Enhancement of Electron Affinity of Benzocycloheptene-1,4,7-trione by Substitution

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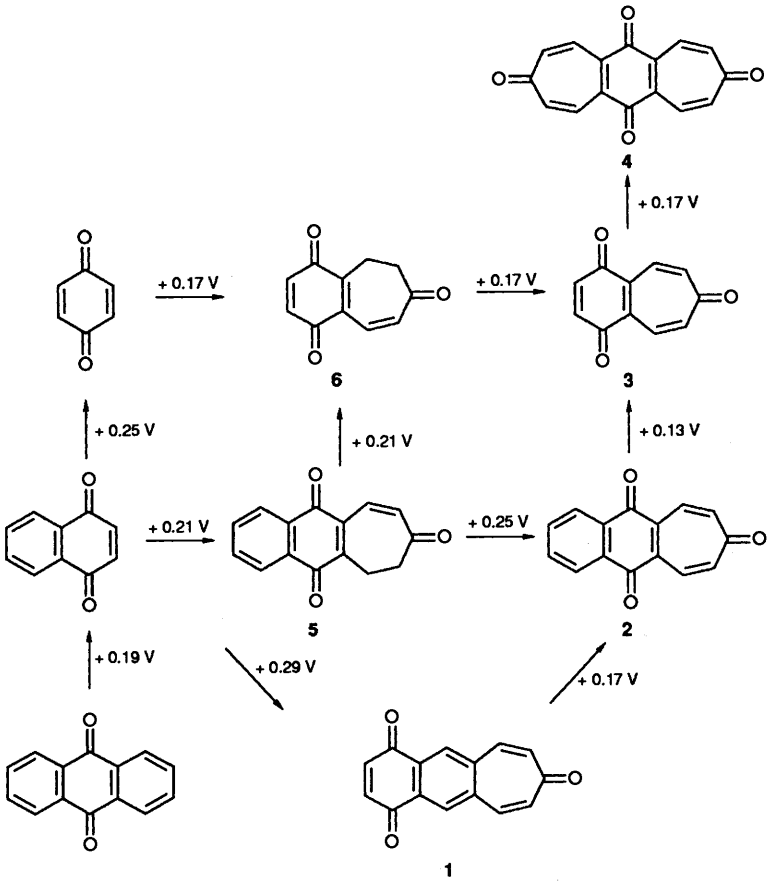
To obtain new efficient electron acceptors, three bromine-substituted benzocycloheptene-1,4,7-triones, **14**, **15**, **16**, and 7-dicyanomethylene-7*H*-benzocycloheptene-1,4-dione **36** have been synthesized. The electron affinities of the bromine-substituted quinones were found to be raised considerably as the number of bromine atoms increased compared with the parent trione **3**. A linear correlation between E_1^{redox} and E_{LUMO} (MNDO) has been shown. The dicyanomethylene substitution (**36**) of the tropone carbonyl of **3** caused an increase in the electron affinity by E_1 + 0.2 V. To obtain an acceptor carrying electron-withdrawing substituents on C_6 and C_8 of **3**, the 6,8-dimethoxycarbonyl derivative **18** was oxidized and gave a ring-contracted product **22** in fair yield. The formation is discussed in terms of electron distribution in the molecule of the expected product **19**.

We have previously synthesized tropone-annellated quinones **1**–**4** and some of their dihydro derivatives **5**, **6** (Scheme 1).[1,2]

In order to study the effect of substituents introduced into benzocycloheptene-1,4,7-trione **3**, on the electron affinity, we first calculated the coefficients on the atomic orbitals of the lowest unoccupied molecular orbital (LUMO) for the trione **3** by the MNDO method[3] and obtained the values shown in Fig. 1. From this figure, the values on C-5 and C-9 were close to zero, and hence the introduction of substituents at these positions seemed to have little effect on the electron affinity of the trione. Therefore, we studied the synthesis of trione **3** with substituents at positions other than C-5 and C-9.

Results and Discussion

Synthesis and Physical Properties of 2,3-*Dibromo-*, 2,3,6-*Tribromo-*, *and* 2,3,6,8-*Tetrabromobenzocycloheptene*-1,4,7-*trione* **14**–**16**.—As bromine, like chlorine, is strongly electron



Scheme 1 Increments in the first redox potentials are given along the arrows

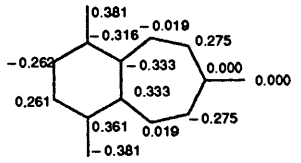
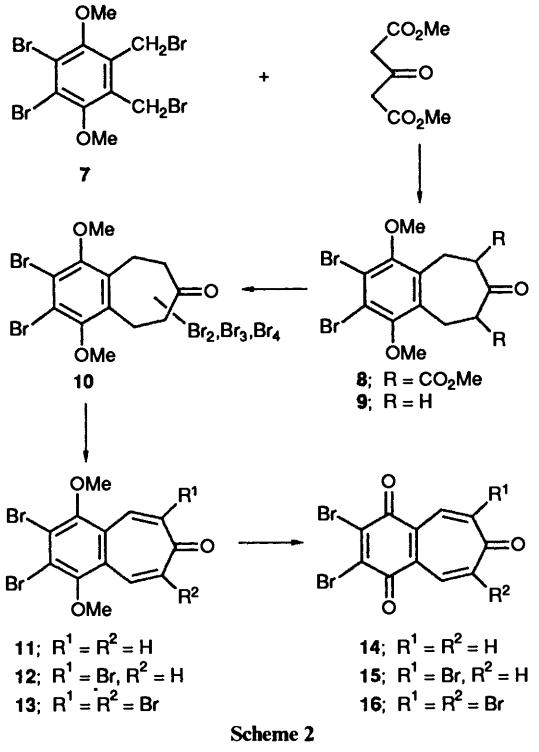


Fig. 1 The coefficients on each atomic orbital of the LUMO calculated by MNDO method on 7*H*-benzocycloheptene-1,4,7-trione **3**

withdrawing,[4,5] and is easily replaced by other groups such as CN, OR *etc.*,[6] bromine-substituted triones may form strong electron acceptors and be useful as precursors of new electron acceptors composed of benzoquinotropones, like bromine-substituted TTFs for the precursors of new electron donors.[6]

The synthesis is outlined in Scheme 2.



Scheme 2

The *o*-xylylene dibromide **7** was condensed with dimethyl 3-oxopentanedioate under previously reported conditions[8] with some modification.[9] Bisdemethoxycarbonylation of the resulting **8** was effected by refluxing with alcoholic potassium hydroxide to give 2,3-dibromo-1,4-dimethoxy-5,6,8,9-tetrahydrobenzocyclohepten-7-one **9**. α-Bromination of **9** with 2.4 molar equivalents of bromine gave a product mixture **10**, which was, without further purification, dehydrobrominated with lithium bromide/lithium carbonate in *N*,*N*-dimethylformamide (DMF) to give **11**, **12** and **13**, including their demethylated products, from which compounds **11** and **12** were separated. The buttressing effect of bromine atoms on C-2 and C-3 seems to have facilitated the cleavage of the methoxy group(s) by lithium bromide at temperatures as low as 100 °C.

As the hydroquinone dimethyl ethers **11** and **12**, unlike the parent benzotropone **17**,[1] were resistant to the usual ammonium cerium(IV) nitrate (CAN) oxidation, the dibromide **11** was oxidized with aq. potassium dichromate in conc. sulfuric acid to give triketone **14** in 49% yield. The yield of **14** was improved to 80% with use of nitric acid (*d* 1.42 g cm^{-3}) as oxidant in cold conc. sulfuric acid. The other precursors, **12** and a mixture of **12** and **13**, were oxidized to the corresponding quinones, **15** and **16**, with this reagent almost in the same yields.

The oxidation of the demethylated mixture of **11**–**13** also gave a mixture of **14**–**16**. The yields of triones **14**, **15** and **16** from tetrahydrotropone **9** were calculated as 18%, 13% and 6%, respectively, based on the isolated compounds.

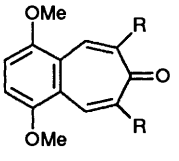
The electronic spectra of the products (**14**, reddish orange; **15**, yellow; **16**, lemon yellow crystals), taken in dichloromethane, are shown in Fig. 2. All three maxima showed steadily bathochromic shifts as the number of bromine atoms increased.

In the ^1H NMR spectra (Table 1), the β-hydrogens of the α,β-unsaturated ketone in the seven-membered ring in **15** and **16** were shifted to lower field by *ca.* 1.00 ppm by the effect of α-bromine substitution, which was larger than the shift (+0.45 ppm) caused by α-methoxycarbonyl substitution (**18**) of **17** (see below). This seems to be caused largely by the −I effect of the bromine atom outweighing its +R effect[4] and by the bulkiness of the bromine atom.

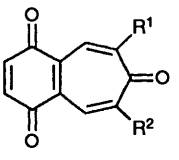
In the ^{13}C NMR spectra of **14**, while the carbonyl carbon signal of tropone was seen in a similar region to that of the parent **3**, those of the quinone shifted to higher field by *ca.* 7.9 ppm, which is the same order as the shift of the signal of the benzoquinone carbonyl induced by α-chlorine substitution.[10] For **15**, three carbonyl carbon signals are seen at 176.1, 175.5 and 170.2 ppm. Though it is regrettable that we could not specify the carbonyl signal of tetrabromide **16** owing to its insolubility in deuteriochloroform, the assignment of the signal at 170.2 ppm to the quinone carbonyl of **15** seems to be unacceptably high because even α-bromine substitution causes a +7.9 ppm shift of quinone carbonyl for **14** against that of **3** and it is not reasonable to assume that γ-bromine of **15** would cause a 6.7 ppm shift of the quinone carbonyl. Therefore, we assigned the peak at 175.5 and 176.1 ppm to quinone carbonyls and that at 170.2 ppm to the tropone carbonyl. The latter shifted extraordinarily (+15.5 ppm) compared with that of **14**.

Unusual Oxidation of 6,8-*Dimethoxycarbonyl*-1,4-*dimethoxybenzocyclohepten*-7-*one* **18**.—*The X-ray structure of the product and theoretical consideration of its formation.* In order to obtain benzocycloheptene-1,4,7-trione substituted with electronegative group(s) at C-6 and/or C-8, we attempted the synthesis of 6,8-dimethoxycarbonylbenzocycloheptene-1,4,7-trione **19**.

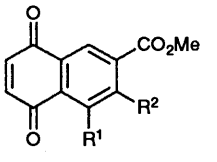
The precursor **18** was prepared by dehydrogenation of 6,7,8,9-tetrahydro-**18**, obtained from 2,3-bis(bromomethyl)hydroquinone dimethyl ether and dimethyl 3-oxoglutarate. Oxidation of compound **18** was carried out using (i) CAN in acetonitrile–$CHCl_3$, (ii) aq. potassium dichromate(VI) in conc. sulfuric acid, and (iii) nitric acid (*d* 1.42 g cm^{-3}) in conc. sulfuric acid. For the first two methods, selected product distribution data under various reaction conditions are shown in Table 2.



17; R = H
18; R = CO_2Me



19; $R^1 = R^2 = CO_2Me$
20; R^1 = H, R^2 = SPh
21; $R^1 = R^2$ = SPh



22; $R^1 = CO_2Me$, R^2 = OH
23; R^1 = OH, $R^2 = CO_2Me$

With excess dichromate, oxidation proceeded with little recovery of the starting material for 10 min of reaction time and gave mainly compound **A** with some by-products. With 4.0 mol equiv. of CAN, it gave solely **A**, which was isolated in 46% yield.

The structure **22** was established by a single crystal X-ray analysis of compound **A** as shown in Fig. 3. The physical data are consistent with this structure (see the Experimental section).

It is very interesting to note that the plane formed by the

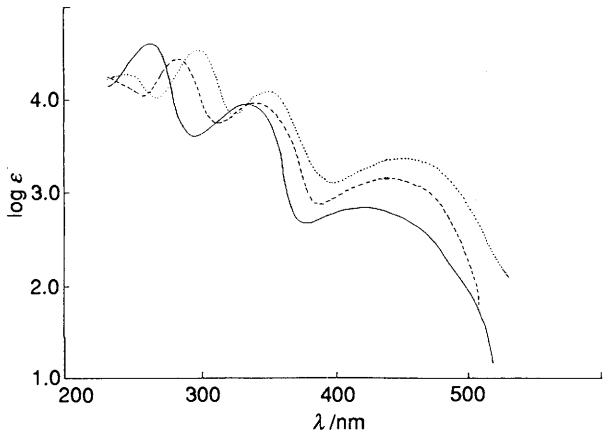


Fig. 2 The electronic spectra of bromine-substituted benzocycloheptene-1,4,7-triones in dichloromethane: **14**, ——; **15**, – – – –; **16**, · · · ·

Table 1 ^1H and ^{13}C NMR data for compounds **3**, **14**, **15** and **16** in $CDCl_3$

Nuclear	Position	3	14	15	16
^1H (400 MHz)					
	5-H	7.99d (*J* 12.5)	7.897d (*J* 11.9)	8.939s	8.960s
	9-H			8.058d (*J* 12.8)	
	6-H	7.25d (*J* 12.5)	7.114d (*J* 11.9)	—	—
	8-H			7.114d (*J* 12.8)	
^{13}C (100 MHz)					
	C(1)=O	184.8	176.9	176.1	
	C(4)=O			175.5	
	C(7)=O	186.1	185.7	170.2	
	Others	144.5	145.0	147.0, 134.9	—
		137.3	140.8	140.9, 134.7	—
		136.3	136.8	140.5, 133.3	—
		131.3	131.5	139.5, 131.2	—

Table 2 Product distributions in the oxidation of diester **18** with potassium dichromate or CAN

Reagent	Molar ratio[a]	Reaction conditions	Product distribution[c] A	18	Others
Aq. $K_2Cr_2O_7$	6.0	0 °C, 5 min	32	13	16
in conc. H_2SO_4	6.0	0 °C, 10 min	41	2	27
Aq. CAN	2.2	r.t.[b] 3 h	30	50	20
in acetonitrile	4.0	r.t.[b] 4 h	100	0	0

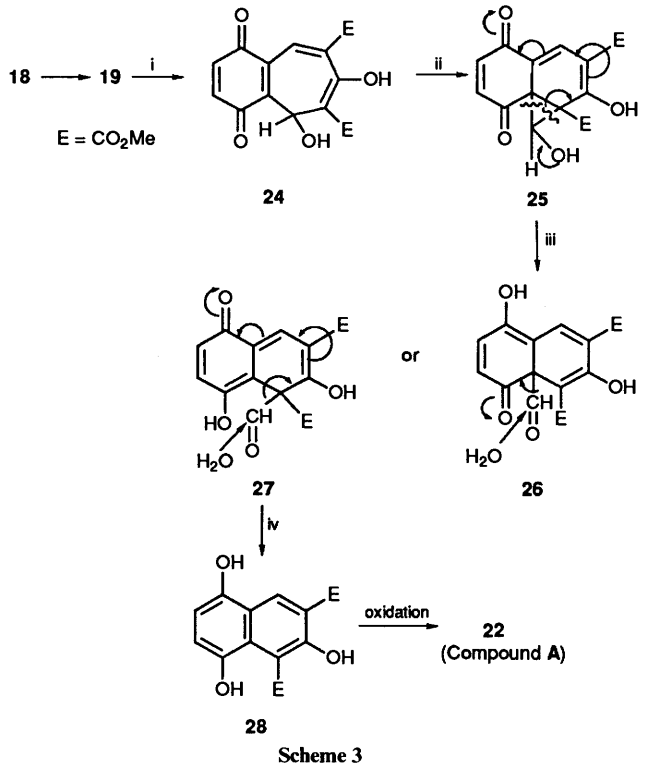
[a] The molar ratios of reagents used against diester **18** are shown. [b] r.t. = room temperature. [c] Each product mixture was roughly separated by silica gel chromatography and the product ratios were estimated by the proton-signal areas of methyl esters.

methoxycarbonyl group adjacent to the quinone carbonyl had a conformation almost perpendicular to the molecular plane of naphthoquinone and another ester carbonyl showed an intramolecular six-membered chelation with the phenolic hydroxy group. This fact is consistent with the IR behaviour of ester carbonyls.

The intramolecular O(5)···O(6) distance was 2.640(3) Å, while the intermolecular contacts of O(5)···O(6′) and O(6)···O(6′) were 2.879(3) and 2.797(2) Å, respectively, suggesting a bifurcated hydrogen bond.

It is known that the oxidation of hydroquinone dimethyl ethers to the corresponding quinones under the above oxidation conditions usually takes place smoothly[1] and the tropone ring may be protected from oxidation under strongly acidic conditions by protonation, forming a hydroxytropylium ion.[2] Therefore, it is reasonable to assume that compound **18** may initially be transformed into the quinone **19**. The reason why quinotropone **19** was further transformed into **22**, while **3** remained unchanged under the oxidation conditions,[1] may be attributed to the susceptibility of **19** to nucleophilic attack at C-5 or C-9 compared with **3**. To check this possibility, we compared the total charge distribution[11] of **19** with that of **3** (Table 3),[3] and found that the former showed a positive charge on C-5 (C-9) while the latter showed negative values on C-2 (C-3), C-5 (C-9), and C-6 (C-8).

Therefore, the reaction of **19** may be considered to proceed as follows (Scheme 3): (i) the initial nucleophilic attack of

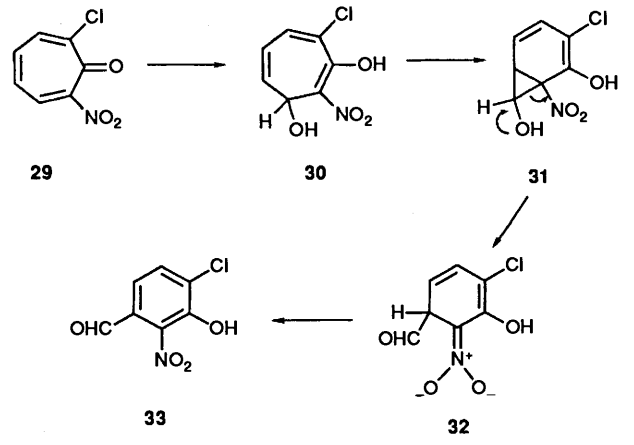


Scheme 3

water may occur at C-5 in conjunction with protonation on the carbonyl oxygen of **19**, then (ii) electrocyclic ring closure of **24** to give norcaradienol **25**,[12] followed by (iii) opening of the three-membered ring to form formyl compounds, **26** or **27**.[13] Finally, (iv) elimination of formic acid followed by oxidation may give **22** *via* **28**.

Similar ring contraction of the tropone ring has been reported in the case of oxidation of 2-chloro-7-nitrotropone **29** with aq. silver nitrate and a similar explanation had been given.[13] We also calculated the total charge densities on every carbon atom of **29** by the MNDO method,[3] and found the most positive value on C-6, where the initial attack of water had been proposed (Table 3). In this case, further oxidation took place and 4-chloro-3-hydroxy-2-nitrobenzaldehyde **33** resulted (Scheme 4).

These experiments showed that benzocycloheptene-1,4,7-triones substituted with strong electron-withdrawing group(s) on C-6 and/or C-8 may undergo ring contraction under the above oxidation conditions.



Scheme 4

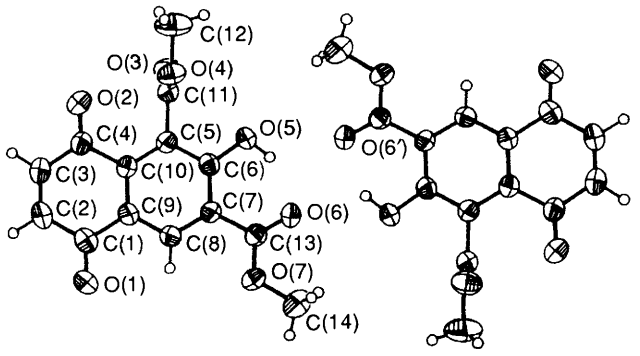
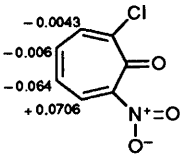


Fig. 3 X-Ray structure (ORTEP drawing) and numbering scheme of atoms for compound **22**. Non-hydrogen atoms are expressed as thermal ellipsoids with 50% probability level and hydrogen atoms as spheres of radius 0.1 Å.

Table 3 Total charge densities on ring-carbons of benzocycloheptene-1,4,7-trione **3**, 6,8-dimethoxycarbonylbenzocycloheptene-1,4,7-trione **19**, and 2-chloro-7-nitrotropone **29** calculated by the MNDO method [3]

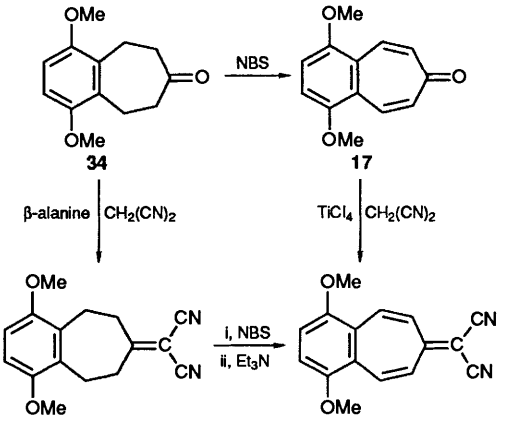
Carbon number	3	19
C-1, C-4	+0.271	+0.272
C-2, C-3	−0.085	−0.083
C-4a, C-9a	−0.051	−0.056
C-5, C-9	−0.013	+0.045
C-6, C-8	−0.095	−0.112
C-7	+0.279	+0.317



29

It should be mentioned here that preliminary *in vitro* experiments on compound **22** for 55 kinds of cancer cell, done at the National Cancer Institute in the USA, showed that it had some selective activity against leukaemia and a number of lung cancers.[14]

Synthesis of 7-(*Dicyanomethylene*)-7H-*benzocycloheptene*-1,4-*dione* **36**.—*The effects of the dicyanomethylene function on electron affinity*. It is well known that substitution of the oxygens of the two carbonyls of *p*-benzoquinone with dicyanomethylene groups results in a considerable increase in E_1, which make it an excellent electron acceptor to form organic metals with TTF.[15] In developing new electron acceptors composed of the framework of benzocycloheptene-1,4,7-trione **3**, it is important to evaluate the effect of dicyanomethylene substitution of the tropone carbonyl in **3**. We synthesized the precursor **37** by two routes shown in Scheme 5.



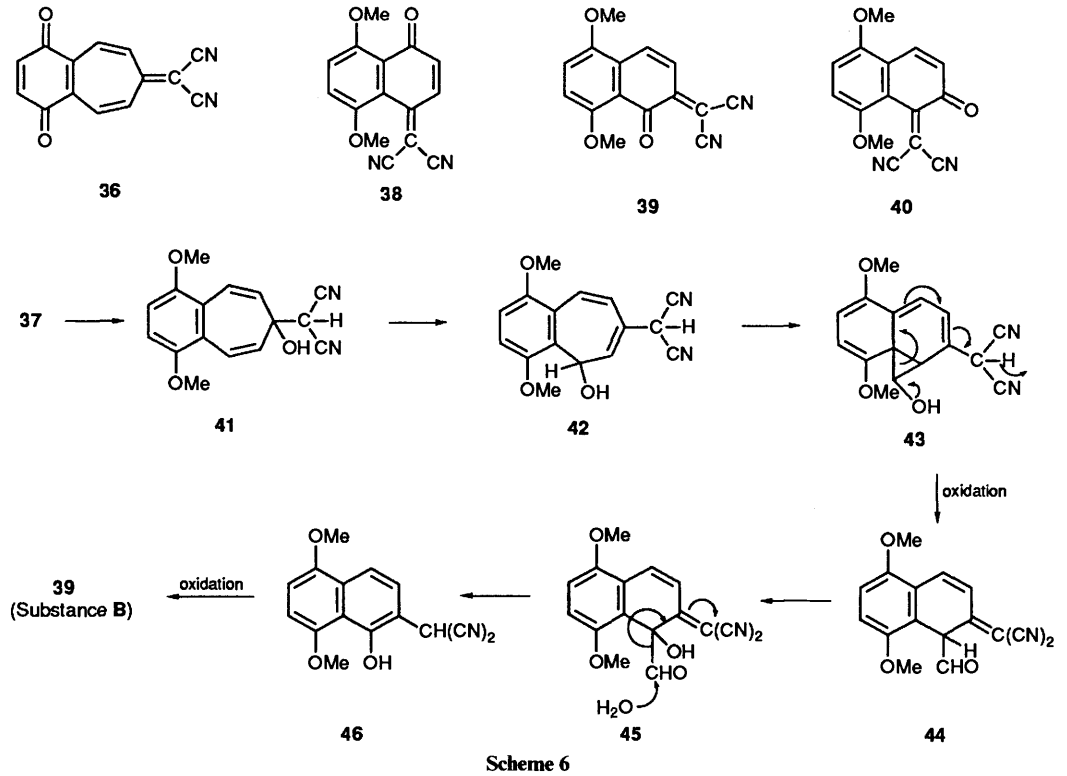
Scheme 5

Though it was found that tropone **17** could be prepared from the tetrahydrotropone **34** merely by refluxing with NBS in carbon tetrachloride, the condensation of tropone **17** with malononitrile gave a rather low yield of dicyanomethylene compound **37**. Therefore, tetrahydrotropone **34** was first condensed with malononitrile in the presence of β-alanine and the resulting dicyanomethylene derivative **35** was brominated with NBS, followed by dehydrobromination with triethylamine to give **37**. Thus, the yield of **37** from **34** was improved considerably (from 26% to 65%).

When CAN oxidation of **37** was carried out in the usual way, the main product was a blue substance **B** (30%) in addition to 2% of quinone **36**. From the spectral properties of the blue crystals, the presence of a 2,3-unsymmetrically disubstituted hydroquinone dimethyl ether, a six-membered ring ethylene group conjugated with an electron-attracting group, and a carbonyl group was suggested. Of the possible structures **38**–**40** which fulfil the spectral requirements, structure **39** was tentatively assigned for the blue compound **B** by consideration of the structure of the starting **37**. The formation of **39** is rationalised as shown in Scheme 6.

Thus, owing to the strong electron-withdrawing effect of cyano groups, the charge distribution on C-7 of **37** becomes positive [C-5 (C-9) −0.026; C-6 (C-8) −0.119; C-7 +0.112], which may be easily hydrated to give a 7*H*-benzocyclohepten-7-ol **41**. This could be rearranged to the 5*H*-benzocyclohepten-5-ol **42**, which is in equilibrium with the norcaradiene valence isomer **43**. This may readily undergo ring opening of the cyclopropanol by recovering aromaticity under the oxidation conditions to give a formyl derivative **44**. Oxidation of the benzylic position of **44** may lead to the α-hydroxy aldehyde **45**, which may be attacked by water and lose formic acid to give **46**. The oxidation of benzylic hydrogen is sometimes encountered with this reagent.[16] The final step may be oxidation of **46** to the *o*-quinomethane **39**.

According to Scheme 6, since the presence of water seemed to be responsible for the formation of the blue product **39**, we studied the oxidation of **37** with CAN in the solid state by mixing without solvent. This technique led us to obtain **36** in 32% yield without contamination by **39**. The product was red crystals, m.p. 230 °C (decomp.), showing a conjugated CN stretching band at 2220 cm^{-1} in its IR spectrum. The X-ray



Scheme 6

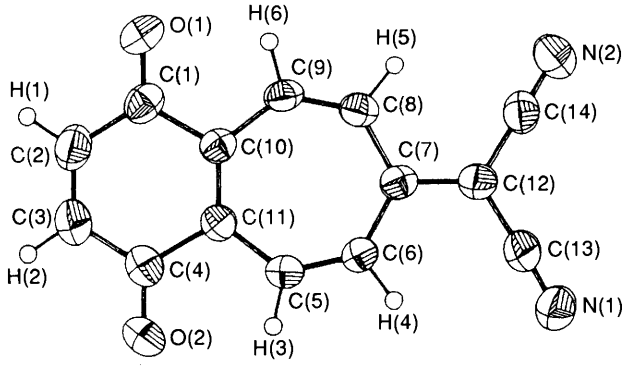


Fig. 4 X-Ray structure (ORTEP drawing) and numbering scheme of atoms for compound **36**. Non-hydrogen atoms are expressed as thermal ellipsoids with 50% probability level and hydrogen atoms as spheres of radius 0.1 Å.

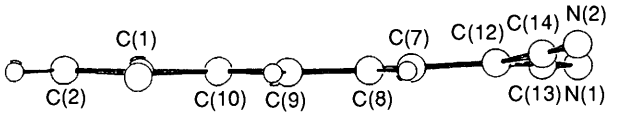


Fig. 5 Side view of molecule **36**. The angles between C(6)–C(7)–C(8) and C(5)–C(6)–C(8)–C(9), C(5)–C(6)–C(8)–C(9) and C(5)–C(9)–C(10)–C(11), C(5)–C(9)–C(10)–C(11) and C(1)–C(4)–C(11)–C(10), and C(1)–C(4)–C(11)–C(10) and C(1)–C(4)–C(3)–C(2) planes are 2.8(3), 1.5(2), 1.5(2), and 1.8(2)°, respectively.

structure of **36** is shown in Figs. 4 and 5. Although the molecular structure of **36** was as flat as 8,8-dicyanomethyleneheptafulvene itself,[17] the $HOMA_d$ value for **36**, which represents the extent of bond alternation (the lower the bond alternation, the nearer this value is to 1) was larger (0.804) than that of 8,8-dicyanoheptafulvene (0.745). The former value is very close to that (0.806) reported for tropone.[18]

Redox Potentials of Compounds **14**, **15**, **16** *and* **36**.—The CV curves of compounds **14**–**16** were obtained in dichloromethane containing 0.1 mol dm^{-3} tetrabutylammonium perchlorate. The three bromides gave reversible CV curves in the region +0.5 to *ca.* 1.1 V. The first and second redox potentials are listed in Table 4 together with those of other compounds obtained previously.[1,2,9]

The log K_{sem} values were obtained from eqn. (1);[19] the values

$$\log K_{sem} = (E_1 - E_2)0.059 \quad (1)$$

of the bromides fell in the range 11.0–11.4, showing that the relative thermodynamic stabilities of semiquinones or anion radicals were increased by bromine substitution.[20] The stepwise increase in the electron affinities of benzocycloheptene-1,4,7-trione by bromine substitution is apparent. It should be mentioned here that the tetrabromide **16** was the first compound to show a positive E_1 value.

The CV curves (Ag/AgCl) of **36** measured in CH_2Cl_2 and acetonitrile containing 0.1 mol dm^{-3} tetrabutylammonium perchlorate are shown in Fig. 6.

The first reduction potential (E_1) showed a reversible curve but the second one exhibited two reduction peaks (E_3 and E_2) corresponding to one-electron reduction. The former (E_3) of the second peaks is observed clearly in acetonitrile with a scan rate of 250 mV s^{-1} and in dichloromethane with a scan rate of 50 mV s^{-1}. But, with a faster scan rate in dichloromethane, E_3 was difficult to observe. These phenomena are explained when we assume an equilibrium between two molecules of anion radical **47** and an associate (or complex) **48** between a neutral **36** and its dianion **49**. E_2 corresponds to the second redox potential of an anion radical **47** to dianion **49** and E_3 is the redox potential of the bimolecular complex **48**. The overall transformations are shown in Scheme 7.

When the scan rate is faster than the establishment of association, E_1 and E_2 are observed but in the case of a slower scan rate in a non-polar solvent, or an even faster scan rate in a polar solvent, in addtion to E_1, both E_2 and E_3 are observable. In a polar solvent, the equilibrium $2A^{\cdot -} \rightleftharpoons A{\cdot}A^{2-}$ may be established faster than in a non-polar solvent. The structure of the complex **48** is not clear; it may have a covalent bond or be

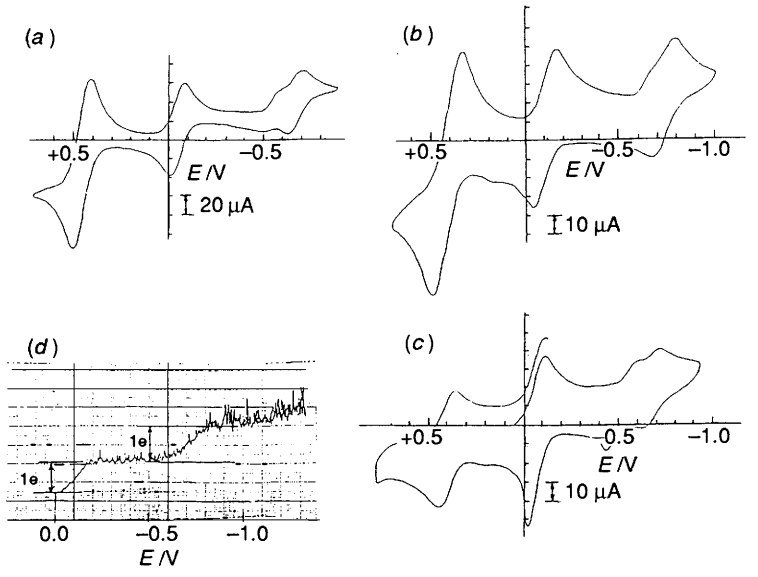
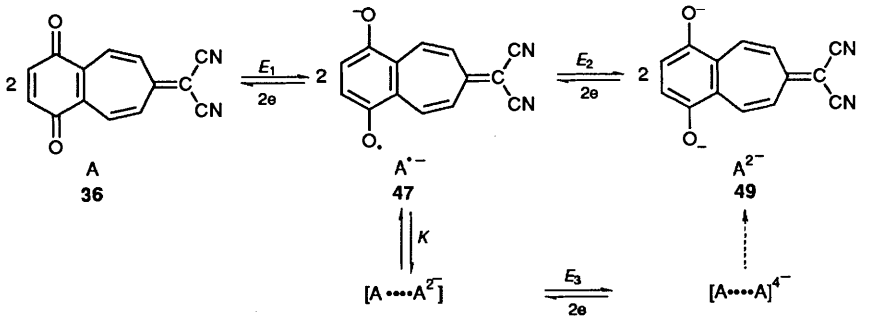


Fig. 6 Redox diagrams of **36**. (*a*) CV curve in dichloromethane with a scan rate 25 mV s^{-1}. (*b*) CV curve in dichloromethane with a scan rate 250 mV s^{-1}. (*c*) CV curve in acetonitrile with a scan rate 250 mV s^{-1}. (*d*) Steady state voltammetry in a stirred solution of dichloromethane.



Scheme 7

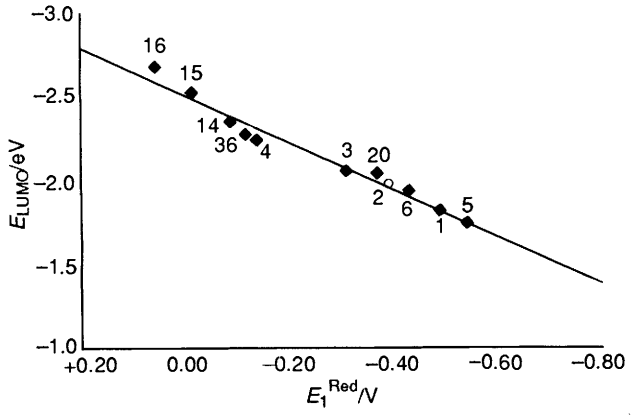


Fig. 7 A correlation line between E_1^{redox} of quinotropones listed in Table 4 and the corresponding E_{LUMO} values calculated by the MNDO method

simply a CT complex. A similar phenomenon was observed in the case of an azulene-annellated naphthoquinone.[21]

The Relationship between Redox Potentials and the Corresponding E_{LUMO} *Values.*—The plots of the E_1 values of hitherto obtained tropone-annellated quinones listed in Table 4, together with compound **36** against the corresponding E_{LUMO} values obtained by the MNDO method of MO calculations were found to fall almost on a straight line with gradient −1.39 (Fig. 7). From this line, we can estimate E_1 values of unknown tropone-annellated quinones by MNDO calculations with considerable accuracy.

Experimental

General.—The NMR spectra were taken on JEOL Model GX400 or FX100 Ft-NMR spectrometers. *J*-Values are in Hz. The IR spectra were recorded on a JASCO Model A-102 spectrometer and the UV on Hitachi Recording spectrometer 323 or on a Shimadzu Model UV-160A spectrometer with a colour X-Y plotter Model P/N 206-15788.

2,3-*Dibromo*-5,6-*bis*(*bromomethyl*)*hydroquinone Dimethyl Ether* **7**.—To a solution of 2,3-dibromo-5,6-dimethylhydroquinone dimethyl ether (4.50 g, 14 mmol), prepared from 2,3-dimethylhydroquinone,[1] dissolved in tetrachloromethane (250 cm^3) was added dropwise a solution of bromine (4.58 g, 28.6 mmol) in tetrachloromethane (50 cm^3) under external irradiation with a high pressure mercury lamp (Ushio USH-500D) through a filter (Toshiba UV-35). After 1 h irradiation, as the red colour of bromine faded to pink-orange, the solution was washed successively with 5% aq. sodium thiosulfate, water, and saturated brine, and then dried. Evaporation of the solvent gave crude crystals which were washed with hexane. Pale yellow crystals of **7** (5.51 g, 82%), m.p. 104–105 °C (from hexane–dichloromethane) (Found: C, 25.0; H, 2.05. $C_{10}H_{10}Br_4O_2$ requires C, 24.90; H, 2.07%); δ_H(100 MHz; $CDCl_3$) 4.73 (4 H, s), 3.95 (6 H, s).

2,3-*Dibromo*-6,8-*dimethoxycarbonyl*-1,4-*dimethoxy*-5,6,8,9-

Table 4 Redox potentials of tropone-annellated quinones

Compound	Solvent	E_1/V	E_2/V	log K_{sem}
1	CH_3CN (SCE)[a]	−0.50	—	—
1	CH_2Cl_2 (Ag/AgCl)[b]	−0.54	−0.89	6.03
2	CH_3CN (SCE)[a]	−0.35	—	—
5	CH_3CN (SCE)[a]	−0.55	—	—
3	CH_3CN (SCE)[a]	−0.23	−0.92	11.90
3	CH_2Cl_2 (Ag/AgCl)[b]	−0.31	−0.90	10.17
6	CH_3CN (SCE)[a]	−0.38	—	—
4	CH_2Cl_2 (Ag/AgCl)[b]	−0.14	−0.74	10.34
20	CH_3CN (Ag/AgCl)[b]	−0.25	−0.73	8.27
20	CH_2Cl_2 (Ag/AgCl)[b]	−0.37	−0.86	8.45
21	CH_3CN (Ag/AgCl)[b]	−0.30	−0.80	8.62
36	CH_2Cl_2 (Ag/AgCl)[b]	−0.11	−0.71	10.34
14	CH_2Cl_2 (Ag/AgCl)[b]	−0.085	−0.73	11.12
15	CH_2Cl_2 (Ag/AgCl)[b]	−0.015	−0.665	11.03
16	CH_2Cl_2 (Ag/AgCl)[b]	+0.045	−0.615	11.38
Anthra-quinone	CH_2Cl_2 (Ag/AgCl)[b]	−0.93	—	—

[a] The cyclic voltammograms were run on a potentiometer, Model HA-305 (Hakuto-Denko Co. Ltd.), using platinum wire electrodes (SCE) at room temperature. A solution of each substrate was made in acetonitrile containing tetrabutylammonium perchlorate (10^{-1} mol dm^{-3}). [b] The redox potentials were recorded on a BAS voltammetry control unit, Model CV-1B, in an appropriate solvent containing tetrabutylammonium perchlorate (10^{-1} mol dm^{-3}) as the supporting electrolyte. Ferrocene was added after several runs as an internal standard (+0.4 V). Graphite rod was used as a working electrode.

tetrahydrobenzocyclohepten-7-one **8**.—A solution of the tetrabromide **7** (3.77 g, 7.82 mmol), dimethyl 3-oxoglutarate (1.35 g, 9.39 mmol) and benzyltriethylammonium chloride (0.68 g) in dichloromethane (25 cm^3) was stirred vigorously at 40 °C with 20% aq. potassium hydrogencarbonate (25 cm^3) for 48 h. After more dichloromethane had been added, the organic layer was separated and washed successsively with water and saturated brine, and then dried. After evaporation of the solvent, the remaining liquid was crystallized by trituration with diethyl ether. Pale yellow crystals **8** (2.46 g, 63.6%); m.p. 167–169.5 °C; ν_{max}(Nujol)/cm^{-1} 1740 (ester carbonyl), 1700 (ketone). This compound was used without further purification.

2,3-*Dibromo*-1,4-*dimethoxy*-5,6,8,9-*tetrahydrobenzocyclohepten*-7-*one* **9**.—The crude diester **8** (2.4 g, 4.86 mmol) dissolved in 0.5 mol dm^{-3} 85% ethanolic potassium hydroxide (23.2 cm^3, 11.7 mmol) was stirred under reflux for 20 h. After cooling, separated crystals were filtered off and washed with cold methanol. The mother liquid was diluted with the same volume of water, concentrated to half volume, and extracted with diethyl ether. The ether solution was washed and dried as usual. After evaporation of the solvent, the residual crystals were washed with cold methanol. The combined crystals (total 1.48 g, 80.5%) **9**, leaflets, m.p. 149–150 °C (from EtOH) (Found: C, 41.4; H, 3.8. $C_{13}H_{14}Br_2O_3$ requires C, 41.27; H, 3.70%); ν_{max}(Nujol)/cm^{-1} 1700; δ_H(100 MHz; $CDCl_3$) 3.70 (6 H, s), 3.02–2.90 (4 H, m), 2.57–2.45 (4 H, m).

Bromination and Dehydrobromination of the Tetrahydrobenzocyclohepten-7-*one* **9**.—To a solution of the tropone **9** (1.84 g, 4.84 mmol) dissolved in tetrachloromethane (50 cm^3) was added, dropwise with stirring, a solution of bromine (1.8 g, 11.6 mmol) in tetrachloromethane (20 cm^3). The red colour of bromine faded rapidly at first, but the decolouration became slower later. After the addition, the red solution was stirred overnight. The organic layer was decolourized with 5% aq. sodium hydrogen sulfite and washed successively with water and saturated brine, and then dried. Evaporation of the solvent gave a mixture of bromides as a yellow liquid (2.14 g). This liquid (2.14 g), anhydrous lithium bromide (0.827 g, 9.52 mmol), and lithium carbonate (0.910 g, 12.3 mmol) suspended in anhydrous DMF (25 cm^3) was stirred at 100 °C under nitrogen for 2 h. After cooling, the mixture was concentrated to dryness under reduced pressure and the residue was triturated with 1 mol dm^{-3} hydrochloric acid until it reacted acid to an indicator (methyl red). After addition of water, the solution was extracted with dichloromethane. The organic extracts were washed with saturated brine and dried. After evaporation of the solvent, the remaining dark brown oil (1.58 g) was chromatographed on the degassed silica gel (30 g) with benzene–ethyl acetate (95:5 v/v) as the eluent. From the third fraction (TLC R_f = 0.18 with the same solvent), the dibromide **11** (317 mg) was obtained as colourless needles, m.p. 194–195.5 °C (from acetonitrile) (Found: C, 41.9; H, 2.7. $C_{13}H_{10}Br_2O_3$ requires C, 41.74; H, 2.69%); δ_H(100 MHz, $CDCl_3$) 7.89 (2 H, d, *J* 13.5; 5-H, 9-H), 6.84 (2 H, d, *J* 13.5, 6-H, 8-H), 3.88 (6 H, s, 2 OMe). The first (R_f 0.64; 301 mg) and the second fractions (R_f 0.43; 135 mg) contained a mixture of **12** and **13**, and **12**, respectively. The fourth fraction (R_f 0.06; 298 mg) was a demethylated mixture of **11**, **12** and **13**. They were oxidized without further purification (see below).

2,3-*Dibromobenzocycloheptene*-1,4,7-*trione* **14**.—(*a*) *Oxidation of compound* **11** with dichromate. To an ice-cooled solution of compound **11** (47 mg, 0.126 mmol) dissolved in cold conc. sulfuric acid (3 cm^3) was added dropwise an aq. solution of potassium dichromate (222 mg, 0.75 mmol) with stirring. Stirring was continued for 5 min after the addition, during which some foaming and change of colour (dark brown to green) in solution were observed. The reaction mixture was poured onto ice and extracted with dichloromethane. The organic solution was washed with water and saturated brine, and dried. Evaporation of the solvent gave a yellow powder, which was recrystallized from hexane–dichloromethane **14** (18 mg, 41%). For the physical data of **14**, see below.

(*b*) *Oxidation of compound* **11** *with nitric acid.* To a solution of the dibromide **11** (317 mg, 0.848 mmol) dissolved in cold conc. sulfuric acid (2 cm^3) with ice cooling was added dropwise nitric acid (*d* 1.42 g cm^{-1}; 12 drops) and stirring was continued until the red colour of the reaction mixture turned to orange (5 min). The mixture was then diluted with water and extracted with dichloromethane. The extracts were washed successively with water and saturated brine, and then dried. After evaporation of the solvent, the residue was solidified, and recrystallized from hexane–dichloromethane to give golden yellow crystals **14** (80%; TLC R_f 0.27 with benzene–ethyl acetate 95:5 v/v), m.p. 187–190 °C (decomp.) (Found: C, 38.65; H, 1.15. $C_{11}H_4Br_2O_3$ requires C, 38.41; H, 1.17%); ν_{max}(Nujol)/cm^{-1} 1668, 1638, 1594, 1519, 1510, 1240, 1132; $\lambda_{max}(CH_2Cl_2)$/nm 263 (log ε 4.59), 335 (3.95), 420 (2.82); *m*/*z* 346 (13%, M^+ + 4), 344 (21, M^+ + 2), 342 (10, M^+), 235 (100). For other spectral data, see the text.

2,3,6-*Tribromobenzocycloheptene*-1,4,7-*trione* **15**.—A similar experiment to the above for **11** was carried out with the tribromide **12** (135 mg, 0.299 mmol) to give **15** (100 mg, 79%), m.p. 262–265 °C (decomp.) (Found: C, 31.15; H, 0.65. $C_{11}H_3Br_3O_3$ requires C, 31.24; H, 0.72%); ν_{max}(Nujol)/cm^{-1} 1670, 1660, 1633, 1605, 1588, 1570, 1243, 1048; $\lambda_{max}(CH_2Cl_2)$/nm 283 (log ε 4.43), 341 (3.96), 436 (3.14); *m*/*z* 426 (14%, M^+ +6), 424 (37, M^+ + 4), 422 (36, M^+ + 2), 420 (M^+), 315 (100). For other spectral data, see text.

2,3,6,8-*Tetrabromobenzocycloheptene*-1,4,7-*trione* **16**.—Similar oxidation of a mixture (215 mg) of **12** and **13** gave bromides **15** and **16**, which were separated by silica gel chromatography. The R_f values (benzene–ethyl acetate 95:5 v/v) for **15** and **16** were 0.43 and 0.56, respectively, on silica gel TLC. These were

separated with silica gel column chromatography to give tetrabromide **16** (102 mg) and tribromide **15** (72.5 mg), **16** lemon yellow crystals, m.p. 278–281 °C (decomp.) (from hexane–dichloromethane) (Found: C, 26.3; H, 0.35. $C_{11}H_2Br_4O_3$ requires C, 26.33; H, 0.40%); ν_{max}(KBr)/cm^{-1} 1673, 1626, 1575, 1553, 1227; λ_{max}(CH_2Cl_2) 244 (log ε 4.28), 299 (4.54), 351 (4.08), 448 (3.36); *m/z* 506 (10%, M^+ + 8), 504 (47, M^+ + 6), 502 (70, M^+ + 4), 500 (48, M^+ + 2), 498 (12, M^+), 393 (100). For other spectral data, see the text.

Condensation of 2,3-*bis*(*bromomethyl*)-1,4-*hydroquinone Dimethyl Ether with Dimethyl* 3-*Oxoglutarate*.—The dibromide, m.p. 64–65 °C (10.9 g, 33 mmol) and dimethyl 3-oxoglutarate (6.96 g, 39.6 mmol) in dichloromethane (60 cm^3) was stirred under reflux with 20% aq. potassium hydrogen carbonate (40 cm^3) in the presence of benzyltriethylammonium chloride for 3 days. More dichloromethane was added and the organic layer washed with water and saturated brine and then dried. After evaporation of the solvent, the residual brown oil partially crystallized. The filtered solid was recrystallized from ethanol to give 5,6,8,9-tetrahydro-**18** (3.6 g, 32.5%), m.p. 129–130 °C (from ethanol) (Found: C, 60.5; H, 6.0. $C_{17}H_{20}O_7$ requires C, 60.71; H, 5.99%).

6,8-*Dimethoxycarbonyl*-1,4-*dimethoxybenzocyclohepten*-7-*one* **18**.—The above diester (1.0 g, 2.98 mmol) and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) (2.7 g, 11.9 mmol) in dioxane (20 cm^3) were stirred under reflux for 3 h in the presence of toluene-*p*-sulfonic acid (280 mg). The precipitated white solid was filtered and the filtrate was concentrated to dryness. The residue dissolved in chloroform was washed with water and saturated brine and then dried. After evaporation of the solvent, the residual semisolid was recrystallized from methanol to give yellow crystals **18** (500 mg, 50.3%), m.p. 177–178 °C (Found C, 61.2; H, 4.85. $C_{17}H_{16}O_7$ requires C, 61.44; H, 4.85%); δ_H(400 MHz, $CDCl_3$) 3.86 (6 H, s), 3.90 (6 H, s), 7.06 (2 H, s), 8.66 (2 H, s); δ_C(100 MHz, $CDCl_3$) 184.6, 166.4, 152.8, 134.6, 134.2, 124.3, 113.7, 52.8, 56.6; ν_{max}(KBr)/cm^{-1} 1723, 1610, 1590.

Oxidation of Diester **18** *with Potassium Dichromate*.—To an ice-cooled solution of **18** (68.2 mg) in sulfuric acid (4.0 cm^3) was added dropwise potassium dichromate (293 mg, 0.96 mmol) in water (2.0 cm^3). The initial violet colour of the solution changed to green after 5 min. After stirring for a further 5 min, the solution was diluted with ice-water and extracted with dichloromethane. Usual work-up gave a yellow oil (30 mg) which showed two spots on TLC (silica gel/hexane–ethylacetate 95:5 v/v). From the ^{1}H NMR spectrum of the mixture, it contained compound **20** as high as 80%.

Oxidation of Diester **18** *with CAN*.—To a solution of the diester **18** (96.7 mg, 0.29 mmol) in acetonitrile (3.6 cm^3) was added dropwise a solution of CAN (645 mg, 1.16 mmol) in water (1.6 cm^3) at 29 °C. Over a period of 6 h, the colour of the solution changed from orange to red, dark brown, and finally cloudy orange. The solution was diluted with water (30 cm^3) and extracted with dichloromethane. The dichloromethane extracts were washed successively with aq. sodium hydrogencarbonate and saturated brine, and then dried. After evaporation of the solvent, a yellow orange oil (74 mg) was obtained and soon solidified. Chromatographic separation on silica gel (benzene–ethyl acetate 95:5 v/v) gave yellow crystals **22** (40 mg), m.p. 204–205 °C (from hexane–dichloromethane) (Found: C, 57.95; H, 3.45; M^+, 290. $C_{14}H_{10}O_7$ requires C, 57.94; H, 3.47%; M, 290); δ_H(400 MHz, $CDCl_3$) 4.044 (3 H, s), 4.095 (3 H, s), 6.978 (1 H, d, *J* 10.4), 7.006 (1 H, d, *J* 10.4), 8.690 (1 H, s), 11.66 (1 H, bs); δ_C(100 MHz, $CDCl_3$) 53.2 (q), 53.5 (q), 116.6 (s), 123.2 (s), 123.6 (s), 130.8 (d, *J* 170), 132.2 (s), 138.0 (d, *J* 170), 139.1 (d, *J* 170), 162.2 (s), 166.1 (s), 169.1 (s), 182.5 (s), 183.4 (s); λ_{max}(CH_2Cl_2)/nm 217 (log ε 4.43), 256 (4.26), 376 (4.49); *m/z* 291 (10.5%), 290 (M^+, 64), 259 (39.5), 258 (60), 228 (55.5), 227 (100), 199 (14.5); ν_{max}($CHCl_3$)/cm^{-1} 3150–3500, 1740, 1685 (sh), 1675.

Improved Synthesis of **3**.—*Synthesis of benzotropone* **17** *from* 1,4-*dimethoxy*-5,6,8,9-*tetrahydrobenzocyclohepten*-7-*one* **34**. A solution of **34** (1.06 g, 4.57 mmol), *N*-bromosuccinimide (NBS) (1.94 g, 10.8 mmol), a small amount of azobis(isobutyronitrile) (AIBN) dissolved in carbon tetrachloride (50 cm^3) was stirred under reflux for 4 h. The yellow colour of the reaction mixture turned to pink and red crystals floated on the liquid surface. These crystals were filtered and dissolved in dichloromethane, which was washed successively with 1 mol dm^{-3} aq. sodium hydroxide, water, and saturated brine, and then dried. After evaporation of the solvent, yellow crystals were obtained, **17** 676 mg (67%), m.p. 132–133 °C (from benzene)[1] (Found: C, 72.15; H, 5.65. $C_{13}H_{12}O_3$ requires C, 72.21; H, 5.59%).

Oxidation of Compound **17** *with Nitric Acid*.—To an ice-cooled solution of tropone **17** (114 mg, 0.528 mmol) dissolved in conc. sulfuric acid was added 3 drops of nitric acid (*d* = 1.42 g cm^{-3}) and the solution was stirred for 5 min. This solution was poured onto ice and extracted with dichloromethane to give a yellow organic solution. From this extract trione **3** (76.1 mg, 78%) was obtained as yellow-brown crystals, m.p. 123 °C (decomp.) (from hexane–dichloromethane), *m/z* 187 (5.9%), 186 (M^+, 47), 159 (12), 158 (100), 130 (77), 104 (71), 102 (75).

7-*Dicyanomethylene*-1,4-*dimethoxy*-6,7,8,9-*tetrahydro*-5H-*benzocycloheptene* **35**.—A solution of **34** (1.16 g, 5.27 mmol), malononitrile (347 mg, 5.26 mmol), and β-alanine (5 mg) in ethanol (70 cm^3) was stirred under reflux for 1 h. After concentration to dryness, the residue taken up in dichloromethane was filtered and the filtrate was concentrated to dryness to give colourless crystals (1.28 g, 90%), **35**, m.p. 202 °C (from ethanol) (Found: C, 71.55; H, 6.0; N, 10.45. $C_{16}H_{16}N_2O_2$ requires C, 71.62; H, 6.01; N, 10.44%); ν_{max}($CHCl_3$)/cm^{-1} 2220, 1473, 1460, 1255, 1210, 1073; δ_H(100 MHz, $CDCl_3$) 2.64–2.88 (4 H, dm), 2.96–3.20 (4 H, dm), 3.78 (6 H, s), 6.75 (2 H, s); δ_C(25 MHz, $CDCl_3$) 185.9, 150.6, 129.8, 111.8, 109.6, 84.5, 56.2, 35.5, 22.9.

7-*Dicyanomethylene*-1,4-*dimethoxy*-7H-*benzocycloheptene* **37**.—(*a*) *From compound* **17**. In an anhydrous dichloromethane (2.0 cm^3) solution of **17** (206 mg, 0.95 mmol), was dissolved titanium(IV) chloride (0.80 cm^3, 2.8 mmol). To this solution, malononitrile (624 mg, 9.44 mmol) and anhydrous pyridine (1.37 g, 17.3 mmol) were added and the resulting solution was stirred under reflux for 2.5 h. After cooling, the solution was poured onto ice and extracted with dichloromethane. The organic layer was separated, washed with water and saturated brine, and then dried. The product was recrystallized from chloroform to give orange crystals **37** (91.3 mg, 36%), m.p. 251–253 °C (Found C, 71.7; H, 4.5; N, 10.6. $C_{16}H_{12}N_2O_2$ requires C, 71.71; H, 4.58; N, 10.60%); ν_{max}(Nujol)/cm^{-1} 2200, 1620, 1413, 1323, 1259, 1071; λ_{max}(CH_2Cl_2)/nm 375 (log ε 4.52), 410 (4.31), 430 (4.27), 454 (3.78); δ_H(400 MHz, $CDCl_3$) 3.92 (6 H, s), 7.09 (2 H, s), 7.12 (2 H, dd, *J* 12.2), 8.01 (2 H, dd, *J* 12.2).

(*b*) *From compound* **35**. Dicyanomethylene derivative **35** (504 mg, 1.88 mmol) dissolved in carbon tetrachloride (90 cm^3) was stirred with NBS (832 mg, 4.42 mmol) under reflux for 3 h. The separated succinimide was filtered off and the filtrate was stirred with triethylamine (10 cm^3) for several min. The precipitated triethylammonium chloride was filtered and the filtrate was washed with water and saturated brine, and then dried. The crystals obtained after evaporation of the solvent were

Table 5 Atomic co-ordinates for compound **22**

Atom	*x*	*y*	*z*
C(1)	0.8383(3)	0.1307(2)	0.7240(2)
C(2)	0.9525(3)	0.1808(2)	0.6631(3)
C(3)	0.9080(3)	0.2106(2)	0.5375(3)
C(4)	0.7418(3)	0.1962(1)	0.4508(3)
C(5)	0.4540(3)	0.1406(1)	0.4366(2)
C(6)	0.3404(3)	0.0952(1)	0.4921(2)
C(7)	0.3885(3)	0.0626(1)	0.6253(2)
C(8)	0.5511(3)	0.0747(1)	0.6985(2)
C(9)	0.6656(3)	0.1183(1)	0.6438(2)
C(10)	0.6172(3)	0.1514(1)	0.5114(2)
C(11)	0.3901(3)	0.1771(3)	0.2971(2)
C(12)	0.3444(4)	0.1523(2)	0.0614(3)
C(13)	0.2655(3)	0.0146(2)	0.6808(2)
C(14)	0.1993(4)	−0.0529(2)	0.8702(3)
O(1)	0.8872(2)	0.1001(1)	0.8371(2)
O(2)	0.7074(2)	0.2197(1)	0.3328(2)
O(3)	0.3297(2)	0.2448(1)	0.2788(2)
O(4)	0.4018(2)	0.1234(1)	0.2007(2)
O(5)	0.1870(2)	0.0867(1)	0.4123(2)
O(6)	0.1349(2)	−0.0092(1)	0.6118(2)
O(7)	0.3130(2)	−0.0015(1)	0.8116(2)

Table 6 Atomic co-ordinates with esds in parentheses for compound **36**

Atom	*x*	*y*	*z*
C(1)	1.0342(3)	0.4427(2)	0.6824(4)
C(2)	1.0166(4)	0.3706(2)	0.6064(4)
C(3)	0.8704(4)	0.3392(2)	0.5719(5)
C(4)	0.7182(4)	0.3747(2)	0.6098(4)
C(5)	0.5748(3)	0.4775(2)	0.7226(4)
C(6)	0.5363(3)	0.5400(1)	0.7942(4)
C(7)	0.6420(3)	0.5980(1)	0.8688(4)
C(8)	0.8200(3)	0.5993(1)	0.8667(4)
C(9)	0.9181(3)	0.5498(2)	0.8067(4)
C(10)	0.8834(3)	0.4803(1)	0.7292(4)
C(11)	0.7315(3)	0.4483(1)	0.6929(4)
C(12)	0.5707(3)	0.6548(1)	0.9467(4)
C(13)	0.3936(4)	0.6591(2)	0.9458(4)
C(14)	0.6682(4)	0.7124(2)	1.0355(4)
N(1)	0.2527(3)	0.6610(1)	0.9448(4)
N(2)	0.7497(3)	0.7566(1)	1.1099(4)
O(1)	1.1700(2)	0.4715(1)	0.7052(3)
O(2)	0.5836(3)	0.3454(1)	0.5723(4)

recrystallized from chloroform to give **37** (357 mg, 72% from **35**).

Oxidation of 7-Dicyanomethylene-1,4-dimethoxy-7H-benzocycloheptene **37**.—(*a*) *With aq. CAN.* To a solution of the heptafulvene **37** (100 mg, 0.38 mmol) dissolved in a mixture of acetoninitrile (8 cm^3) and chloroform (16 cm^3) was added dropwise aq. CAN (425 mg, 0.775 mmol) and the resulting solution was stirred for 40 min at room temperature. The solution was diluted with water and extracted with chloroform. The products isolated by the usual method were chromatographed on silica gel (10 g) with benzene–ethyl acetate (95:5 v/v) as the eluent. A blue crystalline product (20.3 mg) and the expected quinone **36** (1.9 mg, 3%) were obtained along with the recovery of starting **37** (32.3 mg, 32%). Blue substance: δ_H(400 MHz, $CDCl_3$) 3.92 (3 H, s), 3.98 (3 H, s), 7.02 (1 H, dd, *J* 10.4), 7.09 (1 H, dd, *J* 9.5), 7.21 (1 H, dd, *J* 9.5), 7.64 (1 H, dd, *J* 10.4); δ_C(100 MHz, $CDCl_3$) 179.4, 157.3, 151.0, 137.5, 137.2, 133.8, 133.4, 124.9, 122.4, 120.5, 116.7, 113.6, 113.1, 56.6, 56.5; ν_{max}(Nujol)/cm^{-1} 2210, 1668, 1605, 1570, 1480, 1400, 1271, 1180, 1078; *m/z* 266 (M^+, 100%), 253 (28), 238 (20), 224 (61).

(*b*) *Solid state oxidation with CAN.* The heptafulvene **37** (125 mg, 0.474 mmol) was thoroughly mixed with powdered CAN (2.28 g, 4.16 mmol) in an agate mortar with an agate pestle. The reaction mixture gradually became hygroscopic and formed a sticky semisolid. The progress of reaction was followed by TLC. After 2 h mixing, the reaction mixture was digested with chloroform and the extract was chromatographed on silica gel to give the quinone **36** (36.9 mg, 33%) along with recovery of **37** (14.7 mg, 12%), **36** m.p. 230 °C (decomp.) (Found: C, 71.4; H, 2.3; N, 11.55%. $C_{14}H_6N_2O_2$ requires C, 71.79; H, 2.58; N, 11.96%); δ_H(400 MHz, $CDCl_3$) 7.65 (2 H, d, *J* 12.2), 7.51 (2 H, d, *J* 12.2), 7.03 (2 H, s); δ_C(100 MHz, $CDCl_3$) 183.7, 160.0, 137.5 (two peaks), 137.2, 133.4, 112.9, 77.2; ν_{max}(Nujol)/cm^{-1} 2220, 1664, 1615, 1291, 1270, 1118; ν_{max}(CH_2Cl_2) 240 (log ε 3.59), 272 (3.75), 292 (3.81), 387 (3.87), 408 (3.65).

Table 7 Selected bond lengths (Å) and angles (°) with esds in parentheses for **22**

C(1)–C(2)	1.466(4)	C(1)–C(9)	1.479(3)
C(1)–O(1)	1.223(3)	C(2)–C(3)	1.324(4)
C(3)–C(4)	1.464(4)	C(4)–C(10)	1.485(3)
C(4)–O(2)	1.216(3)	C(5)–C(6)	1.393(3)
C(5)–C(10)	1.392(3)	C(5)–C(11)	1.503(3)
C(6)–C(7)	1.410(3)	C(6)–O(5)	1.340(3)
C(7)–C(8)	1.386(3)	C(7)–C(13)	1.474(3)
C(8)–C(9)	1.380(3)	C(9)–C(10)	1.405(3)
C(11)–O(3)	1.195(3)	C(11)–O(4)	1.318(3)
C(12)–O(4)	1.450(4)	C(13)–O(6)	1.202(3)
C(13)–O(7)	1.312(3)	C(14)–O(7)	1.463(4)
C(2)–C(1)–C (9)	118.0(2)	C(2)–C(1)–O(1)	120.1(2)
C(9)–C(1)–O(1)	122.0(2)	C(1)–C(2)–C(3)	122.0(3)
C(2)–C(3)–C(4)	122.3(3)	C(3)–C(4)–C(10)	117.8(2)
C(3)–C(4)–O(2)	121.0(2)	C(10)–C(4)–O(2)	121.2(2)
C(6)–C(5)–C(10)	119.7(2)	C(6)–C(5)–C(11)	116.9(2)
C(10)–C(5)–C(11)	123.4(2)	C(5)–C(6)–C(7)	120.2(2)
C(5)–C(6)–O(5)	115.8(2)	C(7)–C(6)–O(5)	123.9(2)
C(6)–C(7)–C(8)	119.1(2)	C(6)–C(7)–C(13)	118.9(2)
C(8)–C(7)–C(13)	122.0(2)	C(7–C(8)–C(9)	121.2(2)
C(1)–C(9)–C(8)	120.3(2)	C(1)–C(9)–C(10)	120.0(2)
C(8)–C(9)–C(10)	119.6(2)	C(4)–C(10)–C(5)	120.2(2)
C(4)–C(10)–C(9)	119.7(2)	C(5)–C(10)–C(9)	120.1(2)
C(5)–C(11)–O(3)	123.2(2)	C(5)–C(11)–O(4)	111.1(2)
O(3)–C(11)–O(4)	125.5(2)	C(7)–C(13)–O(6)	123.0(2)
C(7)–C(13)–O(7)	113.9(2)	O(6)–C(13)–O(7)	123.0(2)
C(11)–O(4)–C(12)	115.9(2)	C(13)–O(7)–C(14)	116.0(2)

Crystal Data for Compound **22**.—$C_{14}H_{10}O_7$, M = 290.23. Monoclinic, a = 8.191(2), b = 16.120(9), c = 10.039(3) Å, β = 102.71(2)°, V = 1293.1(9) $Å^3$ (from 2θ values of 23 reflections, $21 < 2\theta < 26°$). Space group $P2_1/c$, Z = 4, D_c = 1.489, D_m = 1.48 g cm^{-3}, $F(000)$ = 600. Crystal dimensions: 0.25 × 0.4 × 0.45 mm, μ(Mo-Kα) = 1.14 cm^{-1}. Yellow crystals were obtained from benzene by slow evaporation.

Data collection and processing. Rigaku AFC-5 diffractometer, ω–2θ mode with scan width = 1.5 + 0.35 tanθ, scan speed 8 deg min^{-1}, graphite monochromated Mo-Kα radiation, 2546 reflections ($2 < 2\theta < 50°$, index ranges h −9 to 0, k −19 to 0, l −11 to 11), 2277 unique, giving 1645 with $F_o > 3\sigma(F_o)$. At 298 K. No absorption correction.

Structure analysis and refinement. The structure was solved by the direct method (MULTAN78)[22] and refined by block-diagonal least squares (HBLS-V)[23] with anisotropic thermal parameters for non-hydrogen atoms and isotropic ones for the H atoms except H(5), which was constrained. Atomic scattering factors were from ref. 24. All calculations were performed on an ACOS 1000 computer at the Information Processing Center of Kobe University with the UNICS system.[25] The final refinement gave R = 0.0484 and R_w = 0.0570; $w^{-1} = [\sigma^2(F_o) - 0.021\,57\,|F_o| + 0.0185\,|F_o|^2]$; 235 parameters; max. shift/ esd = 0.02, ρ_{max} = 0.16, ρ_{min} = −0.20 e $Å^3$ on final difference Fourier map.

Table 8 Selected bond lengths (Å) and angles (°) with esds in parentheses for **36**

C(1)–C(2)	1.465(4)	C(1)–C(10)	1.500(4)
C(1)–O(1)	1.215(4)	C(2)–C(3)	1.312(5)
C(3)–C(4)	1.469(5)	C(4)–C(11)	1.509(4)
C(4)–O(2)	1.214(4)	C(5)–C(6)	1.345(4)
C(5)–C(11)	1.433(4)	C(6)–C(7)	1.438(4)
C(7)–C(8)	1.446(4)	C(7)–C(12)	1.382(4)
C(8)–C(9)	1.344(4)	C(9)–C(10)	1.435(4)
C(10)–C(11)	1.358(4)	C(12)–C(13)	1.438(4)
C(12)–C(14)	1.433(4)	C(13)–N(1)	1.142(4)
C(14)–N(2)	1.143(4)		
C(2)–C(1)–C(10)	119.4(2)	C(2)–C(1)–O(1)	119.7(3)
C(10)–C(1)–O(1)	120.8(3)	C(1)–C(2)–C(3)	121.3(3)
C(2)–C(3)–C(4)	121.3(3)	C(3)–C(4)–C(11)	119.1(3)
C(3)–C(4)–O(2)	120.2(3)	C(11)–C(4)–O(2)	120.7(3)
C(6)–C(5)–C(11)	131.5(3)	C(5)–C(6)–C(7)	130.5(3)
C(6)–C(7)–C(8)	122.9(2)	C(6)–C(7)–C(12)	118.7(2)
C(8)–C(7)–C(12)	118.4(2)	C(7)–C(8)–C(9)	129.5(2)
C(8)–C(9)–C(10)	132.2(3)	C(1)–C(10)–C(9)	113.9(2)
C(1)–C(10)–C(11)	119.5(2)	C(9)–C(10)–C(11)	126.6(2)
C(4)–C(11)–C(5)	114.0(2)	C(4)–C(11)–C(10)	119.3(2)
C(5)–C(11)–C(10)	126.7(2)	C(7)–C(12)–C(13)	121.7(3)
C(7)–C(12)–C(14)	122.3(3)	C(13)–C(12)–C(14)	115.9(3)
C(12)–C(13)–N(1)	178.6(3)	C(12)–C(14)–N(2)	177.6(3)

Crystal Data for Compound **36**. $C_{14}H_6N_2O_2$, $M = 234.1$. Monoclinic, $a = 8.110(4)$, $b = 18.821(2)$, $c = 7.307(1)$ Å, $\beta = 99.36(2)°$, $V = 1100.5(6)$ Å^3 (from 2θ values of 24 reflections, $20 < 2\theta < 25°$). Space group $P2_1/c$, $Z = 4$, $D_c = 1.414$, $D_m = 1.41$ g cm^{-3}, $F(000) = 480$. Crystal dimensions: 0.01 × 0.4 × 0.5 mm, μ(Mo-Kα) = 0.91 cm^{-1}. Black crystals were obtained from acetonitrile by slow evaporation.

Data collection and processing. Rigaku AFC-5 diffractometer, ω–2θ mode with scan width = 1.2 + 0.35 tanθ, scan speed 4 deg min^{-1}, graphite monochromated Mo-Kα radiation, 2795 reflections ($2 < 2\theta < 55°$, index ranges h 0 to 10, k 0 to 24, l −9 to 9), 2531 unique, giving 1402 with $F_o > 3\sigma(F_o)$. No absorption correction. At 298 K.

Structure analysis and refinement. As for **22**, the final refinement gave $R = 0.0674$ and $R_w = 0.0444$; $w^{-1} = [\sigma^2(F_o) + 0.023\,37\ |F_o| - 0.000\,16|F_o|^2]$; 188 parameters; max. shift/esd = 0.07, $\rho_{max} = 0.20$, $\rho_{min} = -0.22$ e Å^3 on final difference Fourier map.

Molecular structures and numbering of atoms for **22** are shown in Fig. 3 (ORTEP drawing),[26] and those for **36** in Figs. 4 and 5. Atomic coordinates for **22** and **36** are given in Tables 5 and 6. Selected bond lengths for **22** and **36** are listed in Tables 7 and 8. Full crystallographic data are available from the Cambridge Crystallographic Data Center [see Instructions for Authors (1992), *J. Chem. Soc., Perkin Trans. 2*, 1992, issue 1].

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