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$BiBr_3$-catalysed formation of cyclic carbonates from epoxides and DMF: a new oxidation reaction with molecular oxygen

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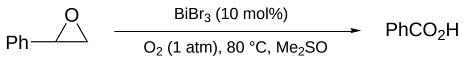
Cyclic carbonates are obtained in good yields from terminal epoxides and DMF in a $BiBr_3$-catalysed reaction with molecular oxygen as the oxidant.

In the course of our ongoing research on the use of bismuth(iii) derivatives as catalysts in oxidation reactions,[1] we have recently found a new $BiBr_3$-catalysed reaction which provides cyclic carbonates from terminal epoxides and DMF. Cyclic carbonates present interesting applications as polar aprotic solvents and as synthetic intermediates in organic synthesis,[2] and they are also important precursors to polycarbonates and other polymeric materials.[3]

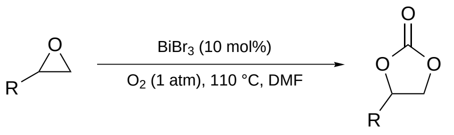
The synthesis of cyclic carbonates from epoxides is generally carried out with carbon dioxide, and various catalysts have been reported for this reaction.[4] To the best of our knowledge, no example in the literature reports the formation of carbonates from epoxides, DMF and O_2. Moreover, there has been no report of the use of $BiBr_3$ as the catalyst in oxidation reactions.

We have recently explored new possibilities for Bi^{III} catalysis in the oxidation of epoxides[5] and α-ketols[6] to carboxylic acids by molecular oxygen. With Bi^{III} mandelate[7] as the catalyst in Me_2SO, a C–C bond cleavage occurs on the oxirane ring or on the ketol, the carboxylic acids being obtained in 40–65% yield. When $BiBr_3$ was taken as the catalyst (10 mol%) for the oxidation of epoxides in Me_2SO under O_2 (1 atm), the corresponding carboxylic acids were also formed. Thus, the reaction of styrene oxide led to benzoic acid in 46% yield [eqn. (1)].



(1)

Interestingly, when the same reaction was carried out in DMF, no oxidative C–C bond cleavage occurred and no carboxylic acid was obtained. The reaction selectively led to the formation of the cyclic carbonate 4-phenyl-1,3-dioxolan-2-one in 56% yield [eqn. (2)]. Thus, the nature of the solvent strongly influences the reaction pathway, determining the nature of the reaction products.



(2)

The formation of cyclic carbonates from epoxides in DMF–O_2 catalysed by $BiBr_3$ appears to be specific to this catalytic system. Thus, when the experiment was carried out with 1,2-epoxydecane as the model epoxide, the corresponding cyclic carbonate was obtained in 70% yield. In the absence of the catalyst, no carbonate was formed. The replacement of $BiBr_3$ by $BiCl_3$ did not afford any carbonate, but led to the synthesis of 2-chloro alcohols (as a mixture of isomers) in 62% yield when 30 mol% $BiCl_3$ was used. It is worth noting that the corresponding bromo alcohols were not isolated in the analogous reaction with $BiBr_3$. Moreover, when Bi^{III} mandelate was used as the catalyst in DMF, no reaction occurred, and the epoxide was quantitatively recovered. The reaction of the epoxide with CO_2 catalysed by $BiBr_3$ in refluxing THF did not give any carbonate.

When the reaction of 1,2-epoxydecane in DMF catalysed by $BiBr_3$ was carried out under an inert atmosphere (N_2), no carbonate was formed, although some polymerisation of the epoxide occurred. Thus, the presence of molecular oxygen is essential for carbonate formation. The consumption of O_2 during the reaction was measured, and reached 1.1 moles of O_2 per mole of epoxide at complete conversion (6 h reaction at 110 °C).

A series of epoxides were reacted in DMF under molecular oxygen (1 atm) at 110 °C, with a 10 mol% of $BiBr_3$ [eqn. (2)]. The results concerning the cyclic carbonate formation are presented in Table 1. The reactions were clean and selective, the only isolated products being the cyclic carbonates, the remaining by-products being attributed to epoxide polymerisation.

Aliphatic as well as aromatic terminal epoxides (entries 1–3) afforded the corresponding cyclic carbonates in good yields. An *o*-chlorine substituent on the aromatic ring (entry 4) was compatible with the reaction conditions, although it slowed the reaction rate, probably due to steric hindrance. Benzylic epoxides (entries 5, 6) and epibromohydrin (entry 7) led to the corresponding cyclic carbonates without elimination. No additional intramolecular cyclisation or double bond modification was observed in the reaction of 7,8-epoxyoct-1-ene (entry 8), indicating that carbonate formation does not involve radical intermediates. Several disubstituted epoxides were also tested

Table 1 Oxidation of terminal epoxides to cyclic carbonates[a]

Entry	R	Reaction time/h	Isolated yield of carbonate (%)
1	Ph	7.5	56
2	C_8H_{17}	6	70
3	C_6H_{13}	8	64
4	*o*-ClC_6H_4	31	68 (conversion 88%)
5	$PhOCH_2$	24	76
6	*p*-$OMeC_6H_4OCH_2$	30	23
7	$BrCH_2$	7	64
8	CH_2=CHC_4H_8	31	32 (conversion 93%)

[a] General reaction conditions: anhydrous DMF (5 ml) was stirred in the presence of $BiBr_3$ (134 mg, 0.3 mmol) at 110 °C for 30 min under molecular oxygen (1 atm), followed by the addition of the epoxide (3 mmol). The reaction was followed by GC until complete conversion of the substrate (unless stated). Acidic hydrolysis with aqueous 0.1 m HCl, diethyl ether extraction, drying of the organic layers with $MgSO_4$ and solvent evaporation led to the cyclic cabonates in the yields shown. The products were analysed by GC, ^1H, ^{13}C NMR and mass spectroscopy, and their spectral data compared with those of authentic samples.

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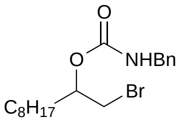
but did not afford cyclic carbonates under the same conditions. *trans*-5,6-Epoxydecane led to decane-5,6-dione in 56% yield.

The reaction presumably involves an epoxide ring opening with the incorporation and oxidation of the carbonyl moiety of DMF, the oxidant being O_2. 1,2-Diketones are not intermediates in this reaction; the reaction of hexane-3,4-dione did not afford any carbonate. In order to quench the amine residue eliminated from DMF, an equivalent amount of benzoyl chloride was added after the reaction with 1,2-epoxydecane. However, no *N*,*N*-dimethylbenzamide was isolated. In a different experiment, the reaction was carried out in *N*-benzylformamide. The epoxide consumption was slow (72 h) and no cyclic carbonate was formed. We could however isolate the carbamate **1**, arising from the oxidation of the benzylamine residue.†



1

Compound **1**, formed in 40% yield and purified by column chromatography, clearly establishes the epoxide–formamide coupling and the oxidation of the formamide group. The presence of a bromide on the less hindered side of the starting epoxide also shows the role of the catalyst in the initial oxirane ring opening. We can assume that an analogue of **1** is likely to be the intermediate in the carbonate formation in DMF. The reaction would be followed by oxygen transfer to the carbamate and ring closure with bromide elimination.

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Footnote

† *Selected data* for compound **1**: ^{1}H NMR ($CDCl_3$): δ 7.65–7.15 (5 H, m), 6.20 (NH, s), 4.50 (2 H, s), 3.85–3.60 (1 H, m), 3.12 (1 H, dd, *J* 15.0, 6.0 Hz), 3.08 (1 H, dd, *J* 15.0, 7.0 Hz), 1.40–0.78 (17 H, m). ^{13}C NMR ($CDCl_3$): δ 164.1, 129.0–127.6, 71.2, 69.1, 53.1, 39.7–14.3; *m/z* (70 eV) 342 and 340 (1 : 1) ($M^+ - 29$, 5), 291(1), 262(3), 149(68), 91(100).

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