Hydrogenation of 7.—A solution of 50 mg of 7 in ~20 ml of ether was catalytically hydrogenated over Adams catalyst at room temperature. The catalyst was filtered and the product was isolated by preparative scale gas chromatography (32 mg). The substance was identical with 9-oxabicyclo[3.3.1]nonane (5).

Iododemercuration of 3 for Various Time Periods.—To determine the extent of isomerization of 4 as a function of time, 3 was treated as above with iodine for varying periods. The reaction mixture was divided in half; one half was dehydrohalogenated in the predescribed manner, and the second half was reduced with lithium aluminum hydride as outlined above. The product distribution results are tabulated in Table I.

TABLE I

| Time, hr | Per cent composition[a] | | | |
| | Dehydrohalogenation | | Reduction | |
	7	8	5	6
4	96	4	50	50
8	92	8	50	50
10	86	14	50	50
12	82	18	50	50

[a] Vpc analyses.

2-Iodo-9-oxabicyclo[4.2.1]nonane (11).—A solution of 4.5 g (0.01 mol) of mercurial iodide 10 and 2.5 g (0.01 g-atom) of iodine in 300 ml of carbon tetrachloride at 0° under a nitrogen atmosphere was stirred for 8 hr while slowly being allowed to come to room temperature. The salts were removed by filtration, and the filtrate was decolorized with aqueous sodium thiosulfate, dried, and concentrated to give 2.3 g (91%) of 11. The nmr spectrum of 11 was characterized by a one-proton multiplet at δ 4.6–4.85, a two-proton multiplet at 3.95–4.55, and a ten-proton multiplet at 1.0–2.5.

Hydride Reduction of 11.—A solution containing 2.5 g (0.01 mol) of 11 in 10 ml of anhydrous ether was reduced with lithium aluminum hydride as described above to give 0.9 g (72%) of a single product, bp 74–76° (24 mm), mp 31°, which was identical in all respects with authentic 1,4-epoxycyclooctane.[3]

Dehydrohalogenation of 1.—A 2.0-g (7.95 mmol) sample of 11 was dehydrohalogenated as above with 1.02 g (9.0 mmol) of potassium t-butoxide in 25 ml of anhydrous tetrahydrofuran. There was obtained 750 mg (76%) of a colorless liquid, vpc analysis of which indicated the presence of 7 (15%) and 8 (85%).

Synthesis and Kinetics of Decomposition of Di-t-butyl Tricarbonate, Di-t-butyl Dithioltricarbonate, and the Related Dicarbonates[1]
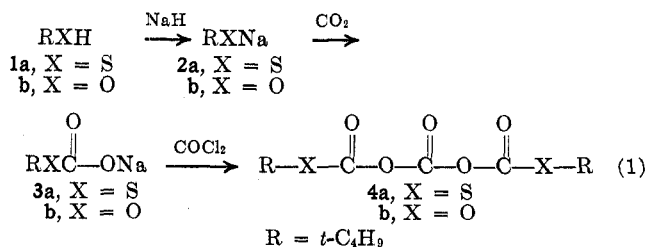
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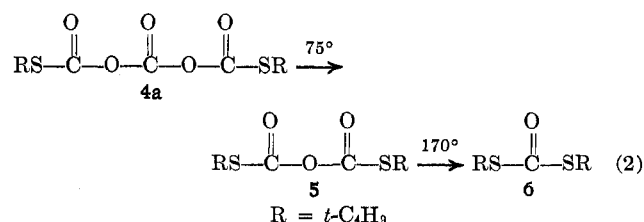Details of the preparation of di-t-butyl dithioltricarbonate, $[(CH_3)_3C\text{-}S\text{-}CO_2\text{-}]_2CO$, and di-t-butyl tricarbonate by the action of phosgene on sodium t-butyl thiolcarbonate and potassium t-butyl carbonate are given. Both tricarbonates decompose when heated above their melting points, the former producing di-t-butyl dithioldicarbonate and carbon dioxide, and the latter fragmenting into isobutene, t-butyl alcohol, and three molecules of carbon dioxide. The decomposition of the di-t-butyl tricarbonate can be arrested at the dicarbonate stage by refluxing the tricarbonate in carbon tetrachloride in the presence of a trace of triethylamine. When heated di-t-butyl dicarbonate fragments into isobutene, t-butyl alcohol, and two molecules of carbon dioxide, whereas di-t-butyl dithioldicarbonate gives the corresponding monocarbonate. Kinetic studies on all of these decompositions in both decalin and chlorobenzene, following the reactions by infrared spectroscopy, have shown them all to be strictly first order, and activation parameters have been determined. The mechanisms of the processes have been discussed.

The action of phosgene on sodium t-butyl thiolcarbonate 3a has been found to give di-t-butyl dithioltricarbonate[2] (eq 1) 4a and by a similar procedure[3] di-t-butyl tricarbonate 4b has been made from potassium t-butyl carbonate 3b; both are crystalline compounds.

$$RXH \xrightarrow{NaH} RXNa \xrightarrow{CO_2}$$

1a, X = S 2a, X = S
b, X = O b, X = O

$$\underset{\substack{\text{3a, X = S} \\ \text{b, X = O}}}{RX\overset{\overset{\displaystyle O}{\|}}{C}\text{-}ONa} \xrightarrow{COCl_2} \underset{\substack{\text{4a, X = S} \\ \text{b, X = O}}}{R\text{-}X\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}O\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}O\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}X\text{-}R} \quad (1)$$

$$R = t\text{-}C_4H_9$$

Several other oxygen tricarbonates 4b, where R is isopropyl or other, were prepared but could not be obtained pure.[3] When heated above its melting point (71–72°)

di-t-butyl dithioltricarbonate 4a decomposes very rapidly with the loss of one molecule of carbon dioxide to give di-t-butyl dithioldicarbonate 5 which, if heated at 170° for 45 min, similarly loses carbon dioxide to yield di-t-butyl dithiolmonocarbonate[4] 6 (eq 2). The same results were observed when the decomposition was effected in decalin and chlorobenzene as solvents.

$$\underset{\textbf{4a}}{RS\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}O\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}O\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}SR} \xrightarrow{75°}$$

$$\underset{\textbf{5}}{RS\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}O\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}SR} \xrightarrow{170°} \underset{\textbf{6}}{RS\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}SR} \quad (2)$$

$$R = t\text{-}C_4H_9$$

In contrast to the behavior of the dithiol tricarbonate 4a, di-t-butyl tricarbonate 4b when heated above its melting point (64.5–65°), fragments into three molecules of carbon dioxide, one molecule of isobutene, and
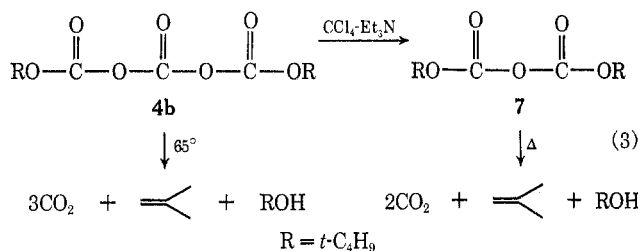
(1) Aided by Grant GP-7874 from the National Science Foundation.
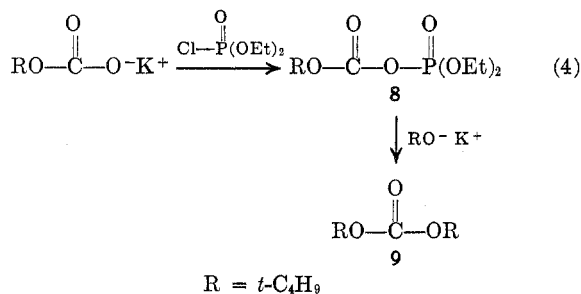(2) A. W. Friederang and D. S. Tarbell, *Tetrahedron Lett.*, 5535 (1968).
(3) C. S. Dean and D. S. Tarbell, *Chem. Commun.*, 728 (1969).
(4) D. S. Tarbell and L. Wei, *J. Org. Chem.*, **33**, 1884 (1968).

one molecule of *t*-butyl alcohol.[3,5] The same results were observed in both decalin and chlorobenzene as solvents. However, in refluxing carbon tetrachloride in the presence of a trace of triethylamine, the decomposition is arrested at the di-*t*-butyl dicarbonate[6,7] 7 stage. All attempts to convert the oxygen dicarbonate into the monocarbonate 9 were unsuccessful, the products being two molecules of carbon dioxide, one molecule of *t*-butyl alcohol, and one molecule of isobutene (eq 3). Further it appears that the di-*t*-

$$RO-\overset{\overset{\displaystyle O}{\|}}{C}-O-\overset{\overset{\displaystyle O}{\|}}{C}-O-\overset{\overset{\displaystyle O}{\|}}{C}-OR \xrightarrow{CCl_4\text{-}Et_3N} RO-\overset{\overset{\displaystyle O}{\|}}{C}-O-\overset{\overset{\displaystyle O}{\|}}{C}-OR$$

$$\textbf{4b} \qquad\qquad\qquad \textbf{7}$$

$$\downarrow 65° \qquad\qquad\qquad \downarrow \Delta \qquad (3)$$

$$3CO_2 + \hspace{-0.3em}=\hspace{-0.6em}<\hspace{0.3em} + ROH \qquad 2CO_2 + \hspace{-0.3em}=\hspace{-0.6em}<\hspace{0.3em} + ROH$$

$$R = t\text{-}C_4H_9$$

butyl monocarbonate[8] 9 does not function as an intermediate, because, when the dicarbonate is decomposed in the presence of the monocarbonate, the monocarbonate remains unchanged in all respects. An authentic sample of di-*t*-butyl monocarbonate 9 was obtained from *t*-butyl carbonic diethylphosphoric anhydride[9] 8, by reaction with potassium *t*-butoxide (eq 4). *t*-Amyl *t*-butyl carbonate was prepared by the same procedure.

$$RO-\overset{\overset{\displaystyle O}{\|}}{C}-O^-K^+ \xrightarrow{Cl-\overset{\overset{\displaystyle O}{\|}}{P}(OEt)_2} RO-\overset{\overset{\displaystyle O}{\|}}{C}-O-\overset{\overset{\displaystyle O}{\|}}{P}(OEt)_2 \quad (4)$$

$$\textbf{8}$$

$$\downarrow RO^-K^+$$

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

$$\textbf{9}$$

$$R = t\text{-}C_4H_9$$

The present paper gives experimental details for the results previously reported[2,3] in preliminary form. It further reports kinetic studies of the transformation of di-*t*-butyl dithioltricarbonate 4a to dicarbonate 5 and 5 to the monocarbonate 6, and also the decomposition of di-*t*-butyl tricarbonate 4b and of di-*t*-butyl dicarbonate 7 into their fragmentation products.

The reactions were readily followed by measuring the decrease in the infrared absorption of the selected carbonyl band. The results are tabulated in Table I. All the reactions gave good first-order constants up to 70–85% completion, and the first-order rate constants were essentially unchanged by a twofold increase in concentration. The rates of the reactions were not affected by the presence of the decomposition products. A typical rate run is shown in Table II.

Discussion of Kinetic Results.—As can be seen from Table I, the rates of decomposition of the dithiol tricarbonate 4a (reaction A, Table I) and of the oxygen

(5) For cleavage of *t*-butyl esters, see R. Altschul, *J. Amer. Chem. Soc.*, **68**, 2605 (1946), and references therein. For synthetic application, see G. S. Fonken and W. S. Johnson, *ibid.*, **74**, 831 (1952).

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(7) W. Thoma and H. Rinke, *Justus Liebigs Ann. Chem.*, **624**, 31 (1959).

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

(9) M. A. Insalaco and D. S. Tarbell, *Proc. Nat. Acad. Sci. U. S.*, **57**, 233 (1967).

TABLE I
KINETICS OF DECOMPOSITION OF TRI- AND DICARBONATES

Temp, °C	Concn, M	First order $k \times 10^5$ sec^{-1}	$\Delta H^{\neq}$, kcal mol^{-1}	$\Delta S^{\neq}$, eu

A. $RS-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-SR \longrightarrow RS-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-SR + CO_2$

Temp, °C	Concn, M	$k \times 10^5$ sec^{-1}	$\Delta H^{\neq}$	$\Delta S^{\neq}$
		In Decalin		
98.10	0.02716	2.66		
105.50	0.02520	6.20	28.14	−4.05
114.75	0.05200	14.4		
		In Chlorobenzene		
62.80	0.02020	3.46		
72.25	0.02035	10.4	24.43	−5.96
82.35	0.02500	28.5		
82.35	0.05000	28.2		

B. $RO-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-OR \longrightarrow 3CO_2 + ROH + \hspace{-0.3em}=\hspace{-0.6em}<$

Temp, °C	Concn, M	$k \times 10^5$ sec^{-1}	$\Delta H^{\neq}$	$\Delta S^{\neq}$
		In Decalin		
101.77	0.02495	2.69		
110.35	0.02495	6.50		
114.35	0.02473	8.58	27.17	−7.22
114.35	0.05015	9.08		
116.60	0.02595	10.37		
120.95	0.02140	17.65		
		In Chlorobenzene		
68.55	0.02534	5.67		

C. $RS-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-SR \longrightarrow RS-\overset{\overset{O}{\|}}{C}-SR + CO_2$

Temp, °C	Concn, M	$k \times 10^5$ sec^{-1}	$\Delta H^{\neq}$	$\Delta S^{\neq}$
		In Decalin		
144.15	0.02775	3.17	29.77	−8.60
151.75	0.02775	5.42		
159.95	0.02315	12.05		

D. $RO-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-OR \longrightarrow 2CO_2 + ROH + \hspace{-0.3em}=\hspace{-0.6em}<$

Temp, °C	Concn, M	$k \times 10^5$ sec^{-1}	$\Delta H^{\neq}$	$\Delta S^{\neq}$
		In Decalin		
143.30	0.02825	2.97		
149.35	0.02763	4.92		
157.81	0.02763	10.71	30.57	−6.53

TABLE II[a]

$RS-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-SR \longrightarrow RS-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-SR + CO_2$

Time $\times 10^{-2}$ sec	OD_t	$\text{Log} \dfrac{OD_t}{OD_0}$	% reaction	First order $k \times 10^5$ sec^{-1}
0	0.4366	0	0	
7.2	0.4013	−0.0367	8.085	11.74
18.0	0.3636	−0.0795	16.72	10.17
36.0	0.3034	−0.1581	30.51	10.11
72.0	0.2068	−0.3245	52.63	10.38
159.6	0.0810	−0.7316	81.45	10.57

[a] Temp, 72.25°; solvent, chlorobenzene; ir band, 1840 cm^{-1}.

tricarbonate 4b (reaction B, Table I) are considerably increased in changing from the nonpolar solvent, decalin, to the more polar chlorobenzene. This indicates that the transition states of the reactions have considerable ionic character. The data is given in Table III; all values but the last in this table were obtained by extrapolation from rate runs made at other temperatures using the temperature coefficients determined. It may

TABLE III
COMPARISON OF REACTION RATES IN
DECALIN AND CHLOROBENZENE AT 68.55°

| Reaction	Solvent	First order $k \times 10^7$ sec^{-1}
A[a]	Decalin	9.34
A	Chlorobenzene	671
B	Decalin	6.98
B	Chlorobenzene	567

[a] Table I.

also be noted that the rates of decomposition for both tricarbonates are essentially similar in decalin and also in chlorobenzene as are their activation parameters in decalin. This would suggest that the slow step in both decomposition reactions, as well as being first order, is the same mechanistically.

The reaction of aninile with both di-*t*-butyl dithioltricarbonate **4a** and di-*t*-butyl tricarbonate **4b** yields diphenylurea. Further work on the reaction of several aromatic amines (to be reported later) has shown that attack of the amines on the tricarbonates is at the central carbonyl group.[10] Nucleophilic attack at either of the other two equivalent carbonyls would be expected to produce the corresponding carbamates, N-phenyl-*t*-butyl thiolcarbamate[11] or N-phenyl-*t*-butyl carbamate[8], as primary products, both of which are stable compounds. Since no such compounds were isolated it may be inferred that the effect of the triethylamine in arresting the decomposition of di-*t*-butyl tricarbonate at the dicarbonate stage is brought about by an association of the tertiary amine moiety at the central carbonyl group, which in some way stabilizes the reactive intermediate long enough for the dicarbonate to form. Hence we may conclude that the slow step involves the loss of the middle carbonyl group in both cases. Further, since the rate of decomposition of di-*t*-butyl dicarbonate into its fragmentation products is much slower than the rate of decomposition of the tricarbonate, the dicarbonate does not function as an intermediate in the latter process.

The formation of isobutene in the decomposition of di-*t*-butyl tricarbonate and di-*t*-butyl dicarbonate illustrates the ready ability of *t*-butyl oxygen compounds to form *t*-butyl carbonium ions and emphasizes the well-known failure of *t*-butyl thiol compounds to reciprocate this behavior[4,5,12,13] and it may well be this behavior which causes the di-*t*-butyl tricarbonate and dicarbonate to fragment, rather than lose one molecule of carbon dioxide, as is the case with the sulfur analogs.

From the activation parameters for the decomposition of di-*t*-butyl dithioldicarbonate and di-*t*-butyl dicarbonate ($\Delta H^{\ddagger}$ 29.77 and 30.57 kcal mol^{-1}, and $\Delta S^{\ddagger}$ −8.60 and −6.53 eu), coupled with the fact that their rate constants are almost the same, it would seem that the slow step is mechanistically the same. Whereas the decomposition of the dithiol dicarbonate **5** produces the corresponding monocarbonate, in the case of the oxygen di-*t*-butyl dicarbonate **7** none of the corresponding monocarbonate is produced, nor does it function as

an intermediate. This would indicate that the first and slow step in both decompositions is the breaking of a C–O bond, the di-*t*-butyl dicarbonate then going on to form its fragmentation products on account of the ready ability of *t*-butyl oxygen compounds to generate *t*-butyl carbonium ions, and the di-*t*-butyl dithioldicarbonate stopping at the monocarbonate stage. Whereas this process is probably an ionic dissociation process, a cyclic transition state as depicted below cannot be ruled out.
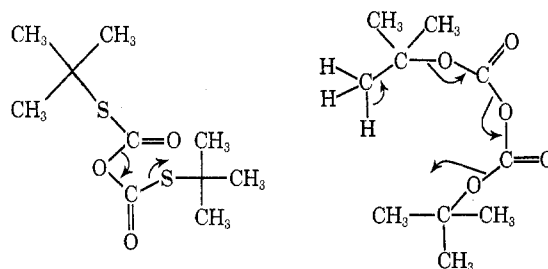
The tricarbonates are a new class of compounds, and there are no close mechanistic analogies. The dicarbonates **5** and **7** are related to the *t*-butylcarbonic[12] and thiolcarbonic anhydrides[4,13] previously studied in these laboratories. Many cases of carbon dioxide evolution which have received detailed kinetic study have involved peroxide derivatives decomposing by a freeradical path.[14] The large solvent effect in the present case indicates a considerable polar character in the transition state.[15] The intensively studied decarboxylation reactions of malonate and β-keto esters[16] do not present many points of similarity to the reactions described in the present paper.

Experimental Section[17]

Di-*t*-butyl Tricarbonate (4b).—Dry carbon dioxide was passed through an ice-cold solution of potassium *t*-butoxide (11.2 g, 0.1 mol) in THF (200 ml, distilled from aluminohydride) with vigorous stirring for 1 hr. Phosgene was then passed into the resulting white gel for 1–1.5 hr with vigorous stirring while the temperature was maintained below 0° (acetone–Dry Ice). The resulting solution was stirred for 1 hr more, again below 0°, and then dry nitrogen was passed through for 1 hr to remove excess phosgene. The bulk of the solvent was removed on a rotary evaporator, at 0° and water pump pressure, and the residue taken up in ice-cold pentane. The precipitated potassium chloride was filtered off and the filtrate evaporated under vacuum at 0° to give a pale yellow oil which crystallized on standing. Recrystallization from pentane gave 6.6 g (50%) of white needles, mp 64.5–65°. The ir spectrum (CCl$_4$) showed carbonyl absorptions at 1845, 1810, and 1780 cm^{-1} and the nmr spectrum showed a singlet at 1.66 ppm.

(10) Diphenyl triketone [J. D. Roberts, D. R. Smith, and C. C. Lee, *J. Amer. Chem. Soc.*, **73**, 618, 5927 (1951)] loses its central carbonyl group, under a variety of conditions, as CO or CO$_2$, with formation of benzoin or benzil.

(11) E. Dyer and J. F. Glenn, *ibid.*, **79**, 366 (1957).

(12) C. J. Michejda and D. S. Tarbell, *J. Org. Chem.*, **29**, 1168 (1964).

(13) T. Parasaran and D. S. Tarbell, *ibid.*, **29**, 2471 (1964).

(14) P. D. Bartlett and R. E. Pincock, *J. Amer. Chem. Soc.*, **82**, 1769 (1960), and earlier papers; T. Koenig and R. Cruthoff, *ibid.*, **91**, 2562 (1969); J. W. Taylor and J. C. Martin, *ibid.*, **89**, 6904 (1967), and earlier papers.

(15) *Cf.* S. J. Rhoads and R. E. Michel, *ibid.*, **85**, 585 (1963).

(16) For leading references, see B. R. Brown, *Quart. Rev. (London)*, **5**, 131 (1951); E. J. Corey, *J. Amer. Chem. Soc.*, **75**, 1163 (1953); R. Steinberger and F. H. Westheimer, *ibid.*, **73**, 429 (1951).

(17) 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 or a Perkin-Elmer 621 spectrometer. The nmr spectra were recorded on a Varian A-60 spectrometer using TMS as an internal standard. Temperature control in the kinetic experiments was achieved by the use of an E. H. Sargent Co. mercury capillary thermoregulator. The temperatures at which the kinetic runs were performed are corrected by calibration against a Dymec Model DY-2801 A quartz thermometer (Hewlett-Packard, Dymec Division, Palo Alto, Calif.).

Anal. Calcd for $C_{11}H_{18}O_7$: C, 50.39; H, 6.92; mol wt, 262. Found: C, 50.71; H, 7.04; mol wt, 270.

Di-*t*-butyl Dicarbonate (7).—Di-*t*-butyl tricarbonate (0.9 g) and triethylamine (5 drops) in 50 ml of dry carbon tetrachloride were refluxed until the ir spectrum of an aliquot indicated that no tricarbonate remained (~30 min). Removal of the solvent at reduced pressure gave 600 mg (81%) of colorless mobile dicarbonate: bp 64° (1.0 mm), mp 23°; lit.[6] bp 56–57° (0.5 mm), mp 21–22°. The ir spectrum showed carbonyl absorptions at 1820 and 1765 cm⁻¹ and the nmr spectrum showed a singlet at 1.61 ppm.

A second run was made in order to determine the quantity of carbon dioxide evolved. The apparatus consisted of a side-arm round bottomed flask equipped with a condenser attached to the top of which were two tubes, connected in series, containing ascarite. The tricarbonate (0.897 g) and 5 drops of triethylamine in 50 ml of dry carbon tetrachloride were placed in the flask and a stream of pure dry nitrogen passed through the apparatus slowly *via* the side arm. (The nitrogen was passed through a third tube of ascarite prior to entry into the apparatus.) The passage of nitrogen was continued for 2 hr and then for further 0.5-hr periods until the weight of the two ascarite tubes attached to the top of the condenser remained constant. The decomposition flask was immersed in an oil bath and heated at approximately 70° for 2 hr. After this initial period the ascarite tubes were weighed at 30-min intervals until their weights remained constant. The weight of carbon dioxide evolved was 120 mg (94% of 1 mol). Work-up of the carbon tetrachloride solution gave 600 mg (81%) of the colorless dicarbonate, mp 23°, bp 64° (1.0 mm).

Thermal Decomposition of Di-*t*-butyl Tricarbonate in the Absence of Solvent.—The tricarbonate (0.572 g, 0.00214 mol) was decomposed at 90–100° exactly as described above. The apparatus also incorporated a Dry Ice–acetone trap containing a solution of bromine in dry chloroform to estimate the isobutene. At the end of the experiment the contents of the trap were evaporated to yield 245 mg (90%) of a pale yellow liquid, bp 149°. Its nmr spectrum was identical with that of 1,2-dibromo-2-methylpropane. The residue in the decomposition flask, 125 mg (76%), bp 82°, had an ir spectrum identical with that of *t*-butyl alcohol. The weight of carbon dioxide evolved was 265 mg (93% of 3 mol).

Thermal Decomposition of Di-*t*-butyl Dicarbonate. A. In the Absence of Solvent.—In the apparatus described above 240 mg (0.001 mol) of di-*t*-butyl dicarbonate was decomposed at 130–140° to give isobutene, *t*-butyl alcohol (not estimated), and carbon dioxide (107 mg, 110% of 2 mol).

B. In Solvent.—In an attempt to isolate di-*t*-butyl monocarbonate, a number of runs were made using various solvents (decalin, chlorobenzene, *o*-dichlorobenzene) and catalysts (N-methylpiperidine, benzoyl peroxide) at various temperatures. In all cases, the dicarbonate decomposed to carbon dioxide, isobutene, and *t*-butyl alcohol. The dicarbonate (282 mg) plus 3 drops of N-methylpiperidine in 10 ml of *o*-dichlorobenzene was heated at 140° in the usual apparatus. Carbon dioxide (114 mg, 104% of 2 mol) was evolved.

C. In the Presence of Di-*t*-butyl Monocarbonate.—Di-*t*-butyl monocarbonate 9 (100 mg) and di-*t*-butyl dicarbonate (100 mg) in 6 ml of pure chlorobenzene were heated at 130–150°. After 1 hr, the dicarbonate absorption in the ir had partially disappeared (40%). After 2 hr the dicarbonate had almost disappeared but the monocarbonate absorptions remained. Removal of the solvent gave unchanged monocarbonate.

Di-*t*-butyl Monocarbonate (9).—A solution of 5.6 g (0.05 mol) of potassium *t*-butoxide in 150 ml of THF was carbonated as described previously. A solution of diethyl chlorophosphate, 8.6 g (0.05 mol) in 30 ml of THF, was added dropwise with stirring over a period of 60 min to the resulting ice cooled gel. The resulting gelatinous, turbid solution was stirred at 0° for a further hour. A solution of 5.6 g of potassium *t*-butoxide in 50 ml of THF was added dropwise with stirring at 0° over a period of 1 hr and the resulting slurry allowed to stir at room temperature overnight. Filtration followed by removal of the solvent at reduced pressure and ambient temperature gave a pale yellow oil. Distillation gave 3.5 g (40%) of colorless mobile di-*t*-butyl monocarbonate, bp 46–50° (1.0 mm), which crystallized on standing. Recrystallization from EtOH–H₂O gave white prisms, mp 40–41° [reported[8] bp 158° (767 mm), mp 39.5–40.5°]. The ir spectrum showed absorption at 1760 cm⁻¹ and the nmr showed a singlet at 1.42 ppm. A second fraction, diethyl *t*-butyl phos-

phate, bp 72° (1 mm), was also collected. A stream of dry nitrogen was passed through the apparatus for the duration of the experiment.

t-Amyl *t*-butyl monocarbonate has been prepared using this method in 60% yield as a colorless mobile liquid, bp 106–109° (6.3–6.5 mm). The nmr spectrum is in agreement with the assigned structure.

Di-*t*-butyl Dithioltricarbonate[2] (4a).—A 50% suspension of sodium hydride in mineral oil (2.5 g, 0.0543 mol) was washed with three 30-ml portions of pure THF to remove the mineral oil. The washed sodium hydride was placed in 250 ml of pure THF and a solution of *t*-butyl mercaptan (4.5 g, 0.05 mol) was added dropwise over a period of 15 min to the stirred suspension under nitrogen. The mixture was then refluxed for 1 hr resulting in the formation of a thick white slurry. This was cooled in a Dry Ice–acetone bath and dry carbon dioxide passed through with vigorous stirring for 3 hr. Phosgene was passed through the resulting colorless gel for 1 hr. A turbid solution formed which was stirred for a further hour and then the excess phosgene was removed by passing dry nitrogen through the solution. The temperature was allowed to warm to 0° and the bulk of the solvent was removed under reduced pressure at this temperature. The addition of ice-cold pentane caused the precipitation of sodium chloride, which was filtered off. Evaporation of the filtrate at 0° gave a pale yellow oil, which crystallized on standing. Recrystallization from pentane yielded 3.7 g (50%) of colorless needles, mp 71–72°. The nmr spectrum showed a singlet at 1.55 ppm. The elemental analysis has been reported previously.[2] Di-*t*-butyl dithioldicarbonate 5 and di-*t*-butyl dithiolmonocarbonate 6 were obtained as previously described.[2]

Reaction of Di-*t*-butyl Dithioltricarbonate with Aniline.—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-*t*-butyl dithioltricarbonate 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 amide product, mp 241–242°, whose ir spectrum was identical with that of diphenylurea. Recrystallization from EtOH–H₂O gave white needles, mp 241–242°. Nothing was isolated from the filtrate.

Reaction of Di-*t*-butyl Tricarbonate with Aniline.—Aniline (50 mg, 0.0054 mol) was added to a solution of 34 mg (0.00013 mol) of the tricarbonate in 4.5 ml of decalin at room temperature. A crystalline white solid appeared after several minutes. Filtration gave 20 mg (82%) of white needles, mp 241–242°, which were identical with diphenylurea.

Kinetic Studies. Purification of Solvents. A. Decalin.—The Eastman Kodak Practical sample was stirred with concentrated H₂SO₄ for 12 hr. The organic phase was separated, washed with water, with saturated Na₂CO₃, again with water, dried with CaH₂, filtered, and fractionally distilled through a 30-cm Vigreux column. The fraction boiling at 191–192° was collected, n^{20}D 1.4774 (lit.[18] *cis* isomer, n^{20}D 1.48113; *trans* isomer, n^{20}D 1.46968).

B. Chlorobenzene.—The "Baker Analyzed" reagent was washed several times with concentrated H₂SO₄, then with aqueous Na₂CO₃ and water, and dried with CaCl₂ and then P₂O₅. The sample was fractionally distilled twice through a 30-cm Vigreux column and the fraction boiling at 128–129° was collected, n^{20}D 1.5244 (lit.[19] n^{20}D 1.5248).

The kinetic runs were done in a constant temperature bath controlled to within ±0.1°.

Pyrex tubes of 8-mm i.d. were cleaned thoroughly by soaking in concentrated H₂SO₄ for 24 hr and then rinsing with water, dilute NH₄OH, water, and then several times with distilled water. Tubes of 20-cm length were drawn out and pulled thin at 16-cm length for convenient sealing. The tubes were dried in an oven at *ca.* 100° for at least 12 hr.

Stock solutions of di-*t*-butyltricarbonate and di-*t*-butyl dithioltricarbonate, which had been recrystallized prior to the kinetic runs and always had a melting range of less than 1°, and di-*t*-butyldicarbonate and di-*t*-butyl dithioldicarbonate which had been purified by distillation, were prepared from weighed samples. Into each tube, 1 ml of stock solution was transferred with a syringe. The solution was degassed, the tubes were flushed with nitrogen and sealed and stored in Dry Ice until the kinetic runs

(18) W. F. Seyer and R. D. Walker, *J. Amer. Chem. Soc.*, **60**, 2125 (1938).
(19) D. D. Perrin, W. L. F. Amerigo, and D. R. Perrin "Purification of Laboratory Chemicals," Pergamon Press, 1966, p 108.

were done. Generally, eight to ten tubes were prepared for each run. The tubes were placed in a metal rack which was then immersed in the thermostated Ucon oil bath (each tube was immersed up to 13 cm). It usually took 1.5–2.5 min for the temperature of the solution to reach equilibrium with the bath temperature. This was taken as the zero time of the reaction; one tube was withdrawn and immersed immediately in a Dry Ice–acetone bath as the zero time. The other tubes were withdrawn at suitable time intervals in the same way. The last tube was usually removed after about three half-lives of the reaction. The tubes were stored in Dry Ice until the ir analyses could be effected.

Analyses of the Kinetic Runs by Infrared Spectroscopy and Treatment of the Data.—The rate of thermal decomposition was followed by measuring the decrease in absorbance of the selected carbonyl band, Table IV, using a Perkin-Elmer Model 621

TABLE IV

Compd	Solvent	Band used, cm^{-1}
Di-t-butyl dithioltricarbonate	Chlorobenzene	1840
Di-t-butyl dithioltricarbonate	Decalin	1837
Di-t-butyl dithioldicarbonate	Decalin	1773
Di-t-butyl tricarbonate	Chlorobenzene	1870
Di-t-butyl tricarbonate	Decalin	1805
Di-t-butyl dicarbonate	Decalin	1775

infrared spectrometer[20] and KBr cells of 0.5-mm thickness. Beer's law was shown to be followed in all cases where the initial

concentration of the tricarbonate or dicarbonate was less than 4×10^{-2} mol.

The spectrum was scanned two to three times in the region of 1950–1650 cm^{-1}. The same procedure was used for all the kinetic runs. Transmittance (T_0 and T_{100}) were adjusted at the carbonyl maximum of the band measured when both cells were filled with pure solvent. To avoid the possibility of setting the pen against the mechanical stop, zero transmittance was set at 0–5% and 100% was set at 95–100%. The true per cent transmittance, T_X, of a sample was thus calculated from the observed transmittance, T_{obsd}, $T_X = (T_{obsd} - T_0)/(T - T_0)$. Each time the sample cell was cleaned with spectroscopic grade carbon tetrachloride and dried under a stream of air, and rinsed two or three times with the sample solution which was warmed to room temperature before analysis.

Generally in the region of 20–80% transmittance, the transmittance could be determined with an accuracy of ±0.3%. Therefore the tricarbonate and dicarbonate solutions were made up at (or uniformly diluted to) such a concentration that the zero time would be around 20–30% and thus two to three half-lives transmittance would be around 80%. From the per cent transmittance, the optical density at time t was obtained, and first-order rate constants were determined from the slope of the first-order plots of log OD_t/OD_0 against time. The activation parameters were calculated from the Eyring equation in the usual way.[21]

The enthalpy of activation, $\Delta H\ddagger$, was obtained at 100° from the Arrhenius energy of activation which was determined from the slope through the points on a plot of log k against $1/T$. The entropy of activation, $\Delta S\ddagger$, was calculated at 100° by substituting the known value of $\Delta H\ddagger$ into the equation.

Registry No.—**4a**, 22085-39-8; **4b**, 24424-95-1.

(20) *Cf.* P. D. Bartlett and R. R. Hiatt, *J. Amer. Chem. Soc.*, **80**, 1398 (1958).

(21) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," Wiley, New York, N. Y., 1961, p 98.

Phenyl Migration in Pseudohalogen Additions to 3,3,3-Triphenylpropene[1]

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Addition of iodine azide (IN$_3$) to tritylethylene (1), unlike to t-butylethylene, leads to complete rearrangement producing 3-azido-2,3,3-triphenyl-1-propyl iodide (2) in 99% yield. Treatment of 2 with potassium t-butoxide gave triphenylacrolein. Under milder conditions it was possible to isolate an intermediate allylic azide. A rearranged product was also noted on iodine isocyanate addition to 1. Similarly, benzonorbornadiene gave a 1,3 adduct resulting from a Wagner–Meerwein phenyl migration and methylenenorbornene produced a rearranged IN$_3$ adduct.

Though electrophilic addition of halogens to terpene olefins often leads to rearrangement of the carbon skeleton,[2] there are reported only few instances of alkyl migration occurring during halogen additions to acyclic olefins. A favorable case such as t-butylethylene, for example, which gives 60% methyl migration in HCl addition, renders no rearranged products when Cl$_2$, Br$_2$, or IN$_3$ is added to it under ionic conditions.[3] The first example of rearrangement in an acyclic system appears to be the Cl$_2$ addition to *trans*-di-t-butylethylene.[4]

Many more examples exist for phenyl migration. Although addition of HBr in acetic acid to allylbenzene gives only the normal adduct in 92% yield,[5] the presence

of two of three allylic phenyl groups or of a hydroxy group augments rearrangement by stabilizing the carbonium ion resulting from phenyl migration.[6,7] Such an example is shown below for bromine addition to 2-phenyl-3-buten-2-ol.
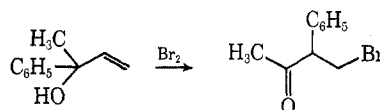
Recent studies on the reaction of olefins with iodine azide (IN$_3$) revealed that such additions occur with a remarkably high degree of stereo- and regioselectivity,[8] suggesting a three-membered ring iodonium ion intermediate. Thus n-butylethylene adds IN$_3$ to yield 2-

(1) Stereochemistry. LIV. For the previous paper in this series, see A. Hassner, F. P. Boerwinkle, and A. B. Levy, *J. Amer. Chem. Soc.*, **92**, 4879 (1970).

(2) See, for instance, H. Kwart, *ibid.*, **75**, 5942 (1953); L. Kaplan, H. Kwart, and P. von R. Schleyer, *ibid.*, **82**, 2341 (1960).

(3) (a) G. C. Ecke, N. E. Cook, and F. C. Whitmore, *ibid.*, **72**, 1511 (1950); (b) W. H. Puterbaugh and M. S. Newman, *ibid.*, **79**, 3469 (1957); (c) A. Hassner and F. W. Fowler, *J. Org. Chem.*, **33**, 2686 (1968).

(4) W. H. Puterbaugh and M. S. Newman, *ibid.*, **81**, 1611 (1959).

(5) H. E. Carter, *J. Biol. Chem.*, **108**, 619 (1935).

(6) I. V. Bodrikov, V. R. Karwashov, and T. I. Temikova, *Russ. J. Org. Chem.*, **3**, 1640 (1967).

(7) While this work was in progress the addition of bromine to 1 was reported by R. O. C. Norman and C. B. Thomas, *J. Chem. Soc. B*, 598 (1967).

(8) *Regio* is used to describe directional effects in bond making and breaking: A. Hassner, *J. Org. Chem.*, **32**, 2684 (1968).