5-H), 11.0 (broad, 1, NH).

Anal. Calcd for $C_4H_2BrNO_3$: C, 25.03; H, 1.05; Br, 41.63; N, 7.30; O, 25.0. Found: C, 25.02; H, 1.00; Br, 41.48; N, 7.37; O, 25.09.

Method C. Methylation Procedure. This procedure is a modification of Fieser's procedure[9] for methylation of plant phenols. The oxazinedione is refluxed in dry acetone with a slight molar excess of dimethyl sulfate and sodium bicarbonate buffer. Reactions may be followed by TLC. Generally 3–24 hr are required for complete reaction. The reactions are then filtered and the acetone is removed under reduced pressure. The semisolid residues are triturated with hot ethyl acetate and cooled, giving the 3-methylated derivative.

3-Methyl-2*H*-1,3(3*H*)-oxazine-2,6-dione (4a). 2*H*-1,3(3*H*)-Oxazine-2,6-dione (2.5 g, 22 mmol) in acetone (65 ml) was refluxed under nitrogen with dimethyl sulfate (3.2 g, 25 mmol) and sodium bicarbonate (2.5 g, 30 mmol) for 20 hr. Work-up as described above gave 2.0 g (71%) of **2a**, white crystals: mp 110–111° dec; ir ($CHCl_3$) 3130 (m), 1790 (s), 1745 (s), 1715 (s), 1640 (s), 1360 (m) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 3.2 (s, 3, NCH_3), 5.65 (d, 1, J = 7.5 Hz, C_5-H), 7.75 (d, 1, J = 7.5 Hz, C_4-H); MS (70 eV) *m/e* (rel intensity) 127 M^+ (100), 83 M − CO_2 (132), 55 M − C_2O_3 (109), 44 CO_2^+ (70), 42 CON^+ (190).

Anal. Calcd for $C_5H_5NO_3$: C, 47.25; H, 3.96; N, 11.02. Found: C, 47.01; H, 3.90; N, 10.91.

(3,4)-Dimethyl-2*H*-1,3(3*H*)-oxazine-2,6-dione (4b). 4-Methyl-2*H*-1,3(3*H*)-oxazine-2,6-dione (1.7 g, 13.3 mmol) in acetone (40 ml) with dimethyl sulfate (1.9 g, 15 mmol) and sodium bicarbonate (1.5 g, 18 mmol) was refluxed under nitrogen for 22 hr. Work-up as described above gave 1.2 g (64%) of **4b**, white crystals: mp 83–85° dec; ir ($CHCl_3$) 3120 (m), 2960 (m), 1780 (s), 1720 (s), 1630 (s), 1370 (m) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 2.4 (d, 3, J = 1 Hz, CH_3), 3.4 (s, 3, N-CH_3), 5.6 (q, 1, J = 1 Hz, C_5-H).

Anal. Calcd for $C_6H_7NO_3$: C, 51.07; H, 4.99; N, 9.92. Found: C, 50.90; H, 5.23; N, 9.78.

***N*-Chloromaleimide (6).** To a stirred solution of maleimide (2.43 g, 25 mmol) in 40 ml of 53% (w/v) aqueous acetic acid at 0° was added 35 ml of fresh 5.25% aqueous sodium hypochlorite [or pulverized calcium hypochlorite (4.3 g, 30 mmol)] over a period of 10 min. After 0.5 hr, the white precipitate was collected, washed

with ice-cold H_2O, and sucked dry, 1.9 g (58%): mp 101–103.5° dec; [14] ir (mull) 3110 (m), 1765 (m), 1710 (s), 1635 (m), 1320 (s), 1270 (s), 865 (m), 850 (m) cm^{-1}.

2*H*-1,3(3*H*)-Oxazine-2,6-dione (1a). To a stirred dispersion of *N*-chloromaleimide (250 mg, 1.9 mmol) in 10 ml of H_2O at 0° was added dropwise over a period of 0.25 hr a solution of $NaHCO_3$ (180 mg, 2.1 mmol) in 5.0 ml of H_2O. The solid dissolved during the above addition to yield a clear solution. After neutralization with cold dilute H_2SO_4, the solution was saturated with NaCl and the oxazinedione **1a** isolated by ethyl acetate extraction. It was identical with that prepared as described above.

Registry No.—**1a**, 24314-63-1; **1b**, 51440-82-5; **1d**, 53907-40-7; **1e**, 53907-41-8; **1f**, 53907-42-9; **1g**, 53907-43-0; **4a**, 53907-44-1; **4b**, 53907-45-2; **6**, 45514-70-3; maleic anhydride, 108-31-6; trimethylsilyl azide, 4648-54-8; citraconic anhydride, 616-02-4; fluoromaleic anhydride, 2714-23-0; dichloromaleic anhydride, 1122-17-4; bromomaleic anhydride, 5926-51-2.

References and Notes

(1) This research was supported by Grant No. CA-13120-03 from the National Cancer Institute and Contract No. DAMD 17-74-C-4100 from the U.S. Army Medical Research and Development Command. This is Contribution No. 1303 to the Army Research Program on Malaria.

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The Synthesis of 1,3-Diselenole-2-selones and -2-thiones

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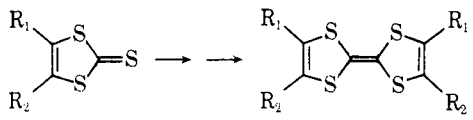
Received September 27, 1974

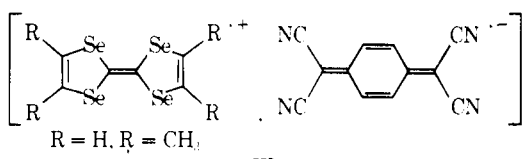
The synthesis and some physical and chemical properties of 1,3-diselenole-2-selones and -2-thiones are reported. The compounds were prepared in a three-step synthesis from *N,N*-pentamethylenediselenocarbamate and appropriate α-halo ketones.

In recent years 1,3-dithiole-2-thiones (I) have gained interest as intermediates in the synthesis of tetrathiafulvalenes (II), which have been used as the donor in several highly conducting organic "metals."[2,3]



I II

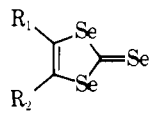
As a part of a systematic study of organic conducting solids,[4] we have been interested in substituting sulfur with selenium in order to increase electronic interactions in the donor stacks of the organic "metals." So far the selenium-containing fulvalenes have shown very promising properties in salts of the general type III.[5,6]



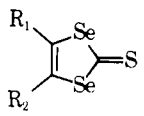
R = H, R = CH_3

III

In order to obtain the tetraselenafulvalenes in question, we have developed a general synthetic route to mono- and disubstituted 1,3-diselenole-2-selones (IV) and -2-thiones (V), which by dechalkogenizing reagents can be coupled to tetraselenafulvalenes.[5,6] Reaction sequences similar to those outlined in Scheme I have been reported for sulfur analogs of some of the compounds described in this paper.[7,8]



IV



V

Recently Engler and Patel[5,9] have prepared 1,3-diselenole-2-selone (IV, $R_1 = R_2 = H$) from sodium acetylide, selenium, and carbon diselenide, utilizing a modified procedure originally developed to prepare 1,3-dithiole-2-thiones.[10,11] Engler and Patel also prepared several thiaselenoles.[9]

Results and Discussion

The compounds in question were all prepared by the general route outlined in Scheme I.

The first step involves nucleophilic substitution of a halogen with the *N,N*-pentamethylenediselenocarbamate anion. The substitution proceeds rapidly, but the solution was usually left 2–4 hr at room temperature to assure complete reaction. In addition to piperidinium *N,N*-pentamethylenediselenocarbamate,[12] we have used the morpholine and pyrrolidine analogs which react as well, but since piperidinium *N,N*-pentamethylenediselenocarbamate is