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SYNTHESIS OF TETRAHYDROXY-1,4-BENZOQUINONE BISCARBONATE AND HEXAHYDROXYBENZENE TRISCARBONATE—NEW ORGANIC CARBON OXIDES

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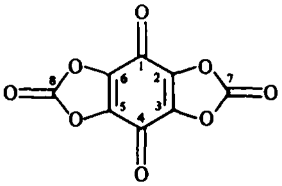
Abstract—Two new organic carbon oxides namely tetrahydroxy-1,4-benzoquinone biscarbonate(**1**) and hexahydroxybenzene triscarbonate(**2**) are reported in this paper, which were isolated as tetrahydrofuran (THF) solvates. Mass spectral and ^{13}C-NMR spectral data of these two compounds are consistent with the structures proposed.

Although organic carbon oxides such as tetrahydroxy-1,4-benzoquinone bisoxalate (**3**) and hexahydrosybenzene trisoxalate (**4**) have been reported, very little work has been carried out in this area.[1,2] The bisoxalate and trisoxalate have been prepared as THF solvates and attempts to desolvate them under reduced pressure have resulted in their decomposition.



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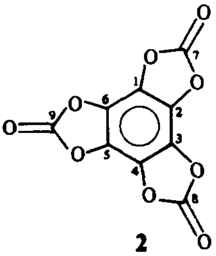

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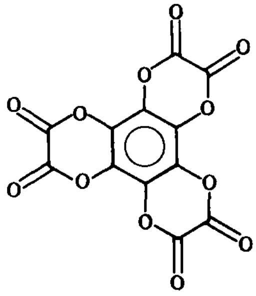

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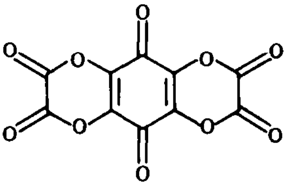

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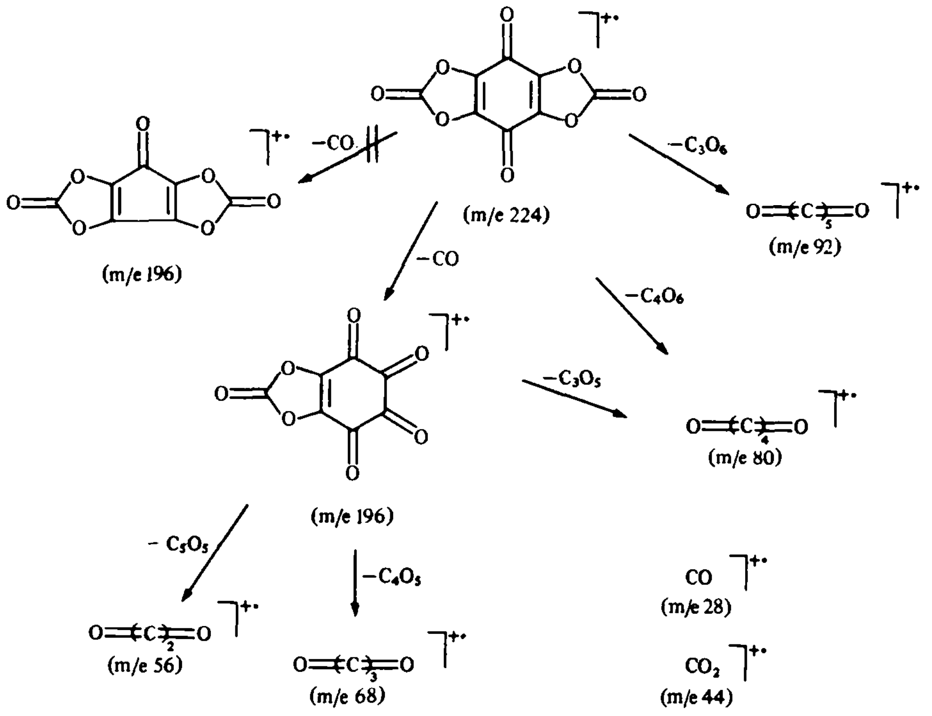
RESULTS AND DISCUSSION

We have prepared the corresponding biscarbonate (**1**) and triscarbonate (**2**) of tetrahydroxy-1,4-benzoquinone (THBQ) and hexahydroxybenzene (HHB) respectively by reacting them with carbonylchloride (phosgene) in THF solutions, hitherto unknown. Tetrahydroxy-1,4-benzoquinone biscarbonate (**1**) was prepared as a THF solvate by refluxing a mixture of THBQ and carbonylchloride (THBQ—$COCl_2$, 1 : 2), in super dry THF. The reaction mixture on concentration and cooling gave bright orange–yellow crystals of **1**. However when the reaction was carried out with a large excess of carbonyl chloride, the crude mixture was found to contain a mixture of **1** and **2** [*m/e* 252 **2** and *m/e* 224 **1**; IR (THF) 1670, 1678 cm^{-1}]. A similar behaviour was also observed in the reaction of THBQ with excess oxalylchloride.[3] The formation of triscarbonate (**2**) and trisoxalate (**4**) when THBQ is reacted with excess carbonylchloride and oxalylchloride respectively, could be via the intermediacy of tetrahydroxy-1,2-benzoquinone. The latter could be formed by a prototropic shift of THBQ. The driving force for the formation of **2** and **4** from THBQ in the presence of excess of these reagents, is the stability conferred by the benzene ring.

Hexahydroxybenzene triscarbonate (**2**) was prepared as a white solid by refluxing a mixture of HHB and excess carbonyl chloride in dry THF. The carbon oxides (**1** and **2**) are extremely sensitive to heat and moisture. On heating they darken and decompose at 45–53° with brisk evolution of gas.

The electron impact mass spectra of **1** and **2** are interesting in that fragmentation occurs by loss of CO and CO_2. A significant feature of the spectra is that no metastable peaks were detected. Metastable studies were unsuccessful due to the instability of these compounds to heat. The mass spectrum of **1** showed a weak molecular ion peak at *m/e* 224 (12% of the base peak at *m/e* 28). The occurrence of base peak at *m/e* 28



Scheme 1.

(CO) and fairly intense peak at *m/e* 44 (CO_2, 55%) suggests that loss of CO and CO_2 is of considerable importance in the fragmentation pattern. Mass spectral behaviour of monocyclic polyoxoenediols[4] has revealed that the characteristic feature of the fragmentation of these compounds is the elimination of CO, followed by ring contraction to yield the next lower member of the series. However the loss of CO from the molecular ion of **1** appears to favour the formation of the carbonate of rhodizonic acid (**5**) rather than cyclopentadienone biscarbonate (**6**). The latter is unlikely since the C—O bond is more labile than the C—C bond. The presence of intense peaks at *m/e* 92 (100%), 80 (62%), 68 (65%) and 56 (50%) are probably due to "diketene" type of fragments [$O{=}(C)_n{=}O$, where $n = 5, 4, 3$ etc.] and can be explained by the fragmentation pattern depicted in Scheme 1.

The mass spectra of the triscarbonate differs from that of the biscarbonate in that it gives an intense molecular ion peak at *m/e* 252 (82% of the base peak at *m/e* 28). Loss of CO_2 from the molecular ion to form an oxirene type of fragment (**7**) appears to be more favoured (*m/e* 208, 20%) than the loss of CO. The general fragmentation pattern of triscarbonate is otherwise similar to that of biscarbonate and the probable fragmentation pathway is represented in Scheme 2.

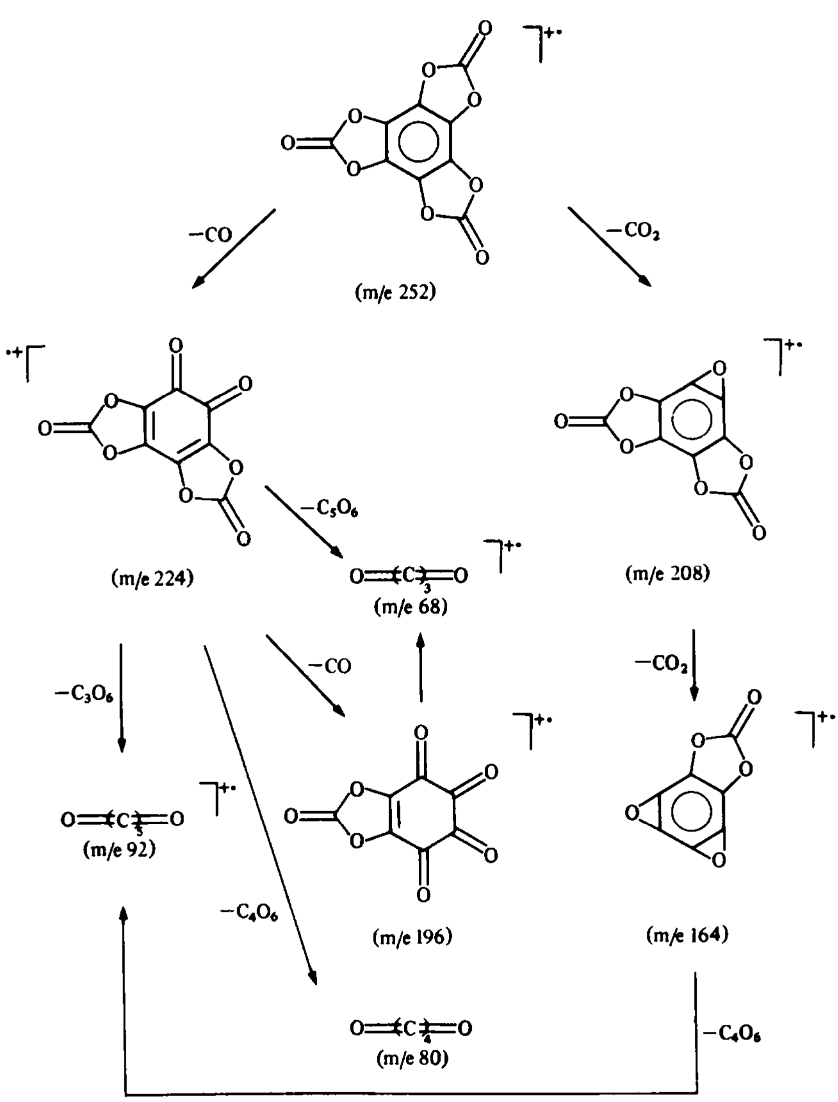
Even though there are no metastable peaks to substantiate the fragmentation pattern presented nevertheless by comparing the fragmentation patterns of stable carbonates such as catechol carbonate (Scheme 3) and ethylene carbonate (Scheme 4), schemes 1 and 2 appear to be the most likely fragmentation pathways for **1** and **2**.

The ^{13}C-NMR spectra of the two new carbon oxides (**1** and **2**) gave further evidence for their respective structures. The solvents used were carefully dried to prevent not only the decomposition of the carbon oxides, as these are very sensitive to moisture but also the hydration of CO groups.[5] The chemical shifts (ppm) of **1** and **2** are shown in Table 1. Compound **1** gave three peaks as expected. If however the biscarbonate of 1,2-benzoquinone is formed by prototropic shift, then this compound should give four peaks instead of the three peaks observed. The ^{13}C-NMR spectrum of **2** gave two peaks, consistent with the proposed structure.

The organic carbon oxides such as the oxalyl and carbonate derivatives of THBQ and HHB represent a class of compounds with a general formula C_nO_n (where $n = 12, 10, 9, 8$). This series could be extended by preparing the oxalyl and carbonate derivatives of other cyclic poly oxoenediols like rhodizonic, croconic and squaric acids. However, attempts to synthesize these carbon oxides were unsuccessful even when anhydrous pyridine and aluminium chloride were used as catalysts. Hexahydroxy-1,4-naphthoquinone (spinochrome-E) is another potential substrate to prepare organic carbon oxides of the type C_nO_{n-2}. Repeated attempts to synthesize spinochrome-E by the method reported in the literature[6] were unsuccessful.

Table 1. ^{13}C-NMR chemical shifts of compounds **1** and **2**

Carbon No.	δ (ppm)
Compound **1**	
(1) C(1), C(4)	169.3
(2) C(7), C(8)	153.7
(3) C(2), C(3), C(5), C(6)	133.4
Compound **2**	
(1) C(7), C(8), C(9)	154.8
(2) C(1)–C(6)	124.7



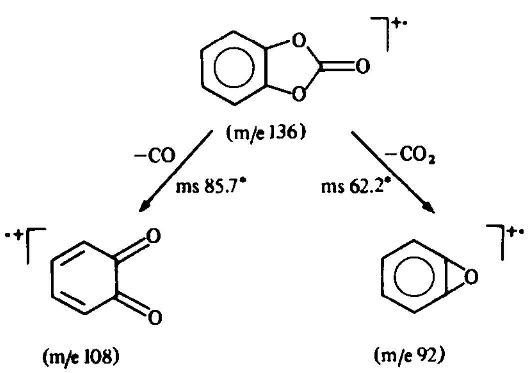
Scheme 2.

EXPERIMENTAL

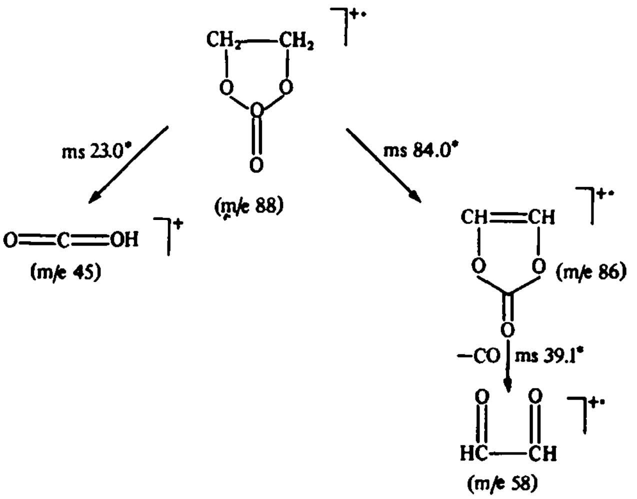
Most of the reagents and chemicals used were of reagent grade purified by recrystallization or distillation as appropriate. Whenever necessary "Analar" reagents were used. THF was dried by refluxing over $LiAlH_4$ for 3–5 days and distilled immediately prior to use. A solution of carbonyl chloride ($COCl_2$) in dry THF was prepared by passing $COCl_2$ into THF for 10–15 hr. IR and UV/visible were recorded for solns in dry THF, using Perkin–Elmer 457 and SP-800 spectrometers respectively. Mass spectra were recorded on an AE-1 MS902 and VG 70-70 spectrometers using direct insertion probe at temps 50°, 100° and 150° and the spectra were recorded at high chart speed. Best results were obtained at 100°. ^{13}C-NMR spectra were recorded on a Varian XL-100-12FT spectrometer for solns in dry THF-d_8 using C_6D_6–TMS as external standard. Elemental analyses were carried out by Butterworth micro analytical laboratory, Teddington, U.K. and micro analytical services at University of Nottingham.

Preparation of tetrahydroxy-1,4-benzoquinone biscarbonate

Tetrahydroxy-1,4-benzoquinone (1.57 g, 9.13×10^{-3} moles) in dry THF (25 cm^3) and a soln of $COCl_2$ (2.11 g, 2.15×10^{-2} moles) in dry THF (50 cm^3) were refluxed for 12.5 hr and the orange–yellow mixture was filtered while hot using an enclosed filter. The filtrate was concentrated by distillation under anhyd conditions, to 25 ml. Bright orange–yellow crystals of 1 were obtained on cooling and recrystallization from THF. The biscarbonate thus prepared was dried under reduced pressure (0.1 Torr) at 25° for 10 hr and found to be a

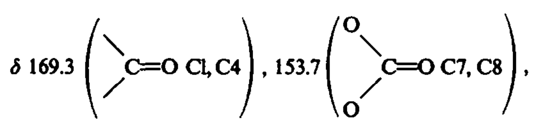


Scheme 3.



Scheme 4.

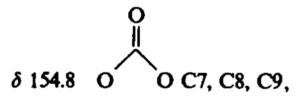
THF solvate (0.87 g, 42.6%), m.p. 45–46° (d); Elemental analysis, Found; C, 48.73, H, 2.94%; Expected for C_8O_8 (0.95 THF), C, 48.42, H, 2.60%; IR (THF) 1662, 1685, 1805, 1820 cm^{-1}; λ max (THF) 223(i), 286 nm (log ε 3.82, 3.89). ^{13}C-NMR (100 mg in 2 cm^3 THF-d_8; C_6D_6, TMS (external std):



133.4 (C=C C2, C3, C5, C6) ppm. M$^{+\cdot}$224 (12%), *m/e* 196 (23%), 92 (100%), 80 (62%), 56 (17%), 44 (55%), 28 (100%).

Preparation of hexahydroxybenzene triscarbonate

HHB[7] (1.95 g, 1.12 × 10^{-2} moles) in dry THF (20 ml) and a soln of $COCl_2$ (3.62 g, 3.70 × 10^{-2} moles) in dry THF (50 cm^3) were refluxed for 8 hr under anhyd conditions and the pale yellow mixture was filtered while hot. White crystals of hexahydroxybenzene triscarbonate were isolated in a manner similar to that described for the biscarbonate (1.33 g, 47.2%), m.p. 51–53° (d); Found; C, 53.01, H, 4.77%; Expected for C_9O_9 2.35 THF, C, 52.42, H, 4.46%; IR (THF) 1835, 1847 cm^{-1}; λ max (THF) 259, 317 nm (log ε 3.85, 3.74); ^{13}C-NMR (120 mg in 2.5 cm^3 THF-d_8; C_6D_6, TMS external std):



124.7 ppm (C=C aromatic); M$^{+\cdot}$(*m/e* 252, 82%), *m/e* 224 (3%), 208 (20%), 196 (35%), 164 (37%), 92 (100%), 80 (60%), 68 (75%), 56 (63%), 44 (65%), 28 (100%).

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