aromatic systems with differentiated oxygens. From this perspective it is likely to be of value in other synthetic enterprises.

Experimental Section[5]

Methyl Undec-2-yn-10-enoate (8). To a solution of 5.65 g (0.0559 mol) diisopropylamine in 20 mL of dry tetrahydrofuran under N_2 and at −78 °C, was added 34.9 mL of a 1.6 M solution of *n*-butyllithium in hexane (0.0559 mol) in a rapid dropwise fashion. The resulting solution was stirred for 45 min at −41 °C. To this solution at −41 °C were added 1.92 g (0.0275 mol) of propiolic acid and then 20 mL of dry hexamethylphosphoramide. This mixture was warmed to −15 °C and stirred for 2 h. A 5.2-g (0.0272-mol) sample of 1-bromo-7-octene (Chemical Samples) was then added dropwise over ca. 10 min. The reaction mixture was then allowed to warm to room temperature and stirred for 18 h.

The reaction mixture was poured into 400 mL of water and extracted (4 × 200 mL) with CH_2Cl_2. The aqueous layer was acidified to pH 1 with 1 N HCl, and the product was extracted (3 × 150 mL) with ether. The combined ether extracts were washed with water and with brine, dried ($MgSO_4$), and freed of solvent to afford 3.33 g (68%) of crude acid **7**: $\bar{\nu}$ ($CHCl_3$) 3600–3000 (br), 2240, 1685 cm^{-1}.

A mixture of 3.17 g of crude acid (2.50 g, 0.0181 mol) of anhydrous potassium carbonate and 6 mL of methyl iodide in 38 mL of dry dimethylformamide was stirred overnight under nitrogen at room temperature. It was poured into 400 mL of water and 350 mL of ether. The organic layer was washed (2 × 150 mL) with water and with brine, dried ($MgSO_4$), and freed of solvent to afford 3.06 g (90%) of the crude ester. Kugelrohr distillation, 65–75 °C (0.25 mm), afforded 2.82 g of the ester **8** as a colorless liquid: $\bar{\nu}$ ($CHCl_3$) 2230, 1715 cm^{-1}; δ ($CDCl_3$) 6.1–5.3 (m, 1 H), 5.03 (br d), 4.78 (br s, 2 H), 3.71 (s, 3 H), 1.0–2.50 (m, 12 H).

Methyl 2-Methoxy-4-(benzyloxy)-6-(oct-7-en-1-yl)benzoate (10). A solution of 0.848 g (0.0044 mol) of **8** and 2.65 g (0.0131 mol) of diene **3** in 2 mL of dry xylene was heated under nitrogen at 141 °C for 18 h. Upon the solution cooled, the solvent was removed in vacuo, and the residue was taken up in 10 mL of tetrahydrofuran and 10 mL of 0.1 N HCl. This mixture was stirred for 1.5 h at room temperature and was poured into 200 mL of ether and 100 mL of H_2O. The organic layer was washed with 1 N HCl (2 × 100 mL) and with brine. It was dried ($MgSO_4$), freed of solvent in vacuo, taken up in 3:1 hexane:ethyl acetate, and filtered through 10 g of Florisil. Concentration afforded 1.33 g of crude **9** which was submitted to the next step.

To a slurry under N_2 of 0.0068 mol of NaH (0.330 g of a 50% emulsion washed with pentane) in 15 mL of dry tetrahydrofuran was added a solution of 1.25 g of crude **9** in 10 mL of tetrahydrofuran at such a rate that the evolution of gas was controlled. After the mixture was stirred for ca. 10 min at room temperature, 3 mL of benzyl chloride followed by 0.800 g (0.001 mol) of sodium iodide was added. This reaction mixture was heated for 16 h under reflux, cooled to room temperature, and poured into 250 mL of water layered with 200 mL of ether. The organic layer when washed with H_2O and with brine, dried ($MgSO_4$), and freed of solvent afforded an oil which, after chromatography on silica gel and elution with 6:1 hexane:ethyl acetate, afforded 0.580 g (35%) of **10** as an oil: δ ($CDCl_3$) 7.38 (br s, 5 H), 6.41 (s, 2 H), 6.18–5.35 (m, 1 H), 5.05 (m and s, 3 H), 4.82 (br s, 1 H), 3.87 (s, 3 H), 3.75 (s, 3 H), 2.72–2.33 (m, 2 H), 2.26–1.83 (m, 2 H), 1.83–0.9 (m, 8 H); the spectrum also included a small signal at δ 7.2–6.8 which arises from an unknown trace impurity; mass spectrum, *m/e* calcd for $C_{24}H_{30}O_4$ 382.2144, found, 382.2119.

Methyl 2-Methoxy-4-(benzyloxy)-6-(8-hydroxyoctyl)-benzoate (1). To a solution of 0.058 g (0.00152 mol) of **10** in 30 mL of dry tetrahydrofuran under nitrogen and at 0 °C was added 2.9 mL of 1.0 M diborane/tetrahydrofuran (0.0029 mol) in a rapid dropwise fashion. The reaction mixture was allowed to warm to room temperature and to stir for 30 min. It was then cooled to 0 °C, and excess diborane was destroyed by the dropwise addition of water. Oxidation was accomplished by addition of 1.3 mL of 10% sodium hydroxide and 1.3 mL of 30% hydrogen peroxide and heating at 50 °C for 30 min.

The reaction mixture was poured into 300 mL of dilute hydrochloric acid and 300 mL of ether. The organic layer was washed with 100 mL of water and brine, dried, and freed of solvent to afford 0.585 g of a crude oil. Chromatography on silica gel using 1:1 hexane:ethyl acetate afforded 0.485 g (80%) of pure hydroxy ester **1** as a colorless oil: NMR and IR spectra were identical with those reported by Gerlach; mass spectrum, *m/e* calcd for $C_{24}H_{32}O_5$ 400.2250 (P), found 400.2249 (P).

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Registry No. **1**, 65716-56-5; **3**, 61539-61-5; **6**, 2695-48-9; **7**, 71819-27-7; **8**, 71819-28-8; **9**, 71838-34-1; **10**, 71819-29-9; propiolic acid, 471-25-0.

(5) Boiling points are uncorrected. Infrared measurements were obtained from a Perkin-Elmer 247 recording spectrometer. NMR spectra were obtained from a Varian Associates T60-A system using tetramethylsilane as an internal standard. Chemical shifts are given in parts per million from Me_4Si (δ). Low-resolution mass spectra were obtained from an LKB-9000 unit by direct insertion. High-resolution mass spectra were obtained from a Varian Associates CH-5 system.

Sulfonamidyls. 3.[1] Electron Spin Resonance Spectroscopic Study of New Acyclic and Cyclic Sulfonamidyl Radicals

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In two earlier communications[1] we have reported electron spin resonance (ESR) spectral data for *N*-alkylsulfonamidyl[1a] ($R_1SO_2\dot{N}R_2$) and *N*-alkoxysulfonamidyl radicals[1b] ($R_1SO_2\dot{N}OR_2$).[2] In a subsequent Japanese paper[3] ESR spectra were described for some *N*-arylsulfonamidyl radicals and, very recently, ESR data for an additional *N*-alkoxysulfonamidyl were reported by Forrester et al.[4] We have proposed[1] that sulfonamidyls reside in a π-electronic ground state, but noted some interesting differences between the ESR spectral features of sulfonamidyls and the corresponding carboxamidyls ($R_1C\dot{O}NR_2$), reported previously.[5,6]

In this note we present new ESR data which shed further light upon the structure of sulfonamidyl radicals. In all cases these rather short-lived radicals were produced by photolysis of the corresponding *N*-bromosulfonamides directly in the cavity of the ESR spectrometer at low temperatures. Alternatively, two *N*-alkoxysulfonamidyls were also generated by hydrogen abstraction from the parent sulfonamide by *tert*-butoxyl radicals, obtained from thermolysis of di-*tert*-butyl peroxyoxalate (DBPO).

$$\underset{\text{Y = alkyl, alkoxy}}{\overset{\displaystyle Br}{\overset{|}{RSO_2NY}}} \xrightarrow{h\nu} RSO_2\dot{N}Y \xleftarrow{t\text{-BuO}\cdot} \underset{\text{Y = alkoxy}}{\overset{\displaystyle H}{\overset{|}{RSO_2NY}}}$$

In order to examine the possibility that the smaller nitrogen hyperfine splitting constants (hfc's) of acyclic

(1) (a) Part 1: G. Zomer and J. B. F. N. Engberts, *Tetrahedron Lett.*, 3901 (1977); (b) Part 2: H. Teeninga and J. B. F. N. Engberts, *Recl. Trav. Chim. Pays-Bas*, **97**, 59 (1978).

(2) After our communications we were informed by Dr. R. W. Gellert that ESR spectral properties of several sulfonamidyls have been described in his M.S. thesis, Kansas State University, 1973. However, to the best of our knowledge, this work has not been published.

(3) Y. Miura, Y. Nakamura, and M. Kinoshita, *Bull. Chem. Soc. Jpn.* **51**, 947 (1978).

(4) A. R. Forrester, E. M. Johansson, and R. H. Thomson, *J. Chem. Soc, Perkin Trans. 1*, 1112 (1979).

(5) W. C. Danen and R. W. Gellert, *J. Am. Chem. Soc.*, **94**, 6853 (1972).

(6) T. Koenig, J. A. Hoobler, and W. R. Mabey, *J. Am. Chem. Soc.*, **94**, 2514 (1972).

0022-3263/79/1944-4717$01.00/0

Table I. ESR Spectral Data[a] of the Cyclic Sulfonamidyls (1 and 2) and of the Corresponding Nitroxides (3 and 4)

radical	A_N, G	A_H, G	g
1	13.2	1.3 (6 H)	2.0040
2	13.1	*b*	2.0042
3	11.8		2.0061
4	11.0		2.0060

[a] In 2:1 (v/v) $CFCl_3$-CH_2Cl_2 at −50 °C. [b] See text and Table II.

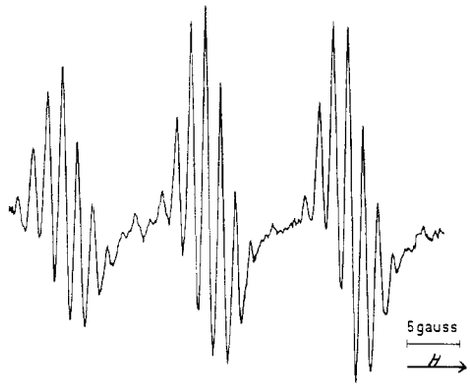


Figure 1. ESR spectrum of 1 in 2:1 (v/v) $CFCl_3$–CH_2Cl_2 at −50 °C.

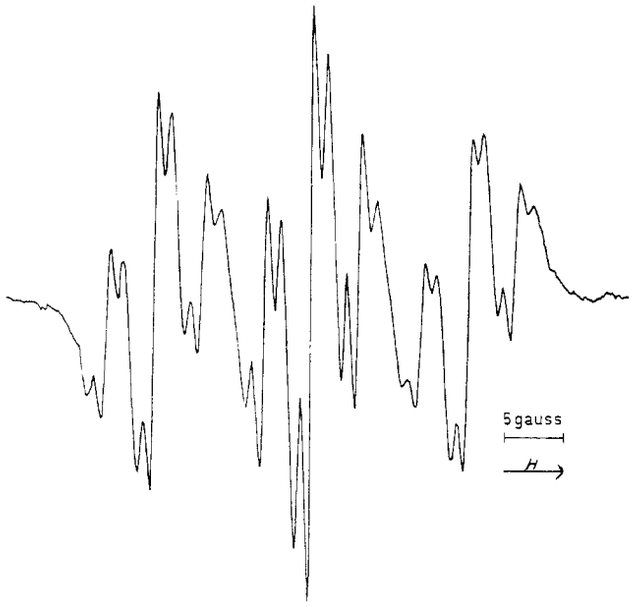
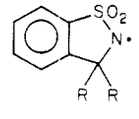
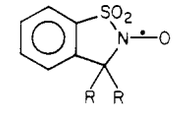


Figure 2. ESR spectrum of 2 in 2:1 (v/v) $CFCl_3$–CH_2Cl_2 at −90 °C.

sulfonamidyls as compared with those for the corresponding carboxamidyls (~13 vs. ~16 G) would reflect a bias toward sp hybridization of the nitrogen atom in the sulfonamidyls, some cyclic sulfonamidyl radicals were prepared and studied by ESR. Results for two 3,3-dialkyl-1,2-benzisothiazoline 1,1-dioxide systems, 1 and **2**, are given in Table I and representative spectra are displayed in Figures 1 and 2. Data for the corresponding nitroxides **3** and **4** are given for comparison. Since the



1, R = Me
2, R = Et



3, R = Me
4, R = Et

nitrogen hfc's for the acyclic and cyclic sulfonamidyls are virtually identical, we conclude that a tendency toward sp hybridization at nitrogen (with a SNR_2 angle of 180° and the unpaired electron on nitrogen in a pure p orbital lying in the plane of the σ framework) cannot be invoked to account for the relatively low A_N values. The magnitude of hydrogen hfc's for the γ protons in **1** is reminiscent of that found in rigid systems.[7] Interestingly, the hfc's for the two diastereotopic γ protons (H_a and H_b) in **2** exhibited a pronounced temperature dependence (Table II). Therefore, it appears that a dynamic process is involved, most likely arising from a rotational barrier about one (or more) bond(s) and reflecting steric crowding in the radical. At about −80 °C a preferred conformation is frozen out on the ESR time scale which shows resolvable H_a and H_b protons. Apparently, there is effective rotational averaging at higher temperatures under which conditions H_b cannot be resolved.[8]

Table II. Temperature Dependence of A_{H_γ} in 2[a]

T, °C	A_{H_a}, G	A_{H_b}, G
60	2.38 (2 H)	*b*
−25	2.85 (2 H)	*b*
−80	3.88 (2 H)	0.60 (2 H)
−103	3.93 (2 H)	1.13 (2 H)

[a] In 2:1 (v/v) $CFCl_3$-CH_2Cl_2. A_N = 13.1 G. [b] Not resolvable.

Table III. Hyperfine Splitting Constants and g Values for Some Sulfonamidyls and Sulfonyl Nitroxides[a]

	R	Y	A_N, G	$A_H^{t\text{-Bu}}$, G	$A_H^{CH_3}$, G	g
			RSO_2NY			
5	Me_2N	*t*-Bu	13.0	0.60 (9 H)	0.30 (3 H)	2.0043
6	MeO	*t*-Bu	13.0	0.62 (9 H)	0.31 (3 H)	2.0044
7[b]	Me	O-*t*-Bu	11.8		*c*	2.0052
8[b]	*p*-NO_2-C_6H_4	O-*t*-Bu	11.3			2.0048
9	Me_2N	O-*t*-Bu	11.8	*d*	0.70 (6 H)	2.0052
			$RSO_2N(O)Y$			
10	Me_2N	*t*-Bu	12.8			2.0059
11	MeO	*t*-Bu	11.8			2.0059

[a] In 2:1 (v/v) $CFCl_3$-CH_2Cl_2 at ca. −50 °C. [b] Also obtained from the parent *N*-alkoxysulfonamide through hydrogen abstraction by *tert*-butoxyl radicals generated from thermolysis of DBPO in benzene at 40 °C. [c] Not resolvable. [d] $A_{N'}$ = 0.23 G (second nitrogen).

Substituent effects on the ESR spectral parameters of a series of sulfonamidyls **5**–**9** are listed in Table III. Some data for corresponding nitroxides **10**–**11** are given for comparison.[9] The small variation of A_N upon variation of R strongly suggests that there is little or no spin delocalization onto the sulfonyl group. The same conclusion has been drawn previously for sulfonylcarbinyl radicals,[10]

(7) T. Toda, E. Mori, H. Horiuchi, and K. Murayama, *Bull. Chem. Soc. Jpn.*, **45**, 1802 (1972).

(8) Coupling to only a single proton of a pair of methylene groups has recently been observed for the 3,3-dimethyl-1-oxa-4-azaspiro[4.11]hexadec-4-yloxy radical: M. J. Heinig, G. R. Eaton, and S. S. Eaton, *Org. Magn. Reson.*, **11**, 211 (1978).

(9) For a discussion of the ESR spectral properties of sulfonyl nitroxides, see: (a) Th. A. J. W. Wajer, H. W. Geluk, J. B. F. N. Engberts, and Th. J. de Boer, *Recl. Trav. Chim. Pays-Bas*, **89**, 696 (1970); (b) G. Rawson and J. B. F. N. Engberts, *Tetrahedron*, **26**, 5653 (1970). As argued previously, the influence of a sulfonyl group, compared with that of a comparable acyl group, on a nitrogen radical center is different for amidyl and nitroxide radicals.

(10) P. M. Carton, B. C. Gilbert, H. A. H. Laue, R. O. C. Norman, and R. S. Sealy, *J. Chem. Soc., Perkin Trans. 2*, 1245 (1975).

largely on the basis of A_{H_γ} hfc's. However, the A_N values of the *N*-alkoxysulfonamidyl radicals **7–9** are ~1.5 G smaller than those for *N*-alkylsulfonamidyls, consistent with some spin delocalization onto oxygen of the alkoxy group.[1b] We note that the nitrogen hfc's of *N*-alkoxy-

$$\underset{\text{A}}{R_1SO_2\dot{N}-\bar{O}-R_2} \longleftrightarrow \underset{\text{B}}{RSO_2\bar{N}-\dot{O}^{+}-R_2}$$

carboxamidyls are about 5 G smaller than those of *N*-alkylcarboxamidyls, indicating that resonance hybrids comparable to B are probably more important than in the case of *N*-alkoxysulfonamidyl radicals. This provides further evidence for the notion that structurally related sulfonyl and acyl groups exert different effects on a nitrogen free radical center. At present ab initio quantum mechanical calculations are in progress to probe the electronic structure of sulfonyl- and carbonyl-substituted aminyl radicals.

Finally, we report that alkylsulfonyloxyaminyl radicals can be generated by hydrogen abstraction from the parent *O*-sulfonyl hydroxylamine. Thus, irradiation of the *O*-sulfonyl hydroxylamines **12** (R = 2,6-Me_2-4-*t*-BuC_6H_2) or **13** (R = 4-MeC_6H_4) in tetra (CCl_4) or benzene or, alternatively, treatment of **12** or **13** with lead tetraacetate (or lead dioxide) in the same solvents at room temperature, leads to the production of radicals with A_N = 14.8 G and g = 2.0045. We assign these spectra to the corresponding sulfonyloxyaminyl radicals. The ESR spectral data may be compared with those of acyloxyaminyls obtained by Forrester et al.[11] and are very similar. When samples of **12** and **13** are irradiated in the presence of di-*tert*-butyl

$$\underset{\textbf{12, 13}}{RSO_2ONHBu\text{-}t} \rightarrow RSO_2\dot{O}NBu\text{-}t$$

peroxide, the ESR spectra exhibited triplets with A_N = 12.3 G (from **12**) and A_N = 13.3 G (from **13**), respectively. Both radicals had g = 2.0060. Presumably, the corresponding sulfonyl nitroxides are generated under these conditions.[9] Although different routes for the production of these nitroxides may be imagined, a tentative mechanism is the following:

$$RSO_2ONHBu\text{-}t \xrightarrow[h\nu]{(t\text{-}BuO)_2} RSO_2\dot{O}NBu\text{-}t \rightarrow RS\dot{O}_2 + t\text{-}BuN{=}O \rightarrow RSO_2N(\dot{O})Bu\text{-}t$$

Experimental Section

Melting points were taken on a Mettler FP2 melting point apparatus. ESR spectra were recorded on a Varian E-4 apparatus. The spectrometer was fitted with a Varian A-1268 variable temperature controller, checked with a copper–constantan thermocouple. All solutions used for ESR experiments were purged with nitrogen for 30 min in order to remove dissolved oxygen. The g values (±0.0002) were measured using α,α'-diphenyl-β-picrylhydrazyl as a reference compound (g = 2.0037). Photolyses were carried out using a Philips SP-500 W lamp. ^{1}H NMR spectra were obtained using a Hitachi Perkin-Elmer Model R24B spectrometer. Chemical shifts are expressed as δ values in parts per million relative to Me_4Si = 0.

Infrared spectra were recorded on a Perkin-Elmer 125 spectrophotometer. The *N*-alkyl-*N*-bromosulfonamides were prepared from the reaction of the parent sulfonamide with *tert*-butyl hypobromite.[12] The cyclic *N*-bromosulfonamides and the *N*-alkoxy-*N*-bromosulfonamides were obtained from the reaction of the corresponding cyclic sulfonamide or *N*-alkoxysulfonamide with sodium hypobromite.[13] All *N*-bromosulfonamides contained 10–15% of the parent sulfonamides. The purity of the acyclic *N*-alkyl-*N*-bromosulfonamides was estimated by IR and NMR spectroscopy, and that of the cyclic *N*-alkyl-*N*-bromosulfonamides and the *N*-alkoxy-*N*-bromosulfonamides by IR spectroscopy.

***N,N*-Dimethyl-*N'*-*tert*-butylsulfamide.** *tert*-Butylamine (11.0 g, 0.15 mol) was added dropwise at room temperature to a stirred solution of *N,N*-dimethylsulfamoyl chloride (7.2 g, 0.05 mol) in dichloromethane (50 mL). After stirring overnight the solution was poured out in water. The organic layer was separated and washed twice with 20 mL of 1 M HCl and once with water (20 mL) and was then dried over $MgSO_4$. The solvent was removed in vacuo and the crude product was crystallized from *n*-hexane to yield 5.4 g (60%) of pure sulfamide: mp 58–59 °C; NMR ($CDCl_3$) δ 1.34 (s, 9 H), 2.78 (s, 6 H), 4.4 (br s, 1 H); IR (Nujol) 3330, 1385, 1195 cm^{-1}. Anal. Calcd for $C_6H_{16}N_2O_2S$: C, 40.00; H, 8.89; N, 15.56; S, 17.78. Found: C, 39.79; H, 8.92; N, 15.55; S, 17.68.

***N*-*tert*-Butoxy-*p*-nitrobenzenesulfonamide** was prepared by the method of Reagan and Nickon.[14] The compound was crystallized from ethanol–water and then from ether–*n*-pentane: yield 67%; mp 144–145 °C; NMR ($CDCl_3$) δ 1.25 (s, 9 H), 6.75 (br s, 1 H), 7.97–8.43 (m, 4 H); IR (KBr) 3208, 1529, 1341, 1159 cm^{-1}. Anal. Calcd for $C_{10}H_{14}N_2O_5S$: C, 43.79; H, 5.14; N, 10.21; S, 11.69. Found: C, 43.57; H, 5.14; N, 10.20; S, 11.65.

***N,N*-Dimethyl-*N*-*tert*-butoxysulfamide.** A solution containing *O*-*tert*-butylhydroxylamine hydrochloride (1.0 g, 8 mmol), *N,N*-dimethylsulfamoyl chloride (1.1 g, 7.5 mmol), and triethylamine (1.6 g, 16 mmol) in 1:1 (v/v) acetonitrile–DMF 80 mL was stirred for 2 h at room temperature. After removal of the solvent in vacuo at 50 °C, ether was added to the residue and the triethylammonium salt was filtered off. After evaporation of the ether an oil was obtained which crystallized slowly. The pure sulfamide was obtained upon sublimation at 60 °C (10 mm): yield 0.1 g (15%); mp 98–101 °C; NMR ($CDCl_3$) δ 1.27 (s, 9 H), 2.98 (s, 6 H), 6.95 (br s, 1 H); IR (KBr) 3222, 1301, 1153 cm^{-1}. Anal. Calcd for $C_6H_{16}N_2O_3S$: C, 36.72; H, 8.22; N, 14.27; S, 16.34. Found: C, 36.73; H, 8.17; N, 14.14; S, 15.99.

***N*-*tert*-Butoxymethanesulfonamide** was prepared by a method reported previously.[14] The organic layer was washed once with 1 M HCl. The pure compound was obtained upon crystallization from benzene–*n*-hexane: yield 60%; mp 63–64 °C; NMR ($CDCl_3$) δ 1.30 (s, 9 H), 3.04 (s, 3 H), 6.76 (br s, 1 H); IR (KBr) 3194, 1335, 1163 cm^{-1}. Anal. Calcd for $C_5H_{13}NO_3S$: C, 35.91; H, 7.84; N, 8.37; S, 19.17. Found: C, 35.76; H, 7.85; N, 8.34; S, 18.88.

***N*-*tert*-Butyl-*O*-(2,6-dimethyl-4-*tert*-butylphenylsulfonyl)hydroxylamine (12).** A solution of *N*-*tert*-butylhydroxylamine (0.9 g, 0.01 mol) in 30 mL of dichloromethane was added dropwise in 20 min to a stirred solution of 2,6-dimethyl-4-*tert*-butylbenzenesulfonyl chloride[15] (2.6 g, 0.01 mol) and triethylamine (2 g, 0.02 mol) in 30 mL of dichloromethane. After standing overnight the solution was washed three times with 5% aqueous HCl and once with water. After drying over $MgSO_4$ and evaporation of the solvent in vacuo, the crude material was crystallized from 2:1 (v/v) petroleum ether (40–60)–chloroform to yield 1.2 g (51%) of pure material: mp 94–95 °C; NMR ($CDCl_3$) δ 1.00 (s, 9 H), 1.30 (s, 9 H), 2.70 (s, 6 H), 5.3 (br s, 1 H), 7.18 (s, 2 H); IR (Nujol) 3310, 1280, 1190 cm^{-1}. Anal. Calcd for $C_{16}H_{27}NO_3S$: C, 61.34; H, 8.63; N, 4.47; S, 10.22. Found: C, 61.40; H, 8.72; N, 4.39; S, 10.19.

***N*-*tert*-Butyl-*O*-(*p*-tolysulfonyl)hydroxylamine (13)** was prepared similarly: yield 60%; mp 88–90 °C; NMR ($CDCl_3$) δ 0.95 (s, 9 H), 2.45 (s, 3 H), 7.30–7.95 (m, 4 H); IR (Nujol) 3320, 1390, 1180 cm^{-1}. Anal. Calcd for $C_{11}H_{17}NO_3S$: C, 54.30; H, 7.04; N, 5.76; S, 13.18. Found: C, 54.27; H, 7.00; N, 5.77; S, 13.13.

Registry No. **1**, 71750-18-0; **2**, 71750-19-1; **3**, 71750-20-4; **4**, 71750-21-5; **5**, 71750-22-6; **6**, 71750-23-7; **7**, 71750-24-8; **8**, 71750-25-9; **9**, 71750-26-0; **10**, 71750-27-1; **11**, 71750-28-2; **12**, 71750-29-3; **13**,

(11) A. R. Forrester, J. Henderson, E. M. Johansson, and R. H. Thomson, *Tetrahedron Lett.*, 5139 (1978).
(12) R. S. Neale and N. L. Marcus, *J. Org. Chem.*, **34**, 1808 (1969).
(13) E. E. J. Dekker, J. B. F. N. Engberts, and Th. J. de Boer, *Recl. Trav. Chim. Pays-Bas*, **97**, 39 (1978).
(14) M. T. Reagan and A. Nickon, *J. Am. Chem. Soc.*, **90**, 4096 (1968).
(15) E. H. Huntress and J. S. Autenrieth, *J. Am. Chem. Soc.*, **63**, 3446 (1941).

71750-30-6; *N,N*-dimethyl-*N'*-*tert*-butylsulfamide, 71750-31-7; *tert*-butylamine, 75-64-9; *N,N*-dimethylsulfamoyl chloride, 13360-57-1; *N*-*tert*-butoxy-*p*-nitrobenzenesulfonamide, 71750-32-8; *N,N*-dimethyl-*N*-*tert*-butoxysulfamide, 71750-33-9; *O*-*tert*-butylhydroxylamine hydrochloride, 39684-28-1; *p*-toluenesulfonyl chloride, 98-59-9; *N*-*tert*-butoxymethanesulfonamide, 71750-34-0; *N*-*tert*-butoxyhydroxylamine, 71750-35-1; 2,6-dimethyl-4-*tert*-butylbenzenesulfonyl chloride, 70823-04-0.

Electrochemical Generation of the Azo Linkage. Synthesis of Bicyclic Azo Compounds, Precursors of 1,3-Diyls

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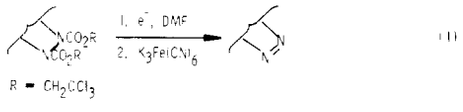
In conjunction with our efforts to utilize cyclopenta-1,3-diyls (e.g., **1**; see Scheme I) as useful intermediates for the synthesis of linearly fused tricyclopentanoids (e.g., hirsutene, hirsutic acid, the coriolins, capnellane), bicyclo[5.3.0]decanes (e.g., damsin, the mexicanins, helenalin, etc.), and modified prostaglandins,[1] we required a route to bicyclic azo compounds (e.g., **2**) subject to the following conditions: (1) reactions leading to **2** must be conducted at or below room temperature to avoid or at least minimize thermal decomposition of the product; (2) the reagents, reaction conditions, and byproducts must be compatible with the survival of the C_7–C_8 π system for a variety of different substituents A and B; (3) the sequence should bypass the formation of hydrazo compounds since they are often unstable. Furthermore, the conditions used to effect their conversion to azo compounds are often incompatible with the survival of the product; (4) the sequence must (obviously) be efficient.

Table I displays several routes for the conversion of dicarbamates to azo compounds along with comments regarding specific disadvantages of these methods especially in relation to the synthesis of compounds such as **2** for a variety of substituents A and B.

In this paper we describe a new electrochemical method for the synthesis of azo compounds which fulfills the conditions described above. The method, illustrated in eq 1, utilizes a controlled-potential reductive cleavage of a



(1)

bis(2,2,2-trichloroethyl) dicarbamate followed by oxidation using aqueous potassium ferricyanide at 0 °C. Undoubtedly, the ferricyanide oxidation could be replaced by an electrochemical oxidation, but, considering the convenience and efficiency of the present procedure, we see no compelling reason to do so.

Scheme I

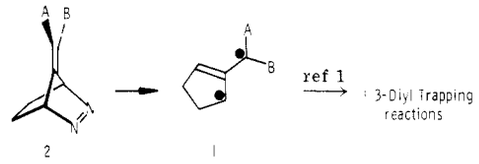
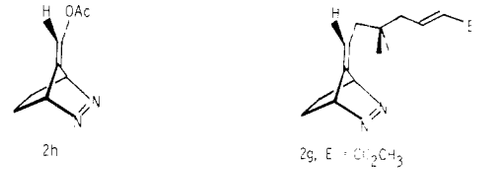


Table II summarizes our results. The reduction potentials were determined by using cyclic voltammetry and are reported vs. a silver–silver chloride reference electrode in DMF with 0.1 N lithium perchlorate as the supporting electrolyte. The choice of a silver–silver chloride rather than a calomel (SCE) reference electrode was suggested by the well-established problems of using an aqueous calomel electrode in a nonaqueous solvent.[8] While there are several ways to obviate these problems,[9] we decided to opt for the silver–silver chloride electrode since it is known to be compatible with a number of organic solvents.[10] (For comparison, one might wish to note that E = −0.045 V vs. SCE for Ag/AgCl(s), KCl(s).)[11]

Two entries deserve special comment. Entry **3h** illustrates the synthesis of a bicyclic azo compound which we have been unable to synthesize by using any other method. An obvious limitation upon any method which might be used to synthesize **2h** is the acid and base sensitivity of



the enol acetate group along with the propensity of C_7 to become sp^3 rather than sp^2 hybridized. Thus, the result is significant even though the yield for the formation of **2h** is only a modest 40–50%. Entry **3g** illustrates that use of the method in an instance where there is more than one readily reduced functional group. In this case, reductive cleavage of the trichloroethyl group occurs in preference to the reduction of the α,β-unsaturated ester unit.[12] This result was anticipated on the basis of the results of cyclic voltammetry studies. Presumably, if required, even greater selectivity could be achieved through the use of a tribromo- rather than a (trichloroethoxy)carbonyl group.[13]

Experimental Section

^{1}H NMR spectra were obtained by using a Varian T-60 spectrometer. The spectral data are reported in δ relative to $(CH_3)_4Si$ as an internal standard with $CDCl_3$ as the solvent. The dicarbamates were prepared by using a Diels–Alder reaction of the appropriate fulvene and bis(2,2,2-trichloroethyl) azodicarboxylate followed by selective monohydrogenation at atmospheric pressure by using 10% Pd/C as the catalyst or, in the case of **3a**, by

(1) Tricyclopentanoids, see: (a) Little, R. D.; Bukhari, A.; Venegas, M. G. *Tetrahedron Lett.* **1979**, 305–8. (b) Venegas, M. G.; Little, R. D. *Ibid.* **1979**, 309–12. (c) Little, R. D.; Muller, G. W. *J. Am. Chem. Soc.* **1979**, in press. Bicyclo[5.3.0]decanes and modified prostaglandins, unpublished results of L. Dang and L. Brown, respectively.

(2) For examples, see inter alia: (a) Gassman, P. G.; Mansfield, K. H. *Org. Synth.* **1969**, *49*, 1. (b) Berson, J. A.; Bushby, R. J.; McBride, J. M.; Tremelling, M. J. *J. Am. Chem. Soc.* **1971**, *93*, 1544. (c) Zimmerman, H. E.; Boettcher, R. J.; Buehler, N. E.; Keck, G. E.; Steinmetz, M. G. *Ibid.* **1976**, *98*, 7680.

(3) Wildi, E. A.; Carpenter, B. K. *Tetrahedron Lett.* **1978**, 2469.

(4) Little, R. D.; Venegas, M. G. *J. Org. Chem.* **1978**, *43*, 2921–3.

(5) Heyman, M. A.; Snyder, J. P. *Tetrahedron Lett.* **1973**, 2859.

(6) Masamune, S.; Nakamura, N.; Spadara, J. *J. Am. Chem. Soc.* **1975**, *97*, 918.

(7) For example, see: Semmelhack, M. F.; Foos, J. S.; Katz, S. *J. Am. Chem. Soc.* **1973**, *95*, 7325.

(8) Lund, H.; Iversen, P. *Org. Electrochem.* **1973**, 204–8.

(9) For example, see ref 8 and: Coetzee, J. F.; Padmanabhan, J. R. *J. Phys. Chem.* **1962**, *66*, 1708.

(10) See ref 8 and: Synnott, J. C.; Butler, J. N. *Anal. Chem.* **1969**, *41*, 1890.

(11) See p 207 of ref 8.

(12) Baizer has extensively studied the electrochemistry of α,β-unsaturated esters and nitriles. For example, see: (a) Wagenknecht, J. H.; Baizer, M. M. *J. Org. Chem.* **1966**, *31*, 3885. (b) Anderson, J. D.; Baizer, M. M.; Petrovich, J. P. *Ibid.* **1966**, *31*, 3890. (c) Petrovich, J. P.; Anderson, J. D.; Baizer, M. M. *Ibid.* **1966**, *31*, 3897.

(13) The preparation of bis(2,2,2-trichloroethyl) azodicarboxylate is described in: Little, R. D.; Venegas, M. G. *Org. Synth.*, in press.

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