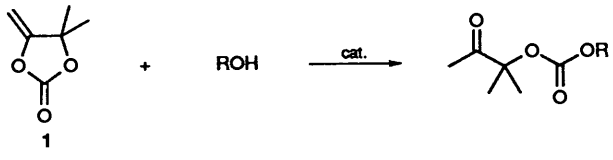
Direct Access to β-Oxopropyl Carbonates from Bulky Alcohols

Jean Marc Joumier, Christian Bruneau and Pierre H. Dixneuf*
Laboratoire de Chimie de Coordination Organique, URA CNRS 415, Campus de Beaulieu, Université de Rennes, 35042 Rennes, France

Cyclic α-methylene carbonates react with bulky alcohols in the presence of catalytic amounts of either 2-hydroxypyridine and potassium cyanide or DBN to give β-oxopropyl carbonates.

Functional unsaturated carbonates are of interest as useful reagents in synthesis or as monomers for the preparation of transparent polymers.[1] Allyl[2] and prop-2-ynyl[3] carbonates are commonly used for the generation of organic allyl and allenyl intermediates *via* decarboxylation by palladium(0) catalysts under mild conditions, whereas dienyl carbonates are active Diels–Alder dienes.[4] The potential of β-oxopropyl carbonates has recently been shown for selective access either to (*E*)-α-enones,[5] or to ketonic cyclopropane derivatives[6] by catalytic activation with palladium(0) complexes. β-Oxopropyl carbonates are usually obtained from chloroformates,[7] by catalytic oxidation of allyl carbonates,[8] or by addition of alcohols to the α-methylene carbonate **1**, prepared in one step from prop-2-ynyl alcohol derivatives and carbon dioxide.[9] However, the latter method, based on triethylamine and potassium cyanide catalysis, is restricted to primary, secondary and non-sterically hindered alcohols. We now report two ways to generate unsymmetrical β-oxopropyl carbonates from **1** and bulky or tertiary alcohols.



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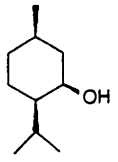
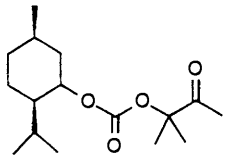
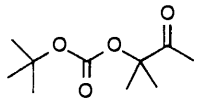
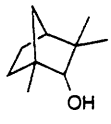
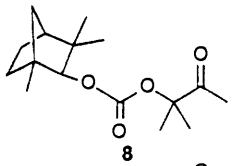
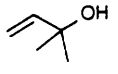
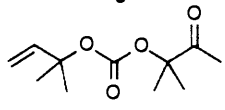
Results and Discussion

Ghosh *et al.*[10] have recently shown that di(2-pyridyl) carbonate reacts with hindered alcohols and that the resulting mixed 2-pyridyl carbonate, on reaction with amines, affords functional carbamates and releases 2-hydroxypyridine. We have adapted this reactive 2-pyridyl carbonate concept to produce bulky β-oxopropyl carbonates from 2-hydroxypyridine and the carbonate **1**. In fact, 1 equiv. of 2-hydroxypyridine **10** does not appear to react with the carbonate **1**, even in the presence of KCN. However, in the presence of both 2-hydroxypyridine (1 mmol) and KCN (1 mmol), the carbonate **1** (20 mmol) reacted with menthol **2** (10 mmol) in ethyl acetate at room temperature to give a 58% isolated yield of the carbonate **6** after 40 h. When the reaction was carried out at 60 °C for 16 h, an 88% isolated yield (95% VPC yield) of **6** was obtained (Table 1).

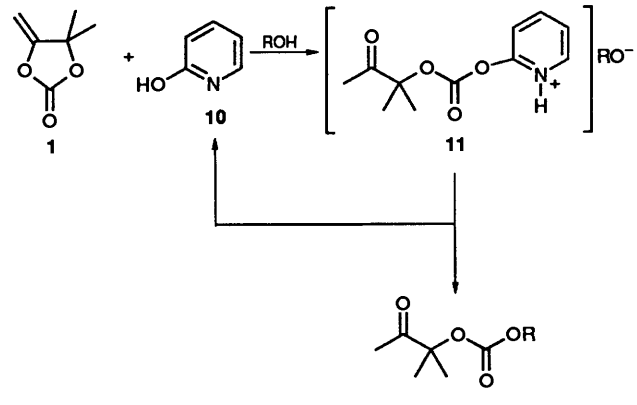
Under similar conditions, sterically hindered *tert*-butyl alcohol **3** and fenchyl alcohol **4**, respectively, gave 78 and 50% yields of carbonates **7** and **8**. Although the method of access to carbonates is efficient, the formation of **6** and **8** took place with partial racemization (d.e. = 87 and 82% respectively). The formation of these latter carbonates can be explained by the addition of the bulky alcoholate to the reactive mixed intermediate β-oxopropyl-2-pyridyl carbonate **11**, in a reaction similar to that of di(2-pyridyl) carbonate[10] (Scheme 1).

We have studied an alternative route to carbonates based on the generation of alcoholates from bulky secondary and tertiary

Table 1 β-Oxopropyl carbonates from tertiary and hindered alcohols and carbonate **1**[a]

Alcohol	Carbonate	Conditions	Yield (%)
 **2**	 **6**	I 60 °C 16 h	88[b] (95)[c]
2	**6**	II 20 °C 4 h	95[b]
 **3**	 **7**	I 60 °C 12 h	78[b]
 **4**	 **8**	I 60 °C 26 h	50[b]
 **5**	 **9**	II 20 ° 60 h	(60)[c]

[a] *General conditions:* **I**, carbonate **1** (20 mmol), alcohol (10 mmol), EtOAc (5 cm^3), KCN (1 mmol), 2-hydroxypyridine (1 mmol); **II**, carbonate **1** (8 mmol), alcohol (4 mmol), DBN (4 mmol).[b] Isolated yield based on the alcohol. [c] Yield determined by VPC.

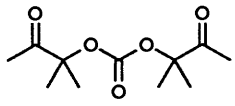


1 **10** **11**

Scheme 1

alcohols, by the more basic 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) in the presence of the carbonate **1**. Thus, in the presence of 1 equiv. of DBN, menthol **2** (1 equiv.) reacted with the carbonate **1** (2 equiv.) in the absence of solvent, to give the carbonate **6** in 95% yield (Table 1), after only 4 h at room temperature. However, though the reaction was much faster, a similar partial racemization took place.

Because the formation of carbonates from tertiary allylic alcohols is difficult to achieve, except in the presence of *both* chloroformate and lithium alcoholate,[11] we have treated alcohol **5** with the carbonate **1** in the presence of DBN. After 60 h at 20 °C, the carbonate **9** was formed in 60% yield and the parallel formation of the carbonate **12** was observed. The formation of



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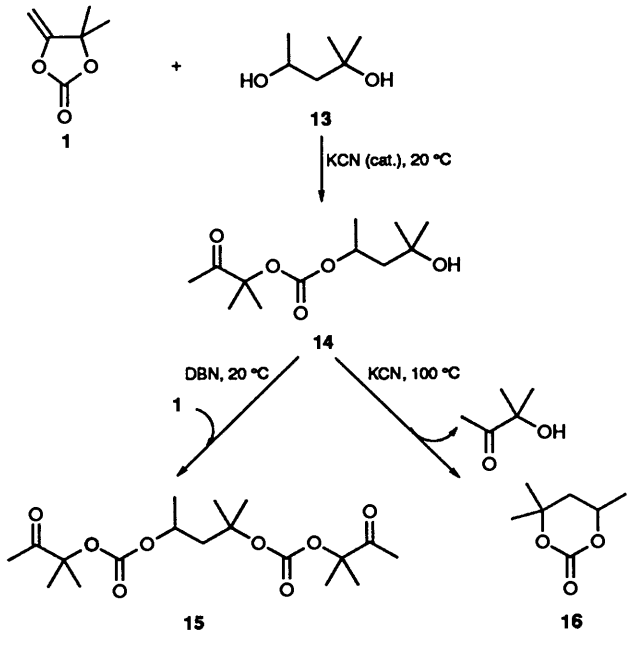
the symmetrical carbonate **12** resulted from the opening of carbonate **1** by traces of water in the presence of DBN, to afford 3-hydroxy-3-methylbutan-2-one which gave a subsequent addition to carbonate **1**.

The carbonation of mixed secondary and tertiary diols could be achieved selectively (Scheme 2). The secondary hydroxy group of the diol **13** was first carbonated using conditions specific to non-sterically hindered alcohols,[9] by reaction of the carbonate **1** in the presence of KCN at 20 °C and led to the carbonate **14** in 70% yield. The mixed hydroxy carbonate **14** was further treated with the carbonate **1** under the conditions required for the addition of tertiary alcohols, and the unsymmetrical biscarbonate **15** was thus obtained in 94% yield



Scheme 2

in the presence of DBN at 20 °C. When the carbonate **14** was heated at 100 °C for 20 h with a catalytic amount of KCN (5%), the cyclic carbonate **16**, resulting from intramolecular transcarbonation, was isolated in 70% yield.

Conclusion

The above results significantly broaden the scope of formation of functional carbonates as it is now possible to prepare selectively β-oxopropyl carbonates from bulky and tertiary alcohols and diols, and this opens the use of carbonates for organic synthesis and polymerization.

Experimental

On a Bruker AC 300 WPB spectrometer (*J* values in Hz) ^{1}H NMR spectra were recorded at 300 MHz and IR spectra were recorded on a Nicolet 205 FTIR spectrometer. Vapour phase chromatography was performed with a Hewlett Packard HP5890 Serie II chromatograph. A 30 m capillary column coated with FFAP and heated from 90 to 220 °C min^{-1} was used. Mass spectra were performed with a Varian Mat 311 at the CRMPO, Rennes (France) and elemental analyses were carried out by the CNRS, Vernaison (France).

Alcohols **2–5** and **13** were commercially available and used without further purification, and carbonate **1** was prepared from carbon dioxide and 2-methylbut-3-yn-2-ol according to ref 9. The d.e. of compounds **6** and **8** were determined from the ^{1}H NMR signals of the acetyl groups of the two diastereoisomers.

Synthesis of Carbonates **6–9**, **12** *and* **14–16**.—*Method I*. The cyclic carbonate **1** (20 mmol), the alcohol (10 mmol), potassium cyanide (1 mmol) and 2-hydroxypyridine **10** (1 mmol) were stirred under nitrogen at 60 °C. The linear carbonates **6**, **7** and **8** were isolated by distillation under reduced pressure.

Method II. The cyclic carbonate **1** (8 mmol), the alcohol (4 mmol) and DBN (4 mmol) were stirred under nitrogen at 20 °C until complete conversion of the alcohol into the desired carbonate. The linear carbonates **6**, **9** and **12**, and the cyclic carbonate **16** were isolated by distillation under reduced pressure or recrystallization.

1,1-*Dimethyl*-2-*oxopropyl menthyl carbonate* **6**. Method **II**, colourless oil (95%); distilled under reduced pressure (1 mmHg, b.p. 100 °C); δ_H(300 MHz; $CDCl_3$) 4.48 (1 H, td, ^3J 11.0 and ^3J 4.4, 1-H), 2.16 (3 H, s, MeCO), 2.05–1.93 (2 H, m, 2-H and 6-H), 1.79–1.61 (2 H, m, 4-H and 3-H), 1.51 and 1.49 (6 H, 2 s, Me_2C), 1.48–1.39 (2 H, m, 8-H and 5-H), 1.08 (1 H, m, 6-H), 0.99–0.84 (2 H, m, 4-H and 3-H), 0.93 and 0.91 (6 H, 2 d, ^3J 2.9 and 2.4, Me_2CH) and 0.79 (3 H, d, ^{3}J 6.9, 7-Me); ν/cm^{-1} 1735 (C=O) (Found: C, 67.2; H, 9.8%; M$^+$, 284.200. $C_{16}H_{28}O_4$ requires C, 67.56; H, 9.93%; *M*, 284.199).

tert-*Butyl* 1,1-*dimethyl*-2-*oxopropyl carbonate* **7**. Method **I**, white solid (78%); distilled under reduced pressure (1 mmHg, b.p. 100 °C); δ_H(300 MHz; $CDCl_3$) 2.10 (3 H, s, MeCO), 1.45 (9 H, s, Me_3C) and 1.43 (6 H, s, Me_2C); ν/cm^{-1} 1740 and 1730 (C=O) (Found: 59.2; H, 9.0%; M$^+$, 202.121. $C_{10}H_{18}O_4$ requires C, 59.37; H, 8.98%; *M*, 202.120).

1,1-*Dimethyl*-2-*oxopropyl fenchyl carbonate* **8**. Method **I**, white solid (50%); δ_H(300 MHz; $CDCl_3$) 4.15 (1 H, s, 1-H), 2.09 (3 H, s, MeCO) 1.75 (1 H, m, 5-H), 1.71 (1 H, m, 3-H), 1.70 (1 H, m, 4-H), 1.54 (1 H, m, 7-H), 1.44 and 1.43 (6 H, 2 s, Me_2C), 1.42 (1 H, m, 4-H), 1.17 (1 H, 7-H), 1.06 and 1.05 (6 H, 2 s, 8-Me and 10-Me) and 0.80 (3 H, s, 9-Me); ν/cm^{-1} 1735 and 1725 (C=O) (Found: C, 67.9; H, 9.2. $C_{16}H_{26}O_4$ requires C, 68.04; H, 9.29%).

1,1-*Dimethyl*-2-*oxopropyl* 1,1-*dimethylprop*-2-*enyl carbonate* **9**. Method **II**, colourless liquid (60%); distilled under reduced pressure (1 mmHg, b.p. 90 °C); δ_H(300 MHz; $CDCl_3$) 6.05 (1 H, dd, ^3J 11.0 and 17.6, C*H*=CH_2), 5.20 (1 H, dd, $^3J_{trans}$ 17.6, ^2J 0.6, =CH_2), 5.11 (1 H, dd, $^3J_{cis}$ 11.0, ^2J 0.6, =CH_2), 2.12 (3 H, s, MeCO), 1.53 (6 H, 2 s, Me_2CCO) and 1.46 (6 H, s, Me_2CC=); ν/cm^{-1} 1715 (C=O) and 1665 (C=C).

Bis(1,1-*dimethyl*-2-*oxopropyl*) *carbonate* **12**. Method **II**, colourless liquid; distilled under reduced pressure (1 mmHg, b.p. 90 °C); δ_H(300 MHz; $CDCl_3$) 2.16 (6 H, s, MeCO) and 1.50 (12 H, s, Me_2C); ν/cm^{-1} 1745 and 1725 (C=O) (Found: C, 57.3;

H, 7.9%; M^+, 230.115. $C_{11}H_{18}O_5$ requires C, 57.36; H, 7.88%; *M*, 230.115).

1,1-*Dimethyl*-2-*oxopropyl* 3-*hydroxy*-1,3-*dimethylbutyl carbonate* **14**. Colourless oil obtained by addition of 2-methylpentan-2,4-diol **13** (1 equiv.) to the carbonate **1** at 20 °C for 16 h in the presence of KCN (0.05 equiv.) (74%); distilled under reduced pressure (1 mmHg, b.p. 50 °C); δ_H(300 MHz; $CDCl_3$) 4.96 (1 H, m, MeC*H*), 2.10 (3 H, s, MeCO), 2.05 (1 H, s, OH), 1.86 (1 H, dd, ^3J 8.5 and ^2J 15.0, CH_2CH), 1.60 (1 H, dd, ^3J 3.4 and ^2J 15.0, CH_2CH), 1.44 and 1.43 (6 H, 2 s, Me_2CCO), 1.26 (3 H, d, ^3J 6.3, MeCH) and 1.19 and 1.18 (6 H, 2 s, Me_2COH); ν/cm^{-1} 3428 (OH) and 1735 (C=O) (Found: C, 58.3; H, 8.9%. $C_{12}H_{22}O_5$ requires C, 58.50; H, 9.01%).

Bis(1,1-*dimethyl*-2-*oxopropyl*) 2-*methylpentane*-2,4-*diyl dicarbonate* **15**. Method **II**, white solid (94%); isolated by chromatography on silica with a diethyl ether–hexane mixture (3:7); δ_H(300 MHz; $CDCl_3$) 4.96 (1 H, m, MeC*H*), 2.24 (1 H, dd, ^3J 8.8 and ^2J 15.3, CH_2CH), 2.12 and 2.11 (6 H, 2 s, 2 MeCO), 1.95 (1 H, dd, ^3J 3.1 and ^2J 15.3, CH_2CH), 1.45 (6 H, s, 2 Me), 1.43 (9 H, s, 3 Me), 1.41 (3 H, s, Me) and 1.25 (3 H, d, ^3J 6.3, MeCH); ν/cm^{-1} 1744, 1735 and 1725 (C=O) (Found: C, 57.8, H, 8.0. $C_{18}H_{30}O_8$ requires C, 57.72; H, 8.08%).

4,4,6-*Trimethyl* 1,3-*dioxane*-2-*one* **16**. White solid obtained by heating **14** at 100 °C for 20 h in the presence of 5 mol% KCN (77%); recrystallized from diethyl ether and hexane; δ_H(300 MHz; $CDCl_3$) 4.58 (1 H, qdd, ^3J 12.0, 6.2 and 3.1, MeC*H*), 1.92 (1 H, dd, ^2J 14.1 and ^3J 3.1, CH_2), 1.70 (1 H, dd, ^2J 14.1 and ^3J 12.0, CH_2), 1.40 (6 H, s, Me_2C) and 1.35 (3 H, d, ^3J 6.2, *Me*CH); ν/cm^{-1} 1720 (C=O) (Found: C, 58.2; H, 8.45. $C_7H_{12}O_3$ requires C, 58.30; H, 8.39%).

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