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THE PREPARATION AND CHARACTERIZATION OF DI-t-BUTYL DITHIOL TRICARBONATE

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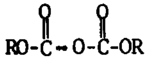
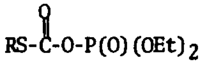
Di-t-butyl dicarbonate (1) has been prepared by reaction of potassium t-butyl carbonate with phosgene in about 5% yield.[1] In order to identify the products of the decomposition of the thiolcarbonic phosphoric anhydride 2 [2] we attempted to synthesize di-t-butyl dithiol dicarbonate (4) by the analogous reaction of sodium t-butyl thiolcarbonate with phosgene (eq. (1)).



$\mathrm{RO-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-OR}$

1

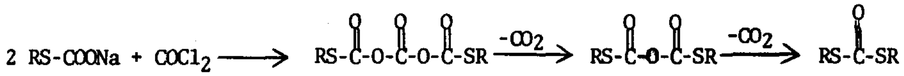


$\mathrm{RS-\overset{O}{\overset{\|}{C}}-O-P(O)(OEt)_2}$

2

R = t-butyl

(1)



$$\mathrm{2\ RS-COONa + COCl_2 \longrightarrow RS-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-SR \xrightarrow{-CO_2} RS-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-SR \xrightarrow{-CO_2} RS-\overset{O}{\overset{\|}{C}}-SR}$$

3 4 5

We obtained in good yield a crystalline product (mp 64-67° after recrystallization from pentane); its infrared spectrum showed the expected two carbonyl bands. The elemental analysis, however, did not correspond to the dicarbonate 4, but to di-t-butyl dithiol *tri*-carbonate (3) (calcd for $C_{11}H_{18}S_2O_5$: C, 44.88; H, 6.16; S, 21.78. Found: C, 45.08; H, 6.18; S, 21.67), which was expected to be a very unstable intermediate in the above reaction (1). The structure of 3 was confirmed by osmometric molecular weight determination (calcd 294; Found: 300 (solvent: benzene)) and by comparison of the ir and nmr spectra with the dicarbonate 4 and the monacarbonate 5 [3], as shown in the Table.

TABLE: Spectra of Di-t-butyl Dithiol Carbonates

Compound	nmr[a]	ir[b]	
		C=O	CO-O-CO
tricarbonate 3	1.55 (s)	1835, 1750	920
dicarbonate 4	1.51 (s)	1770, 1710	940
monocarbonate 5	1.47 (s)	1635	—

[a] Varian A-60, carbon tetrachloride solution, TMS as internal standard, δ (ppm) values.

[b] Beckman IR-10, carbon tetrachloride solution, wave numbers (cm^{-1}).

As far as we know this is the first synthesis of a compound with the structure type 3. The oxygen analog of 3 decomposes immediately to 1.[1] By contrast, 3 is unexpectedly stable. If heated under vacuum to 55° for 7 hours, it loses about 40% of its weight; this, however, is due to sublimation and not to decomposition, sublimate and residue have the same mp and ir spectra as the starting material. If heated under vacuum above its melting point, e.g. in a bath of 75°, 3 decomposes very rapidly to give the dicarbonate 4 (bp 79-80°/0.05 mm, mp 27-33), which was identified by its spectra (Table) and elemental analysis (calcd for $C_{10}H_{18}S_2O_3$: C, 47.97; H, 7.25. Found: C, 48.29; H, 7.53). The dicarbonate 4 decomposes to the known[3] monocarbonate 5 when heated at atmospheric pressure for 45 min. at 170°.

ACKNOWLEDGMENT

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