Preparation and Reactions of Bifunctionalized Tetrathiafulvalenes

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Bifunctionalized tetrathiafulvalene (TTF) derivatives suitable for polycondensations were prepared. The desulfurization–coupling of 4-carbomethoxy-1,3-dithiole-2-thione (**3**) with triethyl phosphite gave, in fair yield, 2,6(7)-bis(carbomethoxy)-TTF (**6**), which was converted to TTF-2,6(7)-dicarboxylic acid (**9**), 2,6(7)-bis(hydroxymethyl)-TTF (**18**), the bis acetic anhydride, **19**, of the diacid **9**, and bisanilide **20** of the diacid **9**. The attempted coupling of 1,3-dithiole-2-thione-4-carboxylic acid (**2**) with triethyl phosphite failed to produce diacid **9**, but 4-carboethoxy-1,3-dithiole-2-thione (**10**) was formed. 4-Carbomethoxy-1,3-dithiole-2-thione (**3**), 4,5-biscarboethoxy-1,3-dithiole-2-thione (**1**), and 4-(*p*-nitrophenyl)-1,3-dithiole-2-thione 4-carboxylate (**4**) were each coupled to give their corresponding bifunctionalized TTF derivatives in the presence of trivalent phosphines.

Charge transfer salts of tetrathiafulvalenes (TTF)[1] and tetraselenafulvalenes (TSeF)[2,3] with tetracyanoquinodimethane (TCNQ) have attracted widespread interest owing to their quasi-metallic electrical conductivity. Preparative methods for TTF and TSeF have been reviewed[4] and two groups have recently reported polymers containing TTF structures.[5,6] We report the synthesis of several difunctionalized TTF monomers suitable for polycondensation studies. Thus, TTF-2,6(7)-dicarboxylic acid (**9**), the bis acetic anhydride of TTF-2,6(7)-dicarboxylic acid (**19**), the bisanilide of TTF-2,6(7)-dicarboxylic acid (**20**), and 2,6(7)-bis(hydroxymethyl)-TTF (**18**) were prepared from 2,6(7)-bis(carbomethoxy)tetrathiafulvalene (**6**). Furthermore, 2,6(7)-bis(*p*- and *m*-hydroxyphenyl)tetrathiafulvalenes (**15** and **16**) were prepared by base-catalyzed coupling of 4-(*p*- and *m*-acetoxyphenyl)-1,3-dithiolium perchlorates (**11** and **12**), respectively. In addition, the synthesis and coupling of a series of substituted 1,3-dithiole-2-thiones were carried out.

Results

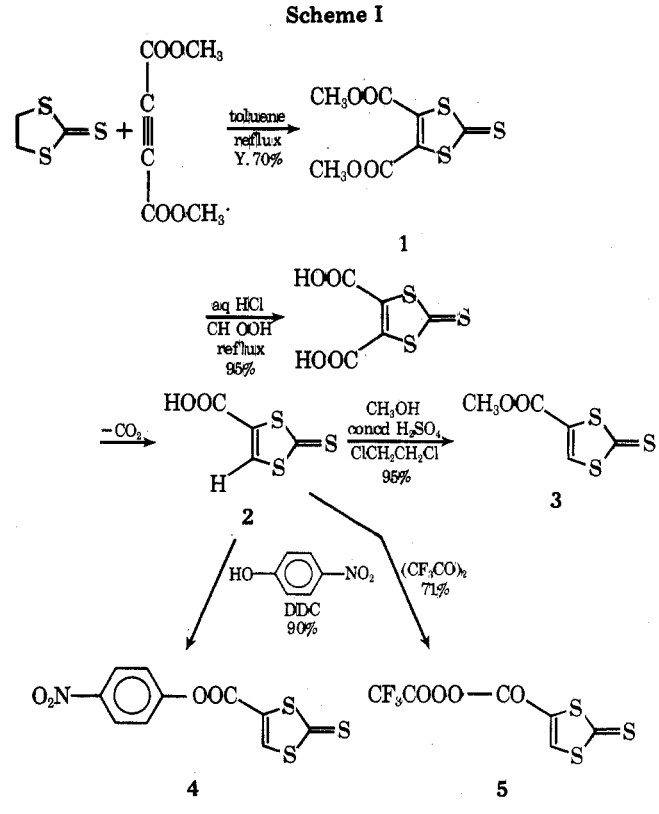
Preparations of 1,3-Dithiole-2-thiones. Several substituted 1,3-dithiole-2-thiones were prepared in order to study their coupling via desulfurization with trivalent phosphorus compounds. It is known that TTF derivatives which have electron-withdrawing substituents may be coupled in fair yields in this manner. Example preparations by this route include 2,3,6,7-tetrakis(trifluoromethyl)-TTF,[7] 2,3,6,7-tetracyano-TTF,[8] and dibenzo-TTF.[9,10]

4-Substituted 1,3-dithiole-2-thiones, precursors of difunctionalized TTFs, were derived from 1,3-dithiole-2-thione-4-carboxylic acid (**2**). Compound **2** was easily obtained by decarboxylation of 1,3-dithiole-2-thione-4,5-dicarboxylic acid,[11] which was prepared by reaction of dimethyl acetylenedicarboxylate with ethylene trithiocarbonate, followed by hydrolysis.[12] The reactions are summarized in Scheme I.

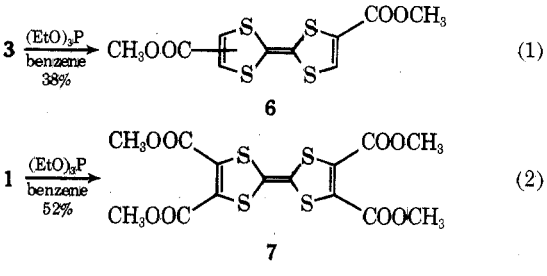
Acid **2** was easily esterified by Clinton's method[13] to give 4-carbomethoxy-1,3-dithiole-2-thione (**3**) in 89% yield. Reaction of **2** and *p*-nitrophenol with dicyclohexylcarbodiimide (DDC) afforded *p*-nitrophenyl 1,3-dithiole-2-thione-4-carboxylate (**4**) in 90% yield, while treatment of **2** with trifluoroacetic anhydride gave the bistrifluoroacetic anhydride, **5**, of the acid **2**, in 71% yield. These 1,3-dithiole-2-thiones were then used for the desulfurization–coupling reactions.

Preparation of Tetrathiafulvalenes by Desulfurization of 1,3-Dithiole-2-thiones. Treatment of either 4-carbomethoxy-1,3-dithiole-2-thione (**3**) or 4,5-bis(carbomethoxy)-1,3-dithiole-2-thione (**1**) with triethyl phosphite in refluxing benzene resulted in the formation of 2,6(7)-bis(carbomethoxy)- and 2,3,6,7-tetrakis(carbomethoxy)tetrathiafulvalenes (**6** and **7**) in 38 and 52% yields, respectively (see eq 1 and 2). The desulfurization–coupling of **1** with triphenylphosphine also gave TTF tetraester **7**, but the yield was only 22%.

Scheme I

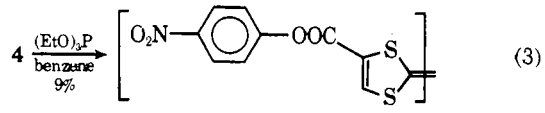


TTF diester **6** was also prepared by the reaction of methyl propiolate with carbon disulfide, a known but low-yield route.[12,14] Tetraester **7** was prepared directly from dimethyl acetylenedicarboxylate and carbon disulfide according to the literature.[7] In contrast to the ready coupling of **1** and **3**, desulfurization of 1,3-dithiole-2-thiones **2**, **4**, and **5** did not proceed smoothly. Bis(*p*-nitrophenyl) TTF diester **8** was obtained in only 9% yield in triethyl phosphite promoted coupling of ester **4** (eq 3) and tarry products predominated. Since aromatic nitro compounds are known to react readily with deoxygenating agents such as $(EtO)_3P$,[15] this result is not surprising.



(1)

(2)



(3)

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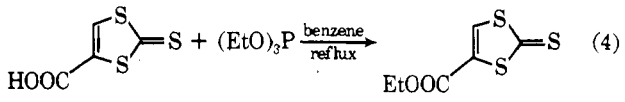
The reaction of 1,3-dithiole-2-thione-4-carboxylic acid with triethyl phosphite did not produce 2,6(7)-tetrathiafulvalenedicarboxylic acid (9). Instead 4-carboethoxy-1,3-dithione-2-thione (1) was produced in 36% yield (see eq 4). The results of coupling thiones 1, 2, and 4 are summarized in Table I.



(4)

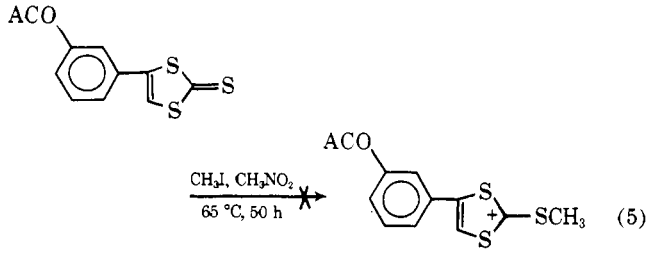
2 10

Preparation of 2,6(7)-Bis(*p*- and *m*-hydroxphenyl)-tetrathiafulvalenes by Deprotonation of 1,3-Dithiolium Cations (Scheme II). The most suitable method for preparation of the bisphenol monomers 15 and 16 appeared to be the coupling of their corresponding 1,3-dithiolium cations (i.e., 11 and 12) by triethylamine-promoted deprotonation. Thus, 11 and 12 were designated as key intermediates. The overall synthesis is summarized in Scheme II.

Many TTF derivatives, which do not have electron-withdrawing substituents, have been prepared by the coupling reaction of cations upon deprotonation with triethylamine.[4,12,16] It is known that 1,3-dithiolium-2-carbenes, produced by deprotonation of 1,3-dithiolium cations, react rapidly with alcohols to give 2-alkoxy-1,3-dithioles.[7,17] Thus, we prepared 4-(*p*- and *m*-acetoxyphenyl)-1,3-dithiolium perchlorates (11 and 12) as intermediates for use in coupling reactions to produce the bisacetates 13 and 14, respectively. Perchlorates 11 and 12 were obtained as shown in Scheme II according to the procedure of Takamizawa.[18] Perchlorates 11 and 12 were reluctantly chosen as intermediates only after it was shown that hydrogen sulfate salts were difficult to prepare reproducibly.

Preparation of *p*- and *m*-hydroxyphenacylpiperidinocarbodithioate was achieved by reaction of corresponding hydroxyphenacyl bromides with carbon disulfide and piperidine. Acid-catalyzed cyclizations gave 4-(*p*- or *m*-hydroxyphenyl)-1,3-dithiole-2-ylidene piperidinium fluoroborates in good yield. The phenolic hydroxyl groups were acylated by acetic anhydride and then the piperidinium salts were reduced with sodium borohydride. Treatment of the resulting 2-piperidino-1,3-dithioles with perchloric acid gave perchlorate salts 11 and 12.

We were unsuccessful in obtaining 4-(*m*-acetoxyphenyl)-1,3-dithiolium tetrafluoroborate by the S-methylation of 4-(*m*-acetoxyphenyl)-1,3-dithiole-2-thione with methyl iodide, followed by sodium borohydride reduction and treatment with fluoroboric acid. The S-methylation failed (eq 5). Thus, the

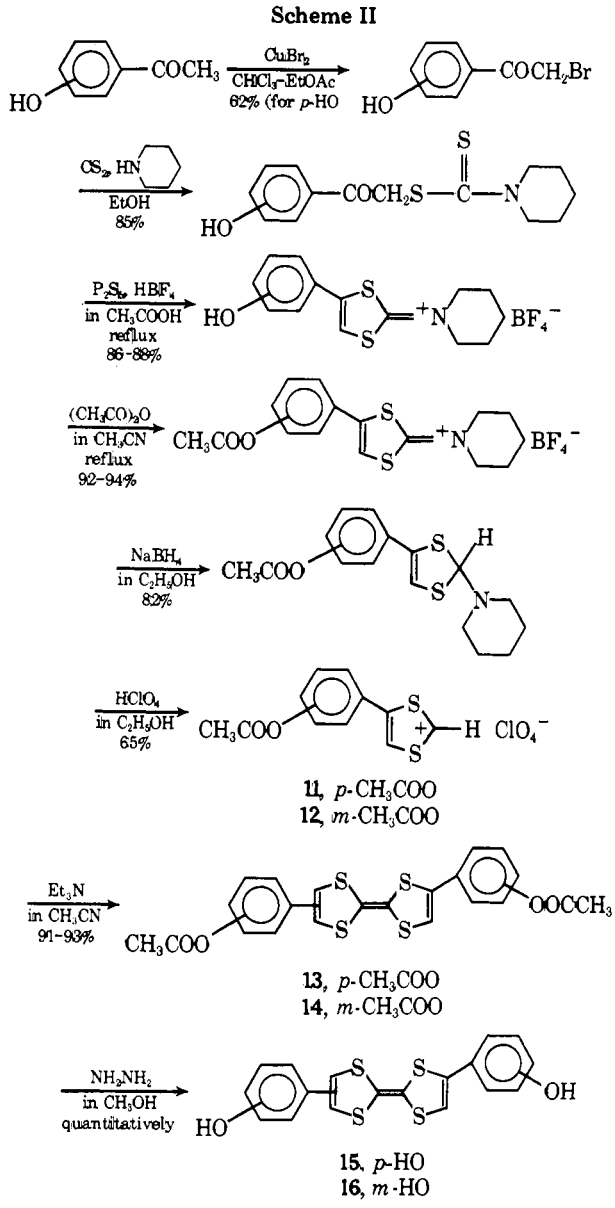


(5)

route involving 2-piperidino-1,3-dithiole intermediates (Scheme II) as the precursors to 11 and 12 was dictated.

Perchlorate salts 11 and 12 were successfully coupled in acetonitrile by treatment with excess triethylamine to produce 2,6(7)-bis(*p*- and *m*-acetoxyphenyl)-TTF (13 and 14). Bisacetates 13 and 14 were easily converted to 2,6(7)-bis(*p*- and *m*-hydroxyphenyl)-TTF (15 and 16) by treatment with hydrazine in methanol. This scheme constitutes an efficient, high-yield route to monomers 15 and 16. No attempts were made to optimize the yields of any of the steps in this scheme. Monomers 15 and 16 were prepared for use in the synthesis of TTF-containing polyesters, polyurethanes, and polycarbonates.

Scheme II



11, *p*-CH_3COO
12, *m*-CH_3COO

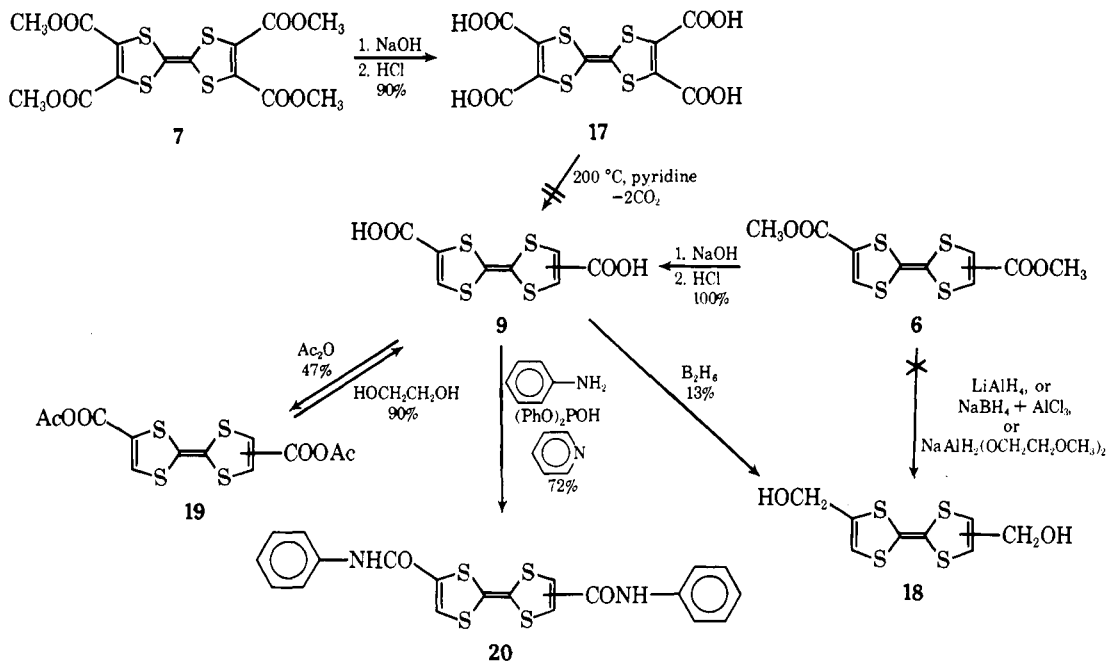
13, *p*-CH_3COO
14, *m*-CH_3COO

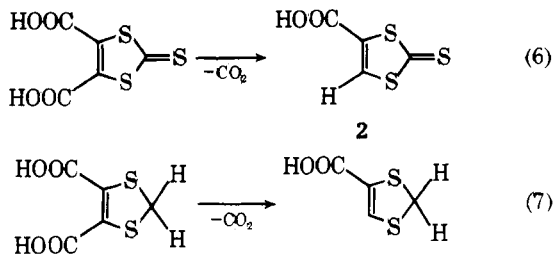
15, *p*-HO
16, *m*-HO

Reactions of Some TTF Derivatives (Scheme III). TTF diester 6 and TTF tetraester 7 were readily hydrolyzed to the corresponding diacid 9 and tetraacid 17 by 1 N NaOH. Decarboxylation of the tetraacid 17 to the diacid 9 was tried at 200 °C in the presence of pyridine, but 17 was quite stable and recovered unchanged. This result was unexpected because both 1,3-dithiole-2-thione-4,5-dicarboxylic acid and 1,3-dithiole-4,5-dicarboxylic acid were readily decarboxylated, without pyridine, to acid 2 and 1,3-dithiole-4-carboxylic acid, respectively, in good yields[11,19] (see eq 6 and 7). Therefore, tetraacid 17 was not a suitable precursor for entry into a series of difunctional TTF monomers.

Diester 6 appeared to be a likely intermediate for the preparation of difunctional monomers such as diol 18. However, 6 was not reduced by $LiAlH_4$, $LiAlH_4 + AlCl_3$, or $NaAlH_2(OCH_2CH_2OCH_3)_2$ to 18. These reductions were tried at temperatures below 70 °C in ether, THF, and benzene.[20] This

Scheme III



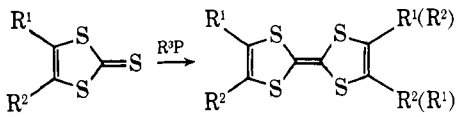


resistance to reduction is puzzling. However, reduction of diacid **9** with diborane in diglyme gave dialcohol **18** in a low yield.

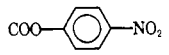
Reaction of diacid **9** with acetic anhydride gave TTF bisanhydride **19** in 47% yield. It was hoped that bisanhydride **19** upon reaction with ethylene glycol would produce 2,6(7)-bis(2-hydroxycarbethoxy)tetrathiafulvalene, a diol which could presumably be polycondensed with diacid **9**. However, reaction of ethylene glycol with **19** gave the TTF diacid **9**. Condensation of diacid **9** with aniline readily give bisanilide **20** in *N,N*-dimethylformamide (D) at 70 °C using diphenyl phosphite–pyridine as a dehydrating reagent. This reagent has previously been used to catalyze polyamide formation.[5,21]

Charge-Transfer Complexes of TTF Derivatives with TCNQ and DDQ. A preliminary study of the ability of TTF derivatives **6**, **13**, **14**, **15**, **16**, **18**, and **20** to form salts or charge-transfer complexes with TCNQ and DDQ was made (Table II). Hot acetonitrile solutions of TCNQ or DDQ were added to hot acetonitrile solutions of the TTF derivative. In the cases of compounds **13**, **14**, **15**, **16**, and **18** complexes with DDQ precipitated when the solutions were slowly cooled to room temperature. TCNQ may form charge-transfer complexes with TTF derivatives **13**, **14**, **15**, **16**, and **18** in solution but precipitation of a complex from acetonitrile occurred only for diols **15**, **16**, and **18**. Compounds **6** and **20**, which have electron-withdrawing substituents, did not form complexes with either TCNQ or DDQ.

Table I. Desulfurization of 1,3-Dithiole-2-thiones



6-8

R^1	R^2	R	Yield, %	Product
$COOCH_3$	H	C_2H_5O	38	6
$COOCH_3$	$COOCH_3$	C_2H_5O	52	7
$COOCH_3$	$COOCH_3$	C_6H_5	22[a]	7
	H	C_2H_5O	9	8

[a] 69% of dimethyl 1,3-dithiole-2-thione-4,5-dicarboxylate was recovered.

Table II. Complex Formation of TTF Derivatives with DDQ and TCNQ[a]

TTF donor	Acceptor	Formula	Found (calcd), % C	H	N
13[b]	DDQ	$C_{30}H_{16}N_2O_6S_4Cl_2$	51.36 (51.50	2.31 2.31	4.14 4.00)
14[c]	DDQ	$C_{30}H_{16}N_2O_6S_4Cl_2$	51.42 (51.50	2.41 2.31	4.56 4.00)
18	DDQ	$C_{16}H_8N_2O_4S_4Cl_2$	39.10 (39.42	1.64 1.71	5.70 5.86)[d]
18	TCNQ	$C_{20}H_{12}N_4O_2S_4$	51.51 (51.70	2.43 2.60	11.88 12.06)

[a] TCNQ and DDQ complexes of **15** and **16** did not give satisfactory analyses for 1:1 or 1:2 complexes. [b] Mp 175–177 °C. [c] Mp 137–139 °C. [d] Cl found, 14.68; calcd, 14.43.

The ir spectra of the DDQ complexes with **13, 14, 15, 16,** and **18** showed the expected low frequency $\nu_{C=O}$ at 1550–1560 cm^{-1} expected of the DDQ radical anion. This may be contrasted with $\nu_{C=O}$ 1680 cm^{-1} in DDQ itself, which was not present in the spectra of the complexes. Absorptions at 1480–1470 and 1350–1340 cm^{-1} also were found in each complex. Each of the TCNQ complexes (with **15, 16,** and **18**) contained nitrile stretching bands about 30–40 cm^{-1} lower than the 2310-cm^{-1} band of TCNQ itself. This implies that $TCNQ^-$ has been formed in the complexes. Ueno and Okawara[22] reported that several TTF derivatives reacted with DDQ in mole ratios which depended upon the partilar substituents present in TTF. The DDQ complexes of **13, 14,** and **18** and the TCNQ complex of **18** gave satisfactory analyses for 1:1 complexes, but the analyses for both DDQ and TCNQ complexes of **15** and **16** could not be fit to integral ratios. Phenolic compounds bring about nucleophilic displacement in both TCNQ and DDQ and if a small fraction of the complexes prepared here underwent this reaction, the analytical results would be explained.

Experimental Section

Melting points were uncorrected. Infrared spectra were obtained as potassium bromide disks with a Beckman IR-33. Nuclear magnetic resonance spectra were obtained using a Perkin-Elmer Hatachi Model R-20B spectrometer. *m*- and *p*-hydroxyphenacyl bromide were prepared according to the literature[23] with the single exception that a longer reflux time (3–4 h) was employed.

Methyl 1,3-Dithiole-2-thione-4-carboxylate (3). Esterification of 1,3-dithiole-2-thione-4-carboxylic acid (2) was carried out by Clinton's method.[13] A mixture of 1,3-dithiole-2-thione-4-carboxylic acid (**2,** 35.6 g, 0.2 mol), 20 ml of methanol, 4 ml of concentrated sulfuric acid, and 80 ml of ethylene dichloride was refluxed for 13 h and then chilled in an ice bath. The solid was collected and washed (with aqueous sodium bicarbonate and water, successively) to give 18.2 g of the ester **3.** The filtrate and the washings were combined, and the organic layer was further washed (with aqueous sodium bicarbonate and water). Concentration of the organic layer gave additional crystals of ester **3** (16.0 g) for a total of 34.2 g (89% yield). The aqueous layer was acidified with 3 N HCl to recover 2.8 g of the acid **2.** After recrystallization from carbon tetrachloride, **3** melted at 105–107 °C: ir (KBr) 3060, 3020, 2975, 1715, 1528, 1436, 1295, 1285, 1200, 1072, 1053 cm^{-1}; NMR ($CDCl_3$) δ 3.90 (s, 3 H), 7.96 (s, 1 H). Anal. Calcd for $C_5H_4O_2S_3$: C, 31.23; H, 2.10; S, 50.02. Found: C, 31.27; H, 2.07; S, 50.04.

4-(*p*-Nitrophenyl) 1,3-Dithiole-2-thione-4-carboxylate (4). To a solution of 3.56 g (0.02 mol) of **2** and 3.34 g (0.024 mol) of *p*-nitrophenol in 40 ml of THF was added 4.94 g (0.024 mol) of dicyclohexylcarbodiimide at 0–5 °C under stirring. The reaction mixture was kept at room temperature for 2 h and then filtered. The precipitate was washed with acetone. The filtrate and the washings were combined, and volatiles were removed to give 5.40 g (90%) of the ester **4,** which was purified by recrystallization from toluene: mp 156–157 °C; ir (KBr) 3070, 1715, 1610, 1585, 1505, 1485, 1348, 1263, 1200, 1160, 1075, 1000 cm^{-1}. Anal. Calcd for $C_{10}H_5NO_4S_3$: C, 40.12; H, 1.68; N, 4.68. Found: C, 40.34; H, 1.80; N, 4.51.

Trifluoroacetic Anhydride 5. Tetrahydrofuran (THF, 50 ml) was stirred while 5.34 g (0.03 mol) of **2** and 3.04 g (0.03 mol) of triethylamine were dissolved while stirring. The solution was cooled to 0–5 °C and a solution of 8.4 g (0.04 mol) of trifluoroacetic anhydride in 10 ml of THF was added dropwise at 5–10 °C. The cooling bath was removed and the stirring was continued for 3 h. Volatiles were removed under reduced pressure. The residue was stirred with a little water and filtered to give 5.83 g (71%) of the yellow-brown crystals. Recrystallization from toluene gave crystals which melted at 130–132 °C: ir (KBr) 3095, 3070, 1770, 1705, 1520, 1280, 1225, 1190, 1140, 1060, 990 cm^{-1}. Anal. Calcd for $C_6HF_3O_3S_3$: C, 26.38; H, 0.37; F, 20.78; S, 35.07. Found: C, 26.13; H, 0.56; F, 19.92; S, 36.01. After a second recrystallization from cyclohexane, the mp was 132.5–133 °C. Analysis gave F, 20.42; S, 35.73.

2,6(7)-Bis(carbomethoxy)tetrathiafulvalene (6). A mixture of 21.1 g (0.11 mol) of the ester **3,** 36.4 g (0.22 mol) of triethyl phosphite, and 100 ml of benzene was refluxed for 35 h. A red precipitate was formed which was filtered, while the solution was hot, and washed with benzene to give 3.5 g of TTF **6,** mp 242–244 °C. Recrystallization from glyme gave material which melted at 244–246 °C (lit.[12] 244–245 °C). The filtrate and the washings were combined and concentrated under vacuum. To the residue was added 300 ml of methanol to precipitate orange crystals of **6** (3.2 g).[24]

2,3,6,7-Tetrakis(carbomethoxy)tetrathiafulvalene (7). A mixture of 10.0 g (0.04 mol) of dimethyl 1,3-dithiole-2-thione-4,5-dicarboxylate, 10.0 g (0.06 mol) of triethyl phosphite, and 80 ml of benzene was refluxed for 10 h. After cooling to room temperature, benzene was removed under vacuum. To the residue was added 50 ml of ethanol to precipitate the tetraester **7.** The yield was 4.4 g (52%), mp 167–169 °C. Recrystallization from methanol gave red-purple crystals (3.9 g), mp 169–170 °C (lit.[7] 169–170 °C). A mixture of 2.5 g (0.01 mol) of diester **1,** 3.9 g (0.015 mol) of triphenylphosphine, and 20 ml of benzene was refluxed for 24 h. The mixture was developed by dry column chromatography (silica gel) with benzene eluent to separate 2.45 g of triphenylphosphine, 1.73 g (69%) of diester **1,** and 0.48 g (22%) of tetraester **7.**

2,6(7)-Bis(*p*-nitrophenyloxycarbonyl)tetrathiafulvalene (8). A mixture of 5.98 g (0.02 mol) of ester **4,** 6.67 g (0.04 mol) of triethyl phosphite, and 100 ml of benzene was refluxed for 60 h. Precipitates were filtered to give 0.50 g (9%) of crude product, which was twice recrystallized from toluene: mp 280 °C dec; ir (KBr) 1720, 1610, 1590, 1540, 1518, 1485, 1344 cm^{-1}. Anal. Calcd for $C_{20}H_{10}N_2O_8S_4$: C, 44.94; H, 1.89; N, 5.24; S, 23.99. Found: C, 45.36; H, 2.08; N, 5.31; S, 24.42.

Reaction of 1,3-Dithiole-2-thione-4-carboxylic Acid (2) with Triethyl Phosphite. A mixture of 1.78 g (0.01 mol) of **2,** 1.67 g (0.01 mol) of triethyl phosphite, and 20 ml of benzene was refluxed for 30 h. Volatiles were removed in vacuo. The residue was dissolved in chloroform, and developed on dry column (silica gel) with chloroform elution to separate 0.78 g (36%) of ethyl 1,3-dithiole-2-thione-4-carboxylate (**10**). Recrystallization from cyclohexane gave material which melted at 39–41 °C: ir (KBr) 1710, 1540, 1300, 1225, 1090, 1075 cm^{-1}; NMR ($CDCl_3$) δ 1.36 (t, 3 H), 4.35 (q, 2 H), 7.92 (s, 1 H). Anal. Calcd for $C_6H_6O_2S_3$: C, 34.93; H, 2.93; S, 46.62. Found: C, 34.90; H, 2.96; S, 46.58.

***m*-Hydroxyphenacylpiperidinocarbodithioate.** To a solution of piperidine (0.6 mol) in 300 ml of ethanol was added a solution of CS_2 (30 ml) in ethanol (200 ml) under rapid stirring at 5 °C. Crystals of the salt precipitated but the salt was not isolated. A mixture of *m*-hydroxyphenacyl bromide[23] (65 g, 0.30 mol), 75 g (0.30 mol) of piperidinium piperidinocarbodithioate, and 500 ml of ethanol was refluxed for 2 h. After cooling, ethanol was removed in vacuo. Addition of water to the residue resulted in the precipitation of a crystalline material (75.5 g, 85%). Recrystallization from ethanol gave *m*-hydroxyphenacylpiperidinocarbodithioate which melted at 175–176 °C: ir (KBr) 3280, 2940, 1660, 1600, 1575, 1479, 1442, 1423, 1345, 1313, 1272, 1234, 1216, 1160, 1127, 1102, 1028, 1012, 990 cm^{-1}. Anal. Calcd for $C_{14}H_{17}NO_2S_2$: C, 56.94: H, 5.80; N, 4.74. Found: C, 57.56; H, 5.82; N, 4.73. *p*-Hydroxyphenacylpiperidinocarbodithioate was prepared in an identical fashion and gave satisfactory analyses and spectra.

4-(*p*- and *m*-Hydroxyphenyl)-1,3-dithiole-2-ylidenepiperidinium Fluoroborates. A mixture of either *p*- or *m*-hydroxyphenacylpiperidinocarbodithioates (29.5 g, 0.10 mol), 20 ml of hydrofluoroboric acid (42%), 13.0 g of P_4S_{10}, and 300 ml of glacial acetic acid was refluxed for 20 h. Treatment of the solution with charcoal, followed by evaporation of solvent and addition of ethanol to the residue, gave pink crystals. Recrystallization from ethanol gave the pure salt.

4-(*p*-Hydroxyphenyl)-1,3-dithiole-2-ylidenepiperidinium fluoroborate: yield 32.2 g (88%); mp 172–174 °C; ir (KBr) 3400, 1605, 1573, 1532, 1510, 1445, 1372, 1280, 1255, 1228, 1210, 1078, 1110–1020 cm^{-1}. Anal. Calcd for $C_{14}H_{16}NOS_2BF_4$: C, 46.04; H, 4.42; N, 3.84. Found: C, 46.16; H, 4.23; N, 3.93.

4-(*m*-Hydroxyphenyl)-1,3-dithiole-2-ylidenepiperidinium fluoroborate: yield 31.4 g (86%); mp 185–186 °C; ir (KBr) 3420, 3080, 2940, 1603, 1567, 1532, 1490, 1478, 1464, 1446, 1320, 1280, 1180, 1110–1030, 852, 796, 775 cm^{-1}. Anal. Calcd for $C_{14}H_{16}NOS_2BF_4$: C, 46.04; H, 4.42; N, 3.84. Found: C, 46.24; H, 4.41; N, 3.95.

4-(*p*- and *m*-Acetoxyphenyl)-1,3-dithiole-2-ylidenepiperidinium Fluoroborates. A mixture of 18.3 g (0.05 mol) of the 4-(*p*- or *m*-hydroxyphenyl)-1,3-dithiole-2-ylidenepiperidinium fluoroborate, 30 ml of acetic anhydride, and 300 ml of acetonitrile was refluxed for 20 h. Volatiles were removed in vacuo. To the residue was added ethanol to give pink crystals. Recrystallization from ethanol gave the pure material.

4-(*p*-Acetoxyphenyl)-1,3-dithiole-2-ylidenepiperidinium fluoroborate: yield 18.2 g (94%); mp 161–163 °C (methanol); ir (KBr) 3020, 2950, 2840, 1755, 1567, 1526, 1496, 1437, 1372, 1210, 1167, 1120–1030, 914, 857, 786 cm^{-1}. Anal. Calcd for $C_{16}H_{18}NO_2S_2BF_4$: C, 47.19; H, 4.45; N, 3.44. Found: C, 46.74; H, 4.35; N, 3.48.

4-(*m*-Acetoxyphenyl)-1,3-dithiole-2-ylidenepiperidinium fluo-

roborate: yield 18.7 g (92%); mp 159–160 °C (ethanol); ir (KBr) 2980, 2950, 1760, 1565, 1525, 1472, 1437, 1372, 1210, 1160, 1120, 1030, 923, 904 cm^{-1}. Anal. Calcd for $C_{16}H_{18}NO_2S_2BF_4$: C, 47.19; H, 4.45; N, 3.44. Found: C, 46.65; H, 4.35; N, 3.86.

4-(*p*-Acetoxyphenyl)-2-piperidino-1,3-dithiole. To a suspension of 8.2 g (0.02 mol) of 4-(*p*-acetoxyphenyl)-1,3-dithiole-2-ylidenepiperidinium fluoroborate in 200 ml of ethanol, 3.0 g of sodium borohydride was added in small portions. The reaction mixture was stirred for 30 min at 0 °C. Addition of water precipitated 5.3 g (82%) of yellow solid. Recrystallization from ethanol–water gave yellow crystals (4.8 g) which melted at 77–79 °C: ir (KBr) 2940, 2850, 2805, 1765, 1748, 1541, 1503, 1438, 1370, 1308, 1215, 1195, 1167, 1095, 990 cm^{-1}. Anal. Calcd for $C_{16}H_{19}NO_2S_2$: C, 60.04; H, 5.88; N, 4.49. Found: C, 59.78; H, 5.96; N, 4.36. 4-(*m*-Acetoxyphenyl)-1,3-dithiole-2-ylidenepiperidinium fluoroborate was prepared in a similar manner. After the addition of water (500 ml in a 20-mmol scale preparation), the product was extracted with ether and dried (Na_2SO_4), and the ether was removed in vacuo. The residue was dissolved in 80 ml of ethanol and this was used directly, without further purification, to produce dithiolium salts **11** or **12** described below.

2,6(7)-Bis(*p*- and *m*-acetoxyphenyl)tetrathiafulvalenes (13 and 14). To a suspension of 1.61 g (0.5 mmol) of 4-(*p*-acetoxyphenyl)-2-piperidino-1,3-dithiole in 20 ml of ethanol, 3 ml of perchloric acid (60%) was added dropwise with stirring at 0–5 °C to form yellow crystals. Filtration and washing with ether gave 1.1 g (65%) of the 4-(*p*-acetoxyphenyl)-1,3-dithiolium perchlorate salt, **11**. 4-(*m*-Acetoxyphenyl)-1,3-dithiolium perchlorate (**12**) was obtained from 4-(*m*-acetoxyphenyl)-2-piperidino-1,3-dithiole by the same procedure with an overall yield from 4-(*m*-acetoxyphenyl)-1,3-dithiole-2-ylidenepiperidinium fluoroborate of 87%. Salts **11** and **12** had ir absorption bands at 3020, 1755, 1370, 1215, 1205, 1142, 1115, 1090 cm^{-1}. *Caution!* the reaction scale should be kept to about 0.5 mmol (1.61 g) of 4-(*p*- or *m*-acetoxyphenyl)-2-piperidino-1,3-dithiole, and salts **11** and **12** should be precipitated in a few minutes, where filtered. They should be washed thoroughly with ether. In our hands, 1-g lots of **11** and **12** could be stored safely, but caution should be always exercised and several small lots should not be combined.[25] Perchlorate salts **11** and **12** are stable in solution, and larger scale preparations of **13** and **14** than those described below can be conducted. For example, reactions on a 5-g (of **11** or **12**) scale were conducted.

Perchlorate salt **11** (1 g) was dissolved in 40 ml of acetonitrile. The solution was magnetically stirred at 0 °C and 2 g triethylamine in 10 ml of acetonitrile was added. After stirring for 1 h, water was added, precipitating crystals (0.64 g, 91%) identified as diacetate **13**. Diacetate **14** was obtained in 93% yield by the same method.

2,6(7)-Bis(*p*-acetoxyphenyl)tetrathiafulvalene (**13**): orange crystals, mp 228–230 °C (benzene); ir (KBr) 1738, 1550, 1505, 1375, 1220–1195, 1167, 1017, 911, 843, 780, 762 cm^{-1}. Anal. Calcd for $C_{22}H_{16}O_4S_4$: C, 55.91; H, 3.41. Found: C, 55.42; H, 3.52.

2,6(7)-Bis(*m*-acetoxyphenyl)tetrathiafulvalene (**14**): orange crystals, mp 185–186 °C (ethanol); ir (KBr) 1760, 1603, 1370, 1205, 1147, 1016, 918, 760 cm^{-1}. Anal. Calcd for $C_{22}H_{16}O_4S_4$: C, 55.91; H, 3.41. Found: C, 55.99; H, 3.35.

2,6(7)-Bis(*p*- and *m*-hydroxyphenyl)tetrathiafulvalenes (15 and 16). To a suspension of 0.47 g (1.0 mmol) of **13** in 20 ml of methanol, 3 ml of hydrazine hydrate was added. The reaction mixture was stirred at room temperature. Methanol was removed in vacuo. The residue was cooled to ~5 °C and filtered, and the filtrate was washed with small amounts of methanol and acetonitrile to give orange crystals of **15** in quantitative yield. Similarly, **16** was obtained quantitatively.

2,6(7)-Bis(*p*-hydroxyphenyl)tetrathiafulvalene (**15**): mp 207–208 °C (methanol); ir (KBr) 1600, 1548, 1502, 1455, 1382, 1248, 1172, 919, 825, 760 cm^{-1}. Anal. Calcd for $C_{18}H_{12}S_4O_2$: C, 55.64; H, 3.11. Found: C, 55.43; H, 3.25.

2,6(7)-Bis(*m*-hydroxyphenyl)tetrathiafulvalene (**16**): mp 224–225 °C (methanol); ir (KBr) 1595, 1548, 1445, 1268, 1226, 1169, 990, 842 cm^{-1}. Anal. Calcd for $C_{18}H_{12}S_4O_2$: C, 55.64; H, 3.11. Found: C, 56.03; H, 3.37.

Hydrolysis of Esters 6 and 7. Hydrolysis of diester **6** was conducted as reported previously[12] giving **9** quantitatively. The dark purple solid was recrystallized from pyridine to give yellow-orange crystals, which became dark purple upon drying at 70–80 °C under vacuum, mp >350 °C (lit.[12] >350 °C). Anal. Calcd for $C_8H_4O_4S_4$: C, 32.87; H, 1.38. Found: C, 32.74; H, 1.32. TTF ester **7** was hydrolyzed under similar conditions, yield 90%. Recrystallization from water gave purple, crystalline material, which did not melt below 300 °C: ir (KBr) 1650, 1570, 1360, 1095, 755 cm^{-1}. Anal. Calcd for $C_{10}H_4O_8S_4$: C, 31.58, H, 1.06; S, 33.71. Found: C, 31.82; H, 1.21; S, 33.19.

2,6(7)-Bis(hydroxymethyl)tetrathiafulvalene (18). Diacid **9** (5.84 g, 0.02 mol) was cautiously added to sodium borohydride (2.76 g, 70 ml of 1.0 M solution in diglyme) after a thorough nitrogen purge. A 200-ml three-necked flask equipped with a pressure-equalized dropping funnel, magnetic stirrer, nitrogen inlet, and an outlet for hydrogen and excess diborane was used for this reaction. The diborane outlet capillary was connected to a mercury-immersed capillary safety release valve. Boron trifluoride etherate (5.7 g, 0.04 mol) in 30 ml of diglyme was added to the solution over a period of 1 h through the separatory funnel. After an additional 3 h at room temperature, the reaction mixture was poured onto crushed ice and kept in a refrigerator overnight. This caused the precipitation of a solid which was collected on a filter, washed with ice–water, and dried. The yield of the crude product was 0.67 g (13%), mp 172–176 °C dec. Recrystallization from ethanol gave yellow-brown crystalline material, which melted at 178–180 °C dec: ir (KBr) 3350, 3260, 3070, 3030, 2960, 2930, 1580, 1460, 1372, 1232, 1090, 1013 cm^{-1}; NMR (Me_2SO-d_6) δ 4.24 (d, 2, OCH_2), 5.49 (t, 1, CH), 6.53 (s, 1, OH). Anal. Calcd for $C_8H_8O_2S_4$: C, 36.34; H, 3.05; S, 48.50. Found: C, 35.87; H, 3.15; S, 48.10.

Bis Acetic Anhydride of Tetrathiafulvalene-2,6(7)-dicarboxylic Acid (19). In a mixture of 20 ml of acetic anhydride and 30 ml of THF, 1.18 g (4 mmol) of diacid **9** was suspended. This suspension was refluxed for 24 h and then the remaining diacid was filtered (0.41 g of diacid **9**). The filtrate was evaporated in vacuo to give a residue which was recrystallized from acetonitrile to give 0.46 g of **19**, mp ~350 °C (gradually dec). The yield was 47% based on diacid **9** originally charged to the reactor: ir (KBr) 3060, 3030, 1803, 1705, 1545, 1380, 1275, 1150, 1015, 990 cm^{-1}. Anal. Calcd for $C_{12}H_8O_6S_4$: C, 38.29; H, 2.14. Found: C, 37.64; H, 2.18.

Reaction of Bis Acetic Anhydride 19 with Ethylene Glycol. To 20 ml of THF was added 0.02 g of **19** and 2 ml of ethylene glycol. This solution was refluxed for 3 h; THF was removed, and to the residue was added a small amount of methanol. A solid was collected on a filter and identified[12] as diacid **9**, 0.14 g (90%).

Bisanilide 20 of Tetrathiafulvalene-2,6(7)-dicarboxylic Acid (9). To 0.59 g (2 mmol) of diacid **9** and 0.38 g (4 mmol) of aniline in 20 ml of *N,N*-dimethylformamide (DMF) was added 5 ml of pyridine and 1.40 g (6 mmol) of diphenyl hydrogen phosphonate. The reaction mixture was stirred at 70 °C for 10 h. The mixture was poured into water and a precipitate was collected by filtration and washed with acetone. After drying, the yield of **9** was 0.64 g (72%), mp 224 °C dec. Recrystallization from acetonitrile gave diacid **9**: mp 224–226 °C dec; ir (KBr) 3330, 3060, 3020, 1630, 1595, 1540, 1495, 1440, 1320, 1260 cm^{-1}. Anal. Calcd for $C_{20}H_{14}N_2O_2S_4$: C, 54.28; H, 3.19; N, 6.33. Found: C, 54.24; H, 3.48; N, 6.24.

Charge Transfer Complexes of TTF Derivatives with TCNQ and DDQ. To a hot solution of the TTF derivative (0.2 mmol) in 30 ml of acetonitrile was added a hot solution of TCNQ (0.4 mmol) or DDQ (0.4 mmol) in acetonitrile. The mixture slowly cooled to room temperature, was filtered, washed with acetonitrile, and vacuum dried. The results are summarized in Table II.

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Registry No.—**1**, 7396-41-0; **2**, 1004-08-6; **3**, 55526-01-7; **4**, 59269-67-9; **5**, 59269-68-0; **6**, 51751-18-9; **7**, 26314-39-6; **8**, 59269-69-1; **9**, 51751-19-0; **10**, 59269-70-4; **11**, 59269-72-6; **12**, 59269-74-8; **13**, 59269-75-9; **14**, 59269-76-0; **15**, 59269-77-1; **16**, 59269-78-2; **17**, 59269-79-3; **18**, 58268-45-4; **19**, 59269-80-6; **20**, 59269-81-7; *p*-nitrophenol, 100-02-7; trifluoroacetic anhydride, 407-25-0; triethyl phosphite, 122-52-1; *m*-hydroxyphenacyl bromide, 2491-38-5; piperidinium piperidinocarbodithioate, 98-77-1; *m*-hydroxyphenacylpiperidinocarbodithioate, 59269-82-8; *p*-hydroxyphenacylpiperidinocarbodithioate, 24372-67-6; 4-(*p*-hydroxyphenyl)-1,3-dithiole-2-ylidenepiperidinium fluoroborate, 59269-83-9; 4-(*m*-hydroxyphenyl)-1,3-dithiole-2-ylidenepiperidinium fluoroborate, 59269-85-1; 4-(*p*-acetoxyphenyl)-1,3-dithiole-2-ylidenepiperidinium fluoroborate, 59269-87-3; 4-(*m*-acetoxyphenyl)-1,3-dithiole-2-ylidenepiperidinium fluoroborate, 59269-89-5; 4-(*p*-acetoxyphenyl)-2-piperidino-1,3-dithiole, 59269-90-8; perchloric acid, 7601-90-3; acetic anhydride, 108-24-7; aniline, 62-53-3; 4-(*m*-acetoxyphenyl)-2-piperidino-1,3-dithiole, 59269-91-9.

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(25) The formation of hexafluorophosphate salts would probably be a preferable route, but it was not done in this study.

Tetrazolo[1,5-*b*]-1,2,4-triazines. Syntheses and Structure Determination

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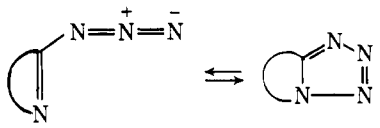
Several 3-azido-1,2,4-triazines were prepared by treating the corresponding 3-hydrazino derivatives with nitrous acid. The azidotriazines spontaneously cyclized into a tetrazolo isomer. These transformations were studied using nuclear magnetic resonance and infrared spectroscopic methods. The tetrazolo isomers were proven to be tetrazolo[1,5-*b*]-1,2,4-triazines by an x-ray crystallographic study on the 5-*p*-chlorophenyl derivative.

Azido-substituted π-deficient nitrogen heterocyclic systems have been extensively investigated.[1] These studies have established that the equilibrium



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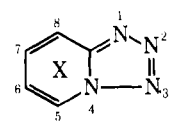
is strongly controlled by (a) the π deficiency of the nitrogen heterocycle; (b) the polarity of the solvents; and (c) to some extent, temperature. The following interpretive statement has been made:[1]

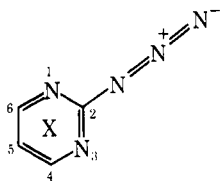
"In azolazines, the azine part of the molecule is responsible for the magnitude of the charge on the N-atom common to both rings. If the negative charge can be further delocalized on other N-atoms in the *m*-position of the azine ring, this enhances the stability of the azido form."

By way of recapitulating the data, the following compounds exist, in dimethyl sulfoxide, as the tetrazolo derivatives:[2-6]



3, X = nil
4, X = N, at position 5
5, X = N, at position 6
6, X = N, at position 7

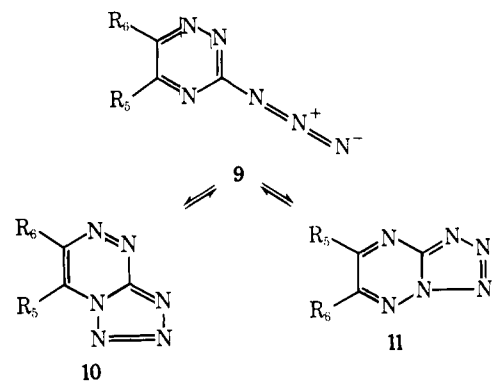
When a nitrogen is substituted at position 8 in the above structure, the azido heterocycles are formed in dimethyl sulfoxide.[7] For example:



7, X = nil (10% in this form)
8, X = N, at position 5 (100% in this form)

The formation of these azido compounds is greatly enhanced by nonpolar solvents (compound **7** in chloroform solution is reported to exist totally in the azido form).[8]

In view of our extensive interest in 1,2,4-triazines and the potential dual possibility of cyclization (**10**, **11**), we decided to study the behavior of some 3-azido-1,2,4-triazines (**9**).



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