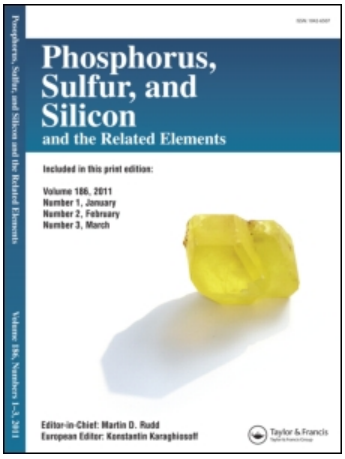

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B. Wladislaw[a]; L. Marzorati[a]; C. Di Vitta[a]; I. De Arruda Campos[a]
[a] Instituto de Química, Uniuersidade de São Paulo, São Paulo, Brazil

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SOME NEW SULFUR AND SELENIUM SUBSTITUTED BENZOQUINONE-CYCLOPENTADIENE DIELS-ALDER ADDUCTS. PART II. MONOSUBSTITUTED ADDUCTS

B. WLADISLAW,† L. MARZORATI, C. DI VITTA and I. P. de ARRUDA CAMPOS

Instituto de Química, Universidade de São Paulo, Caixa Postal 20.780, São Paulo, Brazil

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Some new sulfur and selenium monosubstituted benzoquinone-cyclopentadiene Diels–Alder adducts having the *endo* configuration have been synthesized and characterized.

Key words: Chlorobenzoquinone-cyclopentadiene adduct; sulfur; selenium; *endo* configuration; ^{13}C NMR spectra.

INTRODUCTION

We have been interested, for the purpose of photocyclization studies,[1,2] to obtain monosulfenylated and selenylated benzoquinones-cyclopentadiene adducts having an *endo* configuration. Only two representatives of this serię of compounds have been reported in the literature: 4-mercaptotolyl[3] and 1-phenyl, 5-mercaptotetrazol[4] substituted derivatives. The first compound was obtained by treating benzoquinone with a thiol, prior to Diels–Alder reaction with cyclopentadiene. The second one was prepared by the reaction of the epoxide of the unsubstituted benzoquinone-cyclopentadiene adduct with thiol.

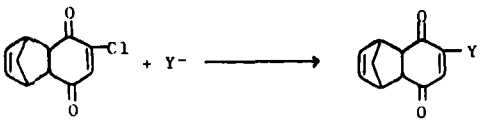
In the preliminary studies[5] we verified that both methods failed when aliphatic thiols were employed. Thus, the addition of ethanethiol to benzoquinone lead to formation of the tetraethylthio-substituted benzoquinone and the reaction of ethanethiol with the epoxide of the benzoquinone-cyclopentadiene adduct afforded the corresponding aromatized ethylthio-substituted adduct.

In view of these observations, the addition–elimination method, which has been found to be successful in the case of the disubstituted benzoquinone–cyclopentadiene adducts seemed to merit investigation.

RESULTS

Scheme 1 illustrates the reaction between the chlorobenzoquinone–cyclopentadiene adduct (**1**) and some sulfur and selenium nucleophiles to give the corresponding monosubstituted adducts (**2a–h**).

† To whom correspondence should be addressed.



1 2a-h

Y = SMe (a); SEt (b); $SCH_2\phi$ (c); $S\phi$ (d); SC_6H_4-OCH_3(p) (e);
SC_6H_4-NO_2(p) (f); $SO_2\phi$ (g); $Se\phi$ (h)

SCHEME 1

Table I shows the yields, physical constants and microanalytical results of the compounds (**2a–h**) and Table II the ^1H NMR and IR data of the same compounds.

The configuration of these compounds was determined by analysis of the ^{13}C NMR spectra, which showed that, similar to the corresponding disubstituted adducts,[1] the double-bond carbons (C-6, 7) chemical shifts are in the 135–136 ppm region and the methylene bridge carbon (C-9) in the ~49 ppm region, which support an *endo* configuration.

EXPERIMENTAL

All melting points are uncorrected. The IR spectra were run on a Perkin Elmer 283 or 180 spectrometer (Grating) in KBr. ^1H and ^{13}C NMR spectra were recorded, on a Varian T-60 or on a Bruker AC-80 spectrometer, respectively. The carbon and hydrogen analyses were carried out on a Perkin Elmer elemental analyser 240-B. Chlorobenzoquinone[6] and the corresponding adduct[7] with cyclopentadiene (**1**) were prepared according to literature procedures.

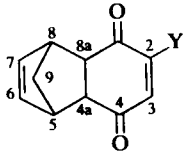
TABLE I

Yields, physical data and microanalyses of monosubstituted benzoquinone-cyclopentadiene adducts

Compounds	Y	Yield (%)	m.p. (°C)	Molecular formula	Calcd./Found (%) C	H	N
2a	SCH_3	78	153–4	$C_{12}H_{12}O_2S$ (220.29)	65.43 65.34	5.49 5.48	— —
2b	SC_2H_5	74	87–8	$C_{13}H_{14}O_2S$ (234.27)	66.64 66.74	6.02 6.22	— —
2c	$SCH_2C_6H_5$	72	138–40	$C_{18}H_{16}O_2S$ (264.33)	72.94 72.72	5.45 5.47	— —
2d	SC_6H_5	68	128–30	$C_{17}H_{14}O_2S$ (282.36)	72.31 72.47	5.00 5.05	— —
2e	$SC_6H_4OCH_3$(p)	70	109–10	$C_{18}H_{16}O_3S$ (312.39)	69.20 69.47	5.17 5.48	— —
2f	$SC_6H_4NO_2$(p)	43	134–6	$C_{17}H_{13}NO_4S$ (327.36)	62.37 62.10	4.01 4.28	4.28 4.15
2g	$SO_2C_6H_5$	66	118–20	$C_{17}H_{14}O_4S$ (314.36)	64.95 65.22	4.50 4.44	— —
2h	SeC_6H_5	47	120–22	$C_{17}H_{14}O_2Se$ (329.26)	62.01 62.14	4.29 4.16	— —

TABLE II

^{1}H NMR and IR data for monosubstituted benzoquinone-cyclopentadiene adducts



	Y	^{1}H NMR (δ in ppm, 10% (v/v) in $CDCl_3$)					
		4a, 8a	5, 8	6, 7	9	3	Y
2a[a]	SCH_3	3.24(m, 2H)	3.53(m, 2H)	6.00(m, 2H)	1.53(m, 2H)	6.16(s, 1H)	2.23(s, 3H)
2b[a]	SC_2H_5	3.22(m, 2H)	3.52(m, 2H)	6.01(m, 2H)	1.49(m, 2H)	6.17(s, 1H)	1.36(t, J = 6.8 Hz, 3H) 2.69(q, J = 6.8 Hz, 2H)
2c[a]	$SCH_2C_6H_5$	3.20(m, 2H)	3.44(m, 2H)	5.99(m, 2H)	1.45(m, 2H)	6.32(s, 1H)	3.85(bs, 2H) 7.27(bs, 5H)
2d[a]	SC_6H_5	3.18(m, 2H)	3.53(m, 2H)	6.00(m, 2H)	1.45(m, 2H)	5.71(s, 1H)	7.02(s, 5H)
2e[b]	$SC_6H_4OCH_3$(p)	3.21(m, 2H)	3.48(m, 2H)	6.07(m, 2H)	1.49(m, 2H)	5.74(s, 1H)	3.82(s, 3H) 6.93(d, J = 8.8 Hz, 2H) 7.30(d, J = 8.8 Hz, 2H)
2f[a]	$SC_6H_4NO_2$(p)	3.28(m, 2H)	3.56(m, 2H)	6.08(m, 2H)	1.56(m, 2H)	5.80(s, 1H)	7.60(d, J = 9.0 Hz, 2H) 8.24(d, J = 9.0 Hz, 2H)
2g[b]	$SO_2C_6H_5$	3.28(m, 2H)	3.49(m, 2H)	5.77(dd, J = 6.0; 2.1 Hz, 1H) 6.06(dd, J = 6.0; 2.0 Hz, 1H)	1.50(m, 2H)	7.30(s, 1H)	7.62(m, 3H) 7.98(dd, J = 6.8; 3.5 Hz, 2H)
2h[b]	SeC_6H_5	3.22(m, 2H)	3.48(m, 2H)	6.08(bs, 2H)	1.51(m, 2H)	6.08(bs, 1H)	7.40–7.60(m, 5H)

[a] D_{co} (cm^{-1}): 1670, 1640.
[b] D_{co} (cm^{-1}): 1670.

*Mono substituted benzoquinone-cyclopentadiene adducts (**2a–h**). General Procedure.*

To a stirred solution of chlorobenzoquinone-cyclopentadiene adduct (**1**) (4.8 mmol) in 5 ml of dry methanol was added, dropwise, a solution of sodium thiolate, in dry methanol (5 ml) prepared from sodium methoxide (4.7 mmol) and the corresponding thiol (5.1 mmol). When the addition was completed, the solid product was isolated by filtration, washed at least 3 times with n-pentane (5 ml) and recrystalized from methanol. p-Nitrophenylthiolate and phenylselenolate were prepared as in the previous paper.[1] For mps, yields, ^{1}H NMR and IR data of compounds **2a–h** see Tables I, and II. ^{13}C-NMR (δ ppm; 40% v/v, $CDCl_3$): **2a** 48.83(C-9); 134.68, 135.67 (C-7). **2c** 49.08(C-9); 134.55, 135.52(C-6,7). **2d** 48.76(C-9); 134.38, 135.12(C-6,7). **2e** 48.87(C-9); 134.70, 135.67(C-6,7). **2f** 48.98(C-9); 134.80, 135.86(C-6,7). **2g** 49.01(C-9), 134.21, 135.47(C-6,7). **2h** 48.92(C-9); 134.83, 135.71(C-6,7).

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