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Oxalyl Chloride as a One and Two Carbon Synthon.
A Cyclic Carbonate with a Tetraoxa[3.3.3]propellane Skeleton.

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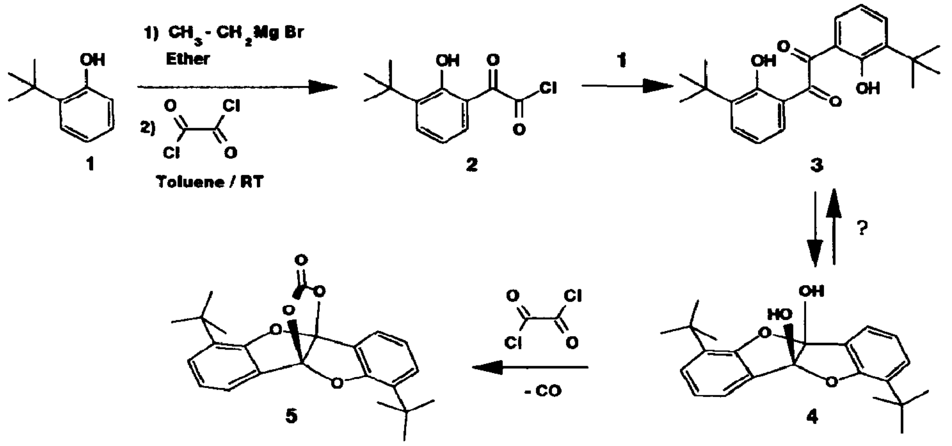
Abstract: The chelation-directed reaction of bromomagnesium-2-*tert*-butylphenolate with oxalyl chloride yields the pentacyclic carbonate **5** along with the expected glyoxalyl chloride **2**. Oxalyl chloride serves both as a C-acylation and esterification reagent.

Derivatives of 2-hydroxyarylglyoxylic acid can be prepared from the bromomagnesium salts of phenols by regiospecific reaction with oxalyl chloride at room temperature [2]. Since the 2-hydroxybenzoyl group is found in the structure of commercial UV absorbers such as the 2-hydroxybenzophenones [3], we were interested in using these glyoxylic compounds as intermediates. In our hands, however, the reported yields of esters were difficult to reproduce [4], which led us to investigate the by-products of the reaction. We wish to report the isolation of one of them, the cyclic carbonate **5**, for which we propose the following reaction scheme (Scheme 1):

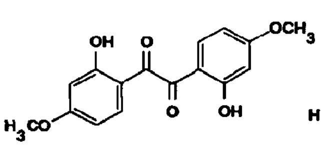


Scheme 1

The formation of the diacylated compound **3** is favoured under the conditions of ref.[2] by the excess of **1** present in the mixture. Double ketalization leads to the diol **4**. Trapping by oxalyl chloride followed by decarbonylation affords the cyclic carbonate **5**. The isolated yield of **5** was 8-13%, which rules out the esterification by traces of phosgene contained in the oxalyl chloride [5]. Similar cyclocondensations with acyclic 1,2-diols have been described recently [6]. The structure **5** was established by spectroscopic and chemical analysis [7]. The bridgehead carbons exhibit a signal at 93.0 ppm, and the C=O a signal at 157.4 ppm (the double IR band at 1820 and 1840 cm^{-1} is in good agreement with the spectrum of ethylene carbonate). The diol **4** was not identified. No trace of a cyclic oxalate formed from **4** could be detected [8].

In the absence of steric hindrance in the 2-position, no cyclization was observed. For instance, resorcinol monomethylether gave **6** [9] (17-25%) as the main by-product, which is consistent with scheme 1, but no cyclic carbonate. The expected ester **7** was obtained in 25-34% yield.

Quenching the intermediate chloride **2** with 2-propanol (50°C, 8 h) afforded the known ester **8**[1] in 37 % yield, but this is a slow process, since analogous quenching by methanol at RT (3h) led to the isolation of the corresponding acid (60-70%) formed by hydrolysis during the subsequent work-up, with only traces of the methyl ester [10]. Replacing oxalyl chloride by oxalyl monochloride monoethylester did not yield the arylglyoxylic ester, but the mixed oxalate **9** in 75% yield.



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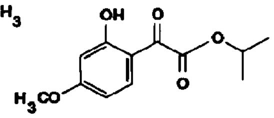

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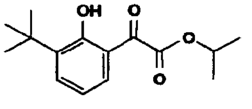

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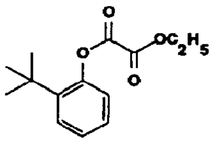

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The 2,4,6,9-tetraoxatricyclo[3.3.3.$0^{1,5}$]undecane skeleton of **5** was hitherto unknown. There are few reports of furo[3,2-b]furan derivatives featuring the *cis*-diol group of **4** at the ring junction [11].

References and notes

1. Diploma student, on leave from the Ecole Nationale Supérieure de Chimie de Mulhouse, Mulhouse, France, spring 1994.
2. Bigi, F.; Casiraghi, G.; Casnati, G.; Sartori, G. *J. Chem. Soc. Perkin Trans. I*, **1984**, 2655-2657.
3. Gugumus, F. Light stabilizers. In, *Plastics Additives Handbook*; Gächter, R.; Müller, H.; Klemchuk, P. P. Eds.; Hanser Verlag: Munich, 1990; pp. 129-270.
4. Reactions were run under argon atmosphere, using commercially available anhydrous solvents (Fluka).
5. Moreover, an example of the low reactivity of phosgene towards a glycol has been reported [6].
6. Iida, T; Itaya, T. *Tetrahedron*, **1993**, *49*, 10511-10530.
7. Compound **5**. Colorless crystals, mp 204-205 °C (AcOEt); ^1H NMR ($CDCl_3$) δ 1.38 (s, 18 H), 7.10 (t, 2H), 7.34 (d, 2H), 7.47 (d, 2H); ^{13}C NMR ($CDCl_3$) δ 29.1, 34.4, 93.0, 122.6, 123.1 124.2 129.6, 135.7, 151.1, 157.4; IR (KBr) ν_{max} cm^{-1} 1820, 1840; MS (CI, *iso*-butane) *m/z* 381 (MH^+); Anal. Calcd. for $C_{23}H_{24}O_5$: C 72.59; H 6.36. Found: C 72.38, H 6.46.
8. Such an oxalate is expected to be unstable [6].
9. Van Allan, J. A. *J. Org. Chem.*, **1958**, *23*, 1679-1682.
10. To optimize the yields, G. Sartori suggests to add absolute THF to the reaction mixture containing the acid chloride, followed by an excess of lithium alcoholate in the corresponding alcohol at 0°C (G. Sartori, personal communication).
11. Krueger, H. R.; Weyerstahl, P.; Marschall, H.; Nerdel, F. *Chem. Ber.* **1972**, *105*, 3553-3565. Krueger, H. R.; Marschall, H.; Weyerstahl, P.; Nerdel, F. *Chem. Ber.* **1973**, *106*, 91-104. Kuszmann, J.; Medgyes, G.; Jerkovics, G. *Carbohydr. Res.* **1987**, *164*, 459-464. Angyal, S. J.; Craig, D. C.; Kuszmann, J. *Carbohydr. Res.* **1989**, *194*, 21-29.

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