Synthesis of Cyclic Carbonates by a Novel Carbonate Rearrangement

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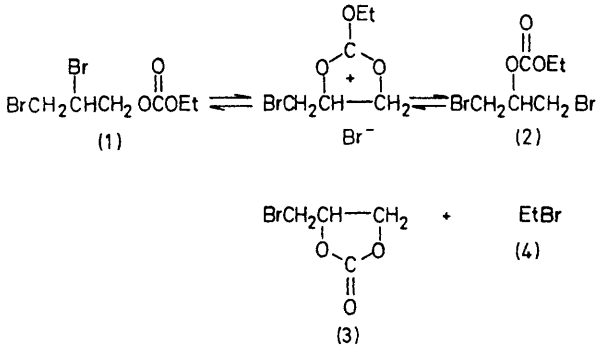
Summary 2,3-Dibromopropyl ethyl carbonate (**1**) and 1,3-dibromo-2-propyl ethyl carbonate (**2**) equilibrate at 180° with concomitant formation of 3-bromopropylene carbonate (**3**) and ethyl bromide (**4**).

RECENTLY we reported the thermal isomerization of 2,3-dihalogenopropyl acetates to 1,3-dihalogeno-2-propyl acetates and suggested that the rearrangement proceeded *via* an acetoxonium ion intermediate.[1] Extension of this rearrangement to the carbonate has provided further evidence for the cyclic intermediate and has led to a novel cyclic carbonate synthesis and rearrangement. Compound (**1**) on heating (sealed tube) at 180° isomerizes to (**2**) as evidenced by the appearance of a multiplet at δ 5·00 ($CDCl_3$) for the methine hydrogen of (**2**). On further heating a triplet appears at δ 1·67 ($CDCl_3$) for ethyl bromide. Pyrolysis of either (**1**) or (**2**) at 195—205° and 1 atm. gave, after purification of both the volatile products and residue by distillation, 88 ± 2% of (**3**) and 90 ± 2% of (**4**). The formation of ethyl bromide *via* bromide ion attack on the ethereal carbon is analogous to the formation of alkyl halides in the Arbuzov reaction.[2]

Similarly, 2-bromoethyl ethyl carbonate gave comparable yields of ethylene carbonate and (**4**), whereas 3-bromopropyl ethyl carbonate on prolonged heating at 250° did not give the corresponding 6-membered ring cyclic carbonate. Analysis of the pyrolysis distillate showed diethyl carbonate and trace amounts of (**4**), ethanol, and allylic material. The n.m.r. spectrum of the residue was consistent with 3-bromopropyl carbonate. The ease of formation of the 5-membered ring relative to the 6-membered ring is in agreement with previous studies on the ease of ring formation.[3]



(*Received, 8th November* 1973; *Com.* 1542.)

[1] R. G. Pews and R. A. Davis, *J.C.S. Chem. Comm.*, 1973, 269.
[2] A. J. Kirby and S. G. Warren in 'The Organic Chemistry of Phosphorus', Elsevier, Amsterdam, p. 38.
[3] E. L. Eliel in 'Stereochemistry of Carbon Compounds', McGraw-Hill ,New York, p. 198.