Dialkyl Dithiol Tricarbonates and Dialkyl Tricarbonates

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Summary The action of phosgene on sodium t-butyl carbonate gives the crystalline di-t-butyl tricarbonate, m.p. 64—65°, which when subjected to heat breaks down into 3 moles of carbon dioxide, one mole of isobutene and one mole of t-butyl alcohol.

THE synthesis and thermal decomposition of di-t-butyl dithiol tricarbonate (I) has been described,[1] eq. 1; $R = Bu^t$.

We now report that the corresponding oxygen compound has been obtained in good yield as a crystalline solid, m.p. 64—65°, with the correct elemental analysis and molecular weight, by a similar procedure (Eq. 2; $R = Bu^t$).

Unlike the dithiol tricarbonate (I), when heated above its melting point in the absence of solvent, di-t-butyl tricarbonate (II) fragments into 3 moles of carbon dioxide, 1 mole of t-butyl alcohol and 1 mole of isobutene. However, when heated under reflux in carbon tetrachloride in the presence of a trace of triethylamine, 1 mole of carbon dioxide is lost, resulting in the formation of the known dicarbonate (III).[2,3] Attempts to decompose (III) to the monocarbonate were unsuccessful under all of the conditions tried, the products being 2 moles of carbon dioxide, 1 mole of t-butyl alcohol and 1 mole of isobutene. This behaviour emphasizes the well known failure of t-butylthiol compounds to form t-butyl carbonium ions.[4,5,6]

$$\begin{tikzcd} \mathrm{RSH} \arrow[r, "\mathrm{NaH}"] & \mathrm{RSNa} \arrow[r, "\mathrm{CO_2}", "-60^\circ"'] & \mathrm{RSCO_2Na} \arrow[r, "\mathrm{COCl_2}", "-60^\circ"'] & {} \\ & & & \mathrm{RSCO_2CO_2COSR} \arrow[d, "75^\circ"] & \text{(I)} \\ & & \mathrm{RSCOSR} \arrow[r, "140^\circ"] & \mathrm{RSCO_2COSR} & \text{(1)} \end{tikzcd}$$

$$\begin{tikzcd} \mathrm{ROK} \arrow[r, "\mathrm{CO_2}", "\text{tetrahydrofuran}"'] & \mathrm{ROCO_2K} & \mathrm{ROCO_2CO_2CO_2R} \arrow[l, "\mathrm{COCl_2}"', "-60^\circ"] & \text{(II)} \end{tikzcd}$$

$$\begin{tikzcd} & 3\mathrm{CO_2} + \mathrm{Bu^tOH} + \mathrm{CH_2{:}CMe_2} & & \text{(2)} \\ \text{(II)} \arrow[ur, "70^\circ"] \arrow[dr, "\mathrm{CCl_4{-}Et_3N}"] & & & \\ & \underset{\text{(III)}}{\mathrm{ROCO_2CO_2R}} \arrow[r, "130^\circ"] & 2\mathrm{CO_2} + \mathrm{Bu^tOH} + \mathrm{CH_2{:}CMe_2} & \end{tikzcd}$$

Other tricarbonates prepared include di-isopropyl dithiol tricarbonate and di-isopropyl tricarbonate. It has not been possible to obtain these pure since they decompose

TABLE. *Spectral data*

R		RCO_2CO_2COR	RCO_2COR	RCOR
Bu^t·S–	i.r.[a] n.m.r.[b]	1850, 1735 1·55 s	1770, 1710 1·51 s	1635 1·47 s
Pr^i·S–	i.r. n.m.r.	1840, 1750 3·59 sept. *J* 7 1·42 d *J* 7	1775, 1720 3·53 sept. *J* 7 1·39 d *J* 7	1645 3·73 sept. *J* 7 1·32 d *J* 7
Bu^t·O–	i.r. n.m.r.	1845, 1810, 1780 1·66 s	1820, 1765 1·61 s	
Pr^i·O–	i.r. n.m.r.	1865, 1815, 1780 4·98 sept. *J* 6·25 1·39 d *J* 6·25	1825, 1770 4·88 sept. *J* 6·25 1·34 d *J* 6·25	1750 4·76 sept. *J* 6·25 1·25 d *J* 6·25

[a] Beckman IR-10, wave numbers (cm.$^{-1}$).

[b] Varian A-60, (CCl_4) Me_4Si as internal standard, δ (p.p.m.) values, *J* in Hz.

readily to their corresponding dicarbonates. The assignments were made on the basis of the similarities of their spectral properties (i.r., n.m.r.) with the known examples and the measurement of the quantity of carbon dioxide evolved in their decomposition from tricarbonate. Di-isopropyl dicarbonate,[2] at 130°, and di-isopropyl dithiol dicarbonate, at room temperature, both lose one mole of carbon dioxide in the presence of a trace of *N*-methylpiperidine to give the known monocarbonate[7] and dithiolmonocarbonate.[4]

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