ft × 0.125 in. UCW-982 on Chromosorb W column at 160 °C). All ^{1}H NMR and IR spectra were recorded by using Varian A-60 and Beckman Acculab 7 spectrometers, respectively. All *N*,*N*-dialkylacrylamides were prepared by condensation of acryloyl chloride with the appropriate secondary amine by using standard procedures and were distilled prior to use:[10] *N*,*N*-dimethyl, bp 37–38 °C (1.0 mm); *N*,*N*-diethyl, bp 65–67 °C (1.0 mm); *N*,*N*-di-*n*-propyl, bp 62–64 °C (2.0 mm); *N*,*N*-di-*n*-butyl, bp 80–81 °C (1.0 mm); *N*,*N*-di-*n*-octyl, bp 155–156 °C (1.0 mm). All acrylamides gave the expected IR and ^{1}H NMR spectra. Samples of *N*,*N*-dimethylacrylamide, *N*,*N*-diethylacrylamide, and *N*,*N*-di-*n*-butylacrylamide obtained commercially (Polysciences) gave identical results.

***N*,*N'*-Dimethyl-*N*,*N'*-ethylenebis(acrylamide).**[12] To a cooled solution (−30 °C) of acryloyl chloride (9.0 g, 0.10 mol) in $CHCl_3$ (75 mL) was added dropwise a mixture of *N*,*N'*-dimethylethylenediamine (4.4 g, 0.05 mol) and triethylamine (10.2 g, 0.1 mol). The mixture was then warmed to room temperature and stirred for an additional 2 h, and the solvent was evaporated under reduced pressure. Hexane (100 mL) was then added and the mixture filtered. Evaporation of the solvent from the filtrate followed by column chromatography of the residue on neutral alumina, using $CHCl_3$ as eluent, afforded 8.5 g (86%) of *N*,*N'*-dimethyl-*N*,*N'*-ethylenebis(acrylamide) as a colorless oil: ^{1}H NMR ($CDCl_3$) 6.0–6.9 (m, 4 H, CH=CH), 5.68 (m, 2 H, HCH=C), 3.62 (s, 4 H, CH_2N), 3.06 (s, 6 H, CH_3N); IR (neat) C=O 1635 (s, C=O), 1610 (m, C=C) cm^{-1}; exact mass calcd for $C_{10}H_{16}N_2O_2$ 196.2512, found 196.1227 (Midwest Center for Mass Spectroscopy, Lincoln, NE).

Polymerization Reactions. Procedures similar to that described below were used for preparing all of the polymers described in Table I. A mixture of *N*,*N*-diethylacrylamide (1.2 g, 10 mmol), *N*,*N'*-dimethyl-*N*,*N'*-ethylenebis(acrylamide) (0.019 g, 0.1 mmol), azobis(isobutyronitrile) (0.016 g, 0.1 mmol), and 2 mL of benzene was placed in a 50-mL culture tube and sealed with a Teflon-lined screw cap. The tube was heated for 3 h at 80 °C, and the resulting gel was isolated by filtration. Successive washing with two 10-mL portions of water, two 25-mL portions of distilled THF, and two 25-mL portions of toluene followed by drying [110 °C, 24 h (1.0 mm)] yielded 1.11 g of copolymer (90%). The resin was crushed with a mortar and pestle prior to use, yielding particles of ~20–40 mesh. When *N*,*N*-di-*n*-octylacrylamide was copolymerized with 1 or 5 mol % *N*,*N'*-dimethyl-*N*,*N'*-ethylenebis(acrylamide), intractable and highly sticky polymers were formed. In all other cases, polymerization proceeded smoothly, affording resins which were convenient to handle.

Triphase Displacement. All triphase reactions were carried out in 50-mL culture tubes, using established procedures.[7] In all cases, vigorous stirring was employed (ca. 1000 rpm, using a Teflon-coated magnetic stirring bar (0.5 × $^5/_{16}$ in. octagonal bar with pivot ring)). Reaction of 0.37 mmol of *n*-decyl methanesulfonate in 3 mL of toluene with 5 mL of a saturated aqueous sodium chloride solution catalyzed by 0.1 g of 10% cross-linked poly(*N*,*N*-di-*n*-octylacrylamide) at 90 °C afforded a 42% yield of *n*-chlorodecane after 24 h. By use of similar reaction conditions and catalyst, potassium iodide displacement on 1-bromooctane yielded 36% 1-iodooctane; all other poly(acrylamide) gels listed in Table I produced less than 4% yields of alkyl chloride or iodide.

Cross-linked *N*,*N*-di-*n*-octylacrylamide used to convert *n*-decyl methanesulfonate to *n*-decyl chloride was recovered by filtration, washed with two 10-mL portions of water and two 10-mL portions of toluene, and dried [110 °C, 6 h (1 mm)]; the yield of recovered catalyst was 98%. Two successive reuses gave identical results. A small preparative-scale synthesis of *n*-decyl chloride was also performed, using 4.0 g (17 mmol) of *n*-decyl methanesulfonate, 4.0 g of polymer, 80 mL of toluene, and 50 mL of saturated aqueous sodium chloride. After 24 h at 90 °C, a quantitative conversion was obtained (GLC). Distillation of the organic phase yielded 2.24 g (75%) of *n*-decyl chloride (bp 62–63 °C (1.0 mm)) which was spectroscopically identical with an authentic sample.

Biphase Displacement. A 50-mL culture tube containing a Teflon-coated magnetic stirring bar was charged with 2 mL of dry dioxane, 0.058 g (0.5 mmol) of sodium phenoxide, 0.358 g (2.0 mmol) of 1-bromoheptane, 0.02 g (0.118 mmol) of *n*-dodecane (internal standard), and 0.050 g of poly(acrylamide). The tube was sealed with a Teflon-lined screw cap, placed in an oil bath maintained at 75 °C, and monitored (GLC) by withdrawing 1-μL aliquots from the liquid phase.

Acknowledgment. We are grateful to Professor A. Guyot (CNRS, France) for valuable discussions.

Registry No. *N*,*N*-Dimethylacrylamide, 2680-03-7; *N*,*N*-diethylacrylamide, 2675-94-7; *N*,*N*-di-*n*-propylacrylamide, 68404-19-3; *N*,*N*-di-*n*-butylacrylamide, 2274-13-7; *N*,*N*-di-*n*-octylacrylamide, 7773-87-7; acryloyl chloride, 814-68-6; *N*,*N'*-dimethylethylenediamine, 110-70-3; *N*,*N'*-dimethyl-*N*,*N'*-ethylenebis(acrylamide), 60134-80-7; *n*-decyl methanesulfonate, 41233-29-8; *n*-chlorodecane, 1002-69-3; 1-bromooctane, 111-83-1; 1-iodooctane, 629-27-6; sodium phenoxide, 139-02-6; 1-bromoheptane, 629-04-9; phenyl *n*-heptyl ether, 32395-96-3; *N*,*N*-dimethylacrylamide *N*,*N'*-dimethyl-*N*,*N'*-ethylenebis(acrylamide) copolymer, 76832-62-7; *N*,*N*-diethylacrylamide *N*,*N'*-dimethyl-*N*,*N'*-ethylenebis(acrylamide) copolymer, 76832-63-8; *N*,*N*-di-*n*-propylacrylamide *N*,*N'*-dimethyl-*N*,*N'*-ethylenebis(acrylamide) copolymer, 76832-64-9; *N*,*N*-di-*n*-butylacrylamide *N*,*N'*-dimethyl-*N*,*N'*-ethylenebis(acrylamide) copolymer, 76832-65-0; *N*,*N*-di-*n*-octylacrylamide *N*,*N'*-dimethyl-*N*,*N'*-ethylenebis(acrylamide) copolymer, 76832-66-1.

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Selective Electrochemical Reductive Acetylation of Aromatic Nitrosulfones[1]

LeRoy H. Klemm*

Department of Chemistry, University of Oregon, Eugene, Oregon 97403

Quentin N. Porter*

Department of Organic Chemistry, University of Melbourne, Parkville, Victoria 3052, Australia

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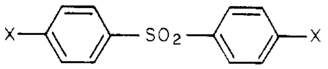
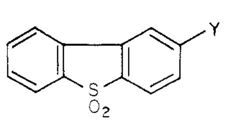
Loev et al. reported good prophylactic activity of 4,4'-bis(*N*,*O*-diacetylhydroxylamino)diphenyl sulfone (**1c**) vs. the malarial parasite *Plasmodium berghei*.[2] However, their synthesis of **1c** by successive steps of chemical reduction of nitro sulfone **1a** to the unstable hydroxylamino sulfone **1b** and subsequent acetylation thereof (31% overall yield) was fraught with experimental difficulties of reproducibility, side reactions, and purification. Also, an attempt to convert **1a** to **1b** by catalytic hydrogenation was abandoned because of the formation of complex mixtures.[2] We now report the successful, convenient one-step electrochemical reductive acetylation of **1a** to **1c** in 74–80% yield and the extension of this methodology to produce **2b** directly from **2a** (83%).



1a, X = NO_2
b, X = NHOH
c, X = $\underset{\mathrm{Ac}}{\underset{|}{\mathrm{N}}}\mathrm{OAc}$
d, X = H



2a, Y = NO_2
b, Y = $\underset{\mathrm{Ac}}{\underset{|}{\mathrm{N}}}\mathrm{OAc}$
c, Y = H

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[1] (a) Paper 5 in the series on Reductive Acetylation of Nitro Compounds. For Paper 4 see: Klemm, L. H.; Barnish, I. T.; McCoy, D. R. *J. Heterocycl. Chem.* **1977**, *14*, 299. (b) Experiments conducted at the University of Melbourne.

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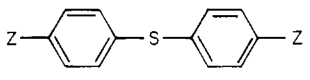
Table I. Cyclic Voltammetric Peak Potentials, E_p, for Some Aromatic Nitro Sulfides and Nitro Sulfones[a]

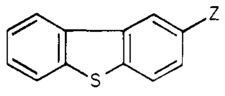
compd no.	reductive E_p, V[b] without Ac_2O	reductive E_p, V[b] with Ac_2O[d,e]	oxidative E_p, V[b,c]
3b	−1.04[f]	−1.03	+1.72
1a	−0.99[d]	−0.91	none
4a[g]	none[f]	none	+1.30, 1.60, 2.08
4b	−1.06, −1.30[d]	−1.01	+1.60
2a	−1.07, −2.01[f]	−0.91	none

[a] E_p was measured with two Pt electrodes, 0.1 M $LiClO_4$ in MeCN as solvent–electrolyte, and a scan rate of 100 mV/s. [b] Referred to a Ag/0.1 M Ag^+ electrode in MeCN. [c] For the range of 0 to +2.2 V. [d] For the range of 0 to −1.5 V. [e] Values vary by ±0.02 V as the concentration of Ac_2O in the catholyte is changed from ca. 1% to 15%. [f] For the range of 0 to −2.5 V. [g] Reference compound.

One-step electrochemical reductive acetylation (47–87% yield) of nitro- and nitrosoarenes and -alkanes in anhydrous acetonitrile–acetic anhydride–sodium perchlorate (as solvent–electrolyte) at a constant mercury cathode potential of −0.9 to −1.3 V (vs. the Ag/Ag *p*-toluenesulfonate or Ag/AgI reference electrode) to yield *N,O*-diacetylhydroxylaminoarenes and -alkanes was reported by Klemm et al.[3] From polarographic data[4] for diphenyl sulfone (**1d**), dibenzothiophene 5,5-dioxide (**2c**), and various nitroarenes we anticipated that the nitro group in a nitro sulfone should be preferentially reducible, unless unforeseen factors such as group interaction or competitive molecular orientation of the substrate at the cathode would markedly alter this order. To check on possible functional group interactions and/or competitions we measured both reductive and oxidative cyclic voltammetric peak potentials for **1a**, **2a**, their synthetic precursory nitro sulfides (**3b** and **4b**), and dibenzothiophene (**4a**). These data are presented in Table I.



3



4

a, Z = H; b, Z = NO_2

All four nitro compounds investigated showed reduction peaks at −1.03 ± 0.04 V without added Ac_2O and at −0.98 ± 0.07 V with added Ac_2O. These closely similar values plus the fact that dibenzothiophene shows no reduction[5] in the range of 0 to −2.5 V imply that the nitro group is, indeed, the electrophore[6] in these molecules. All of the reduction processes were irreversible, as were the oxidative processes (determined on fresh samples). For dibenzothiophene it has been found[5] that the first oxidative peak corresponds to the loss of one electron from the sulfur atom. The orders in electrooxidizability (as measured by E_p) of **4a** > **4b** > **2a** and **3a**[7] > **3b** > **1a** are likewise consistent with preferential electron loss from the sulfur atom in our nitro sulfides and with the electronegative character of the nitro group(s) therein.

On the basis of the data of Table I macroscale syntheses of **1c** and **2b** were conducted in the manner used previously for nitroarenes.[3] No difficulty was encountered in the formation of bothersome byproducts. However, the nitro sulfones have limited solubility in the solvent–electrolyte so that vigorously stirred suspensions of these substrates (which dissolve as electrolysis proceeds) were used. The reaction was also followed by coulometry and by observing the accumulation of an insoluble precipitate of NaOAc. Equation 1 is the balanced (half-reaction) for the chemical

$$\mathbf{2a} + 4e^- + 4NaClO_4 + 3Ac_2O \rightarrow \mathbf{2b} + 4NaOAc\downarrow + 4ClO_4^- \quad (1)$$

transformation of **2a** at the cathode. The *N,O*-diacetylhydroxylamino sulfones **1c** and **2b** are characterized by strong infrared absorption bands at 1790 (OAc), 1690 (NAc), ca. 1300, and 1150 cm^{-1} (SO_2), by two 3-H singlets at ca. 2.4 (NAc) and 2.6 (OAc) ppm in the NMR spectrum, and by facile loss of two (or more) molecules of ketene from the parent ion in mass spectrometry. As evidenced by very low R_f values in thin-layer chromatography with chloroform–silica gel, the diacetylhydroxylamino group forms strong hydrogen bonds.[8]

The present electrochemical methodology should be useful in synthesizing a variety of *N,O*-diacetylhydroxylamino sulfones in quantities from 10 mg to 1 g. Unfortunately, a limited search for a suitable solvent–electrolyte combination in which complete solubility (desired especially for runs on a larger scale) of the starting nitro sulfones occurs was unsuccessful. However, addition of Me_2SO to the solvent mixture does improve solubility (see Experimental Section). One might note that low proton availability is needed in the catholyte in order to avoid competitive formation of acetylamino products from a six-electron reduction process.

Experimental Section

Infrared spectra were determined with a Perkin-Elmer 157G instrument on KBr pellets, ^1H NMR spectra, with a JEOL FX-100 instrument by Gill Hosken on Me_2SO-d_6 solutions, mass spectra, with a Vacuum Generators 70/70 double-focusing instrument at 70 eV (in general) by Athole Wedgwood, and elemental analyses, by Australian Microanalytical Service, Port Melbourne, Victoria.

Starting Materials. 4,4′-Dinitrodiphenyl sulfide[9] (**3b**): mp 162–164 °C; IR 1490 and 1330 cm^{-1} (NO_2), 840 (2 vicinal aromatic H); ^1H NMR δ 8.13 (dd, J_{AB} = 9 Hz, $\Delta\delta$ = 60.4 Hz); mass spectrum, *m/z* 276 (100%, M), 246 (25%, M − NO), 184 (51%, M − $2NO_2$), 139 (31%). 4,4′-Dinitrodiphenyl sulfone[10,11] (**1a**): mp 250–254 °C; IR 1530, 1340, 1300, and 1150 (NO_2 and SO_2), 1100, 850, 755, 725, 675 cm^{-1}; ^1H NMR δ 8.56 (dd, J_{AB} = 9 Hz, $\Delta\delta$ = 11.6 Hz); mass spectrum, *m/z* 308 (6%, M), 292 (6%, M − O), 170 (100%, $O_2NC_6H_4SO$), 122 (17%, $O_2NC_6H_4$), plus fragments <100. 2-Nitrodibenzothiophene[12] (**4b**) (obtained from reagent-grade **4a**): mp 194–195 °C (sintering at 188 °C); IR 1520, 1340, 1300, and 1150 (NO_2 and SO_2), 770, 740, 700 cm^{-1}; ^1H NMR δ 9.47 (t, J = 1.4 Hz, 1 H), 8.7–9.0 and 8.2–8.4 (2 m, 1 H each), 8.51 (d, J = 1.4 Hz, 2 H), 7.7–8.0 (m, 2 H); mass spectrum, *m/z* 229 (100%, M), 199 (21%, M − NO), 183 (82%, M − NO_2), 171 (17%, M − CNO_2), 139 (68%, M − CNO_2S). 2-Nitrodibenzothiophene 5,5-dioxide[13] (**2a**): mp 260–262 °C (sintering at 258 °C); IR 1520, 1340, 1300, and 1150 (NO_2 and SO_2), 770, 740, 700 cm^{-1}; ^1H NMR δ 7.8–8.8 (complex m, 6 H), 9.26 (d, J = 1.8 Hz, 1 H); mass spectrum, *m/z* 262 (21%), 261 (100%, M), 231 (22%, M − NO), 187 (43%, M

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Table II. TLC Data for Some Aromatic Sulfur Compounds on Silica Gel GF-254

compd no.	R_f with		
	$CHCl_3$	$CHCl_3$-EtOAc[a]	EtOAc
4a	0.73	0.83	0.85
4b	0.73	0.84	0.86
2a	0.49	0.78	0.83
2b	0.03	0.47	0.63
3b	0.63	0.85	0.87
1a	0.42	0.77	0.86
1c	0.02	0.24	0.51

[a] 1:1 by volume.

$- NO_2 - CO$), 151 (25%), 150 (58%, M $-$ HNO_4S), 139 (37%), 115 (86%), plus fragments <100.

Cyclic voltammetry was conducted in a three-compartmental H-cell bearing two Pt foil electrodes (1 cm^2 each), a ground-glass Luggin capillary insert (into the working-electrode chamber) for connection to a reference electrode, and a solvent–electrolyte of 0.1 M reagent-grade, anhydrous $LiClO_4$ in purified[14] CH_3CN in all compartments. Compartments were separated by glass frits (G-4). The reference electrode consisted of an Ag wire in 0.1 M reagent-grade Ag salt (usually *p*-toluenesulfonate, but nitrate was used in a few oxidative runs). The solvent–electrolyte was preelectrolyzed[5] so as to remove extraneous peaks in the potential range to be investigated. The substrate (5–13 mg) was added to the working electrode compartment (bearing 7–9 mL of solvent–electrolyte), air in the compartment was displaced by nitrogen, and the voltammogram was obtained by means of a Princeton Applied Research modular instrument (units 173, 175, 176, and 178) which generates a time-dependent triangular voltage input at the working electrode and transmits a voltage output to an X-Y recorder (a Houston Instrument Omnigraph 2000). Reductive cyclic voltammograms were also recorded after addition of varying amounts (1–15 vol %) of purified Ac_2O to the cathode chamber. Data obtained are presented in Table I.

Synthetic electrochemical reductive acetylation was conducted in a larger three-compartmental H-cell whith the following items placed in the cathode chamber: 14 mL of Hg (cathode), a 2.5-cm magnetic stirring bar, 100 mL of 0.72 M $NaClO_4$ in MeCN-Ac_2O (10:1 v/v), and a Ag/0.1 M AgOTs in MeCN reference electrode insert. The anode was Pt foil. The same solvent–electrolyte (prepared from anhydrous $NaClO_4$,[15] laboratory reagent CH_3CN, and Ac_2O—mixture dried over 4-Å molecular sieves for at least 3 days before use) was also placed in the other compartments. Preelectrolysis was continued at a constant cathode potential of -1.3 V until the background current fell to a low value (2–4 mA). The substrate was then added to the cathode chamber and electrolysis was conducted in a nitrogen atmosphere at -1.1 to -1.3 V with vigorous stirring at room temperature and an initial current of 50–90 mA. Coulometry was obtained by plotting the current as a function of time.

2-(*N,O*-Diacetylhydroxylamino)dibenzothiophene 5,5-Dioxide (2b). Electrolysis of 310 mg of **2a** occurred over a period of 128 min (coulomb uptake 479, 104% of theory). The catholyte was filtered by suction to collect precipitated NaOAc (washed with MeCN, dried in vacuo, yield 391 mg, 100%; identified by infrared spectrum). The filtrate was rotoevaporated at 40 °C to remove MeCN, diluted with 100 mL of CH_2Cl_2, allowed to stand for 30 min, and refiltered to remove salts. Rotoevaporation of the filtrate (40 °C) gave a yellow liquid which crystallized on standing. Washing the crystals with ethyl acetate and reworking the mother liquors (evaporation at 50 °C (1 torr)) gave a total yield of 326 mg (83%) of orange product, mp 212–219 °C, converted to white needles on recrystallization from absolute ethanol (charcoal): mp 218–219.5 °C dec; IR (vida supra); ^1H NMR δ 2.39 (s, NAc), 2.55 (s, OAc), 7.7–8.8 (m, aromatic H); mass spectrum, *m/z* 332 (26%, M + 1), 331 (0.4%, M), 290 (26%), 289 (100%, M $-$ $CH_2{=}C{=}O$), 272 (23%), 248 (22%), 247 (100%, M $-$ 2 $CH_2{=}C{=}O$), 231 (29%), 139 (25%), 43 (100%, Ac).

Anal. Calcd for $C_{16}H_{13}NO_5S$: C, 58.00; H, 3.95; N, 4.23; S, 9.7. Found: C, 57.94; H, 4.11;, N, 4.20; S, 9.5.

Compound **2b** was dried and stored in the dark, for it appeared to undergo photooxidation (to a cream or orange product) on the laboratory bench.

4,4′-Bis(*N,O*-diacetylhydroxylamino)diphenyl Sulfone (1c). By the foregoing procedure 299 mg of **1a** was electrolyzed for 290 min (103% coulomb uptake) to yield 534 mg (84%) of NaOAc and 323 mg (74%, mp 183.5–186.5 °C) of **1c**: orange prisms, mp 184.5–185.5 °C from absolute ethanol (charcoal) (lit.[2] mp 186–188 °C); IR (vide supra); ^1H NMR δ 2.36 (s, 6 H, NAc), 2.57 (s, 6 H, OAc), 8.07 (dd, J_{AB} = 9 Hz, $\Delta\delta$ = 24.4 Hz, 8 aromatic H); mass spectrum (15 eV, 200 °C probe), *m/z* 449 (0.5%, M + 1), 448 (not observed, M), 406 (15%, M $-$ $CH_2{=}C{=}O$), 364 (26%, M $-$ 2 $CH_2{=}C{=}O$), 348 (11%), 322 (8%, M $-$ 3 $CH_2{=}C{=}O$), 320 (16%, M $-$ 2 Ac $-$ $CH_2{=}C{=}O$), 306 (24%), 304 (21%), 60 (22%), 43 (100%, Ac).

For a larger run, electrolysis was repeated with a suspension of 1.03 g of **1a** in 100 mL of 0.72 M $NaClO_4$ in MeCN–Me_2SO–Ac_2O (5:5:1). After 22 h (without coulometry) the reaction was stopped (3 mA) and the catholyte was poured directly into 1.5 L of water. The beige precipitate of **1c** was collected and dried in the dark, yield 1.20 g (80%), mp 175–180 °C.

Chromatography. TLC data for **1c**, **2b**, and the compounds studied in cyclic voltammetry are shown in Table II. It is apparent that the diacetylhydroxylamino sulfones should be easily separable from precursory nitro sulfones on a silica gel column with chloroform as an eluting solvent.

Acknowledgment. L.H.K. is pleased to acknowledge a grant-in-aid from the University of Melbourne for pursuit of this research during his sabbatical leave, 1979–1980.

Registry No. 1a, 1156-50-9; **1c**, 36679-41-1; **2a**, 72469-59-1; **2b**, 76917-03-8; **3b**, 1223-31-0; **4a**, 132-65-0; **4b**, 6639-36-7.

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Photolysis of *cis*-1,2,6-Octatriene

Hiroko I. Karan

Natural Science and Mathematics, Medgar Evers College, City University of New York, Brooklyn, New York 11225

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The photochemistry of allenic compounds has drawn little attention; the first report of allene photolysis appear in the work of Collin and Lossing.[1] Ward and Karafiath[2] reported the first benzene-sensitized photolysis of allenes, 1,2,6-heptatriene and 1,2,6-cyclononatriene, and observed a single primary product for each reaction. Betouski and Deyrup[3] reported the photolysis of *trans*-1,2,6-cyclononatriene to study the photochemical Cope rearrangement. Although other allenes such as derivatives of 1,2,6-heptatriene and 2,3,7-octatriene have been reported as intermediates of oxy-Cope rearrangements,[4] their photochemistry has not been studied extensively. In the present work, *cis*-1,2,6-octatriene was prepared in order to study further the mechanism of allene photochemistry. The benzene-sensitized photolysis of *cis*-1,2,6-octatriene gave not only the trans isomer but also several other primary products which were identified as all having the same molecular weight (*m/e* 108).

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