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Synthesis and mass spectral fragmentations of new spiro heterocycles

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Abstract

The reaction of dichlorodiphenoxymethane (**2**) with *ortho*-functionlized benzoic acids **1a–c** yielded the spiro derivatives of bezodioxinone **4a**, benzoxazinone **4b** and benzodioxepinone **4c**. The same reaction with 1,8-diaminonaphthalene afforded the spiro perimidine **6**, while with 1,1′-binaphthyl-2,2′-diol gave the semi-cyclized derivative 2,2-diphenoxydinaphthodioxepine **8**.

Keywords: Spiroorthocarbonate; Azaspiro compounds; Oxaazaspiro compounds

Spiroorthocarbonates (SOCs) and related compounds have received a great deal of attention as monomers since on polymerization undergo minimal shrinkage [1–3]. These monomers are highly desirable in the field of materials such as dental fillings, high strength composites, precision castings and adhesives [4–7].

The synthetic routes to SOCs are varied and mainly consist of organotin compounds. Sakai et al. reported a novel multi-step synthesis of SOCs from organotin derivatives and carbone disulfide [8,9], while a group of other workers prepared SOCs by utilizing tetraalkylorthocarbonates and diols in the presence of *p*-toluenesulfonic acid as an acid catalyst [10]. Other approaches mainly involve cyclocondensation of diols with thiophosgene [11] or with dichlorodiphenoxymethane [12].

As an entry into the synthesis of new spiro heterocycles analogues of SOC, we have utilized the latter compound as a suitable quadro-functional electrophilic reagent.

Our synthesis of the spiroorthocarbonates (SOCs) **4a–c** is shown in Scheme 1. We envisioned that nucleophilic displacement of the chlorine atoms in dichlorodiphenoxymethane (**2**) with *ortho*-functionalized benzoic acids **1a–c** should afford an intermediate **3** which was on further reaction with the second molecule of **1a–c** would provide the desired SOCs analogues **4a–c**, respectively.

2,2′-Spirobi[benzo][1,3]dioxine-4-one (**4a**) was obtained in 47% yield by treatment of salicylic acid (**a**) with dichlorodiphenoxymethane (**2**) in dichloromethane and pyridine. The structure of cyclized product was confirmed by spectral and analytical data. In the ^{1}H NMR spectrum, a multiplet at δ 7.3 ppm is assignable to the protons of the phenyl nuclei. The IR spectrum exhibited two characteristic absorption bands at ν 1750 and 1150 cm^{-1} belonging to C=O and C–O stretching vibrations, respectively. The mass spectrum showed the expected molecular ion peak at 284.

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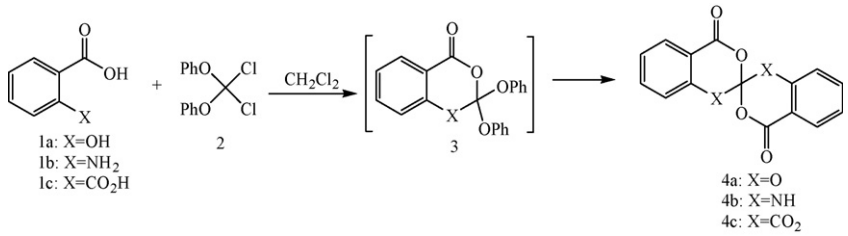
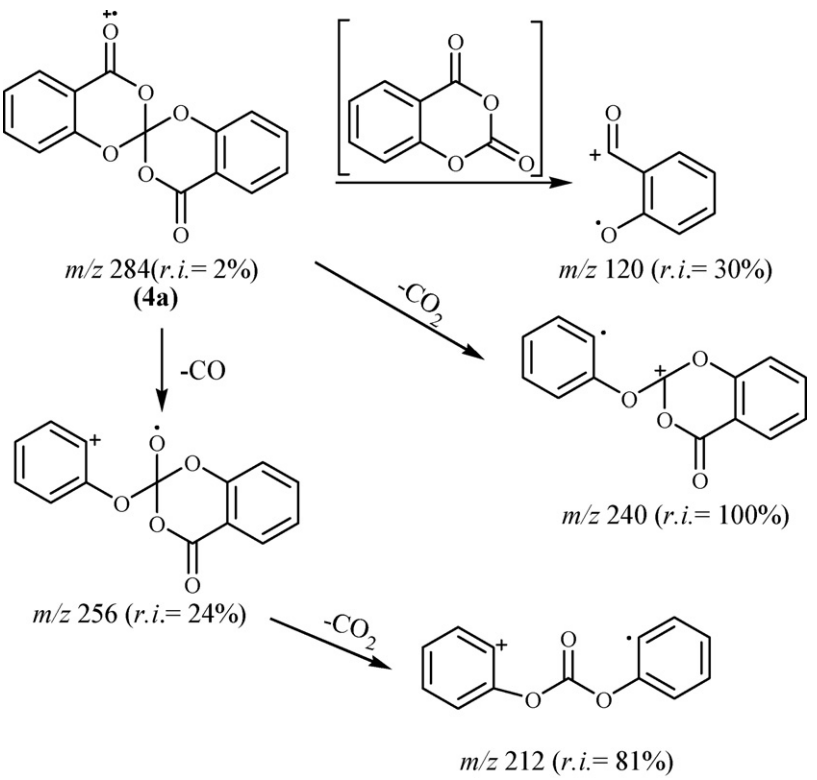


Scheme 1.

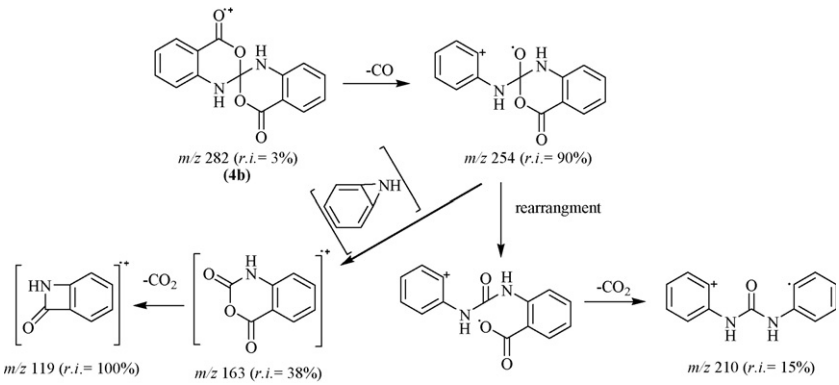
The fragmentation pattern of the product under electron impact ionization (Scheme 2) is in accordance with the proposed structure. All these data plus the microanalytical data strongly support the formation of the spiro compound **4a**.

Repeating the reaction of **2** with anthranilic acid (**1b**) led again to a spiro compound which was identified as **4b** on the basis of its IR, ^{1}H NMR and mass spectral analysis. The IR spectrum showed absorption bands at 3350 and 3050 cm^{-1} assignable to N–H and C–H stretching vibrations of the phenyl nuclei, and two bands at 1670 and 1250 cm^{-1} pertaining to C=O and C–H stretching vibrations, respectively. The ^{1}H NMR exhibited signals belonging to benzene ring hydrogens as a multiplet at 7.4–8.0 ppm, and a singlet at δ 10.5 ppm related to NH hydrogen which was removed on deuteration. The mass spectrum showed the expected molecular weight (M^+ = 282) and confirms the loss of the two molecules of HCl and phenol during cyclization. The fragmentation pattern of the product is indicative of the proposed structure to **4b** (Scheme 3).

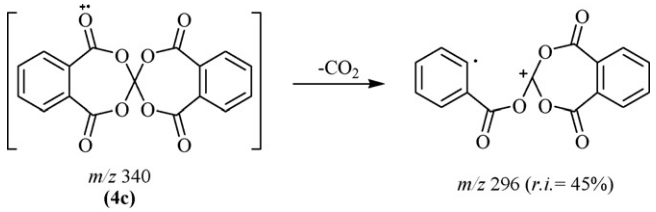
The reaction of **2** with phthalic acid (**1c**) gave a product which was identified as compound **4c**, according to its spectral data. This compound which can be easily hydrolysed in acid media, did not show the molecular ion peak at *m/z* 340 in its mass spectrum but instead showed a peak at *m/z* 296 which resembles the loss of a molecule of CO_2 from the molecular ion as shown in Scheme 4.



Scheme 2.



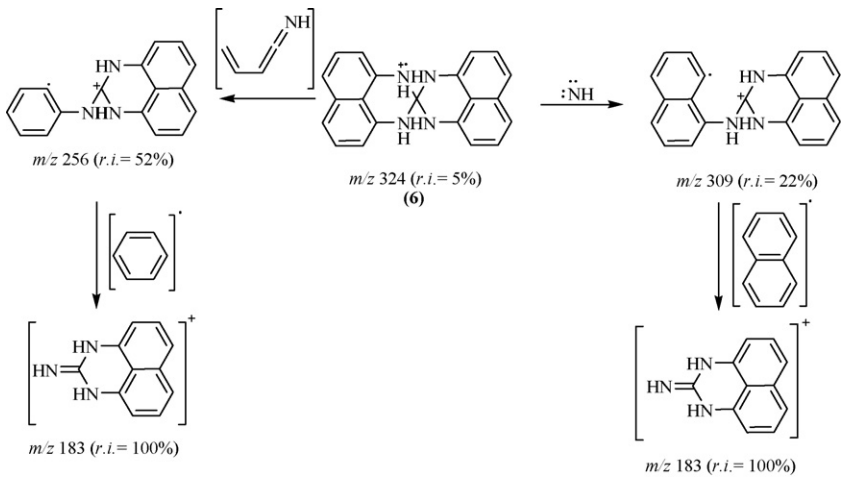
Scheme 3.



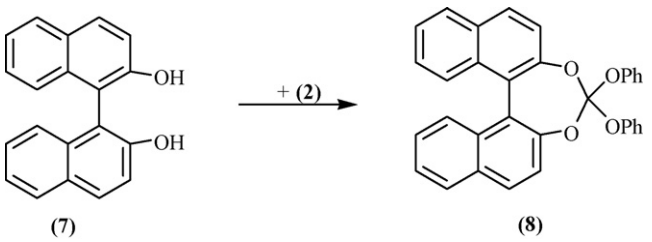
Scheme 4.

Treatment of **2** with 1,8-diaminonaphthalene (**5**) gave the spiro compound **6**. The structure of this compound was confirmed from analytical data. The ^{1}H NMR spectrum exhibited signals assignable to γ hydrogen of the aromatic ring at 6.5 ppm (^2J = 8 Hz). A multiplet at δ 7.1 ppm belonging to the other aromatic ring hydrogens and the protons of four NH groups at δ 10.0 ppm which were removed on deuteration. The IR spectrum showed an absorption band at 3400 cm^{-1} assignable to NH groups, and two absorptions bands at 3060 and 1300 cm^{-1} attributed to C–H and C–N stretching vibrations. The fragmentation pattern of this compound is in accord with the designated structure (Scheme 5).

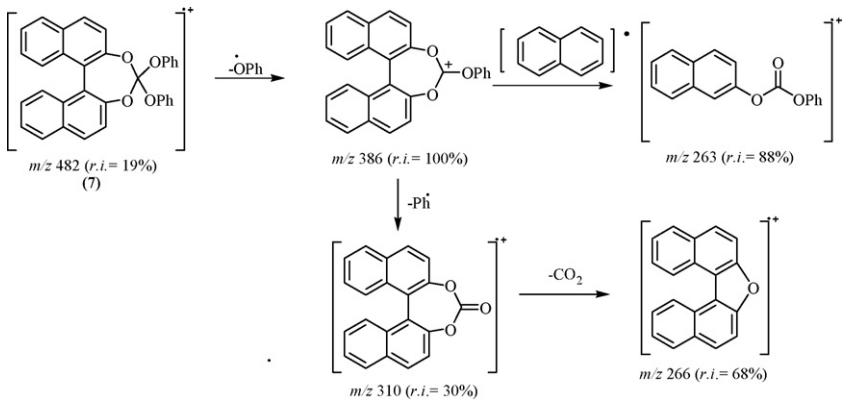
Unexpectedly, the reaction of **2** with 1,1′-binaphthyl-2,2′-diol (**7**) which was prepared in our laboratory according to the literature [13] did not go to completion and only gave the semi-cyclized product **8** (Scheme 6).



Scheme 5.



Scheme 6.



Scheme 7.

The absence of the OH stretching vibration in the IR spectrum of this compound, the appearance of the C–O vibration band at 1110 cm^{-1} plus a molecular ion peak at *m/z* 482 and the mass fragmentation pattern of this compound (Scheme 7) clearly confirm the formation of compound **8**.

1. Experimental

Melting points were recorded on an Electrothermal type 9100 melting point apparatus. The IR spectra were obtained on a 4300 Shimadzu spectrometer. The ^1H NMR (100 MHz) spectra were recorded on a Bruker AC l00 spectrometer. The mass spectra were scanned on a Varian Mat CH-7 instrument at 70 eV. Elemental analysis was performed on a Thermofinnigan Flash EA 1112 microanalyzer.

*1.1. General procedure for the preparation of spiro heterocycles **2a–c**, **6** and **8***

A solution of each compound **2a–c** (20 mmol) was prepared in CH_2Cl_2 (30 mL) and pyridine (40 mmol) was a basic catalyst. Then a solution of compound **2** (10 mmol) in CH_2Cl_2 (10 mL) was added dropwise at room temperature while stirring vigorously under an atmosphere of nitrogen. Stirring was continued for 6 h. The reaction mixture was washed with water (20 mL), then saturated sodium sulphate solution (2 mL × 40 mL) and finally, water (2 mL × 40 mL). The organic layer was dried over anhydrous sodium sulphate and after the solvent was evaporated, the residue was recrystallized from ethyl acetate. For compound **6** and **8**, the amounts are like the procedure of compound **2a–c**, but the refluxing condition was applied, the organic layer was washed with 2% NaOH solution (2 mL × 40 mL), and the residue was recrystallized from a suitable solvent as mentioned bellow.

*1.2. 2,2′-Spirobi[benzo][1,3]dioxine-4-one (**4a**)*

Reaction of salicylic acid (**1a**) with dichlorodiphenoxymethane (**2**): yield (47%), mp: 56–58 °C, ^1H NMR (100 MHz, $CDCl_3$, δ ppm): 7.3 (m, 8H, aromatic hydrogens). IR (KBr disc) ν 3100, 1750, 1600, 1510, 1250, 1150 cm^{-1}, EIMS *m/z* 284. Anal. Calcd. for $C_{15}H_8O_6$:C, 63.39; H, 2.84. Found: C, 63.50; H, 2.89.

*1.3. 2,2′-Spirobi[1,2-dihydro-4H-3,1-benzoxazine-4-one] (**4b**)*

Reaction of anthranilic acid (**1b**) with dichlorodiphenoxymethane (**2**): yield (55%), mp: 92–93 °C, ^{1}H NMR (100 MHz, $CDCl_3$, δ ppm): 7.4–8.0 (m, 8H, aromatic hydrogens), 10.5 ppm (s, 2H, NH). IR (KBr disc) ν 3350, 3050, 1670, 1600, 1510, 1450, 1250 cm^{-1}, EIMS *m/z* 282. Anal. Calcd. for $C_{15}H_{10}N_2O_4$:C, 63.83; H, 3.57, N, 9.92. Found: C, 63.78; H, 3.51, N, 9.81.

*1.4. 3,3′-Spirobi[2,4-benzodioxepine-1,5-dione] (**4c**)*

Reaction of phthalic acid (**1c**) with dichlorodiphenoxymethane (**2**): yield (40%), mp: 71–73 °C, ^{1}H NMR (100 MHz, $CDCl_3$, δ ppm): 7.1 (m, 8H, aromatic hydrogens), IR (KBr disc) ν 3090, 1750, 1590, 1480, 1250, 1170 cm^{-1}, EIMS *m/z* 340 not found. Anal. Calcd. for $C_{17}H_8O_8$:C, 60.01; H, 2.37. Found: C, 59.92; H, 2.25.

*1.5. Spirobi[2,3-dihydro-1H-perimidine] (**6**)*

Reaction of 1,8-diamininaphthalene (**1d**) with dichlorodiphenoxymethane (**2**): recrystallization solvent, ethanol:water (90:10), yield (53%), mp: 170 °C (decomposed), ^{1}H NMR (100 MHz, DMSO-d_6, δ ppm): 6.5 (4H, γ hydrogens) 7.1 (m, 8H, α and β hydrogens) 10.0 (s, 4H, NH). IR (KBr disc) ν 3400, 3060, 1600, 1570, 1300 cm^{-1}, EIMS *m/z* 324. Anal. Calcd. for $C_{21}H_{16}N_4$:C, 77.76; H, 4.97; N, 17.27. Found: C, 77.62; H, 4.91; N, 17.13.

*1.6. 2,2-Diphenoxydinaphtho[2,1-d:1,2-f][1,3]dioxepine (**8**)*

Reaction of 1,1′-binaphthyl-2,2′-diol (**1e**) with dichlorodiphenoxymethane (**2**): recrystallization solvent: toluene, yield (70%), mp: 231 °C, ^{1}H NMR (100 MHz, $CDCl_3$, δ ppm): 7.3–7.9 (m, aromatic hydrogens). IR (KBr disc) ν 3070, 1590, 1510, 1220, 1110 cm^{-1}, EIMS *m/z* 482. Anal. Calcd. for $C_{33}H_{22}O_4$:C, 82.14; H, 4.60. Found: C, 82.03; H, 4.57.

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