Syntheses and Reactions of 3,4-Dialkyl-1,3,4-thiadiazolidine-2,5-diones

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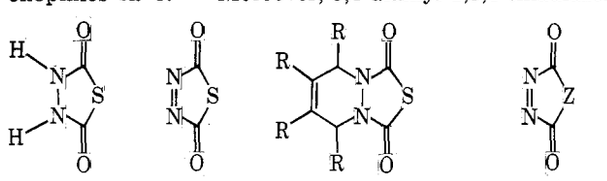
The oxidation of 1,3,4-thiadiazolidine-2,5-dione (**1**) to 1,3,4-thiadiazole-2,5-dione (**2**) is reported. As a dienophile **2** is as reactive as 4-phenyl-1,2,4-triazoline-3,5-dione but decomposes to nitrogen, carbon monoxide, and carbon oxysulfide in acetone at temperatures above −35°. The fragmentation of 3,4-dialkyl-1,3,4-thiadiazolidine-2,5-diones, obtained by $[4_\pi + 2_\pi]$ cycloadditions of **2** followed by reduction or by alkylation of **1**, has been investigated. Reaction to produce a carbon-carbon bond between the alkyl groups is successful only for the conversion of 5,6,7,8-tetrahydro-5,8-methanopyridazino[1,2-*c*]-2-thia-4,9-diazole-1,3-dione (**11a**) to bicyclopentane. An early literature claim of the synthesis of **1** is corrected.

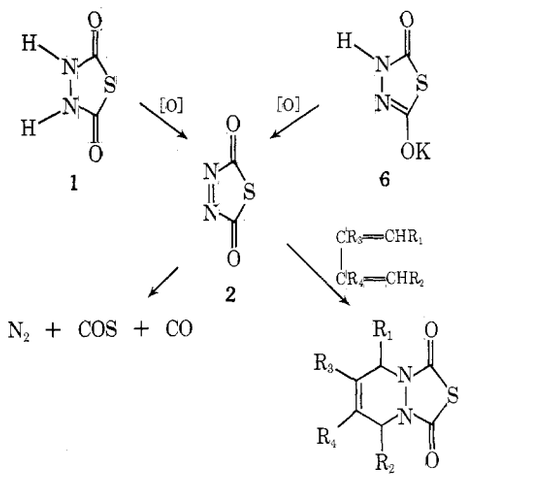
The 1,3,4-thiadiazolidine-2,5-dione ring system appears to have interesting synthetic potential. Oxidation of the parent system **1**[1] should give 1,3,4-thiadiazole-2,5-dione[2,3] (**2**), a species which would be a highly reactive dienophile, and would give adducts, **3**, which should be more amenable to subsequent conversions than those from the related dienophiles **4a–c**.[4–11] Moreover, 3,4-dialkyl-1,3,4-thiadiazolidine-2,5-diones, whether **3**, cycloaddition products of **1**, or **5**, alkylation products of **1**, could undergo a symmetry-allowed fragmentation, giving an azo compound, carbon monoxide, and carbon oxysulfide,[12] or even the latter two products along with nitrogen and carbon–carbon bond formation. Those processes find analogy in a number of reactions, some of which are exceptionally useful.[13] The oxidative conversion of **1** to **2** and the trapping of **2** by $[4_\pi + 2_\pi]$ cycloadditions have been noted.[2,3] We wish to describe our work on this oxidation and trapping, report a comparison of the dienophilic activity of **2** to **4a**, note the syntheses of derivatives of **1** by alkylation procedures, and report one successful case of carbon–carbon bond formation by fragmentation of a derivative of **1**.



Results and Discussion

Diels–Alder Reactions of 1,3,4-Thiadiazole-2,5-dione (2). 1,3,4-Thiadiazole-2,5-dione (**2**) is generated by oxidation of 1,3,4-thiadiazolidine-2,5-dione (**1**) or its monopotassium salt (**6**) with cupric chloride, lead tetraacetate, or *tert*-butyl hypochlorite at 0° in a suitable solvent and may be trapped with reactive dienes to give Diels–Alder adducts. Reaction of dienes with **1** and cupric chloride in dimethylformamide (DMF) gives adducts **3a** from cyclopentadiene (65%), **3b** from 1,3-cyclohexadiene (43%), **3c** from 2,3-dimethylbutadiene (23%), and **3d** from isoprene (4%). Although 1,3-butadiene is unreactive under these conditions, adduct **3e** can be produced in 49% yield by reaction of **1** and *tert*-butyl hypochlorite with the diene in acetone at −78°. The three oxidants give comparable yields of adduct **3a** from **1** and cyclopentadiene in DMF at 0°.

In the absence of a suitable trapping diene, compound **2** decomposes to nitrogen, carbon monoxide, and carbon oxysulfide, as shown by gas chromatographic analysis. An analogous fragmentation has been reported for 1,2,4-triazoline-3,5-dione.[14] Oxidation of **6** with *tert*-butyl hypochlorite in acetone at −78° produces a violet solution, λ_{max} 553 ± 3 nm (ε 170 ± 30). A shoulder on this absorption at 625 nm is consistent with the shift expected for the O,O band of the n, π* transition of **2** relative to analogous transition of closely related compounds.[15] If the acetone solution is allowed to warm to −35°, the color quickly fades.



3a, $R_1 + R_2 = CH_2$; $R_3 = R_4 = H$
b, $R_1 + R_2 = CH_2CH_2$; $R_3 = R_4 = H$
c, $R_1 = R_2 = H$; $R_3 = R_4 = CH_3$
d, $R_1 = R_2 = R_3 = H$; $R_4 = CH_3$
e, $R_1 = R_2 = R_3 = R_4 = H$

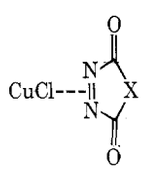
[O] = $CuCl_2$, $Pb(OAc)_4$, +OCl

The potential Diels–Alder dienes hexachlorocyclopentadiene, norbornadiene, 1,3-cyclooctadiene, 1,3-cycloheptadiene, 1,4-diphenyl-1,3-butadiene, 1,3-cycloheptadiene, 1,4-diphenyl-1,3-butadiene, tetraphenylcyclopentadienone, anthracene, furan, and thiophene were found to be unreactive with **2** generated from cupric chloride and **1** in DMF or aqueous acetone. The adduct yields for the dienes reactive with **2** are subject to the same rationales which have been given for the corresponding reactions with maleic anhydrides in terms of conformations of the dienes.[16] The dienophile **2** gives lower yields with the reactive dienes than does 4-phenyl-1,2,4-triazoline-3,5-dione (**4a**) and **4a** is reactive with a number of the above dienes[7] which fail to yield adducts with **2**. Apparently a decreased probability of productive collisions of **2** with unreactive dienes is sufficient to allow competitive decomposition of **2**.

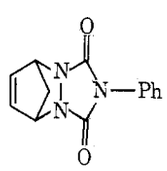
Solvent has a pronounced effect upon the reaction. In general, polar solvents increase the rate of oxidation of **1** and **6** to give **2**, which appears to be stable in such solvents; hexamethylphosphoramide, DMF, and 50% aqueous acetone give equally good yields of adducts. Methylene chloride, which is commonly used for reactions of triazol-

inediones with olefins,[6] is not a suitable solvent for formation and reactions of thiadiazoledione **2** with dienes at 0 or −78°, apparently because the rate of oxidation of **1** and **6** is much slower in this solvent than in more polar solvents. Moreover, **2** itself appears to be less stable in methylene chloride, since an acetone solution of **2** when mixed with methylene chloride at −78° decomposes at −53°, 18° below the temperature at which an acetone solution of **2** decomposes. Methanol, 95% ethanol, and pyridine, when used as solvents with cupric chloride, **1**, and cyclopentadiene, give **3a** in either lower yield or lower purity than when DMF is used as solvent.

The formation of adducts of **2** from different precursors and with different oxidizing agents and the low-temperature ultraviolet spectrum provide evidence for the intermediacy of free **2**. The oxidations can be rationalized through the generally accepted pathways for the oxidants used.[17-19] It seems likely that **2** and **4a**, formed in cupric chloride oxidations of **1** and 4-phenylurazole (**8**), respectively (*vide infra*), are in equilibrium with the copper complexes **7a** and **7b**.[13a-f] The visible–ultraviolet spectra of the solutions resulting from oxidation do not show absorptions due to the dienophiles **2** and **4a**,[15] but do exhibit absorptions at 386 nm (ϵ 22 and 33, respectively, for **7a** and **7b**), tentatively attributable to the n–π^* absorption of the azo function.[20] The expected Diels–Alder products **3a** and **8** are formed in the presence of cyclopentadiene under these conditions.



7a, X = S
b, X = NPh



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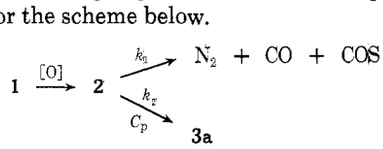
Competition of 1,3,4-Thiadiazole-2,5-dione (2) and 4-Phenyl-1,2,4-triazoline-3,5-dione (4a) for Cyclopentadiene. A matter of considerable interest is a comparison of the Diels–Alder reactivity of 1,3,4-thiadiazole-2,5-dione (**2**) with 4-phenyl-1,2,4-triazoline-3,5-dione (**4a**); the latter species is one of the most potent and useful dienophiles.[4-7,13k,q,r,21] Since **2** is less stable than **4a** at ambient temperature, any comparison of **2** and **4a** must be made under conditions such that unimolecular decomposition of **2** does not occur to a significant extent.

A limit on the ratio of decomposition to trapping in oxidation of **1** with cupric chloride in DMF at 0° may be obtained from the data given in Table I, which shows the yield of adduct **3a** as a function of cyclopentadiene concentration. The proportion of **2** undergoing bimolecular trapping to that undergoing unimolecular decomposition is $k_2(Cp)/k_1$ for the scheme below.



If it is assumed that $k_2/k_1 = 100\ M^{-1}$, the values given in the last column of the table are obtained. The discrepancy between those values and the observed yields in the fourth column show that the k_2/k_1 ratio must be greater than 100 M^{-1}, and the correspondence of the theoretical and observed yields over a variation of 1.0 to 0.1 in the cyclopentadiene:**1** ratio suggests that little fragmentation of **2** occurs.

To assess the relative reactivity of **2** and **4a**, a solution of **2** prepared by oxidation of **6** with *tert*-butyl hypochlorite in acetone at −78° was mixed with an equimolar quantity of **4a** and the dienophiles were allowed to react with a limiting quantity of cyclopentadiene. The ratio of adducts **3a**:**8** was observed to be 1.0 to 1.5, depending upon the amount of **6** oxidized. The quantity of **2** present in solution was determined by uv analysis of **6** remaining after oxidation, and it was assumed that the oxidation product was entirely undecomposed **2**. This assumption is justified because greater than 95% trapping occurred at the lowest cyclopentadiene concentration used and the yields of **3a** formed by reaction of cupric chloride or lead tetraacetate with **1** and cyclopentadiene at 0° in DMF were comparable with yields of **3a** obtained by reaction of **2** generated from *tert*-butyl hypochlorite and **1** or **6** with cyclopentadiene at −78° in acetone.

Table I
Yield of Adduct 3a for the Oxidation of 1 by Cupric Chloride in Dimethylformamide at 0° with Varying Ratios of Cyclopentadiene to 1

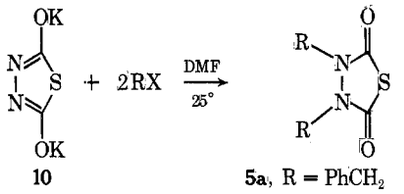
[Cp], mmol	M	$[C_p]/[1]$	[3a], theor, mmol	[3a], found, mmol	[3a] calcd if $k_2/k_1 = 100\ M^{-1}$, mmol
0.06	0.006	0.11	0.06	0.06	0.02
0.12	0.011	0.29	0.12	0.11	0.06
0.24	0.020	0.45	0.24	0.24	0.16
0.6	0.040	1.1	0.52	0.53	0.40
1.2	0.060	2.3	0.52	0.52	0.45

The relative reactivities of **2** and **4a** were also assessed from *in situ* reactions carried out with cupric chloride as oxidizing agent for **1** and 4-phenylurazole (**9**) in the presence of limiting cyclopentadiene or limiting oxidant. These experiments suffer from an additional complication in that the rate constants for oxidation of the precursors now become part of the overall rate expression for the formation of adducts. However, the apparent reactivities of **2** and **4a** in no instance differ by more than an order of magnitude from the ratios obtained in the competition between preformed **2** and **4a**. Thiadiazolidinedione **1** does appear to be oxidized slightly faster than **9**.

It is not surprising that the relative reactivity of **2** should be comparable to that of **4a**, since it is known that *N*-phenylmaleimide, maleic anhydride, and *N*-methylmaleimide have Diels–Alder reactivities which differ by less than an order of magnitude on a scale where tetracyanoethylene exceeds dicyanoethylene in reactivity by nearly six orders of magnitude.[21c] The competition experiments indicate that **2** may be slightly more reactive than **4a** with cyclopentadiene, but for most purposes, the two dienophiles can be considered of comparable reactivity. On the other hand, the competing unimolecular decomposition of **2** which can occur with unreactive dienes (*vide supra*) clearly limits the synthetic utility of this dienophile.

Alkylation of Potassium Salts (6, 10) of 1,3,4-Thiadiazolidine-3,5-dione (1). The monopotassium salt **6** and dipotassium salt **10** can be prepared quantitatively from 1,3,4-thiadiazolidine-2,5-dione (**1**) and potassium hydroxide.

Four alkyl halides were allowed to react with **10** in DMF at room temperature to give dialkylation products: **5a** from benzyl bromide, **5b** from methyl iodide, and **5c** from allyl bromide. Reaction of **10** and *tert*-butyl bromide gave a low yield of **5d**, characterized by ir and nmr spectroscopy. The reaction of monopotassium salt **6** with benzyl bromide and methyl iodide gave dialkylated thiadiazolidinediones **5a** and **5b** and no monosubstituted product.

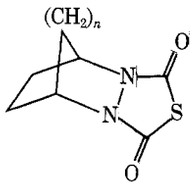


10

5a, R = $PhCH_2$
b, R = CH_3
c, R = CH_2=$CHCH_2$
d, R = $(CH_3)_3C$

The position of alkylation was established for **5a** by treatment with basic peroxide to give benzaldehyde benzylhydrazone in 65% yield. The other alkylated products **5b–d** are presumed to be di-N-alkylated as well, based upon the similarity in location and appearance of their carbonyl bands to the carbonyl bands of **5a** and **3a–e.**

Reduction of Diels–Alder Adducts. Reduction of adduct **3a** with diimide[22] using short reaction times gave the hydrogenated compound **11a.** Attempted catalytic hydro-

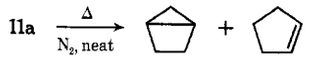


11a, $n = 1$
b, $n = 2$

genation of **3a** over 5% Pd/C gave an unidentified mixture of products having wide melting point ranges. However, catalytic hydrogenation of adduct **3b** over 5% Pd/C gave **11b.**

Decomposition of Thiadiazolidinedione Derivatives. 3,4-Dialkyl-1,3,4-thiadiazolidine-2,5-diones could participate in a symmetry-allowed fragmentation process which would lead to nitrogen, carbon monoxide, carbon dioxide, and carbon–carbon bond formation between the alkyl groups.[12,13a–p] Alternatively, formation of a cis azo compound could intervene but lead to the same result; the well-recognized thermal and photochemical decomposition[13a–p] of a variety of azo compounds provides analogy for the suggested process. Corey and Snider have shown that the thiadiazolidinedione ring can be opened hydrolytically and oxidatively.[3]

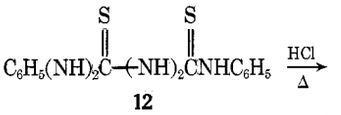
Attempts were made to promote ring fragmentatin in a number of ways, including thermolysis, photolysis, abstraction of sulfur or carbon monoxide, and oxidative attack at the carbonyl group. However, only the thermal decomposition of the reduced cyclopentadiene adduct **11a** gave the desired reaction. When heated to 300–350° for 0.5 hr under a stream of nitrogen, **11a** gives a 4.5:1 mixture of bicyclopentane and cyclopentene in 18% yield. The temperature



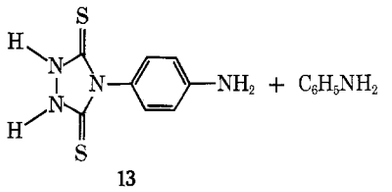
required to force the decomposition is substantially higher than the 180–195° required to convert 2,3-diazabicyclo[2.2.1]hept-2-ene to bicyclopentane in 90–93% yield[13b] and the azo compound could well be an intermediate in this process.[13b] Compounds **11b** and **5a** gave only tar when heated under similar conditions.

The photochemical extrusion of sulfur from sulfides with trialkyl phosphites[23] seemed especially promising; however, photochemical and thermal reactions of **5a** with triethyl and triphenyl phosphites did not produce identifiable products, and starting material was recovered in most cases. Several transition metal species were allowed to react with **5a** and **11a** with the expectation that sulfur and/or carbon monoxide would be extruded. Tris(triphenylphosphine)rhodium chloride seemed an especially propitious reagent, since it is known to promote the conversion of a thioanhydride to an olefin.[24] Reaction of tris(triphenylphosphine)rhodium chloride with **11a** in refluxing carbon tetrachloride for 2 hr gave 49% recovery of starting material and no detectable bicyclopentane, cyclopentene, or 2,3-diazabicyclo[2.2.1]hept-2-ene, although isolation of triphenylphosphine sulfide in 39% yield indicated that some reaction had occurred. Treatment of **5a** with 5% Pd/C and hydrogen-free Raney Ni was also unproductive.

Structural Assignment of 4-(*p*-Aminophenyl)-1,2,4-triazolidine-3,5-dithione (13). An early report[25] claims synthesis of the parent system **1.** Repetition of the synthesis by treatment of thioamide **12** with hot hydrochloric acid gave aniline and, after recrystallization from ethanol, a $C_8H_8N_4S_2$ compound having the same melting point as reported. This compound is a para-substituted aromatic



12



13

species, as determined by an AA′BB′ aryl pattern in the nmr spectrum and a strong 825-cm^{-1} band in the ir spectrum. In addition, the nmr spectrum shows four exchangeable hydrogen atoms consisting of two singlets having equal areas. The product, assigned structure **13,** apparently arises from a combination of cyclization and a rearrangement analogous to the benzidine rearrangement.[26,27]

Experimental Section

Melting points were determined with a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were taken on Perkin-Elmer 137, 237B, or 521 spectrophotometers and are calibrated against a polystyrene reference band at 1601 cm^{-1}. Nmr spectra were obtained with Varian A-56/60, A-60A, T-60, or HA-100 spectrometers with the assistance of Mr. Robert Thrift and associates. Chemical shifts and chemical shift differences are reported as δ units in parts per million relative to tetramethylsilane as internal standard. Mass spectra were recorded at 70 eV by Mr. J. C. Cook and associates using a Varian MAT CH-5 mass spectrometer. The mass spectral data processing equipment employed was provided by NIH Grants CA 11388 and GM 16864, from the National Cancer Institute and the National Institute of General Medical Sciences, respectively. Elemental analyses were performed by Mr. J. Nemeth and associates. Gas chromatography was performed on a Varian Aerograph A90-P3, with columns and column conditions as indicated. Reactions were carried out at ambient temperature unless otherwise specified. Photolyses were performed with a Rayonet photochemical reactor fitted with 16 low-pressure (2537 Å) or medium-pressure (3000 Å) mercury vapor lamps or with a General Electric 275-W ultraviolet sun lamp.

Materials. Elution chromatography was carried out on Brinkmann 0.05–0.2 mm silica gel. Thin layer chromatography was performed using Eastman silica gel coated strips which were developed with iodine. Commercially available liquid reagents, solid inorganic reagents, and reagent solvents were used without further purification, unless otherwise noted. All organic solid reagents were recrystallized before use to a satisfactory degree of purity. Lead tetraacetate was determined by iodine titration to be 91% pure. *tert*-Butyl hypochlorite was prepared from Clorox and *tert*-butyl alcohol. Potassium azodicarboxylate was synthesized by the method of Thiele.[28] Cyclopentadiene, prepared by thermally cracking dicyclopentadiene, was stored at −20° and its purity was established by nmr analysis to exceed 98%. Dimethyl sulfoxide was distilled from calcium hydride under a nitrogen atmosphere at re-

duced pressure and stored unnnnder argon over Linde 4A molecular sieve.

1,3,4-Thiadiazolidine-2,5-dione (1) was prepared in 47% yield according to the procedure of Rüfenacht by the acidic hydrolysis of 2-methoxy-1,3,4-thiadiazole-5(4*H*)-one.[1] Analytical material, obtained on one recrystallization from 50% aqueous methanol, had mp 250–252° dec (lit.[1] mp 245–248°); ir (KBr and Nujol mull) 3200–2000 (broad cyclic amide NH) and 1690, 1640 cm^{-1} (broad, amide C=O, C=N); nmr (DMSO-d_6) no proton absorption; mass spectrum (70 eV) *m/e* (rel intensity) 118 (6), 116 (10), 62 (21), 60 (100), 58 (25), 44 (36), 43 (21), 32 (100), 30 (22), 28 (34), consistent with the structure of **1**.[1]

5,8-Dihydro-5,8-methanopyridazino[1,2-*c*]2-thia-4,9-diazole-1,3-dione (3a). A From 1 with Cupric Chloride as Oxidant. Anhydrous cupric chloride (1.08 g, 8.02 mmol) in 8 ml of DMF was mixed with cyclopentadiene (2 ml, 24 mmol) at 0° under nitrogen, and **1** (197 mg, 1.66 mmol) in 4 ml of DMF was then added rapidly. After the reaction had been allowed to proceed for 20 min, the solution was poured into 200 ml of anhydrous ether and washed five times with 20-ml portions of water. The ethereal extract was dried ($MgSO_4$) and concentrated to give 196 mg (1.08 mmol, 65%) of **3a**, mp 64–76°, recrystallized from ether–pentene: mp 86.5–87.0° (lit.[3] mp 83.5–84.5°), with bubbling at 105° and pyrolysis at 155°; uv max (methanol) 209 nm (ϵ 7330) and 243 (7410); ir (Nujol) 1670 cm^{-1} (C=O); nmr ($CDCl_3$) δ 6.59 (triplet 2, J = 1.5, 1.5 Hz, =CH), 5.21 (multiplet, 2, J = 1.5, 1.5 Hz, =CCH), and 2.37 and 2.07 ppm (two triple doublets, 2, J = 1.5, 9 Hz, CH_2); decoupling of the bridgehead protons causes collapse of the vinylic protons from a triplet to a singlet and collapse of the methano protons from two triple doublets to two doublets; mass spectrum (70 eV) *m/e* (rel intensity) 182 (16), 122 (7), 121 (10), 79 (16), 67 (6), 66 (100), 65 (11), 60 (6), 40 (13), 39 (18), 28 (13).

Anal. Calcd for $C_7H_6N_2O_2S$: C, 46.14; H, 3.32; N, 15.38; S, 17.60. Found: C, 46.30; H, 3.45; N, 15.57; S, 17.53.

B. From 1 with Lead Tetraacetate and *tert*-Butyl Hypochlorite as the Oxidants. When lead tetraacetate was used as oxidant at 0° in DMF, **3a** was obtained in 75% yield; use of the conditions of Corey and Snider[3] at −78° gave **3a** in 82% yield. With *tert*-butyl hypochlorite as oxidant at 0° in DMF, **3a** was produced in 76% yield.

C. From 6 and the Above Oxidants. When cupric chloride was used as oxidant at 0° in DMF with **6**, **3a** was obtained in 38% yield; use of lead tetraacetate under similar conditions gave **3a** in 20% yield. With *tert*-butyl hypochlorite as the oxidant at 0° in DMF, **3a** was obtained in 58% yield; and with acetone solvent at −78°, **3a** was produced in 30–50% yield based upon partial oxidation of the monopotassium salt.

5,8-Dihydro-5,8-ethanopyridazino[1,2-*c*]-2-thia-4,9-diazole-1,3-dione (3b) was prepared in 43% yield from 1,3-cyclohexadiene, **1**, and cupric chloride in DMF: mp 137–11h139°, recrystallization from ether, mp 144.0–145.0° (lit.[3] mp 139.5–140°); ir (Nujol) 1680 cm^{-1} (C=O); nmr (acetone-d_6) δ 6.57 (triplet, 2, J = 2 Hz, =CH), 5.1 (multiplet, 2, =CCH), and 2.4–1.6 ppm (multiplet, 4, CH_2); mass spectrum (70 eV) *m/e* (rel intensity) 196 (26), 136 (3), 118 (19), 108 (6), 81 (9), 80 (57), 79 (100), 78 (13), 77 (21), 67 (12), 66 (22), 60 (11), 52 (11), 51 (11), 50 (10), 41 (8), 39 (23), 28 (88), 27 (15), 17 (22).

Anal. Calcd for $C_8H_8N_2O_2S$: C, 48.96; H, 4.11; N, 14.28; S, 16.34. Found: C, 49.04; H, 4.09; N, 14.41; S, 16.54.

5,8-Dihydro-6,7-dimethylpyridazino[1,2-*c*]-2-thia-4,9-diazole-1,3-dione (3c) was prepared in 23% yield from 2,3-dimethylbutadiene, **1**, and cupric chloride in DMF: mp 134–155°, recrystallization from methylene chloride-hexane, mp 160–161° (lit.[3] mp 153.5–154.4°); ir (Nujol) 1650 cm^{-1} (C=O); nmr ($CDCl_3$) δ 4.13 (singlet, 4, CH_2) and 1.78 ppm (singlet, 6, CH_3); mass spectrum (70 eV) *m/e* (rel intensity) 200 (6), 199 (12), 198 (100), 138 (2), 137 (2), 123 (7), 110 (13), 95 (3), 82 (31), 67 (45), 54 (13), 41 (24), 39 (20), 28 (29).

Anal. Calcd for $C_8H_{10}N_2O_2S$: C, 48.46; H, 5.08; N, 14.13; S, 16.18. Found: C, 48.62; H, 4.92; N, 14.25; S, 16.15.

5,8-Dihydro-6-methylpyridazino[1,2-*c*]-2-thia-4,9-diazole-1,3-dione (3d) was prepared in 4% yield from isoprene, **1**, and cupric chloride in DMF: mp 99–103°, further recrystallization gave mp 103–104° (lit.[3] mp 99–100°); ir (Nujol) 1670 cm^{-1} (C=O); nmr ($CDCl_3$) δ 5.63 (multiplet, 1, =CH), 4.20 (sharp multiplet 4, $=CCH_2$), and 1.87 ppm (sharp multiplet, 3, CH_3); mass spectrum (70 eV) *m/e* (rel intensity) 185 (12), 184 (100), 124 (10), 96 (24), 68 (49), 67 (28), 53 (28), 39 (24), 28 (60).

Anal. Calcd for $C_7H_8N_2O_2S$: C, 45.64; H, 4.38; N, 15.21; S, 17.41. Found: C, 45.82; H, 442; N, 15.36; S, 17.28.

5,8-Dihydropyridazino[1,2-*c*]-2-thia-4,9-diazole-1,3-dione (3e). To **1** in 20 ml of acetone at −78° was added *tert*-butyl hypochlorite (0.47 ml, 4.1 mmol), causing the solution to turn black-violet. After 1 hr, butadiene (90 ml, *ca.* 1.1 × 10^3 mmol) was condensed into the flask and the violet color discharged. A white, crystalline solid resulted on evaporation under nitrogen. Recrystallization from methylene chloride–pentane gave 175.1 mg (1.03 mmol, 49%) of 5,8-dihydropyridazino[1,2-*c*]-2-thia-4,9-diazole-1,3-dione (**3e**): mp 118.5–120.5°; further recrystallization gave mp 121.0–122.0°; ir (Nujol) 1680 cm^{-1} (C=O); nmr ($CDCl_3$) δ 5.95 (sharp multiplet, 2, =CH) and 4.32 ppm (sharp multiplet, 4, CH_2); mass spectrum (70 eV) *m/e* (rel intensity) 170 (100), 110 (42), 82 (50), 54 (83), 39 (69), 28 (84).

Anal. Calcd for $C_6H_6N_2O_2S$: C, 42.34; H, 3.55; N, 16.46; S, 18.84. Found: C, 42.58; H, 3.61; N, 16.72; S, 19.02.

5,8-Dihydro-5,8-methano-2-phenyl-*s*-triazolo[1,2-*a*]pyridazine-1,3(2*H*)-dione (8) was prepared from 4-phenylurazole, cupric chloride, and cyclopentadiene in DMF under conditions identical with those used for **1** to give **8** in 54% yield, mp 133.5–140.0°; recrystallization from methylene chloride–hexane gave mp 140.5–143.0° (lit.[6] mp 141.5–144°); ir, nmr, and mass spectra and analytical properties consistent with those of the assigned structure **8**.[6]

1,3,4-Thiadiazolidine-2,5-dione Monopotassium Salt (6). Evaporation to dryness of an aqueous solution of **1** (2.46 g, 20.8 mmol) and 85% potassium hydroxide (1.37 g, 20.8 mmol) gave a white solid which, after one recrystallization from methanol–2-propanol, yielded 2.00 g (12.8 mmol, 62%) of monopotassium salt **6**: mp 196–197° dec; ir (Nujol) 3260 (NH), 1650 (C=O), and 1550 cm^{-1} (C=N); nmr (D_2O) no peaks.

Anal. Calcd for $C_2HN_2O_2SK$: C, 15.38; H, 0.65; N, 17.94. Found: C, 15.49; H, 0.74; N, 17.88.

1,3,4-Thiadiazolidine-2,5-dione dipotassium salt (10) was prepared in 44% yield in a manner similar to that for **6** from **1** and 85% potassium hydroxide containing 2.5 molar excess of base. Recrystallization from methanol–2-propanol provided the hygroscopic dipotassium salt **10**: mp 253–260° dec; ir (Nujol) 1650 (C=O) and 1550 cm^{-1} (C=N).

Anal. Calcd for $C_2N_2O_2SK_2$: C, 12.36; N, 14.42. Found: C, 12.51; H, 0.34; N, 13.87.

***N,N'*-Dibenzyl-1,3,4-thiadiazolidine-2,5-dione (5a).** The dipotassium salt **10** (5.00 g, 25.7 mmol) suspended in 180 ml of DMF, was allowed to react with benzyl bromide (7.5 ml, 63 mmol) for 5 days. The reaction mixture was then poured into anhydrous ether and washed five times with water. The ethereal portion was dried ($MgSO_4$) and evaporated to give a mobile, light yellow liquid which crystallized when treated with pentane. One recrystallization from ether–pentane gave 4.90 g (16.4 mmol, 64%) of white crystals of **5a**: mp 113.0–115.0; further recrystallization gave mp 115.0–117.0°; ir (Nujol) 1650 cm^{-1} (C=O); nmr ($CDCl_3$) δ 7.31 (multiplet), 10, ArH) and 4.85 ppm (singlet, 4, CH_2); mass spectrum (70 eV) *m/e* (rel intensity) 298 (3), 119 (2), 92 (8), 91 (100), 65 (9), 28 (5).

Anal. Calcd for $C_{16}H_{14}N_2O_2S$: C, 64.41; H, 4.73; N, 9.39; S, 10.75. Found: C, 64.17; H, 4.77; N, 9.49; S, 10.80.

The dialkylated product **5a** was formed in 73% crude yield when **6** was allowed to react under nitrogen with equimolar benzyl bromide in 5 ml of DMF for 19 days.

***N,N'*-Dimethyl-1,3,4-thiadiazolidine-2,5-dione (5b).** The dipotassium salt **10** (396.7 mg, 2.04 mmol) suspended in 10 ml of DMF was allowed to react with methyl iodide (1.00 ml, 16.1 mmol) under nitrogen for 20 hr. The solution was evaporated to dryness, 1 ml of water was added, and evaporation was repeated. The moist solid was treated with 50 ml of boiling methylene chloride and filtered, and the filtrate was dried ($MgSO_4$) and evaporated to give a light orange oil which crystallized after being scratched with a glass rod to give 153.4 mg (1.05 mmol, 52%) of **5b**, mp 62–68°. Column chromatography with ether eluent and recrystallization from carbon tetrachloride–hexane gave mp 75.0–75.5°; ir (Nujol) 1660 cm^{-1} (C=O); nmr ($CDCl_3$) δ 3.40 ppm (sharp singlet, CH_3); mass spectrum (70 eV) *m/e* (rel intensity) 146 (60), 86 (21), 58 (48), 43 (100), 28 (19).

Anal. Calcd for $C_4H_6N_2O_2S$: C, 32.86; H, 4.14; N, 19.17; S, 21.94. Found: C, 33.09; H, 4.03; N, 19.22; S, 21.88.

The product **5b** was produced in 37% crude yield when the monopotassium salt **6** was allowed to react under nitrogen with an eightfold excess of methyl iodide in 20 ml of DMF for 46 hr. Compound **1** does not react under these conditions.

***N,N'*-Diallyl-1,3,4-thiadiazolidine-2,5-dione (5c)** was prepared in 77% yield from reaction of the dipotassium salt **10** suspended in DMF with a fivefold excess of allyl bromide for 22 hr. Extractive work-up with ether produced **5c**: mp 40–45°; recrystal-

lization from ether–pentane gave mp 49.0–50.0°; ir (Nujol) 1690 cm^{-1} (C=O); nmr ($CDCl_3$) δ 6.2–5.0 (multiplet, 3, =CH) and 4.22 ppm (doublet with fine structure, 2, J = 6 Hz, CH_2); mass spectrum (70 eV) m/e (rel intensity) 199 (2), 198 (16), 157 (2), 69 (10), 41 (100), 39 (19), 28 (6).

Anal. Calcd for $C_8H_{10}N_2O_2S$: C, 48.46; H, 5.08; N, 14.13; S, 16.18. Found: C, 48.53; H, 5.11; N, 14.36; S, 16.23.

***N,N'*-Di-*tert*-butyl-1,3,4-thiadiazolidine-2,5-dione (5d)** was prepared in 6% yield from reaction of the dipotassium salt **10** suspended in DMF with a fivefold excess of *tert*-butyl bromide for 7 days. Extractive work-up with ether gave 27.6 mg (0.12 mmol, 6%) of a solid: mp 101–109°; ir (Nujol) 3100 (medium, NH attributed to 1,3,4-thiadiazolidine-2,5-dione as an impurity) and 1650 cm^{-1} (strong, C=O); nmr ($CDCl_3$) δ 1.68 ppm (singlet, CH_3).

5,6,7,8-Tetrahydro-5,8-methanopyridazino[1,2-*c*]-2-thia-4,9-diazole-1,3-dione (11a) was prepared in 49% yield by reduction of **3a** in methanol for 5 min with diimide generated from 4.5 equiv of potassium azodicarboxylate and excess acetic acid. Material obtained by extractive work-up with ether was recrystallized twice from ether-pentane to give **11a**: mp 79.5–80.0°; uv max (methanol) 222 nm (ϵ 9110); ir (Nujol) 1650 cm^{-1} (C=O); nmr (CCl_4) δ 4.94 (multiplet, 2, CH) and 2.16 ppm (multiplet, 6, CH_2); mass spectrum (70 eV) m/e (rel intensity) 184 (100), 124 (45), 96 (15), 68 (70), 67 (78), 28 (41).

Anal. Calcd for $C_7H_8N_2O_2S$: C, 45.64; H, 4.38; N, 15.21; S, 17.41. Found: C, 45.86; H, 4.27; N, 15.49; S, 17.34.

5,6,7,8-Tetrahydro-5,8-ethanopyridazino[1,2-*c*]-2-thia-4,9-diazole-1,3-dione (11b) was prepared in 47% yield by catalytic reduction of **3b** in ethyl acetate at atmospheric pressure with 5% palladium on carbon. Recrystallizations from methylene chloride–ether–pentane and ether–pentane gave **11b** in 47% yield, mp 99–110°. Additional recrystallization provided a solid: mp 137.0–137.5° (lit.[3] mp 129–131°); ir (Nujol) 1650 cm^{-1} (C=O); nmr ($CDCl_3$) δ 4.67 (multiplet, 2, CH) and 2.00 ppm (multiplet, 8, CH_2); mass spectrum (70 eV) m/e (rel intensity) 198 (59), 110 (38), 82 (28), 67 (100).

Anal. Calcd for $C_8H_{10}N_2O_2S$: C, 48.46; H, 5.08; N, 14.13; S, 16.18. Found: C, 48.80; H, 4.94; N, 14.34; S, 16.18.

4-(*p*-Aminophenyl)-1,2,4-triazolidine-3,5-dithione (13). Phenylthiocarbohydrazide–thiocarbophenylamide (**12**), prepared from phenylthiocarbonylhydrazide[29] and phenyl isothiocyanate, was mixed with 25 ml of concentrated hydrochloric acid and the solution was stirred under reflux for 1.5 hr. Steam distillation after neutralization with sodium carbonate gave a brown solid. Recrystallization of this solid from ethanol gave 0.31 g (1.38 mmol, 22%) of 4-(*p*-aminophenyl)-1,2,4-triazolidine-3,5-dithione (**13**) as a light tan powder: mp 219–220°; further recrystallization gave mp 225.0–225.5° (lit.[25] mp 222°); ir (KBr) 3480, 3380, 3280, 3100 (NH), 1575 (C=N), and 825 cm^{-1} (para-substituted aryl hydrogen bend); nmr DMSO-d_6) δ 7.27 (doublet of triplets, 2, J_o = 8, $J_{m,p}$ = 1.5 Hz, ArH), 7.09 (singlet, 2, NH_2, exchangeable with D_2O), 6.62 (doublet of triplets, 2, J_o = 8, $J_{m,p}$ = 1.5 Hz, ArH), and 5.52 ppm (singlet, 2, thioamide H, exchangeable with D_2O); mass spectrum (70 eV) m/e (rel intensity) 224 (90), 150 (11), 136 (16), 124 (61), 106 (100), 80 (35), 79 (37), 74 (14), 65 (25), 52 (28), 39 (17), 28 (14).

Anal. Calcd for $C_8H_8N_4S_2$: C, 42.84; H, 3.60; N, 24.98; S, 28.59. Found: C, 43.03; H, 3.53; N, 24.99; S, 28.64.

1,3,4-Thiadiazole-2,5-dione (2). The monopotassium salt **6** (312 mg, 2.00 mmol) was allowed to react with *tert*-butyl hypochlorite (0.24 ml, 2.0 mmol) in acetone at −78° under nitrogen for 3⅓ hr, after which time unreacted monopotassium salt was removed by filtration and a violet solution of **2** was obtained. If the solution was allowed to warm to −35°, the color changed to yellow within 20 sec. 1,3,4-Thiadiazole-2,5-dione (**2**) in acetone at −78° gave λ_{max} 550–555 nm ($139 \leq \epsilon \leq 203$). The unreacted monopotassium salt was analyzed by uv analysis in water and the reaction was determined to be 66–96% complete after 3⅓ hr.

Rate of Unimolecular Decomposition of 2 Relative to Trapping by Cyclopentadiene. To determine whether gaseous decomposition of **2** is competitive with its trapping by cyclopentadiene, a series of reactions was run at ambient temperature with cupric chloride oxidant in DMF with a cyclopentadiene/thiadiazolidinedione ratio which varied from 2.0 to 0.1. Analysis of the reaction mixtures was performed by nmr after the usual extractive work-up with biphenyl as an internal standard. The results show (*vide supra*) that competitive unimolecular decomposition of **2** is not a serious problem under these conditions.

Relative Reactivities of 1,3,4-Thiadiazole-2,5-dione (2) and 4-Phenyl-1,2,4-triazoline-3,5-dione (4a). The relative reactivities of **2** and **4a** were evaluated under conditions of competitive reaction of known amounts of the two reagents for a limited quantity of cyclopentadiene; the products were analyzed by nmr.

A. From the Azo Diones. The monopotassium salt **6** of 1,3,4-thiadiazolidine-2,5-dione (89 mg, 0.570 mmol) suspended in 6 ml of acetone was mixed with *tert*-butyl hypochlorite at −78° under nitrogen. This reaction was previously determined (*vide supra*) to give thiadiazoledione **4** in 66–96% yield under similar conditions. After the reaction had been allowed to proceed for 3.5 hr, **4a**[30] (68 mg, 0.380 mmol) in 3 ml of acetone at −78° under argon was rapidly added. After 1 min, cyclopentadiene (21 μl, 0.25 mmol) in 1 ml of acetone at −78° was added. Extractive work-up provided a mixture of 61% **3a** and 39% **8**.

B. From the Hydrazo Diones. 1,3,4-Thiadiazolidine-2,5-dione (**1**, 59.2 mg, 0.500 mmol) and 4-phenylurazole (88.2 mg, 0.497 mmol) were dissolved in 5 ml of DMF and rapidly mixed with a solution of excess cupric chloride (339.2 mg, 2.52 mmol) and limiting cyclopentadiene (21 μl, 0.25 mmol) in 11 ml of DMF at 0°. Extractive product isolation showed 57% of thiadiazoledione adduct **3a** and 43% of phenyltriazolinedione adduct **8**. An experiment in which cupric chloride was limiting and cyclopentadiene was in excess gave an oil which showed 91% **3a** and 9% **8**.

Nmr analysis of product mixtures was carried out by integration of the vinylic proton signals for **3a** and **8** at 396 (δ 6.60 ppm) and 388 Hz (δ 6.47 ppm), respectively, on an expanded 50-Hz sweep width. Standard solutions of the two adducts indicated correct integration within experimental error, and control experiments using excess cyclopentadiene and oxidizing reagent gave the expected proportions of adducts. The identity of the assigned vinylic absorptions was confirmed by addition of authentic samples of **3a** and **8**. Neither adduct was selectively fractionated by the ether–water extractive work-up.

Thermal Decomposition of 5,6,7,8-Tetrahydro-5,8-methanopyridazino[1,2-*c*]-2-thia-4,9-diazole-1,3-dione (11a). Thermolysis of 325 mg (1.76 mmol) of **11a** under a slow nitrogen stream at 300–350° for 30 min in a Woods metal bath gave vapors which were passed through two traps held at 0 and −78°, respectively. After this period of time, the −78° trap was found to contain a 21-mg mixture of bicyclo[2.1.0]pentane and cyclopentene (0.31 mmol, 18%): ir (neat and in CCl_4) 3020, 2900, 2810, 2260 (COS),[31] 1700 (C=O contaminant), 1460, 1440, 1360, 1270, 1240, 1220, 1100, 1050, 1020, 970, 920, 890, 785, 755, 700, cm^{-1}, in agreement with published spectrum[32] of bicyclo[2.1.0]pentane contaminated with cyclopentene, except for impurities at 2260 and 1700 cm^{-1}; nmr (CCl_4) 77% bicyclo[2.1.0]pentane at δ 2.3–1.8, 1.7–1.1, and 0.8–0.3 ppm (multiplets) (lit.[13b] δ 2.4–1.9, 1.7–1.1, and 0.8–0.3 ppm), 17% cyclopentene δ 6.4 and 5.6 ppm, and 6% unidentified absorption at δ 2.9 ppm; mass spectrum (70 eV) m/e (rel intensity) 68 (32), 67 (100), 66 (30), 53 (31), 41 (37), 39 (52) [in addition, a small m/e 184 (0.7) peak is seen owing to contamination by starting material **11a**].

The isolated yield was confirmed by means of gas chromatographic analysis with a 5 ft × 0.25 in. stainless steel 3% SE-30 on 100/120 Varaport 30. Use of three traps containing *n*-octane at 0° with *n*-heptane as an internal standard gave an 18.5% yield of the isomeric pentane products and it was assumed that the thermal conductivities of the products are the same as that of *n*-pentane.

Reaction of *N,N'*-Dibenzyl-1,3,4-thiadiazolidine-2,5-dione (5a) with Basic Hydrogen Peroxide. To 297 mg (0.995 mmol) of **5a** in 10 ml of acetone was added quickly a solution of 30% hydrogen peroxide (1.00 ml, 9.82 mmol) and sodium hydroxide (180 mg, 4.49 mmol) in 5 ml of water. Four sodium hydroxide pellets (*ca.* 360 mg) were added after 45 min; after 70 min, 10 ml of water was added, and the solution was evaporated at reduced pressure at 40° until a moist white solid remained. This solid was dissolved in a mixture of 120 ml of ether and 40 ml of water and the aqueous portion was extracted twice with 50-ml portions of ether. The combined ethereal extracts were washed three times with 10-ml portions of water, dried ($MgSO_4$), and evaporated at reduced pressure at 25° to give 138 mg (0.647 mmol, 65%) of a moist, white solid, mp 60–69°. Recrystallization from ether–pentane gave 35 mg (0.166 mmol, 17%) of odorless plates of benzaldehyde benzylhydrazone: mp 64–70°, mmp 64–71.5° (authentic sample mp[33] 62–70°); ir (Nujol) identical with that of independently prepared material;[33] nmr ($CDCl_3$) δ 7.6–7.2 (multiplet, area 11 ± 1, ArH, CH=N), 5.7 (broad singlet, NH), 4.4 (singlet, 2, CH_2), and 4.1 ppm (broad singlet, area <1, impurity), very similar to that of authentic material.

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Registry No.—**1**, 19692-10-5; **2**, 41316-14-7; **3a**, 4136-15-8; **3b**, 41316-16-9; **3c**, 41316-19-2; **3d**, 41316-17-0; **3e**, 52147-54-3; **4a**, 4233-33-4; **5a**, 52147-55-4; **5b**, 52147-56-5; **5c**, 52147-57-6; **5d**, 52147-58-7; **6**, 52147-59-8; **8**, 15971-63-8; **10**, 52147-60-1; **11a**, 52147-61-2; **11b**, 41316-20-5; **12**, 52147-62-3; **13**, 52147-63-4; cyclopentadiene, 542-92-7; 1,3-cyclohexadiene, 592-57-4; 2,3-dimethylbutadiene, 513-81-5; isoprene, 78-79-5; butadiene, 106-99-0; 4-phenylurazole, 4233-33-4; benzyl bromide, 100-39-0; methyl iodide, 74-88-4; allyl bromide, 106-95-6; *tert*-butyl bromide, 507-19-7; bicyclo[2.1.0]pentane, 185-94-4; cyclopentene, 142-29-0.

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Furazans and Furazan Oxides. V.[1] Tropono[4,5-*c*]-, Thieno[2,3-*c*]-, and Biphenyleno[2,3-*c*]furazan Oxides

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The three title furazan oxides were prepared, and the free energies of activation for their rearrangement were investigated. The relevance of these results to the question of the aromaticity of tropone, thiophene, and biphenylene is discussed. An important factor affecting the ease of the reaction appears to be the size of the ring to which the furazan oxide is fused.

The striking difference (~19 kcal mol^{-1}) between the free energies of activation for the isomerization of a furazan oxide (furoxan[2]) (**1a** ⇌ **1b**) and a benzofurazan oxide (**2a** ⇌ **2b**) has led us to suppose that the reaction may provide a sensitive probe of, and an at least semiquantitative means of determining, the "aromaticity" associated with the ring to which the heterocyclic nucleus is fused. In earlier work,[3] the effect of naphtho[1,2] fusion (**3**) was found to be intermediate (ΔG^* ~19.5 kcal mol^{-1}) between that of benzo fusion (**2**) and "olefin fusion" (*i.e.*, the unfused system, **1**). However, interpretation of the results from polycyclic fused systems was not straightforward: allowance had to be made for changes in the aromaticity of the further fused ring as the one carrying the furoxan becomes more "benzenoid" upon opening of the heterocyclic ring. Nevertheless, we hoped that it might be possible to obtain a comparison between the aromaticities of naphthalene and biphenylene in this way. The problem does not arise when the furoxan is