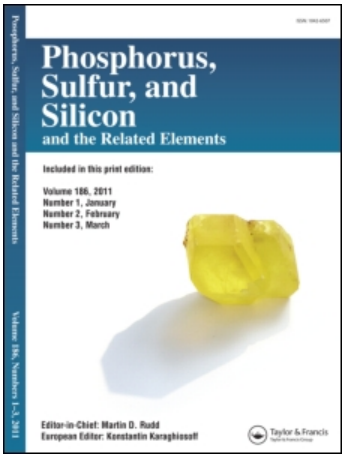


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SYNTHESES OF CYCLOHEPTATRIENES WITH SULFUR FUNCTIONAL GROUPS

Renji Okazaki[a]; Masaharu O-oka[a]; Norihiro Tokitoh[a]; Yoko Shishido[a]; Toshio Hasegawa[a]; Naoki Inamoto[a]
[a] Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo, Japan

To cite this Article Okazaki, Renji , O-oka, Masaharu , Tokitoh, Norihiro , Shishido, Yoko , Hasegawa, Toshio and Inamoto, Naoki(1983) 'SYNTHESES OF CYCLOHEPTATRIENES WITH SULFUR FUNCTIONAL GROUPS', Phosphorus, Sulfur, and Silicon and the Related Elements, 16: 1, 161 — 166
To link to this Article: DOI: 10.1080/03086648308077764
URL: http://dx.doi.org/10.1080/03086648308077764

Phosphorus and Sulfur, 1983, Vol. 16, pp. 161–166
0308-664X/83/1601-0161/$18.50/0

SYNTHESES OF CYCLOHEPTATRIENES WITH SULFUR FUNCTIONAL GROUPS

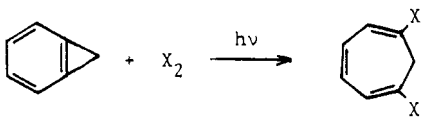
RENJI OKAZAKI, MASAHARU O-OKA, NORIHIRO TOKITOH, YOKO SHISHIDO, TOSHIO HASEGAWA and NAOKI INAMOTO

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo 113, Japan

(*Received December 11, 1982; in final form March 1, 1983*)

Disodium 1,6-disulfido-1,3,5-cycloheptatriene **3**, formed by reduction of **1** with sodium in liq. ammonia, reacts with hydrogen chloride and methyl iodide to give 1,6-dimercapto-, **4**, and 1,6-bis(methylthio)-1,3,5-cycloheptatrienes **5** respectively; however, it is oxidized by bromine to afford cyclic disulfide **6**. 1,6-Diiodo-1,3,5-cycloheptatriene **2** is converted to 1,6-bis(benzylthio)-1,3,5-cycloheptatriene **7** by reaction with sodium phenylmethanethiolate, whereas similar reactions with 1-(2-hydroxyethyl)-6-iodo-1,3,5-cycloheptatriene **9**, obtained from 2 via 1-iodo-6-vinyl-1,3,5-cycloheptatriene **8**, give 1-benzylthio-6-(2-hydroxyethyl)-1,3,5-cycloheptatriene **10**. 1-Benzylthio-6-benzylthioethyl-1,3,5-cycloheptatriene **11** is synthesized by the reaction from **9** via 1-(2-bromoethyl)-6-iodo-1,3,5-cycloheptatriene **10**. Attempts to synthesize thiols from **7**, **11**, and **12** are also described.

During the course of our study on bridged heterocyclic compounds, we required cycloheptatrienes with various heteroatom-containing functional groups. Although some cycloheptatriene derivatives of this type have been reported in connection with studies of the tropylium ion, a non-benzenoid aromatic compound,[1] examples of cycloheptatrienes having sulfur functional groups are very rare.[2] We recently communicated a new synthetic method for 1,6-dithiocyanato- **1** and 1,6-diiodo-1,3,5-cycloheptatrienes **2** using the photoreaction of cyclopropabenzene with thiocyanogen or iodine.[3]



X = SCN or I

1: X = SCN

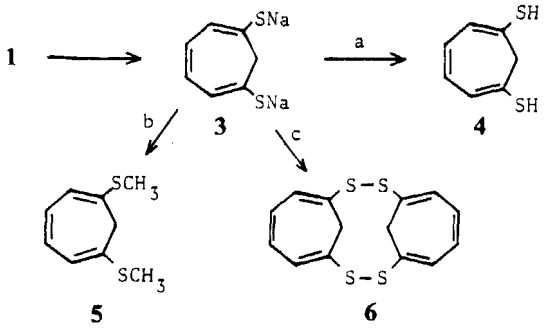
2: X = I

In this paper we delineate the syntheses of 1,6-disubstituted cycloheptatrienes having sulfur functional groups using **1** and **2** as starting materials.

RESULTS AND DISCUSSION

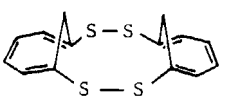
Syntheses with 1,6-Dithiocyanato-1,3,5-Cycloheptatriene **1**

1,6-Dithiocyanato-1,3,5-cycloheptatriene **1** was reduced with sodium in liquid ammonia to dithiolate **3**, which afforded, after acidification, dithiol **4** (Scheme 1). Neat **4** was unstable on exposure to air giving a polymeric product. That **4** has a dithiol structure instead of a tautomeric thione structure is supported by its spectroscopic

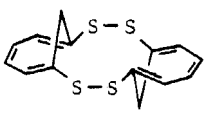


SCHEME 1 a: HCl, 95%; b: CH_3I, 88%; c: Br_2, 40%.

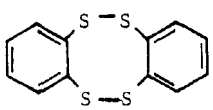
data. The ^1H NMR spectrum shows two methylene (δ 2.69) and four olefin protons (centered at δ 6.25) and two SH protons at δ 3.36 which disappeared upon addition of deuterium oxide. The IR spectrum indicates the presence of an SH group and the electronic spectrum suggests the absence of $n \rightarrow \pi^*$ absorption owing to a thione group. The quenching of **3** with methyl iodide gave **5**, whereas the oxidation of **3** with bromine led to the formation of disulfide **6**. The methylene protons of **6** appeared as an AB quartet, which suggests the nonequivalence of the two protons because of slow flipping in the NMR time scale.



6a



6b



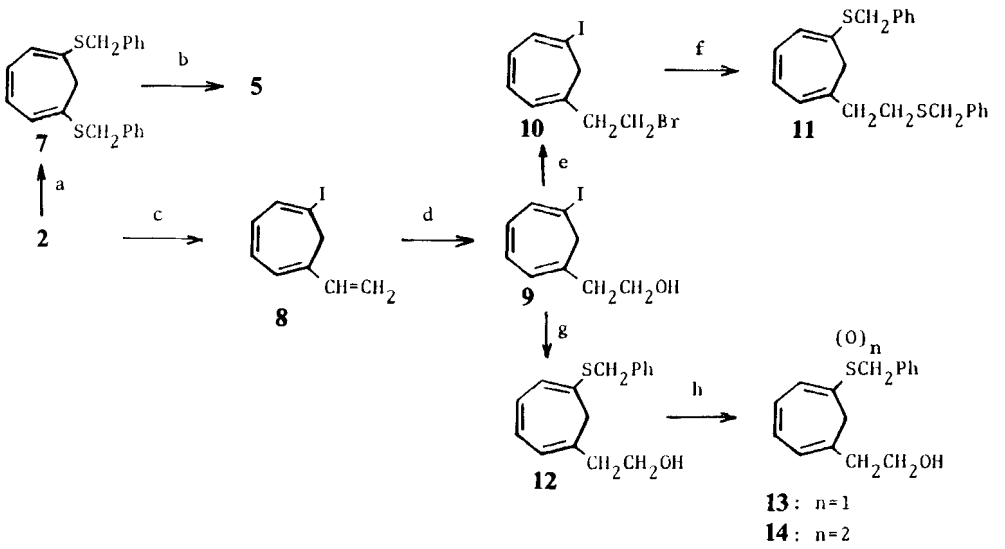
17

However, we cannot determine at present which structure **6a** or **6b** is correct. The formation of disulfide **6** in a moderate yield is interesting in view of the fact that the oxidation of *o*-benzenedithiol with iodine is a very complex reaction and the yield of disulfide **17** is very low (7–17%) even under high-dilution conditions.[4]

Synthesis with 1,6-Diiodo-1,3,5-Cycloheptatriene **2**

The iodine atom of diiodide **2** can be easily converted into sulfur-containing substituents (Scheme 2).

Sodium phenylmethanethiolate reacted with **2** in ethanol in the presence of tetrakis(triphenylphosphine)palladium(0)[5] or in DMF[6] to give **7** in excellent yield. Monoiodide **9**, obtained from **2** via **8**, was also converted to benzyl sulfide **12** by a similar reaction. Cycloheptatrienes having sulfinyl and sulfonyl substituents (i.e., **13** and **14**) were obtained by oxidation of **12** with *m*-chloroperbenzoic acid. The cycloheptatriene with two sulfide functional groups **11** was synthesized from dihalide **10** obtained from **9**. Since a bond between sulfur and a benzyl carbon is known to be cleaved by alkali-metal reduction,[7] attempts to form thiols from benzyl sulfides **7**, **11**, and **12** were carried out. Reduction of **7** with lithium in liquid ammonia led to the formation of dilithium 1,6-disulfido-1,3,5-cycloheptatriene which was quenched



SCHEME 2 a: (i) $PhCH_2SNa$, DMF, 95%, (ii) $PhCH_2SNa$, EtOH, cat $Pd(Ph_3P)_4$; b: (1) Li, liq. NH_3, (2) CH_3I, 90%; c: CH_2=CHMgBr, cat Li_2CuCl_4, 88%; d: 9-BBN, alkaline H_2O_2, 78%; e: Ph_3P–CBr_4, 35%; f: $PhCH_2SNa$, DMF, 96%; g: (i) $PhCH_2SNa$, DMF, 93%, (ii) $PhCH_2SNa$, cat $Pd(Ph_3P)_4$, 80%; h: *m*-chloroperbenzoic acid, **13** 69%, **14** 15%.

with methyl iodide to give the methyl sulfide **5** in good yield. Similar reactions of **11** and **12**, however, resulted in the reduction of the cycloheptatriene moiety and the expected thiols could not be obtained. The reason for this difference is not clear to us at present.

EXPERIMENTAL

Melting points are uncorrected. IR and UV spectra were recorded with Hitachi 260-30 and Hitachi 340 spectrophotometers, respectively. NMR spectra were measured with Hitachi R20B, Varian EM390, and JOEL FX90Q spectrometers using tetramethylsilane as an internal standard. The mass spectra were recorded with Hitachi RMU-60 and JOEL JMS-D300 mass spectrometers. All reactions were carried out under argon unless otherwise noted.

1,6-Dimercapto-1,3,5-cycloheptatriene **4**. To 1,6-dithiocyanato-1,3,5-cycloheptatriene **1**[3] (206 mg, 1.0 mmol) in liq. NH_3 (25 ml) was added sodium (98 mg, 4.3 mmol) at −78°C under nitrogen atmosphere until a blue color persisted. After evaporation of the NH_3, 6 M HCl (30 ml) and ether (30 ml) were added under vigorous stirring. The ether layer was separated and the aqueous layer was extracted with 40 ml of ether. The combined ether solution was dried over anhydrous magnesium sulfate and evaporated to give **4** (149 mg, 95%, oil): NMR ($CDCl_3$) δ 2.69 (s, 2 H), 3.36 (s, 2 H), 6.05–6.45 (m, 4 H); IR (Neat) 2530 cm^{-1} (SH); MS: (*m/e*, rel. intensity) 156 (M^+, 45%), 123 (84), 45 (100); Found: *m/e* 156.0110, Calcd. for $C_7H_8S_2$: *m/e* 156.0068.

1,6-Bis(methylthio)-1,3,5-cycloheptatriene **5**. To **1** (210 mg, 1.02 mmol) in liq. NH_3 (25 ml) was added sodium (98 mg, 4.3 mmol) at −78°C until a blue color persisted. After evaporation of NH_3, the reduction mixture was dissolved in tetrahydrofuran (THF) (10 ml) containing hexamethylphosphoramide (HMPA) (0.5 ml). Methyl iodide (340 mg, 1.2 mmol) was added to the solution, which was stirred at room temperature for 1 h. After evaporation of the THF, to the residue was added 70 ml of ether and 30 ml of water. The extract was washed with 10 ml of water, dried over $MgSO_4$, and concentrated. Chromatography (TLC, silica gel, CCl_4) of the residual oil afforded **5** (194 mg, 88%): mp 36–37°C; NMR ($CDCl_3$) δ

2.32 (s, 6 H), 2.60 (s, 2 H), 5.75–6.45 (m, 4 H); IR (KBr) 3000, 1590, 1585, 1500, 1430, 1410, 1330 cm^{-1}; MS (*m/e*, rel intensity) 184 (M^+, 78%), 169 (17), 137 (100), 121 (28), 91 (23). Anal. Calcd. for $C_9H_{12}S_2$: C, 58.65; H, 6.56; S, 34.79. Found: C, 58.90; H, 6.74; S, 34.32.

2,3,10,11-Tetrathiatricyclo[10.4.1.1^{4,9}]octadeca-4,6,8,12,14,16-hexaene **6**. To an ethanol solution (40 ml) of disodium 1,6-disulfido-1,3,5-cycloheptatriene **3**, which was prepared from dithiol **4** (156 mg, 1 mmol) and sodium (50 mg, 2.1 mmol), was added an ethanol solution (10 ml) of bromine (160 mg, 1 mmol) at −20°C. Stirring was continued at the same temperature for 5 min and then the mixture was raised gradually to room temperature. After stirring for 30 min at ambient temperature, the solvent was evaporated at reduced pressure. To the residue was added 50 ml of dichloromethane and then the precipitates were filtered. The filtrate was washed with 60 ml of water, dried over $MgSO_4$, and concentrated. The product was subjected to chromatography (TLC, silica gel, CCl_4) to give **6** (62 mg, 40%): mp 214°C (dec); NMR (C_6D_6) δ 1.57 (d, J = 14 Hz, 2 H), 5.24 (d, J = 14 Hz, 2 H), 6.1–6.3 (m, 8 H); MS (*m/e*, rel intensity) 308 (M^+, 100%), 155 (92), 154 (80), 153 (92); IR (KBr) 1595, 1490, 1330, 1242, 1070, 840, 720 cm^{-1}. Anal. Calcd. for $C_{14}H_{12}S_4$: C, 54.51; H, 3.92; S, 41.57. Found: C, 54.47; H, 3.81; S, 41.41.

1,6-Bis(benzylthio)-1,3,5-cycloheptatriene **7**

(1) To a suspension of sodium hydride (432 mg, 50% oil dispersion, 9.0 mmol) in THF (10 ml) was added phenylmethanethiol (1.118 g, 9.0 mmol) with stirring at 0°C, during which time a white precipitate of sodium phenylmethanethiolate appeared. After stirring for 30 min at room temperature, THF was removed under reduced pressure. To the crystalline residue was added a solution of 1,6-diiodo-1,3,5-cycloheptatriene[3] **2** (1.03 g, 3 mmol) in dimethylformamide (DMF) (20 ml) with stirring. After stirring for 3 h at 80°C, the reaction mixture was extracted with dichloromethane, the extract was washed with water, dried over $MgSO_4$, and concentrated. Chromatography (silica gel, pentane) of the residual oil gave 958 mg (95%) of **7**.

(2) To an ethanol solution of sodium (135 mg, 5.87 mmol) and phenylmethanethiol (260 mg, 2.22 mmol) was added **2** (293 mg, 0.852 mmol) and, after ten minutes, $Pd(Ph_3P)_4$ (36.1 mg, 0.03 mmol). After the solution was refluxed for 4 h, the ethanol was evaporated under reduced pressure. The red oily residue was dissolved in dichloromethane and the solution was washed with water, dried with anhydrous $MgSO_4$, and evaporated to give an orange oil, which was purified by chromatography (silica gel, pentane–dichloromethane 3 : 1) to give **7** (a yellow oil, 174 mg, 61%). NMR ($CDCl_3$) δ 2.61 (s, 2 H), 3.97 (s, 4 H), 5.86–6.16 (m, 2 H), 6.29–6.59 (m, 2 H), 7.27 (s, 10 H), MS (*m/e*, rel intensity) 336 (M^+, 5%), 259 (3), 245 (5), 136 (18), 135 (6), 92 (9), 91 (100); Found: *m/e* 336.1003, Calcd. for $C_{21}H_{20}S_2$: *m/e* 336.1006.

1,6-Bis(methylthio)-1,3,5-cycloheptatriene **5** *from* **7**. A solution of **7** (196 mg, 0.583 mmol) in THF (15 ml) was added to 25 ml of liq. NH_3 with stirring at −78°C. To the mixture was added lithium (17 mg, 2.43 mmol) with stirring, and lithium disappeared slowly. The color of the solution changed from yellow to blue, and the blue color continued for 30 min. After evaporation of the ammonia, the residue was dissolved in THF (10 ml). Methyl iodide (355 mg, 2.50 mmol) was added to the solution at 0°C. After stirring for 1 h at room temperature, the solvent was removed under reduced pressure. To the residue was added 80 ml of ether and 30 ml of water. The ethereal layer was washed with water, dried over $MgSO_4$, and concentrated. Chromatography (TLC, silica gel, CCl_4) of the residual oil afforded **5** (97 mg, 90%).

1-Iodo-6-vinyl-1,3,5-cycloheptatriene **8**. To a THF solution (2.2 l) of 1,6-diiodo-1,3,5-cycloheptatriene **2** (91.6 g, 266 mmol) cooled to −78°C was added vinylmagnesium bromide (424 mmol) in THF (600 ml) with stirring under a nitrogen atmosphere. Stirring was continued for 15 min at −78°C and a THF solution (150 ml) of dilithium tetrachlorocuprate (Li_2CuCl_4)[8] (16 mmol) was added to the above mixture at −78°C. The temperature of the cooling bath was raised to −55°C and the stirring was continued for 12 h keeping the temperature about −55°C. During this time, the reaction was monitored by gas chromatography (OV-1 column, 120°C).

After the GLC of the reaction mixture showed the disappearance of **2**, the solution was allowed to warm to room temperature and excess Grignard reagent was quenched with water (*ca.* 100 ml). The solution was evaporated to remove most of THF, and the residual solution was extracted several times with 200 ml of dichloromethane. When the separation was difficult, acidification with dilute HCl led to efficient separation. The extract was washed with water, dried over $MgSO_4$, and concentrated.

The NMR spectrum of the residual reddish yellow oil showed exclusive formation of **8** (56.8 g, 88%). It was unstable to heat (above 80°C) and readily polymerized. Although this specimen was pure enough for further reactions, it could be purified by Kugelrohr distillation (50–75°C/0.05 mmHg); NMR (CCl_4) δ 3.10 (s, 2 H), 5.18 (d, 1 H, J = 10 Hz), 5.52 (d, 1 H, J = 17 Hz), 6.00–6.90 (m, 5 H). IR (Neat) 3075, 1670, 1610, 1585, 1500, 1425, 1415 cm^{-1}; MS (*m/e*, rel intensity) 244 (M^+, 28%), 117 (100), 115 (82), 91 (62), Found: *m/e* 243.9778, Calcd. for C_9H_9I: *m/e* 243.9751.

1-(2-Hydroxyethyl)-6-iodo-1,3,5-cycloheptatriene **9**. To a solution of 9-borabicyclo[3.3.1]nonane (30 g, 246 mmol) in THF (550 ml) was added a solution of **8** (44.5 g, 182.3 mmol) in THF (80 ml) with stirring at room temperature, and the mixture was refluxed for 14 h until the disappearance of **8** (TLC and GLC). To the above solution was added 110 ml of ethanol, 60 ml of 16% *aq.* NaOH, and 70 ml of 30% *aq.* H_2O_2 in this order with rapid stirring. The mixture was refluxed for 1 h, and the solvent was evaporated under reduced pressure. After the residual oil was shaken with 200 ml of dichloromethane and 100 ml of water, the organic layer was separated. The aqueous layer was extracted several times with 200 ml of dichloromethane, the combined extracts were dried over $MgSO_4$ and concentrated. Chromatography (silica gel, dichloromethane) of the residual oil afforded 37.1 g (141.7 mmol, 78%) of **9**: NMR ($CDCl_3$) δ 1.94 (br s, 1 H), 2.51 (t, 2 H, J = 7 Hz), 2.92 (s, 2 H), 3.79 (t, 2 H, J = 7 Hz), 5.92–6.80 (m, 4 H); MS (*m/e*, rel intensity) 262 (M^+, 32%), 244 (7), 217 (14), 135 (45), 117 (100), 104 (80), 91 (72), Found: *m/e* 261.9877, Calcd. for $C_9H_{11}OI$: *m/e* 261.9856.

1-Benzylthio-6-(2-benzylthioethyl)-1,3,5-cycloheptatriene **11**. To a stirred acetonitrile solution (10 ml) of tetrabromomethane (1.489 g, 4.48 mmol) and **9** (588 mg, 2.24 mmol), a solution of triphenylphosphine (1.175 g, 4.48 mmol) in acetonitrile (10 ml) was added dropwise at room temperature, and stirring was continued for 6 h. After evaporation of the acetonitrile under reduced pressure, the residual oil was subjected to chromatography (silica gel, ether) to give 1-(2-bromoethyl)-6-iodo-1,3,5-cycloheptatriene **10** (258 mg, 35%, oil): NMR ($CDCl_3$) δ 2.75 (t, 2 H, J = 6 Hz), 2.90 (s, 2 H), 3.45 (t, 2 H, J = 6 Hz), 5.82–6.85 (m, 4 H). To sodium methanethiolate prepared from sodium hydride (3.18 mmol) and phenylmethanethiol (395 mg, 3.18 mmol) was added a solution of **10** (258 mg, 0.794 mmol) in DMF (10 ml). After stirring for 3 h at 100°C, the reaction mixture was shaken with 50 ml of dichloromethane and 30 ml of water. The organic layer was washed with 30 ml of water and evaporated under reduced pressure. To remove remaining DMF the residual oil was extracted with hexane (30 ml), and the extract was washed twice with 30 ml of water, dried over $MgSO_4$, and concentrated. The residual oil was subjected to chromatography (TLC, CH_2Cl_2–pentane 1 : 1) to afford 277 mg (96%, oil) of **11**: NMR ($CDCl_3$) δ 2.40 (s, 2 H), 2.15–2.92 (m, 4 H), 3.71 (s, 2 H), 3.96 (s, 2 H), 5.84–6.10 (m, 2 H), 6.32–6.49 (m, 2 H), 7.29 (s, 10 H); MS (*m/e*, rel intensity) 364 (M^+, 3%), 273 (13), 191 (6), 149 (7), 92 (10), 91 (100); Found: *m/e* 364.1302, Calcd. for $C_{23}H_{24}S_2$: *m/e* 364.1319.

1-Benzylthio-6-(2-hydroxyethyl)-1,3,5-cycloheptatriene **12**

(1) To sodium phenylmethanethiolate prepared from sodium hydride (1.30 mmol) and phenylmethanethiol (0.15 ml, 1.28 mmol) was added a solution of **9** (166 mg, 0.634 mmol) in DMF (5 ml) with stirring at room temperature. After stirring for 4 h at 70°C, the solution was partitioned between 20 ml of dichloromethane and 20 ml of water. The aqueous layer was extracted several times with dichloromethane. The combined organic extracts were washed with water, dried over $MgSO_4$, and concentrated. Chromatography (TLC, silica gel, CH_2Cl_2–pentane 1 : 1) of the residual oil gave **12** (152 mg, 93%, oil). The reaction in *ca.* 10 mmol scale afforded similar results: NMR ($CDCl_3$) δ 1.85 (s, 1 H), 2.43 (t, 2 H, J = 6.0 Hz), 2.50 (s, 2 H), 3.77 (t, 2 H, J = 6.0 Hz), 3.99 (s, 2 H), 5.94–6.15 (m, 2 H), 6.33–6.51 (m, 2 H), 7.27 (s, 5 H); IR (Neat) 3400 cm^{-1}; MS (*m/e*, rel intensity) 258 (M^+, 15%), 236 (6), 167 (13), 149 (12), 135 (10), 105 (10), 91 (100); Found: *m/e* 258.1071, Calcd. for $C_{16}H_{18}OS$: *m/e* 258.1078.

(2) To a solution of sodium (274 mg, 10.8 mmol) in ethanol (25 ml) was added phenylmethanethiol (273 mg, 2.20 mmol) at room temperature and then a solution of **9** (550 mg, 2.10 mmol) in ethanol (5 ml) with stirring. To the mixture was added $Pd(Ph_3P)_4$ (98 mg, 0.084 mmol) in one portion and the solution was refluxed for 3 h. After evaporation of the solvent, the residue was dissolved in 100 ml of dichloromethane and the solution was washed with water, dried over $MgSO_4$, and concentrated. Chromatography as described above gave **12** (431 mg, 1.67 mmol, 80%). The reactions in *ca.* 50 mmol scale afforded similar results.

1-Benzylsulfinyl-6-(2-hydroxyethyl)-1,3,5-cycloheptatriene **13** *and 1-Benzylsulfonyl-6-(2-hydroxyethyl)-1,3,5-cycloheptatriene* **14**. To a dichloromethane solution (100 ml) of **12** (2.74 g, 10.6 mmol) was added at −78°C m-chloroperbenzoic acid (80% purity, 2.29 g, 10.6 mmol) in dichloromethane (100 ml) during 2 h. After stirring at the same temperature for 1 h, the solution was warmed to room temperature. The reaction mixture was shaken with 5% *aq.* sodium bicarbonate, washed with water, dried with anhydrous $MgSO_4$, and the solvent was removed under reduced pressure to give an orange oil. Purification by chromatography (silica gel, ethyl acetate-carbon tetrachloride 3 : 1) afforded **13** (oil, 2.02 g, 69%) and **14** (oil, 0.49 g, 15%). **13**: NMR ($CDCl_3$) δ 2.54 (t, J = 6.0 Hz, 2 H), 2.71 (s, 2 H), 3.14 (br s, 1 H), 3.80 (t, J = 6.0 Hz, 2 H), 4.00 (s, 2 H), 6.00–6.80 (m, 4 H), 7.00–7.47 (m, 5 H); IR (Neat) 3410, 1040 cm^{-1}; MS (*m/e*, rel intensity) 274 (M^+, 2%), 183 (9), 105 (8), 104 (7), 103 (6), 92 (14), 91 (100), 77 (13); Found: *m/e* 274.1007, Calcd. for $C_{16}H_{18}O_2S$: *m/e* 274.1027. **14**: NMR ($CDCl_3$) δ 2.21 (bs, 1 H), 2.52 (t, J = 6.0 Hz, 2 H), 2.55 (s, 2 H), 3.82 (t, J = 6.0 Hz, 2 H), 4.29 (s, 2 H), 6.03–6.95 (m, 4 H), 7.33 (s, 5 H); IR (Neat) 3450, 1300, 1120 cm^{-1}; MS (*m/e*, rel intensity) 290 (M^+, 2%), 199 (13), 169 (8), 156 (15), 139 (17), 118 (21), 117 (29), 105 (25), 104 (21), 92 (23), 91 (100); Found: *m/e* 290.0964, Calcd. for $C_{16}H_{18}O_3S$: *m/e* 290.0976.

REFERENCES AND NOTES

1. K. M. Harmon, "Carbonium Ions," Ed. by G. A. Olah and P. von R. Schleyer (Wiley-Interscience, New York, 1973), Chapter 29.
2. B. Föhlisch and E. Haug, *Chem. Ber.*, **104**, 2324 (1971); M. Cazazza, G. Morganti and F. Pietra, *J. Org. Chem.*, **45**, 2001 (1980) and references cited therein.
3. R. Okazaki, M. O-oka, N. Tokitoh, Y. Shishido and N. Inamoto, *Angew. Chem.*, **93**, 833 (1981); *Angew. Chem. Int. Ed. Engl.*, **20**, 799 (1981).
4. L. Field, W. D. Stephens and E. L. Lippert, Jr., *J. Org. Chem.*, **26**, 4782 (1961); cf. B. Nakhdjavan and G. Klar, *Justus Liebigs Ann. Chem.*, 1683 (1977).
5. Cf. T. Migita, T. Shimizu, Y. Asami, J. Shiobara, Y. Kato and M. Kosugi, *Bull. Chem. Soc. Jpn.*, **53**, 1385 (1980).
6. J. R. Campbell, *J. Org. Chem.*, **29**, 1830 (1964).
7. E. g., W. Schroth and J. Peschel, *Chimia*, **18**, 171 (1964); W. Schroth, F. Billing and G. Reinhold, *Angew. Chem.*, **15**, 685 (1967).
8. J. F. Normant, A. Commercon, G. Cahiea and J. Villieras, *C. R. Acad. Sci. Ser. C*, **278**, 967 (1974); M. Tamura and J. K. Kochi, *Synthesis*, 303 (1971).