tetra-*n*-butyl orthocarbonate (**18f**): bp 85–89° (0.4 mm); ir ($CHCl_3$) 1175, 1120 (ν_{C-O}), 1050, and 970 cm^{-1}; nmr ($CHCl_3$) τ 6.44 (t, 8, J = 6.2 Hz, OCH_2), 8.1–8.8 (m, 16, CCH_2CH_2C), and 9.07 (t, 12, J = 6.1 Hz, CCH_3).

Reaction of Dibutyltin Di-*n*-octoxide (6g) with CS_2.—The dialkoxide **6g** (20 mmol) and equimolar amounts of CS_2 were heated at 120° for 20 hr, and the reaction mixture showed a strong ν_{C-O} band at 1115 cm^{-1} and a very weak $\nu_{C=O}$ band at 1750 cm^{-1} in the ir spectrum, suggesting the formation of tetra-*n*-octyl orthocarbonate. However, the pure orthocarbonate could not be obtained on distillation or column chromatography of the mixture, because it was decomposed to dioctyl carbonate in these procedures.

Reaction of Dioctyltin Di-*n*-hexoxide (6h) with CS_2.—Crude dialkoxide **6h** (10 mmol),[16] prepared *in situ* from dioctyltin dimethoxide and dried 1-hexanol by heating the mixture in a distillation flask to 120° *in vacuo* (20 mm), was allowed to react with CS_2 (0.6 ml) at 120° for 20 hr under argon to give a 49% yield of tetra-*n*-hexyl orthocarbonate (**18h**) and a 20% yield of di-*n*-hexyl carbonate (**19h**) (yields based on the crude **6h** used).

18h: bp 119–121° (0.04 mm); ir ($CHCl_3$) 1118 cm^{-1} (ν_{C-O}); nmr ($CHCl_3$) τ 6.51 (t, 8, J = 6.0 Hz, OCH_2), 8.3–8.9 (m, 32, $C(CH_2)_4C$), and 9.13 (t, 12, J = 5.8 Hz, CCH_3).

Anal. Calcd for $C_{25}H_{52}O_4$: C, 72.06; H, 12.58. Found: C, 72.25; H, 12.74.

19h: bp 61–63° (0.03 mm); ir ($CHCl_3$) 1742 ($\nu_{C=O}$) and 1260 cm^{-1}; nmr (CCl_4) τ 5.87 (t, 4, J = 6.0 Hz, OCH_2), 8.1–8.9 (m, 16, $C(CH_2)_4C$), and 9.11 (t, 6, J = 5.7 Hz, CCH_3).

Anal. Calcd for $C_{13}H_{26}O_3$: C, 67.79; H, 11.38. Found: C, 67.80; H, 11.19.

Reaction of Dioctyltin Di-*n*-octoxide (6i) with CS_2.—Crude dialkoxide **6i** (10 mmol),[16] prepared from dioctyltin dimethoxide and dried 1-octanol as was discussed above, reacted with CS_2 (0.6 ml) at 120° for 20 hr. The reaction mixture showed a strong ether band of tetraalkyl orthocarbonate at 1115 cm^{-1}, but, on distillation (the oil bath temperature used was increased to 220°), di-*n*-octyl carbonate (**19i**) was obtained in a 80% yield suggesting the decomposition of **18g** to **19g**: bp 120° (0.04 mm); ir ($CHCl_3$) 1740 ($\nu_{C=O}$) and 1265 cm^{-1}; nmr ($CHCl_3$) τ 5.85 (t, 4, J = 6.2 Hz, OCH_2), and 8.1–9.3 (m, 30, CC_7H_{15}).

Anal. Calcd for $C_{17}H_{36}O_4$: C, 71.28; H, 11.96. Found: C, 71.46; H, 11.89.

Registry No.—**5a**, 3590-59-8; **5b**, 3590-60-1; **5c**, 3590-63-4; **5d**, 3590-67-8; **5e**, 3744-99-8; **5f**, 3590-62-3; **6a**, 1067-55-6; **6b**, 1067-41-0; **6c**, 3349-35-7; **6d**, 14538-83-1; **6e**, 3349-40-4; **6f**, 3349-36-8; **6g**, 3349-38-0; **13**, 3590-65-6; **18a**, 1850-14-2; **18b**, 78-09-1; **18c**, 597-72-8; **18f**, 25335-30-2; **18h**, 28131-23-9; **19d**, 6482-34-4; **19h**, 7523-15-1; **19i**, 1680-31-5; carbon disulfide, 75-15-0.

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[16] The dialkoxides of dioctyltin were decomposed at ~160° on distillation.

The Reactions of Amines, Alcohols, and Pivalic Acid with Di-*tert*-butyl Dithiol Tricarbonate and Di-*tert*-butyl Tricarbonate[1,2]

C. S. DEAN AND D. S. TARBELL*

Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37203

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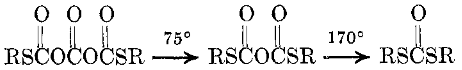
Nucleophilic attack by amines on di-*tert*-butyl dithiol tricarbonate and di-*tert*-butyl tricarbonate is shown to take place at the central carbonyl group. Primary aromatic amines give rise to symmetrical ureas, secondary amines produce the corresponding carbonic carbamic anhydrides, and tertiary amines catalyze the decomposition of the tricarbonates to their corresponding dicarbonates. Ethyl and isopropyl alcohols react to produce the corresponding mixed dicarbonates. Pivalic acid reacts to produce RSCOOCOOCOR (R = *tert*-Bu), almost certainly by attack at the central carbonyl group of the tricarbonate.

The present paper describes the action of primary and secondary amines, of alcohols, and of pivalic acid on the tricarbonates whose preparation and properties were reported previously. The present work will be described most clearly by reference to some of our earlier observations.

The thermal decomposition of di-*tert*-butyl dithiol tricarbonate (**1**) has been shown to give di-*tert*-butyl dithiol dicarbonate (**2**), which may be further decomposed to the corresponding monocarbonate **3**[3–5] (eq 1).

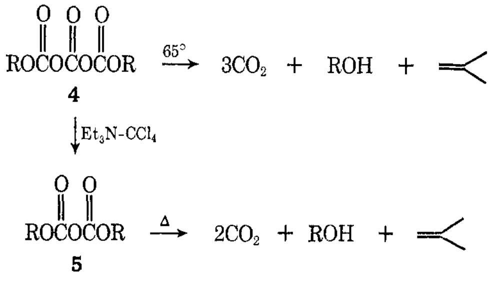


$$\mathrm{RS\overset{\overset{O}{\|}}{C}O\overset{\overset{O}{\|}}{C}O\overset{\overset{O}{\|}}{C}SR \xrightarrow{75^\circ} RS\overset{\overset{O}{\|}}{C}O\overset{\overset{O}{\|}}{C}SR \xrightarrow{170^\circ} RS\overset{\overset{O}{\|}}{C}SR} \qquad (1)$$

1 **2** **3**

R = *tert*-Bu

In contrast to this behavior, di-*tert*-butyl tricarbonate (**4**), when thermally decomposed, fragments into three molecules of carbon dioxide, one molecule of *tert*-butyl alcohol, and one molecule of isobutene[4,5] (eq 2). By refluxing in carbon tetrachloride with a trace of triethylamine, the decomposition is arrested at the di-*tert*-butyl dicarbonate[6,7] **5** stage. Under all of the conditions tried, **5** could not be converted into the known monocar-



(2)

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[1] Aided by Grant GP-7874 from the National Science Foundation.

[2] The nomenclature of the di- and tricarbonates described in this and the preceding papers of this series is a vexing problem. The dicarbonates, ROCOOCOR, have been known for some time (ref 6 and 7 below) and are usually called "pyrocarbonates;" they have received considerable attention as mild acylating agents for compounds of biochemical importance [*e.g.*, N. J. Leonard, J. J. McDonald, and M. E. Reichmann, *Proc. Nat. Acad. Sci. U. S.*, **67**, 93 (1970), and references therein]. R. Sayre [*J. Amer. Chem. Soc.*, **74**, 3647 (1952)] has named EtOCOSCSOEt "diethyl thionothiodiformate" and gives other less descriptive names. In our work, we have preferred the "dicarbonate" and "tricarbonate" scheme to emphasize the similarities between the two types, derived formally from HOCOOCOOH and HOCOOCOOCOOH, as well as from the corresponding sulfur carbonic acids, HSCOOCOSH and HSCOOCOOCOSH. The di- and triphosphates, as in adenosine triphosphate and adenosine diphosphate, are reasonable analogs to our usage.

[3] A. W. Friederang and D. S. Tarbell, *Tetrahedron Lett.*, **55**, 5535 (1968).

[4] C. S. Dean and D. S. Tarbell, *Chem. Commun.*, 728 (1969).

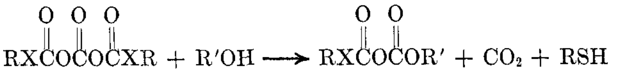
[5] C. S. Dean, D. S. Tarbell, and A. W. Friederang, *J. Org. Chem.*, **35**, 3395 (1970).

[6] J. W. Howe and L. R. Morris, *ibid.*, **27**, 1901 (1962).

[7] W. Thoma and H. Rinke, *Justus Liebigs Ann. Chem.*, **624**, 31 (1959); T. Boehm and D. Mehta, *Ber.*, **71**, 1797 (1938).

bonate,[8] the products being two molecules of carbon dioxide, one molecule of isobutene, and one molecule of *tert*-butyl alcohol (eq 2). The contrast in the decompositions between the oxygen compounds and the sulfur compounds is readily understandable on the basis of the ready ability of *tert*-butyl oxygen compounds to form *tert*-butyl carbonium ions and the well-known failure of *tert*-butyl thiol compounds to reciprocate this behavior.[9] However, the ability of a catalytic quantity of triethylamine to arrest the decomposition of the oxygen tricarbonate at the dicarbonate stage is striking. The action of tertiary amines on the di- and tricarbonates is being investigated further.

The reaction of tricarbonates with alcohols appears to be general. Di-*tert*-butyl dithiol tricarbonate reacts with ethanol in chloroform or carbon tetrachloride solution to give *tert*-butyl thiol ethyl dicarbonate (**6a**) (eq 3). The formation of carbon dioxide in this and the other reactions of nucleophiles with the tricarbonates was shown by a strong band in the ir at 2370 cm^{-1} which disappeared when reaction was complete. Similarly, di-*tert*-butyl tricarbonate reacts with ethanol to produce the corresponding mixed oxygen dicarbonate, *tert*-butyl ethyl dicarbonate (**6c**). A further example is furnished by the reaction of isopropyl alcohol with di-*tert*-butyl dithiol tricarbonate to form *tert*-butyl thiol isopropyl dicarbonate (**6b**).



$$\mathrm{RX\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}XR + R'OH \longrightarrow RX\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}OR' + CO_2 + RSH} \qquad (3)$$

R = *tert*-Bu

6a, R' = C_2H_5; X = S

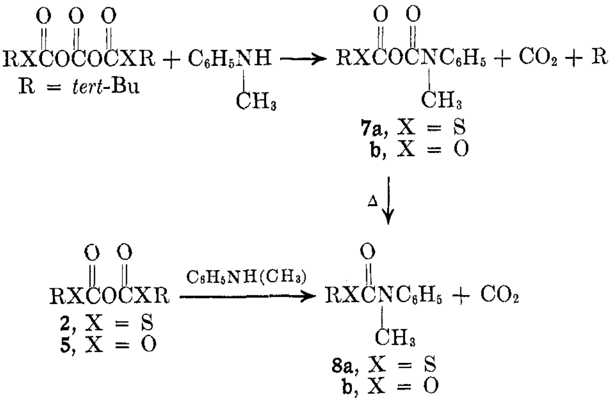
b, R' = $(CH_3)_2CH$; X = S

c, R' = C_2H_5; X = O

Compounds **6a**, **6b**, and **6c** were obtained pure by distillation, and the structures were assigned on the basis of ir and nmr spectra, and the elemental analysis; mass spectroscopy is not useful in the polycarbonate series, because even the monocarbonates fragment extensively, without giving a molecular ion.[10]

All attempts to produce *tert*-butyl thiol *tert*-butyl dicarbonate from di-*tert*-butyl dithiol tricarbonate were unsuccessful. The methods tried included refluxing the tricarbonate in carbon tetrachloride in the presence of *tert*-butyl alcohol, allowing the tricarbonate to stand at room temperature in carbon tetrachloride containing *tert*-butyl alcohol and a catalytic quantity of triethylamine or potassium *tert*-butoxide, and using equimolar quantities of the tricarbonate and potassium *tert*-butoxide at room temperature in tetrahydrofuran solution. In all cases, the decomposition of the tricarbonate, to di-*tert*-butyl dithiol dicarbonate, takes precedence over the formation of the mixed dicarbonate. A similar effect is seen in the reaction of di-*tert*-butyl dithiol tricarbonate with mercaptans. The decomposition of the tricarbonate to di-*tert*-butyl dithiol dicarbonate competes with the formation of the mixed dithiol dicarbonate. Both isopropyl mercaptan and benzyl mercaptan were used and the corresponding mixed dicarbonates, *tert*-butyl thiol isopropyl thiol dicarbonate and *tert*-butyl thiol benzyl thiol dicarbonate were formed in 10–15% yield (nmr).

N-Methylaniline reacts similarly to alcohols, producing carbonic carbamic anhydrides; with di-*tert*-butyl dithiol tricarbonate (**1**) at room temperature, the product formed is *tert*-butyl thiol *N*-methylphenylcarbamic anhydride (**7a**) (eq 4). Similarly, di-*tert*-butyl tricarbonate with *N*-methylaniline produces *tert*-butyl *N*-methylphenylcarbamic anhydride (**7b**). Both of these anhydrides are thermally unstable and may be decomposed with the loss of one molecule of carbon dioxide, the thiol compound giving the known *tert*-butyl thiol *N*-methylphenylcarbamate (**8a**) and the oxygen compound giving *tert*-butyl *N*-methylphenylcarbamate (**8b**). Both of these carbamates can be obtained from di-*tert*-butyl dithiol dicarbonate (**2**) and di-*tert*-butyl dicarbonate (**5**), respectively, by refluxing the dicarbonate with *N*-methylaniline in carbon tetrachloride.



$$\mathrm{RX\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}XR + C_6H_5\underset{\underset{\displaystyle CH_3}{|}}{N}H \longrightarrow RX\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}\underset{\underset{\displaystyle CH_3}{|}}{N}C_6H_5 + CO_2 + ROH}$$

R = *tert*-Bu

7a, X = S

b, X = O

$$\Big\downarrow \Delta \qquad (4)$$

$$\mathrm{RX\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}XR \xrightarrow{C_6H_5NH(CH_3)} RX\overset{O}{\overset{\|}{C}}\underset{\underset{\displaystyle CH_3}{|}}{N}C_6H_5 + CO_2}$$

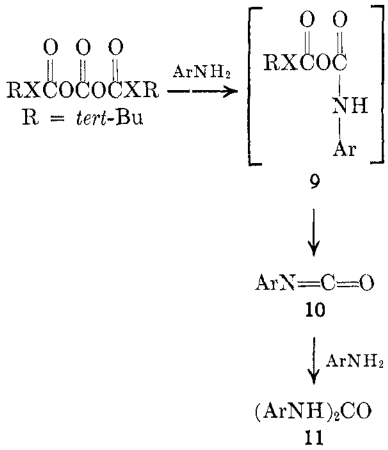
2, X = S

5, X = O

8a, X = S

b, X = O

With primary aromatic amines, both tricarbonates give the isocyanate, which then reacts with a second molecule of amine to give the urea. On the basis of the reactions with alcohols and secondary amines, the reaction presumably proceeds through an intermediate of the type **9** (eq 5) which immediately then forms the isocyanate **10** and finally the symmetrical urea **11**. The primary amines used were aniline, 2,4-dimethylaniline, and 2,6-dimethylaniline. The isocyanates were not isolated, but their presence was shown by the characteristic absorption[11] in the ir at 2270 cm^{-1}, which appeared



$$\mathrm{RX\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}XR \xrightarrow{ArNH_2} \left[RX\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}NHAr\right]_{\mathbf{9}} \longrightarrow \underset{\mathbf{10}}{ArN{=}C{=}O} \xrightarrow{ArNH_2} \underset{\mathbf{11}}{(ArNH)_2CO}} \qquad (5)$$

R = *tert*-Bu

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[8] A. R. Choppin and J. W. Rogers, *J. Amer. Chem. Soc.*, **70**, 2967 (1948).

[9] (a) D. S. Tarbell and L. Wei, *J. Org. Chem.*, **33**, 1884 (1968); (b) C. J. Michejda and D. S. Tarbell, *ibid.*, **29**, 1168 (1964); (c) T. Parasaran and D. S. Tarbell, *ibid.*, **29**, 2471 (1964); (d) R. Altschul, *J. Amer. Chem. Soc.*, **68**, 2605 (1946).

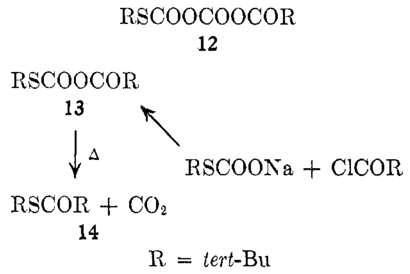
[10] P. Brown and C. Djerassi, *ibid.*, **88**, 2469 (1966); H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, p 484 ff.

[11] W. H. T. Davison, *J. Chem. Soc.*, 3712 (1953); H. Hoyer, *Chem. Ber.*, **89**, 2677 (1956).

during the reaction and then disappeared, because of the reaction with amine to form the urea. The rate of formation of the ureas decreased sharply in going from aniline to 2,6-dimethylaniline, ascribable to the steric effect of the methyl groups.

The reaction of *N*-methylaniline with di-*tert*-butyl and di-*tert*-butyl dithiol dicarbonate can be logically linked to the well-documented reactions with nucleophiles of the *tert*-butyl carbonic carboxylic,[9b] *tert*-butyl thiol carbonic carboxylic,[9c] and *tert*-butyl carbonic phosphoric anhydrides.[12]

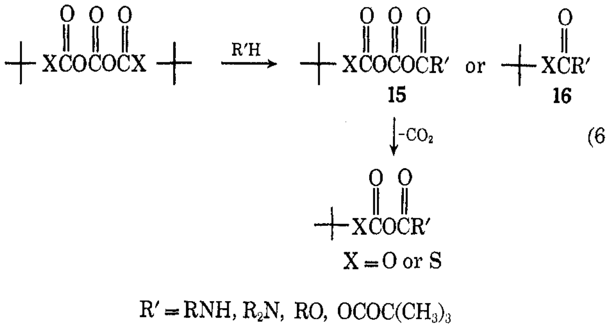
Pivalic acid reacted with the sulfur tricarbonate **1** to yield a mixture of the compounds **12** and **13** (nmr and ir), which gave on distillation at bath temperature of 75° the pure mixed anhydride **13**. This was obtained crystalline and was identical with the product prepared by the usual procedure. Compound **13** readily yielded the simple ester, *tert*-butyl thiol pivalate (**14**). Other acids (benzoic, *p*-nitrobenzoic, and acetic) did not give satisfactory results, partly because the products could not be purified and also because they appeared to disproportionate (especially the acetic acid product). The highly substituted pivalic derivatives did not show this behavior.



Pivalic acid is believed to attack **1** at the central carbonyl group; however, it cannot be stated definitely on the basis of present evidence that the primary product from **1** and pivalic acid is not **15**, formed by attack at the terminal carbonyl. If **15** is formed, however, there is no evidence for it in the ir, which would be very distinctive.

RSCOOCOOCOOCOR + RSH
15

The tricarbonates, however, are a new class of compounds to which there are no close analogies.[13] Even so, all of their above reactions with nucleophilic reagents can be readily rationalized on the basis of nucleophilic attack at the central carbonyl group. Alcohols and mercaptans produce the corresponding mixed dicarbonates **6**, primary amines give the isocyanates *via* the carbonic carbamic anhydride intermediate **9**, and secondary amines give the carbamic anhydrides **7**. (Pivalic acid is discussed above.) Little support can be found for any alternative mechanism whereby one of the other two equivalent carbonyl centers is attacked, as depicted in eq 6.



(6)

One would expect to see at least some, if not exclusive, formation of a monocarbonyl compound of the type **16**, or an indication of the presence of an intermediate of the type **15**, which in itself should be susceptible to further nucleophilic attack as well as decomposition. Such was not the case. Hence the ability of a catalytic quantity of triethylamine to arrest the decomposition of di-*tert*-butyl tricarbonate at the dicarbonate stage, along with its ability to speed up the decomposition of di-*tert*-butyl dithiol tricarbonate to its corresponding dicarbonate, can readily be linked with the above nucleophilic reactions, in that an association of the tertiary amine with the central carbonyl group must be involved. Therefore the evidence would strongly suggest that the thermal decomposition of both tricarbonates involves the loss of the central carbonyl group. Kinetic studies[5] have shown that these decompositions are first order and that the rates are essentially the same for both tricarbonates in chlorobenzene and the same in decalin. Further the rate of reaction decreases sharply in going from the polar solvent chlorobenzene to the nonpolar solvent decalin, which supports an ionic mechanism for the decomposition process.

Experimental Section[14]

Reactions of Alcohols with Tricarbonates. *tert*-Butyl Thiol Ethyl Dicarbonate (6a).—A solution of 294 mg (0.001 mol) of di-*tert*-butyl dithiol tricarbonate[3,5] in 10 ml of chloroform containing 75 mg (0.00166 mol) of ethyl alcohol was heated on a steam bath for 10 min. Removal of the solvent followed by distillation gave 150 mg (73%) of colorless mobile *tert*-butyl thiol ethyl dicarbonate (**6a**) (0.01 mm, bath temperature 80°). The ir spectrum showed carbonyl absorptions at 1800 and 1735 cm^{-1}. The nmr spectrum showed a triplet at 1.37 (J = 7 cps, 3 H), a singlet at 1.33 (9 H), and a quartet at 4.3 (J = 7 cps, 2 H).

Anal. Calcd for $C_8H_{14}O_4S$: C, 46.58; H, 6.68. Found: C, 46.57; H, 6.82.

***tert*-Butyl Ethyl Dicarbonate (6c).**—A similar procedure using ethanol and di-*tert*-butyl tricarbonate[4,5] gave the dicarbonate **6c** in 52% yield, distilled at a bath temperature of 55° (0.025 mm). The ir spectrum showed carbonyl absorptions at 1815 and 1775 cm^{-1}. The nmr spectrum showed a triplet at 1.37 (J = 7 cps, 3 H), a singlet at 1.53 (9 H), and a quartet at 4.25 (J = 7 cps, 2 H).

Anal. Calcd for $C_8H_{14}O_5$: C, 50.53; H, 7.41. Found: C, 50.53; H, 7.38.

***tert*-Butyl thiol isopropyl dicarbonate (6b)** was prepared similarly from the sulfur tricarbonate **1** and isopropyl alcohol in 68% yield as a colorless mobile liquid, distilled at a bath temperature of 80° (0.025 mm). The ir spectrum showed carbonyl

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[12] (a) D. S. Tarbell and M. A. Insalaco, *Proc. Nat. Acad. Sci. U. S.*, **57**, 233 (1967); (b) A. W. Friederang, D. S. Tarbell, and S. Ebine, *J. Org. Chem.*, **34**, 3825 (1969). *Cf.* also K. H. Slotta and H. Dressler *Ber.*, **63**, 888 (1930); R. Sayre, N. J. Leonard, *et al.*, in ref 2 above; J. E. Hodkins, W. P. Reeves, and Y. Liu, *J. Amer. Chem. Soc.*, **83**, 2532 (1961).

[13] M. Zbirovsky and V. Ettel, *Chem. Listy*, **50**, 670 (1956), report compounds obtained from thiophosgene and xanthates of type ROCSSCSSCSOR, which appear to dimerize readily.

[14] Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. All melting points and boiling points are uncorrected unless otherwise specified. Infrared spectra were recorded on a Beckman IR-10 spectrometer and nmr spectra were recorded on a Varian A-60 spectrometer, using TMS as internal standard; nmr spectra are given in parts per million.

peaks at 1800 and 1730 cm^{-1}. The nmr spectrum showed a doublet at 1.34 (J = 6.5 cps, 6 H), a singlet at 1.52 (9 H), and a septet at 4.93 (J = 6.5 cps, 1 H).

Anal. Calcd for $C_9H_{16}O_4S$: C, 49.07; H, 7.32; S, 14.55. Found: C, 49.22; H, 7.33; S, 14.54.

Reactions of Primary Amines with Tricarbonates. Aniline and Di-*tert*-butyl Dithiol Tricarbonate (1).—A solution of 150 mg (0.0016 mol) of freshly distilled aniline in 3 ml of carbon tetrachloride was added to a solution of 150 mg (0.00051 mol) of di-*tert*-butyl dithiol tricarbonate (1) in 3 ml of carbon tetrachloride at 0°. The reactants were allowed to warm to room temperature and stand for 1 hr. A white precipitate formed shortly after the addition was complete. Filtration gave 100 mg (theoretical yield, 92 mg) of product, mp 241–242°, whose ir spectrum was identical with that of diphenylurea. Recrystallization from ethanol–water gave white needles, mp 241–242°. Nothing was isolated from the filtrate.

Aniline and di-*tert*-butyl tricarbonate[4,5] **(4)** reacted similarly to give 82% of diphenylurea.

2,4-Dimethylaniline and Di-*tert*-butyl Dithiol Tricarbonate (1).—2,4-Dimethylaniline (redistilled, 83 mg) was allowed to react with 100 mg of the sulfur tricarbonate 1 in 5 ml of CCl_4 at room temperature; CO_2 was evolved and a white solid began to precipitate after 3 min. The ir spectrum of the reaction mixture showed a strong isocyanate band at 2270 cm^{-1}. The mixture was heated on the steam bath for 15 min, and 75 mg (62%) of bis-2,4-dimethylphenylurea was obtained which melted, from ethanol, at 268–270° (sealed tube) (reported[15] 263–265°).

2,4-Dimethylaniline and di-*tert*-butyl tricarbonate (4) gave 89% of the same urea.

2,6-Dimethylaniline (purified by distillation) with the sulfur tricarbonate 1, and with the oxygen tricarbonate 4, gave similarly a strong absorption for the isocyanate during the reaction, and the corresponding bis(2,6-dimethylphenyl)urea was formed in 50–60% yield, mp 331–332° (sealed tube).[16]

Reactions of Tertiary Amines with Tricarbonates. Triethylamine and *N*-Methylpiperidine.—The decomposition of di-*tert* butyl tricarbonate (4) is arrested at the dicarbonate[4,5] 5, and the decomposition of di-*tert*-butyl dithiol tricarbonate (1) to the dithiol dicarbonate 2 is catalyzed.

Reactions of *N*-Methylaniline with Tricarbonates. A. Di-*tert*-butyl Dithiol Tricarbonate (1).—A solution of 364 mg (0.000356 mol) of *N*-methylaniline (purified by distillation) in 3 ml of CCl_4 was added to a solution of 100 mg (0.00034 mol) of the dithiol tricarbonate 1 at room temperature. The solution became warm and the ir spectrum indicated that reaction was complete after 30 min. Removal of the solvent gave 32 mg (91%) of *tert*-butyl thiol carbonic *N*-methylphenylcarbamic anhydride (7a) as a pale yellow oil. The material could not be purified on account of its instability. The ir spectrum showed absorptions at 1775, 1725, and 1020 cm^{-1}, and the nmr spectrum showed singlets at 1.43 (9 H), 3.33 (3 H), and a broad singlet at 7.27 (5 H).

B. Di-*tert*-butyl Dithiol Dicarbonate (2).—A solution of 107 mg (0.001 mol) of *N*-methylaniline in 4 ml of CCl_4 was added to a solution of 240 mg (0.001 mol) of the dicarbonate 2. The reactants were heated on a steam bath for 1 hr after which time carbamate formation was complete. Removal of the solvent gave 180 mg (81%) of crystalline *tert*-butyl thiol *N*-methylphenylcarbamate (8a). Recrystallization from ethanol–water gave white needles of 8a, mp 54–55.5°.

The same compound was obtained in 45% yield (of recrystallized material) by refluxing *N*-methylaniline with the thiol carbonic carbamic anhydride 7a in CCl_4 for 4 hr. None of the symmetrical bis-*N*-methylphenylurea was found.

C. Di-*tert*-butyl Tricarbonate (4). Formation of *tert*-Butyl Carbonic *N*-Methylphenylcarbamic Anhydride (7b).—A solution of 60 mg (0.00056 mol) of *N*-methylaniline in 3 ml of CCl_4 was added to a solution of 150 mg (0.00057 mol) of the tricarbonate 4 in 3 ml of CCl_4 at room temperature. The solution became warm and carbon dioxide was evolved. The ir spectrum of the reactants showed that the tricarbonate bands had disappeared after 30 min. Removal of the solvent gave 130 mg (92%) of colorless mobile *tert*-butyl carbonic *N*-methylphenylcarbamic anhydride (7b) which was not purified further on account of its instability. The ir spectrum showed absorptions at 1795 and 1745 cm^{-1}. The nmr spectrum showed singlets at 1.43 (9 H), 3.31 (3 H), and 7.28 (5 H).

Thermal Decomposition of *tert*-Butyl Thiol Carbonic *N*-Methylphenylcarbamic Anhydride (7a).—In an apparatus[6] for the estimation of carbon dioxide, 171 mg of the carbonic anhydride 7a was heated at 170–180° in the presence of a trace of *N*-methylpiperidine as catalyst. The decomposition was complete after about 30 min; 26 mg of carbon dioxide (92% of 1 mol) was evolved. The yield of residue was 114 mg (80%). Recrystallization from ethanol–water gave white needles, mp 54–55°, identical with an authentic sample of *tert*-butyl thiol *N*-methylphenylcarbamate (8a).

Thermal Decomposition of *tert*-Butyl Carbonic *N*-Methylphenylcarbamic Anhydride (7b).—The anhydride, 184.5 mg (0.000735 mol), was decomposed at 170–180° exactly as described for the corresponding thiol compound 7a. The yield of carbon dioxide was 37 mg (103% of 1 mol). Distillation of the residue gave 116 mg (76%) of colorless mobile *tert*-butyl *N*-methylphenylcarbamate (8b), bp *ca.* 70° (1 mm). The ir spectrum showed a carbonyl absorption at 1700 cm^{-1}, and the nmr spectrum showed singlets at 1.42 (9 H), 3.21 (3 H), and a broad singlet at 7.18 (5 H).

Anal. Calcd for $C_{12}H_{17}NO$: C, 69.52; H, 8.27; N, 6.76. Found: C, 70.13; H, 8.40; N, 6.85.

The same compound was obtained in 89% yield by the action of *N*-methylaniline on di-*tert*-butyl dicarbonate 5 in refluxing CCl_4.

Reaction of Di-*tert*-butyl Dithiol Tricarbonate (1) with Pivalic Acid.—Pivalic acid (90 mg, 0.01 mol) and di-*tert*-butyl dithiol tricarbonate (294 mg, 0.01 mol) dissolved in 10 ml of CCl_4 were heated on a steam bath for 2 hr, after which time reaction was complete. Removal of the solvent gave 200 mg of crude product which consisted of a mixture of the tri- and dicarbonyl compounds 12 and 13. Distillation caused the tricarbonyl compound to decompose to the dicarbonyl compound, *tert*-butyl thiol carbonic pivalic anhydride (13), which occurred as a white wax, boiling at a bath temperature of about 75°, mp 40–49°. A second distillation gave 100 mg (46%) of a waxy solid, mp 56–59°; the ir spectrum showed absorptions at 1790 and 1725 cm^{-1}. The nmr spectrum showed a singlet at 1.52 (3 H) and at 1.24 (3 H).

Anal. Calcd for $C_{10}H_{18}O_3S$: C, 55.03; H, 8.31; S, 14.69. Found: C, 54.81; H, 8.29; S, 14.44.

***tert*-Butyl Thiol Carbonic Pivalic Anhydride (13).**—Sodium *tert*-butyl thiol carbonate was prepared from 4.5 g (0.05 mol) of *tert*-butyl mercaptan as previously described. A solution of 6.03 g (0.05 mol) of pivaloyl chloride in 30 ml of THF was added dropwise to the stirred carbonate at −60°. The reactants were stirred at this temperature for 2 hr and then for a further 2 hr at 0°. Ice-cold pentane (500 ml) was added, the precipitated NaCl was filtered off, and the solvent was removed at 0°. Distillation gave 4.5 g (41.3%) of the pure anhydride, bp 73° (0.025 mm), mp 57–59°, which was identical with 13 obtained above.

Thermal Decomposition of *tert*-Butyl Thiol Carbonic Pivalic Anhdride (13).—The mixed anhydride (330 mg) was decomposed at 120–140° in the presence of a trace of triethylamine. The yield of residue was 230 mg, which was distilled at a bath temperature of 100° and water pump pressure, to yield 165 mg (75%) of colorless *tert*-butyl thiol pivalate. The ir spectrum showed an absorption at 1675 cm^{-1}, and the nmr showed a singlet at 1.43 (3 H) and at 1.28 (3 H).

Reaction of Di-*tert*-butyl Tricarbonate with Pivalic Acid.—The tricarbonate, 262 mg (0.001 mol), and pivalic acid, 90 mg (0.001 mol), in 10 ml of CCl_4 were heated on a steam bath for 20 min. The ir spectrum indicated that reaction was complete. The nmr spectrum showed the material to consist probably of the symmetrical dicarbonate 5 and the mixed anhydride 13 (O instead of S).

Registry No.—**1**, 22085-39-8; **4**, 24424-95-1; **6a**, 28058-92-6; **6b**, 28058-93-7; **6c**, 19935-69-4; **8b**, 28131-24-0; **13**, 28058-95-9; **14**, 28058-96-0; pivalic acid, 75-98-9.

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[15] J. K. Thomson and F. J. Wilson, *J. Chem. Soc.*, 1262 (1933).

[16] R. A. Franz, *et al.*, *J. Org. Chem.*, **26**, 3309 (1961), report that this urea melts above 300°.