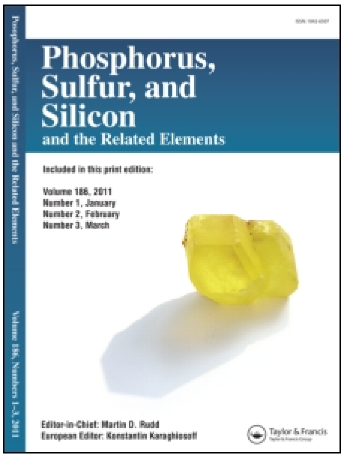

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SOME NEW SULFUR AND SELENIUM SUBSTITUTED BENZOQUINONE-CYCLOPENTADIENE DIELS-ALDER ADDUCTS[1]

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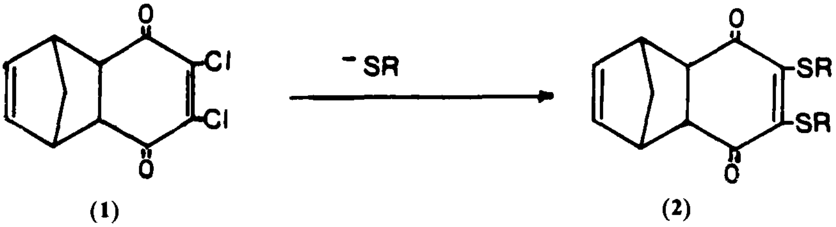
This paper reports the synthesis of new sulfur and selenium-substituted benzoquinone-cyclopentadiene Diels-Alder adducts. Although being of endo configuration, as shown by chemical and spectroscopic proof, they fail to undergo cage-compound formation.

It was reported in a preliminary communication[2] that the reaction of the 2,3-dichlorobenzoquinone-cyclopentadiene Diels-Alder adduct (**1**) with some aliphatic mercaptides afforded the corresponding dialkylthio-substituted adducts (**2a–c**) (Scheme 1).

In order to verify the generality of this reaction it was extended to a wider number of mercaptides, as well as selenium, oxygen and nitrogen nucleophiles.

RESULTS AND DISCUSSION

Tables I and II show the mps, yields, ^{1}H NMR and IR spectra of 16 dialkylthio- and diarylthio-substituted quinones-cyclopentadiene adducts (**2d–l**) and (**2m–s**), respectively. It may be noticed that the reaction occurred also with the highly branched *t*-butyl and triphenylmethyl mercaptides, although in the latter case a lower yield of



R=CH_3(**a**); C_2H_5(**b**); *n*-C_4H_9(**c**)

SCHEME 1

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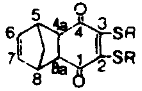
*Author to whom all correspondence should be addressed.

TABLE I

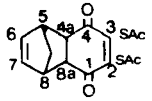
Yields and physical data of dialkylthio-substituted benzoquinone-cyclopentadiene adducts[a]

	R	Yield (%)	Mp (°C)	^{1}H NMR (δ in CDCl$_3$) 4a,8a	5,8	6,7	9	R	ν_{CO}(CHCl$_3$) (cm^{-1})
2d	n-C_3H_7	43	64–5	3.30(m,2 H)	3.40(m,2 H)	6.00(m,2 H)	1.50(m,2 H)	1.10(t,6 H); 1.50(m,4 H); 3.00(t,4 H)	1685
2e	i-C_3H_7	48	104–7	3.20(m,2 H)	3.40(m,2 H)	6.00(m,2 H)	1.00–1.60(m,2 H)	1.00–1.60(m,12 H); 3.95(m,2 H)	1670
2f	t-C_4H_9	45	154–6	3.30(m,2 H)	3.40(m,2 H)	6.00(m,2 H)	1.40(m,2 H)	1.40(s,8 H)	1680
2g	CH_2CO_2Et	40	86–8	3.40(m,2 H)	4.10(m,2 H)	6.10(m,2 H)	1.50(m,2 H)	1.60(t,6 H); 3.40(s,4 H); 4.10(m,4 H)	1680 1730
2h	$CH_2C_6H_5$	57	97–100	2.70(m,2 H)	3.20(m,2 H)	5.60(m,2 H)	1.05–1.50(m,2 H)	4.20(m,4 H); 7.20(s,10 H)	1670
2i	$CH_2C_6H_4OMe(p)$	37	99–101	2.70(m,2 H)	3.20(m,2 H)	5.70(m,2 H)	1.33(m,2 H)	3.73(s,6 H); 4.07(m,4 H); 6.53–7.20(m,8 H)	1675
2j	$CH_2CH{=}CH_2$	25	48.5–49.5	3.09–4.05(m,2 H)	3.09–4.05(m,2 H)	5.97(m,2 H)	1.36(M,2 H)	3.09–4.05(m,4 H); 4.90(m,2 H); 5.10(m,2 H); 5.43–5.86(m,2 H)	1675
2k	$CH(C_6H_5)_2$	53	147–151	2.02(m,2 H)	2.99(m,2 H)	5.58(m,2 H)	0.83–1.29(m,2 H)	6.17(s,2 H) 7.17(m,20 H)	1675
2l	$C(C_6H_5)_3$	15	178–180.5	1.53(m,2 H)	2.70(m,2 H)	5.73(m,2 H)	0.97(m,2 H)	7.20(m,30 H)	1680

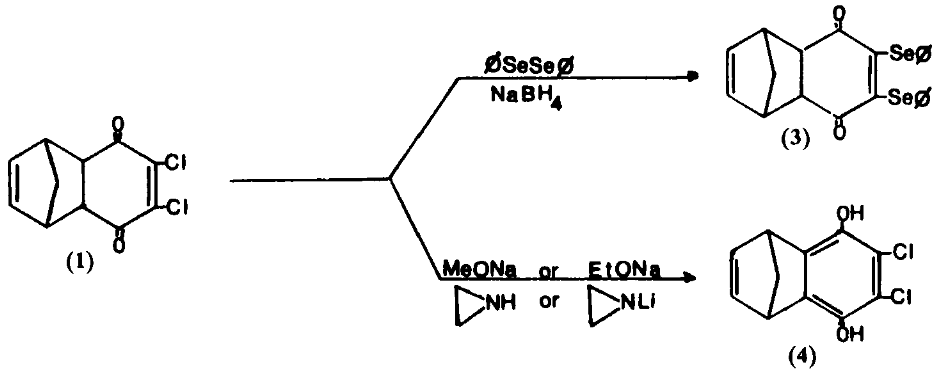
[a] The microanalyses were in satisfactory agreement with the calculated values: C, ±0.2; H, ±0.1.

TABLE II

Yields and physical data of arylthio substituted benzoquinone-cyclopentadiene adducts[a]

	Ar	Yield (%)	Mp (°C)	^{1}H NMR (δ in $CDCl_3$)					$\nu_{CO}(CHCl_3)$ (cm^{-1})
				4a,8a	**5,8**	**6,7**	**9**	**Ar**	
2m	C_6H_5	58	150–3	3.30–3.50(m,2 H)	3.30–3.50(m,2 H)	6.10(m,2 H)	1.40(m,2 H)	7.38(s,10 H)	1682
2n	$C_6H_4CH_3(p)$	95	163–7	3.20(m,2 H)	3.30(m,2 H)	6.00(m,2 H)	1.40(m,2 H)	2.30(s,6 H); 7.10(m,8 H)	1675
2o	$C_6H_4Cl(p)$	63	174–7	3.30(m,2 H)	3.40(m,2 H)	6.00(m,2 H)	1.40(m,2 H)	7.20(m,8 H)	1680
2p	$C_6H_4OCH_3(p)$	99	120–4	3.20(m,2 H)	3.30(m,2 H)	6.00(m,2 H)	1.40(m,2 H)	3.80(s,6 H); 7.00(m,8 H)	1670
2q	$C_6H_4NH_2(p)$	40	200–3	3.10(m,2 H)	3.20(m,2 H)	5.90(m,2 H)	1.30(m,2 H)	5.30(bs,4 H); 6.80(m,8 H)	1670
2r	$C_6H_4NO_2(p)$	59	190*d*	3.40(m,2 H)	3.50(m,2 H)	6.10(m,2 H)	1.50(m,2 H)	7.20(s,8 H)	1680
2s	$C_{10}H_7(\beta)$	68	170–3	3.23–3.40(m,2 H)	3.23–3.40(m,2 H)	6.07(m,2 H)	1.57–1.30(m,2 H)	7.23–7.87(m,14 H)	1675

[a] The microanalyses were in satisfactory agreement with the calculated values: C, ±0.2; H, ±0.1.



SCHEME 2

TABLE III

Physical data and ^1H NMR spectra of the products obtained by reaction of dichloro-adduct (**1**) with selenium, oxygen and nitrogen nucleophiles

No[a]	Mp (°C)	^1H NMR (δ in $CDCl_3$)				
		4a,8a	**5,8**	**6,7**	**9**	
3[b]	152–5	3.20(m,2 H)	3.30(m,2 H)	6.07(m,2 H)	1.40(m,2 H)	7.40(m,10 H)
4	—		4.15(m,2 H)	6.74(m,2 H)	2.09(m,2 H)	5.25(bs,2 H)

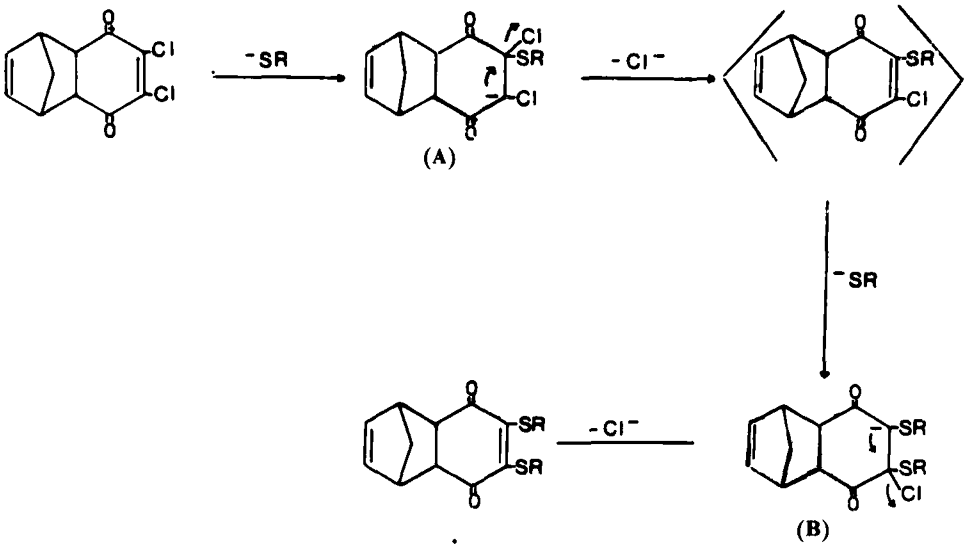
[a] See Scheme 2.
[b] Anal. Calcd. for $C_{23}H_{16}Se_2O_2$: C, 57.03; H, 3.75. Found: C, 57.42; H, 3.65.

the adduct (**21**) was obtained. It is noteworthy that higher yields were obtained in the reactions with the aromatic mercaptides than with aliphatic ones.

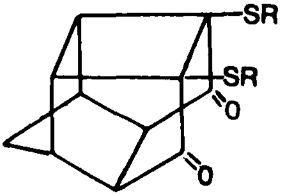
The reaction of the dichloro-adduct (**1**) with selenium, oxygen and nitrogen nucleophiles is shown in the Scheme 2 and the mps and ^1H NMR spectra are included in the Table III. It may be seen that it was possible to obtain the diphenylseleno-substituted adduct (**3**). However, the attempts to prepare the dialkoxy and diaziridinyl-substituted adducts failed. Thus, the reactions of (**1**) with sodium methoxide or ethoxide, aziridine or its lithium salt yielded the dichloro-substituted aromatized product (**4**).

The formation of the aromatized adduct (**4**) may be explained by the high basicity but weak nucleophilicity of the oxygen and nitrogen, in contrast to the sulfur and selenium. Consequently, a removal of the proton in α to the carbonyl group in the dichloro-adduct takes place.

It is noteworthy that in the reaction of (**1**) with the sulfur nucleophiles, it was impossible to isolate the mono-alkylthio-substituted adducts, even when equimolar proportions of the reagents were employed. Two additions with formation of anionic intermediates (*A*) and (*B*), (Scheme 3), followed by two eliminations, are suggested as possibilities, instead of a single intermediate proposed for a monochloro-quinone.[3] It seems reasonable to admit that (*B*), in which the negatively charged carbon is inserted between the carbonyl group and sulfur, should be more stabilized than (*A*). Therefore, the mono-alkylthio-substituted adduct, as soon as it is formed, would undergo transformation into the dialkylthio-adduct.



SCHEME 3

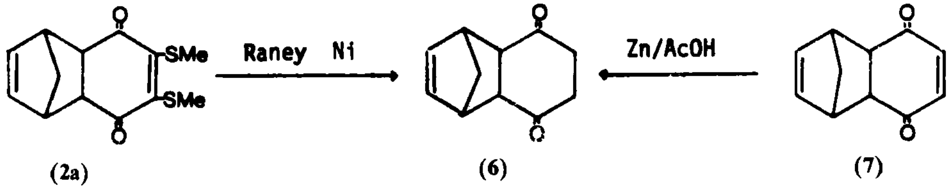


(5)

The dialkylthio-substituted adducts appeared to us to be interesting intermediates for the dialkylthio-substituted cage compounds (**5**), which are not described in the literature. However, when the adducts (**2a**) and (**2h**) were irradiated under the experimental conditions reported for the unsubstituted benzoquinone-cyclopentadiene adduct,[4] the starting materials were recovered. The reason for the failure of this reaction could be either configurational or electronic. Therefore, in the first place, it became necessary to eliminate the possibility of the dialkylthio-substituted adducts being exo.

Evidence for the endo configuration was obtained when the dialkylthio-substituted adduct (**2a**) was submitted to reaction with Raney Nickel[5] and the hydrogenated sulfur-free adduct (**6**), which was obtained as the only product, was shown to be identical to that formed by reaction of the unsubstituted adduct (**7**) of endo configuration with Zn/CH_3CO_2H (Scheme 4).

Furthermore, the endo configuration of the dialkylthio-substituted adducts was confirmed by analysis of the ^{13}C NMR spectra, in comparison with the norbornene series.

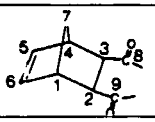


SCHEME 4

It is noteworthy that the literature data[6,7] refer mostly to the mono-substituted exo or endo norbornenes, the endo and exo cyclopentadiene–maleic anhydride adducts being the only examples of the disubstituted norbornenes. It was established that the endo adduct (**8b**) (Table IV) in the ^{13}C NMR spectrum shows an upfield shift of the double-bond carbon signals (C-5,6), in contrast to the exo adduct (**8a**), and that the exo adduct (**8a**) exhibits an upfield shift of the methylene bridge carbon (C-7), in both cases, owing to γ gauche interaction of the carbonyl substituent with one of the protons at C-6 or C-7, respectively. Comparable results were obtained by us with

TABLE IV

^{13}C NMR spectra[a] for some benzoquinones-cyclopentadiene Diels-Alder adducts and some model compounds



No[b]	C-1,4	C-2,3	C-5,6	C-7	C-8,9	C=C (enedione)	CH_3
9a[c]			136.7 134.3	46.4	173.6 172.3	— —	51.0[e] 50.7[e]
9b	47.8	46.0	134.6	48.4	172.5	—	51.1[e]
8a[d]	48.8	46.9	138.8	44.1	171.6	—	—
8b[d]	47.2	46.1	135.6	52.8	171.5	—	—
7	—	48.1	135.0	48.5	199.1	141.8	—
1	49.3	48.4	135.3	48.8	188.5	146.9	—
2a	50.2	46.5	135.8	47.8	191.0	149.9	16.5[f]
2b	50.1	46.4	136.0	47.9	191.5		15.1[g] (27.4)[h]
2e	50.1	46.1	136.2	47.7	192.0	151.0	22.6[i] 24.7[i] (37.1)[j]
2f	50.6	45.1	136.6	47.3	193.6	155.4	32.2[k]
6	51.3	46.9	136.1	48.2	208.8	—	37.4[e]

[a] In ppm from internal TMS for $CDCl_3$ solutions.

[b] See Figure 1, Table I and Scheme 3.

[c] C-1,4 and C-2,3 were not assigned from the signals of 47.0, 46.2 and 44.8 ppm.

[d] Reference 6.

[e] In CO_2Me.

[f] In SCH_3.

[g] In SC_2H_5.

[h] In SC_2H_5.

[i] In Si-C_3H_7.

[j] CH in Si-C_3H_7.

[k] In St-C_4H_9.

[l] CH_2—CH_2.

(8)

exo(a)
endo(b)

(9)

endo-exo(a)
endo-endo(b)

FIGURE 1 Cyclopentadiene-maleic anhydride adducts (**8a**,**b**) cyclopentadiene-fumaric methyl ester adduct (**9a**) and cyclopentadiene-maleic methyl ester adduct (**9b**).

two other disubstituted norbornenes of known configuration, cyclopentadiene–fumaric (**9a**) and–maleic (**9b**) methyl ester adducts, endo–exo and endo–endo, respectively. (Table IV and Figure 1).

Inspection of the molecular models of the benzoquinone–cyclopentadiene adducts indicated that in the case of the exo configuration the carbonyl groups are spatially distant from the double-bond carbons in the cyclopentadiene moiety, but close to the methylene bridge; in the endo configuration, on the other hand, they are quite proximate to the double bond. This seemed to suggest that in these compounds γ effects similar to those in the norbonene derivatives would occur.

The ^{13}CNMR spectra for some dialkylthio-substituted adducts (**2a**,**b**,**e**,**f**) are shown in the Table IV. The data for the unsubstituted (**7**), dichloro-(**1**), and sulfur-free hydrogenated (**6**) adducts are also included. It may be observed that the double-bond carbon (C-5,6) chemical shifts for the dialkylthio-substituted adducts (**2a**,**b**,**e**,**f**) are close to those for the endo dicarboxylic ester (**9b**) and anhydride (**8b**) derivatives, but distant from that for the exo anhydride adduct (**8a**). Furthermore, the dialkylthio-substituted adducts (**2a**,**b**,**e**,**f**) do not exhibit the upfield shift of the methylene bridge (C-7) characteristic for the exo configuration. Similar data were obtained for the unsubstituted (**7**), dichloro (**1**) and endo sulfur-free hydrogenated adducts (**6**).

Once it has been proven that the dialkylthio-substituted adducts are endo, the hypothesis of configuration being responsible for the lack of photocyclization is eliminated.

It is probable that the conjugation between sulfur and double-bond leading to increase of electronic density of the latter could be responsible for the lack of reactivity on irradiation. However, the steric hindrance to cyclization cannot be excluded.

EXPERIMENTAL

Chemicals used were of reagent grade. All melting points were uncorrected. Infrared spectra were measured on a Perkin-Elmer 283A spectrometer. All ^{13}C NMR and ^{1}H NMR spectra were recorded on a Varian FT-80A and a Varian T-60 spectrometers, respectively. The ^{13}C NMR spectra were measured in 40% (v/v) solutions in $CDCl_3$. Compounds (**1**),[8] (**9a**),[9] (**9b**),[10] (**7**)[11] and (**6**)[12] were prepared according to literature procedures.

Preparation of dialkylthio- and diarylthio-substituted quinones-cyclopentadiene adducts. Compounds (**2d–2i**), and (**2m–2q**) were prepared as described previously.[2] For compounds (**2j–2l**) and (**2s**) the solid sodium thiolates were employed which were prepared from equimolar amounts of sodium hydride and thiols. In the case of (**2r**) solid sodium *p*-nitrobenzenethiolate was prepared from the corresponding thiol and sodium hydroxide. For the mps, yields, ^{1}H NMR and IR spectra see Tables I and II.

Preparation of diphenylseleno-substituted adduct (**3**). To a stirred solution of diphenyl diselenide (1.0 g, 3.2 mmol) in 10 ml of dry ethanol, was added 0.3 g of sodium borohydride, in small portions, under nitrogen. The clear solution was added to a suspension of (**1**) (0.4 g, 1.6 mmol) in 4 ml of dry ethanol. The reaction mixture was poured into 20 ml of water. The yellow solid was recrystallized from ethanol to give 0.3 g of (**3**). For mp and ^{1}H NMR spectroscopic data see Table III.

Reaction of (**1**) *with aziridine.* To a stirred solution of 0.24 g (1 mmol) of (**1**) in dry ether was added 0.11 ml (1.9 mmol) of aziridine in 1 ml of dry ether. The solvent was removed and the oily residue was identified by ^{1}H NMR as (**4**). (See Table III).

Reaction of (**1**) *with lithium salt of aziridine.* To a stirred solution of 0.1 ml (1.8 mmol) of aziridine in 2 ml of dry ether was added 1.3 ml of *n*-butyllithium in hexane (1.5 M). This suspension was added to a stirred solution of (**1**) (0.24 g, 1 mmol) in 2 ml of dry ether. After removal of solvent an oily–solid was obtained which was identified by ^{1}H NMR as (**4**). (See Table III).

Reaction of (**1**) *with sodium methoxide in methanol.* A solution of sodium methoxide in methanol prepared from 0.16 g (7 mmol) of sodium and 7 ml of dry methanol was added dropwise to a suspension of (**1**) (0.85 g, 3.5 mmol) in 10 ml of methanol. The reaction mixture was poured into 50 ml of water acidified with HCl, and extracted with ether. The ether extract was dried ($MgSO_4$), the solvent removed and the white solid left was identified as (**4**). (See Table III).

Reaction of (**1**) *with sodium ethoxide in benzene.* To a suspension of (**1**) (0.4 g, 1.6 mmol) in 5 ml of dry benzene, 0.21 g (3.1 mmol) of solid sodium ethoxide was added. The reaction mixture was poured into water, the benzene layer separated and after solvent removal the solid residue was identified as (**4**). (See Table III).

ACKNOWLEDGEMENTS

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