before use. All reactions were carried out under N_2.

Reactions of Nitro Compounds. In a 50-mL centrifuge tube were placed a magnetic stirring bar and a proper amount of Sm powder under air, and the tube was sealed with a serum cap. Pure nitrogen was then passed through, and the Sm was dried by heating under the stream of nitrogen. Two drops of allyl iodide was added by a micro syringe and the metal was heated slightly by a heat gun to activate the Sm metal.[7] Addition of 2 mL of THF gave a dark blue slurry, which after introduction of 0.5 mL of HMPA became purple. To this slurry was dropped the proper amount of nitro compounds with THF (2 mL) and MeOH (2 mL) by a syringe, and the mixture was then stirred at room temperature for the proper time (see the tables, Scheme I, and the related discussion in the text). The products were treated with 2 N HCl and then extracted with ether or CH_2Cl_2 (3 × 30 mL). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. After the solvent was evaporated, the products were isolated by medium-pressure liquid chromatography (silica gel) and identified by NMR, IR, mass spectra, melting point, and retention time comparison with those of authentic samples (Table I). Some physical properties of the products are recorded below.

Azobenzene: mp 68–69 °C (lit.[8] mp 68 °C); mass spectrum, *m/e* 182 (M^+).

Azoxybenzene: mp 35–36 °C (lit.[9] mp 36 °C); mass spectrum, *m/e* 198 (M^+).

4,4'-Dimethylazoxybenzene: mp 68–69 °C (lit.[10] mp 68 °C); ^1H NMR (CCl_4) δ 2.40, 2.43 (a pair of s, 6 H), 7.09–7.40 (m, 4 H), 7.98–8.24 (m, 4 H); mass spectrum, *m/e* 226 (M^+).

4,4'-Dimethoxyazoxybenzene: mp 119–120, 135–137 °C (lit.[10] mp 118, 136 °C); ^1H NMR (CCl_4) δ 3.86 (s, 6 H), 6.94 (d of d, J = 8.0, 1.2 Hz, 4 H), 8.24 (d of d, J = 8, 1.2 Hz, 4 H); mass spectrum, *m/e* 258 (M^+).

4,4'-Dichloroazoxybenzene: mp 156–157 °C (lit.[10] mp 155–156 °C); mass spectrum, *m/e* 267 (M^+).

4,4'-Dichloroazobenzene: mp 188–189 °C (lit.[11] mp 186–187 °C); mass spectrum, *m/e* 251 (M^+).

1,2-Bis(4-chlorophenyl)hydrazine: mp 128–129 °C (lit.[12] mp 122 °C); ^1H NMR (CCl_4) δ 5.48 (br s, 2 H), 6.67 (d, J = 8.0 Hz, 4 H), 7.12 (d, J = 8.0 Hz, 4 H); mass spectrum, *m/e* 253 (M^+).

4,4'-Dibromoazoxybenzene: mp 173–175 °C (lit.[13] mp 175 °C); mass spectrum, *m/e* 356 (M^+).

4,4'-Diiodoazoxybenzene: mp 208–210 °C (lit.[14] mp 207–208 °C); mass spectrum, *m/e* 450 (M^+).

4,4'-Dicyanoazoxybenzene: mp 222–223 °C (lit.[15] mp 221 °C); IR (KBr) 2228 cm^{-1} (CN); mass spectrum, *m/e* 248 (M^+).

4,4'-Dicyanoazobenzene: mp 282 °C (sublime); IR (KBr) 2228 cm^{-1} (CN); mass spectrum, *m/e* 232 (M^+).

4,4'-Diacetylazoxybenzene: mp 191–193 °C; ^1H NMR ($CDCl_3$) δ 2.65, 2.68 (a pair of s, 6 H), 7.86–8.70 (m, 8 H); IR (KBr) 1690 cm^{-1} (CO); mass spectrum, *m/e* 282 (M^+).

Dimethyl 4,4'-azoxycinnamate: mp 221–223, 276–278 °C (lit.[16] mp 219–221, 254–257 °C); ^1H NMR ($CDCl_3$) δ 3.82 (s, 6 H), 6.49 (d of d, J = 16.2, 1.8 Hz, 2 H), 7.48–8.44 (m, 10 H); IR (KBr) 1728 cm^{-1} (CO); mass spectrum, *m/e* 366 (M^+).

Benzo[*c*]cinnoline *N*-oxide (6): mp 139–140 °C (lit.[17] mp 139 °C); mass spectrum, *m/e* 196 (M^+).

Benzo[*c*]cinnoline (2): mp 157–158 °C (lit.[3f] mp 156 °C); mass spectrum, *m/e* 180 (M^+).

Acknowledgment. This research was supported in part by Grant-in-Aids from the Ministry of Education, Science and Culture.

(7) If the Sm metal was not treated with allyl iodide before the reaction much lower yields of the reduction products were obtained, which shows that the metal (surface) must be activated in order to have a high reactivity. See also ref 2d,e.

(8) Corruccini, R. J.; Gilbert, E. C. *J. Am. Chem. Soc.* **1939**, *61*, 2925.
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Regiospecific Synthesis of Arenesulfonamide Derivatives of 3,5-Diamino-1,2,4-triazole[1]

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For several years we have been engaged in a search for new herbicides which act by inhibiting the enzyme acetolactate synthase.[3] We have needed substantial quantities of *N*-(5-amino-1*H*-1,2,4-triazol-3-yl)arenesulfonamides **1** as part of that program. A straightforward approach to **1** involving the reaction of arenesulfonyl chlorides with 3,5-diamino-1,2,4-triazole is not operable due to the multiple sites of reaction for the latter compound toward electrophiles.[4] Consequently, we chose to explore new approaches to **1**.

We have developed a new synthesis of **1** which addresses the problem of regiocontrol in the introduction of the arylsulfonyl functionality (Scheme I). The general strategy is derived from an approach to the regioselective synthesis of derivatives of 3,5-diamino-1,2,4-triazole in which the exocyclic nitrogen atoms bear alkyl groups.[6] We have observed that dimethyl *N*-cyanodithiocarbonimidate (**2**) reacts with arenesulfonamides **3** under basic conditions to give *N'*-cyano-*N*-(arylsulfonyl)-*S*-methylisothioureas **4** in good yield (Table I). The bases that have been employed for this conversion are NaOH or K_2CO_3. Intermediates **4** react with hydrazine to afford **1** (Table II). An excess of hydrazine greater than 2 equiv is required for the latter reaction to proceed at a convenient rate. The examples illustrate the variety of aryl substitutions that are tolerated in this synthesis.

An alternative approach to **4** is illustrated in the synthesis of **4d** in Scheme II. Compound **3d** is reacted with base and CS_2 followed by CH_3I to afford **5** in 61% yield. Reaction of **5** with cyanamide under basic conditions gave **4d** in 69% yield.

Future reports will detail the utilization of **1** in the synthesis of herbicidal arenesulfonamide derivatives of 2-amino-1,2,4-triazolo[1,5-*a*]pyrimidine.[7]

Experimental Section[8]

General Methods. Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. Arenesulfonamides **3d**,[9] **3f**,[10] **3g**,[11] and **3h**[12] were

(1) Presented in part at the 194th National Meeting of the American Chemical Society, New Orleans, LA, September 3, 1987; paper AGRO 162.
(2) (a) Agricultural Products Department. (b) Central Research.
(3) Kleschick, W. A.; Costales, M. J.; Dunbar, J. E.; Meikle, R. W.; Monte, W. T.; Pearson, N. R.; Snider, S. W.; Vinogradoff, A. P., submitted for publication.
(4) A report in the literature[5] describes a "benzenesulfonyl derivative" of 3,5-diamino-1,2,4-triazole. This derivative (mp 225 °C) is clearly different from compound **1a** (mp 293–294 °C) described in this report.
(5) Schulze, W.; Letsch, G.; Fritzsche, H. *J. Prakt. Chem.* **1965**, *30*, 302.
(6) Heitke, B. T.; McCarty, C. G. *J. Org. Chem.* **1973**, *39*, 1522.
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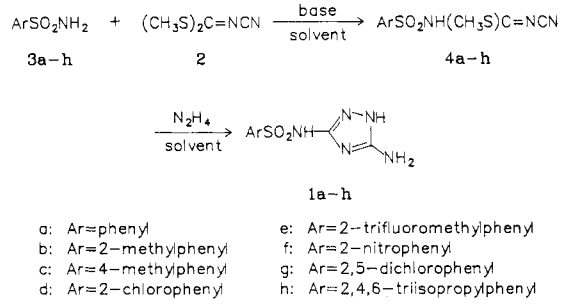
(8) All melting points are uncorrected. NMR chemical shifts are expressed as δ values (ppm) relative to a Me_4Si internal standard. Significant NMR data are tabulated in order: number of protons, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad), coupling constant(s) in hertz.
(9) Allen, C. F. H.; Frame, G. F. *J. Org. Chem.* **1942**, *7*, 15.

0022-3263/88/1953-3120$01.50/0

Scheme I



Scheme II

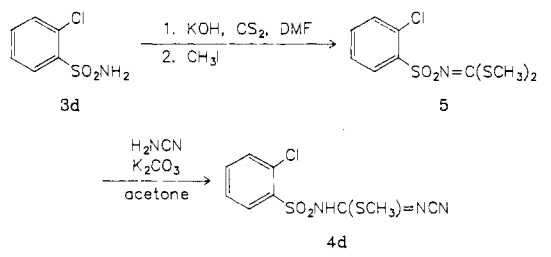


Table I. Preparation of 4[a]

compd	exptl procedure[b]	yield, %	mp, °C
4a	A	45	122 dec
4b	B	87	146–148
4c	B	55	137.5–139
4d	A	69	126.5 dec
4e	A	91	127 dec
4f	A[c]	58	121 dec
4g	B	76	145
4h	B	40	165–165.5

[a] IR and NMR spectral data recorded for all compounds were consistent with the assigned structure. Satisfactory analytical data (±0.40% for C, H, N, Cl, S) were reported for all new compounds listed in the table. [b] See the Experimental Section for a detailed description of the procedure. [c] Experimental procedure A was found to be superior in this instance due to facilitating the removal of a byproduct, 2-(methylthio)nitrobenzene, by trituration with Et_2O.

prepared from the commercially available sulfonyl chlorides by reaction with aqueous ammonium hydroxide.

General Procedure for the Conversion of Arenesulfonamide 3 to *N'*-Cyano-*N*-(arylsulfonyl)-*S*-methylisothiourea 4. Method A. *N'*-Cyano-*N*-[(2-(trifluoromethyl)phenyl)sulfonyl]-*S*-methylisothiourea (4e). A mixture of 58.5 g (0.260 mol) of **3e**, 38.0 g (0.260 mol) of **2**, and 35.9 g (0.260 mol) of powdered, anhydrous K_2CO_3 in 420 mL of acetone was heated at reflux for 17 h. The reaction mixture was cooled to room temperature and filtered. The filtrate was evaporated to afford an amber oil, which solidified upon trituration with Et_2O. The solid was suspended in 130 mL of 2 N HCl (aqueous) and stirred for 90 min. The solid was collected by filtration and dried under vacuum at room temperature[13] to yield 76.9 g (91%) of **4e** as a white solid, mp 127 °C dec: IR (KBr) 2205, 1503, 1434, 1305, 1274, 1184, 1186, 1153, 1116 cm^{-1}; ^1H NMR (acetone-d_6) 8.2–8.6 (1 H, m), 7.8–8.2 (3 H, m), 6.30 (1 H, s), 2.74 (3 H, s). Anal. Calcd for $C_{10}H_8F_3N_3O_2S_2$: C, 37.15; H, 2.49; N, 13.00; S, 19.83. Found: C, 37.02; H, 2.55; N, 12.95; S, 20.00.

Method B. *N'*-Cyano-*N*-[(2,5-dichlorophenyl)sulfonyl]-*S*-methylisothiourea (4g). A solution of 10.6 g (43.2 mmol) of **3g**, 7.15 g (44.0 mmol) of **2**, and 1.8 g (44 mmol) of NaOH in 60 mL of EtOH and 10 mL of H_2O was heated at reflux for 6 h. After cooling to room temperature, the reaction mixture was poured into 600 mL of ice-cold H_2O. The resulting solution was acidified with 6 N HCl (aqueous) to separate 2.2 g of **4g**. Concentration of the filtrate produced an additional 8.5 g of **4g**. The total yield of **4g** after drying under vacuum at room temperature[13] was 10.7 g (76%) of white solid, mp 145 °C: ^1H NMR (DMSO-d_6) 10.10 (1 H, br s), 7.74 (1 H, t), 7.40 (2 H, d), 2.25 (3 H, s). Anal. Calcd for $C_9H_7Cl_2N_3O_2S_2$: C, 33.34; H, 2.18; N, 12.96. Found: C, 33.50; H, 2.39; N, 12.82.

Table II. Preparation of 1[a]

compd	exptl procedure[b]	reactn time, h	yield, %	mp, °C
1a	A	48	70	293–294[c]
1b	A	67	71	254–256
1c	B	0.5	89	314–315
1d	A	192	77	307–309
1e	A	216	78	280.5–282
1f	A	216	82	255–256
1g	B	0.5	57	306–308
1h	B	0.5	84	314 dec

[a] IR and NMR spectral data recorded for all compounds were consistent with the assigned structure. Satisfactory analytical data (±0.40% for C, H, N, Cl, S) were reported for all new compounds listed in the table with the exception of **1g** (Anal. Calcd for $C_8H_7Cl_2N_5O_2S$·HCl: C, 27.88; H, 2.34; N, 20.32. Found: C, 28.36; H, 2.50; N, 19.78). [b] See the Experimental Section for a detailed description of the procedure. [c] This sample was recrystallized from AcOH.

General Procedure for Conversion of *N'*-Cyano-*N*-(arylsulfonyl)-*S*-methylisothioureas 4 to *N*-(5-Amino-1*H*-1,2,4-triazol-3-yl)arenesulfonamides 1. Method A. *N*-(5-Amino-1*H*-1,2,4-triazol-3-yl)-2-methylbenzenesulfonamide (1b). Anhydrous hydrazine (17.5 mL, 17.7 g, 0.552 mol) was added to a suspension of 74.1 g (0.275 mol) of **4b** in 275 mL of CH_3CN. The resulting solution was stirred at room temperature for 67 h, and the solid which separated was collected by filtration, washed with CH_3CN, and dried under vacuum to yield 49.3 g (71%) of **1b** as a white solid, mp 254–256 °C: IR (KBr) 3425, 3320, 1610, 1228, 1141, 1122, 926 cm^{-1}; ^1H NMR (DMSO-d_6) 4.4–10.4 (4 H, br), 7.8–8.1 (1 H, m) 7.0–7.6 (3 H, m), 2.60 (3 H, s). Anal. Calcd for $C_9H_{11}N_5O_2S$: C, 42.68; H, 4.38; N, 27.65; S, 12.66. Found: C, 42.59; H, 4.17; N, 27.79; S, 12.46.

Method B. *N*-(5-Amino-1*H*-1,2,4-triazol-3-yl)-2,5-dichlorobenzenesulfonamide (1g). A mixture of 10.0 g (37.1 mmol) of **4g** and 10 mL (10 g, 0.20 mol) of hydrazine monohydrate in 85 mL of EtOH was heated at reflux for 30 min. After cooling to room temperature, the solid which separated was collected by filtration and suspended in 170 mL of H_2O. The suspension was acidified with concentrated HCl (aqueous) and stirred for 4 h. The solid was collected by filtration and dried under vacuum to yield 5.10 g (57%) of **1g** as a white solid, mp 306–308 °C: ^1H NMR (DMSO-d_6) 8.09 (5 H, br m), 7.93 (1 H, t), 7.55 (2 H, d). Anal. Calcd for $C_8H_7Cl_2N_5O_2S$·HCl: C, 27.88; H, 2.34; N, 20.32. Found: C, 28.36; H, 2.50; N, 19.78.

Preparation of Dimethyl *N*-[(2-Chlorophenyl)sulfonyl]-dithiocarbonimidate (5). Potassium hydroxide (85%, 19.4 g, 0.294 mol) and CS_2 (8.84 mL, 11.2 g, 0.147 mol) were added to a solution of 56.4 g (0.249 mol) of **3d** in 150 mL of DMF, and the solution was stirred at room temperature for 2 h. After the initial exothermic reaction subsided, 19.4 g (0.294 mol) of 85% KOH and 8.84 mL (0.147 mol) of CS_2 were added, and the reaction mixture was stirred at ambient temperature for 2 h. The reaction mixture was cooled to 5 °C, and 19.8 mL (45.1 g, 0.318 mol) of CH_3I was added. After an exothermic reaction subsided, the cooling bath was removed, and an additional 19.8 mL (0.318 mol) of CH_3I was added. The reaction mixture was stirred at room temperature for 18 h and poured onto a mixture of ice and H_2O. The solid which separated was collected by filtration and recrystallized from MeOH to afford 53.2 g (61%) of **5** as a yellow solid, mp 121–122 °C (lit.[14] mp 119–123 °C): IR ($CHCl_3$) 1482, 1302, 1155, 828 cm^{-1}; ^1H NMR ($CDCl_3$) 8.0–8.3 (1 H, m), 7.2–7.6 (3 H, m), 2.53 (6 H, s). Anal. Calcd for $C_9H_{10}ClNO_2S_3$: C, 36.54;

(10) Yale, H. L.; Sowinski, F. *J. Org. Chem.* **1960**, *25*, 1824.
(11) Colgate, R. T.; Rodd, E. H. *J. Chem. Soc.* **1910**, *97*, 1585.
(12) Newton, A. *J. Am. Chem. Soc.* **1943**, *65*, 2439.
(13) Decomposition was observed when samples of **4** were dried at elevated temperatures.
(14) Tseng, C. P. Eur. Pat. Appl. 58476, 1982.

H, 3.41; N, 4.73. Found: C, 36.48; H, 2.91; N, 4.75.

Conversion of 5 to 4d. A mixture of 220 mg (5.23 mmol) of cyanamide, 1.48 g (5.00 mmol) of **5**, and 691 mg (5.00 mmol) of anhydrous, powdered K_2CO_3 in 15 mL of THF was heated at reflux for 19 h. The reaction mixture was cooled to room temperature and filtered. The solid collected was washed with acetone, and the combined filtrates were evaporated at reduced pressure to give an oil, which solidified upon trituration with Et_2O. The solid was collected, washed with Et_2O, and suspended in 2.6 mL of 2 N HCl. After the suspension was stirred for 1 h, the solid was collected by filtration and dried under vacuum at room temperature to afford 1.00 g (69%) of **4d** as a white solid, mp 117–119 °C, which was identical with a sample prepared as described above by IR and ^1H NMR.[13]

Registry No. **1a**, 104667-72-3; **1b**, 104667-74-5; **1c**, 104667-75-6; **1d**, 104692-77-5; **1e**, 104667-73-4; **1f**, 99453-15-3; **1g**·HCl, 99453-18-6; **1h**, 104667-78-9; **2**, 10191-60-3; **3a**, 98-10-2; **3b**, 88-19-7; **3c**, 70-55-3; **3d**, 6961-82-6; **3e**, 1869-24-5; **3f**, 5455-59-4; **3g**, 7720-45-8; **3h**, 105536-22-9; **4a**, 104692-80-0; **4b**, 104667-66-5; **4c**, 104667-67-6; **4d**, 104667-65-4; **4e**, 104667-64-3; **4f**, 99453-14-2; **4g**, 99453-16-4; **4h**, 104667-70-1; **5**, 84346-43-0; cyanamide, 420-04-2.

Supplementary Material Available: Details of reaction scale and stoichiometry and characterization data (physical properties, IR and NMR spectral data, and elemental analyses) for **1** and **4** (4 pages). Ordering information is given on any current masthead page.

X-ray Structure of a Novel [4]Radialene from the Cyclodimerization of an Unsaturated Carbene Derived Pentatetraene[1]

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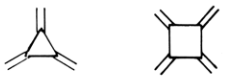
Received January 18, 1988

As a consequence of both their considerable strain energy and possible cyclic delocalization via cross conjugation radialenes represent an inherently interesting class of hydrocarbons.[2] Although both [3]radialene (**1**) and [4]-radialene (**2**) and a few substituted derivatives are known,[2]



1 **2**

we are not aware of any X-ray data on this unusual class of hydrocarbons. Hence, we wish to report the first single-crystal X-ray structure of a novel substituted [4]radialene.

As we reported[3] recently, trapping of carbene **4** with $Me_2C{=}CMe_2$ results in a 47% yield of cumulene **5**, which upon standing at room temperature for several days or heating for a few hours undergoes cyclodimerization to **6** in quantitative yield as shown in Scheme I. Dimer **6** is a stable pale yellow crystalline compound that presumably formed via a thermal [2πa + 2πs] cycloaddition analogous to the known[4] dimerizations of ketenes and allenes.

An ORTEP of **6** is given in Figure 1, and the relevant crystal data, bond distances, and bond angles are in Tables I–III, respectively. The molecule resides on a mirror symmetry so that the carbon atoms C_1, C_2, C_3, C_4, C_8, C_9,

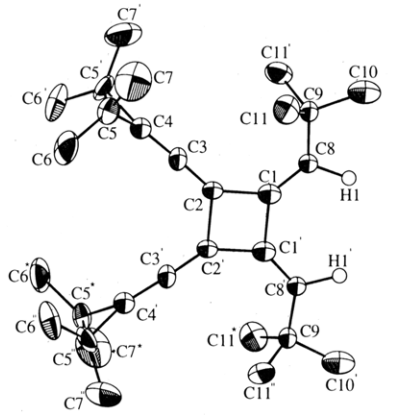
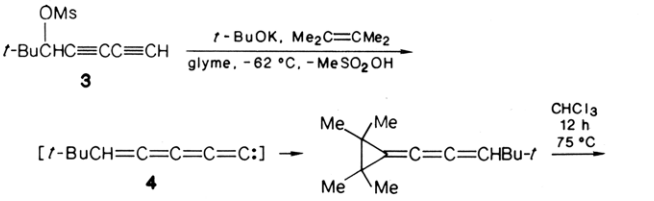


Figure 1.

Scheme I



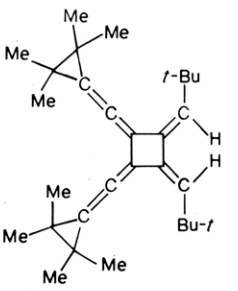


Table I. Summary of Crystallographic Data

molecular formula	$C_{30}H_{44}$
molecular weight	404.69
crystal system	tetragonal
space group	$P\bar{4}2_1m$ (113)
cell dimensions, Å	
a	10.792 (5)
b	10.792 (4)
c	12.022 (5)
volume, Å^3	1400.1
z	2
d(calcd), g/cm^3	0.960
crystal dimensions, mm	0.27 × 0.25 × 0.21
diffractometer	Syntex P$\bar{1}$
radiations, Å	(Mo Kα) 0.710 73
data collection method	2θ:θ
scan speed, deg/min	(variable) 2.5–8.0
reflections measured	659, *h*(0,14), *k*(0,14), *l*(0,18)
scan range	$K_{\alpha 1}$ −1.0 to $K_{\alpha 2}$ +1.0
2θ, deg	2.0–48.0
total bkdg. time/scan time	0.5
no. of reflections between std.	98
total unique data	557
obsd data, $I > 3\sigma I$	227
abs coeff (μ), cm^{-1}	0.496
no. of variables	51
R (averaging)	0.027, 0.025
max shift/error	0.0
R(*F*)	7.51
$R_w(F)$	7.72
goodness of fit	1.914
max diff Fourier peak, e/Å^3	0.52

(1) Abstracted from the Ph.D. Dissertation of A. E. Learned, The University of Utah, 1987.

(2) Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic: New York, 1978.

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