homogeneous conditions it was found that 1.60 mmol of isodurene reacts with 0.80 mmol of CAN to give 0.41 mmol of benzylic acetates and nitrates.

Oxidation of Mesitylene. Isolation of the Reaction Products. A mixture of mesitylene (16.6 mmol) and CAN (33.2 mmol) in acetic acid (200 mL) was treated as above until the red-orange color of CAN faded (45 h). The pale-yellow liquid (2.5 g) obtained after usual workup was chromatographed on silica gel. Elution with $CHCl_3$–light petroleum 1:9 gave 3,5-dimethylbenzyl nitrate (0.93 g, 31% yield) as a colorless liquid: $n^{22}{}_D$ 1.5172 (lit.[30] 1.5172); IR 2920 and 1640 cm^{-1}; ^1H NMR (CCl_4) δ 6.90 (s, 3 H), 5.22 (s, 2 H), 2.27 (s, 6 H). Recovery was not quantitative, since several fractions containing the product in a less pure form were discarded. Elution with pure $CHCl_3$ gave 0.81 g of a mixture of two products, which were later shown to be 3,5-dimethylbenzyl acetate and 2,4,6-trimethylphenyl acetate. Pure samples of the latter compounds were obtained by resolution of the mixture by preparative VPC, on a 2-m column packed with CWX 20M 10% operating at 140 °C. Structure assignments were based on the following properties. 2,4,6-Trimethylphenyl acetate: IR 2920 and 1760 cm^{-1}; ^1H NMR (C_6D_6) δ 6.73 (s, 2 H), 2.10 (s, 3 H), 2.05 (s, 6 H), 1.90 (s, 3 H); mass spectrum (70 eV) *m/e* (rel intensity) 179, M^+ (16), 137 (13), 136 (100), 135 (15), 121 (56), 91 (14), 43 (13). 3,5-Dimethylbenzyl acetate: $n^{20}{}_D$ 1.5032 (lit.[31] $n^{23.5}{}_D$ 1.5028); IR 2920 and 1740 cm^{-1}; ^1H NMR (CCl_4) δ 6.88 (s, 3 H), 4.94 (s, 2 H), 2.27 (s, 6 H), 2.00 (s, 3 H).

Oxidation of Isodurene. Isolation of 2,4,6-Trimethylbenzyl Alcohol. Isodurene (7.5 mmol) was made to react with CAN (15.0 mmol) in acetic acid at 80 °C for 10 min, and the crude reaction product was reduced with $LiAlH_4$. The mixture of alcohols was recrystallized from hexane, and 2,4,6-trimethylbenzyl alcohol, mp 83–85 °C, was obtained in 40% yield.

Acknowledgments. The financial support of C.N.R. is gratefully acknowledged for the part of this work which has been carried out at the University of Perugia.

Registry No.—CAN, 16774-21-3; acetic acid, 64-19-7; 3,5-dimethylbenzyl nitrate, 15285-43-5; acetate, 19082-49-6; 2,4,6-trimethylbenzyl alcohol, 4170-90-5; 3,4,5-trimethybenzyl alcohol, 39126-11-9; 2,6-dimethylbenzyl alcohol, 62285-58-9; 2,3-dimethylbenzyl alcohol, 13651-14-4.

References and Notes

(1) Part 2: E. Baciocchi, L. Mandolini, and C. Rol, *Tetrahedron Lett.*, 3343 (1976).
(2) (a) W. S. Trahanovsky and L. B. Young, *J. Org. Chem.*, **31**, 2033 (1966); (b) L. Syper, *Tetrahedron Lett.*, 4493 (1966); (c) L. A. Dust and E. W. Gill, *J. Chem. Soc. C*, 1630 (1970).
(3) An easier oxidability of the ring acetoxylated product with respect to the other reaction products and the starting material can be reasonably suggested, since it is known that nuclear monoacetates are often much less resistant to oxidation than the parent compound. See L. Eberson, *J. Am. Chem. Soc.*, **89**, 4669 (1967).
(4) D. Benson, "Mechanisms of Oxidation by Metal Ions", Elsevier, New York, N.Y., 1976, p 2, and references cited therein.
(5) It is interesting to note that the isomeric distribution of nitrates and acetates obtained from the reaction of isodurene compares well with the "overall" isomeric distribution determined after conversion of both nitrates and acetates to the corresponding alcohols and VPC analysis. See E. Baciocchi, L. Mandolini, and C. Rol, *Tetrahedron Lett.*, 3787 (1973).
(6) K. Nyberg, *Acta Chem. Scand.*, **25**, 2499 (1971).
(7) (a) J. K. Kochi in "Free Radicals", Vol. I, J. K. Kochi, Ed., Wiley, New York, N.Y., 1973, p 622. (b) R. A. Sheldon and J. K. Kochi, *J. Am. Chem. Soc.*, **90**, 6688 (1968).
(8) (a) We thank a referee for this suggestion; (b) W. S. Trahanovsky and J. Cramer, *J. Org. Chem.*, **36**, 1890 (1971).
(9) T. W. Martin, A. Henshall, J. M. Burk, and R. W. Glass, unpublished work quoted by T. W. Martin, J. M. Burk, and A. Henshall, *J. Am. Chem. Soc.*, **88**, 1097 (1966).
(10) R. O. C. Norman, C. B. Thomas, and P. J. Ward, *J. Chem. Soc., Perkin Trans. 1*, 2914 (1973).
(11) K. Nyberg, *Acta Chem. Scand.*, **24**, 478 (1970).
(12) K. Nyberg, *Chem. Scr.*, **5**, 115 (1974).
(13) K. Nyberg and L. Winstrand, *Chem. Scr.*, **6**, 234 (1974).
(14) K. Nyberg and L. Winstrand, *Acta Chem. Scand., B*, **29**, 629 (1975).
(15) E. I. Heiba, R. M. Dessau, and W. J. Koehl, Jr., *J. Am. Chem. Soc.*, **91**, 6830 (1969).
(16) F. Benington, R. D. Morin, and L. C. Clark, *J. Org. Chem.*, **25**, 1542 (1960).
(17) E. Baciocchi, A. Ciana, G. Illuminati, and C. Pasini, *J. Am. Chem. Soc.*, **87**, 3953 (1965).
(18) E. C. Horning, "Organic Synthesis" Collect. Vol. III, Wiley, New York, N.Y., 1955, p 553.
(19) A. I. Vogel, "Practical Organic Chemistry", 3rd ed, Longmans, Green, and Co., New York, N.Y., p 253.
(20) J. C. Charlton and E. D. Hughes, *J. Chem. Soc.*, 854 (1956).
(21) L. I. Smith and C. L. Moyle, *J. Am. Chem. Soc.*, **58**, 1 (1936).
(22) K. J. P. Orton, J. E. Coates, and F. Burdett, *J. Chem. Soc.*, **91**, 35 (1907).
(23) M. S. Carpenter and W. M. Easter, *J. Org. Chem.*, **19**, 77 (1954).
(24) E. L. Niedzielski and F. F. Nord, *J. Org. Chem.*, **8**, 147 (1943).
(25) R. F. Nystrom and W. G. Brown, *J. Am. Chem. Soc.*, **69**, 2548 (1947).
(26) H. Suzuki, *Bull. Chem. Soc. Jpn.*, **42**, 2618 (1969).
(27) V. F. Raaen and J. F. Eastham, *J. Am. Chem. Soc.*, **82**, 1349 (1960).
(28) W. R. Brasen, C. R. Hauser, *J. Org. Chem.*, **18**, 806 (1953).
(29) L. Zoccolillo and A. Liberti, *J. Chromatogr.*, **77**, 69 (1973).
(30) S. D. Ross, M. Finkelstein, and R. C. Petersen, *J. Am. Chem. Soc.*, **89**, 4088 (1967).
(31) S. D. Ross, M. Finkelstein, and R. C. Petersen, *J. Am. Chem. Soc.*, **86**, 4139 (1964).

A Study of the Mode of Decomposition of Some Carboxylic *tert*-Alkylcarbonic Anhydrides[1a]

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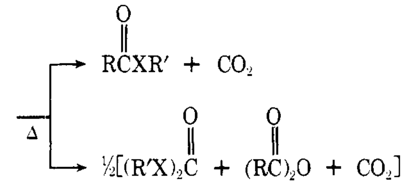
Received March 18, 1977

Three hindered carboxylic carbonic anhydrides—pivalic *tert*-butylcarbonic anhydride, pivalic *tert*-butylthiolcarbonic anhydride, and 2,2-dimethylbutyric *tert*-amylthiolcarbonic anhydride—have been prepared and studied with respect to their mode of decomposition and reactivity with a primary amine. While the products from the decomposition of pivalic *tert*-butylcarbonic anhydride are consistent with an ionic chain mechanism, the products from the decomposition of the two pure thiolcarbonic anhydrides are more consistent with an intramolecular decomposition. In addition, results from the decomposition of a mixture of the two thiolcarbonic anhydrides argue strongly against an ionic chain mechanism. Other considerations are discussed briefly.

There have been numerous reports[2] dealing with the synthesis, reactions, and mode of decomposition of carboxylic carbonic anhydrides 1. In general, this type of compound is thermally unstable, particularly in solution or in the liquid state. Two sets of decomposition products are possible,[3,4] as shown by eq 1 and 2. Usually, mixed anhydrides from alcohols (X = O) tend to give varying ratios of the possible products,[5,6] while anhydrides from thiols (X = S) give primarily thiol ester and carbon dioxide.[7] Although both systems have exhibited first-order or psuedo-first-order decomposition kinetics, the kinetic measurements for thiol-mixed anhydrides were consistent and reproducible, while those for alcohol-mixed anhydrides were erratic and apparently quite succeptible to the influences of trace impurities. It has been proposed that mixed

$$R\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}XR'$$

1, R, R′ = alkyl or aryl, X = O or S
2a, R = R′ = $-C(CH_3)_3$, X = O
b, R = R′ = $-C(CH_3)_3$, X = S
c, R = R′ = $-C(CH_3)_2C_2H_5$, X = S



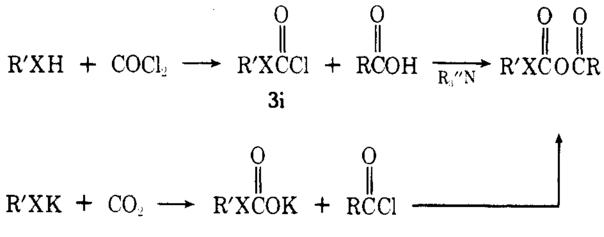
(1)

(2)

anhydrides derived from alcohols decompose by an ionic chain mechanism, while mixed anhydrides from thiols decompose via an intramolecular route.

In order to further investigate these hypotheses, we have studied a new group of anhydrides which are characterized by a tertiary alkyl group adjacent to both the carboxylic and carbonic carbonyls. First, we have compared pivalic *tert*-butylcarbonic anhydride (**2a**) with pivalic *tert*-butylthiolcarbonic anhydride (**2b**). Secondly, we have compared **2b** with 2,2-dimethylbutyric *tert*-amylthiolcarbonic anhydride (**2c**). Finally, we have decomposed a mixture of **2b** and **2c** and analyzed the resulting product mixture to determine whether the decomposition yielded products expected of an intramolecular reaction or those to be expected from an ionic chain mechanism, i.e., crossover products.[8]

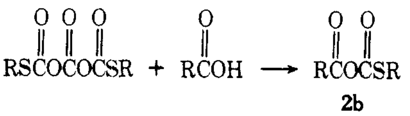
Synthesis of Mixed Anhydrides. The present work with mixed anhydrides indicates that method 3 is preferable for the preparation of anhydrides derived from tertiary thiols and method 4 is preferable for oxygen analogues.[5] The reason for this lies in the stability of the intermediate chlorocarbonate **3**. While tertiary alkyl chlorocarbonates are quite unstable and difficult to work with,[9] the corresponding thiol derivatives are reasonably stable, can be distilled if necessary, and can be stored in the refrigerator for several weeks with no noticeable decomposition. Compound **2b** has been prepared previously[10] in an entirely different fashion (eq 5).



(3)

(4)

X = O or S

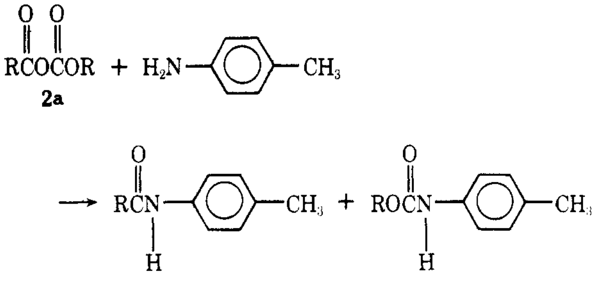


$$RS\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}SR + R\overset{O}{\overset{\|}{C}}OH \longrightarrow R\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}SR \quad (5)$$

2b

R = $-C(CH_3)_3$

Reactions of 2a–c. Because of the hindered nature of these compounds, their utility as possible selective acylating or nitrogen blocking agents was investigated. Leister and Tarbell[11] had previously demonstrated that the reaction of pivalic ethylcarbonic anhydride and *N*-methylaniline led to the formation of only the corresponding ethyl carbamate and none of the possible pivalamide. We found that **2a** reacted with *p*-toluidine (eq 6) to give isolated yields of 66% of the pivalamide **4a** and 32% of the carbamate **4b**. Subsequently, **2b** and **2c** were found to yield mixtures which consisted of approximately the same ratio of amide vs. carbamate on the basis of their IR spectrum and TLC.



2a

(6)

4a, 66% 4b, 32%

Next, a product study of the thermal decomposition of these anhydrides was undertaken. Two different approaches were utilized to give the results shown in Table I. First, the amount of carbon dioxide evolved was measured by absorption on Ascarite; and secondly, the residues from these decompositions were subjected to analysis by VPC. Due to the difference in the stoichiometry between reaction 1 and reaction 2, one can predict the amount of carbon dioxide which should be evolved by comparing the ratio of ester formed to symmetrical anhydride or carbonate.

For the decomposition of **2a**, products identified in order of their relative abundance were carbon dioxide, pivalic anhydride, di-*tert*-butyl carbonate, *tert*-butyl pivalate, *tert*-butyl alcohol, and isobutene. The ratio of pivalic anhydride to *tert*-butyl pivalate was 3.7 to 1.0. This ratio is consistent with 88% of the decomposition occurring by reaction 2.

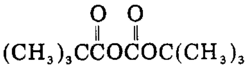
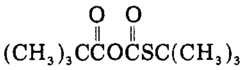
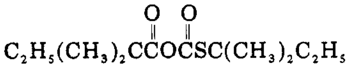
The decompositions of **2b** and **2c** as pure materials led to quite similar product ratios. Both compounds decomposed primarily by reaction 1 to yield 87% of thiol ester and 7% of the symmetrical anhydride in the case of **2b**, and 81% ester to 9% anhydride for **2c**. Products from the decomposition of **2b** were identified as carbon dioxide, *tert*-butyl thiolpivalate (**5**), pivalic anhydride (**6**), and di-*tert*-butyl dithiolcarbonate (**11**). For **2c** the products were carbon dioxide, the *tert*-amylthiol ester from 2,2-dimethylbutyric acid (**9**), 2,2-dimethylbutyric anhydride (**10**), and di-*tert*-amyl thiol carbonate (**12**).

Decomposition of a mixture of **2b** and **2c** led to a mixture which was analyzed by VPC originally to show four major and two minor peaks in addition to carbon dioxide, as noted in Table I. The peaks were identified in order of increasing retention time as *tert*-butyl thiolpivalate (**5**), pivalic anhydride (**6**), *tert*-amyl thiolpivalate (**7**), *tert*-butylthiol 2,2-dimethylbutyrate (**8**), *tert*-amylthiol 2,2-dimethylbutyrate (**9**), and 2,2-dimethylbutyric anhydride (**10**). Since the column temperature was kept below 120 °C during the VPC analysis, it was probable that the symmetrical thiolcarbonates were retained on the column. Subsequent elevation of injection port and column temperature did result indeed in two additional peaks, **11** and **12**, with longer retention times, which were the expected symmetrical thiolcarbonates. The course of the crossover experiment may be summarized by eq 7.

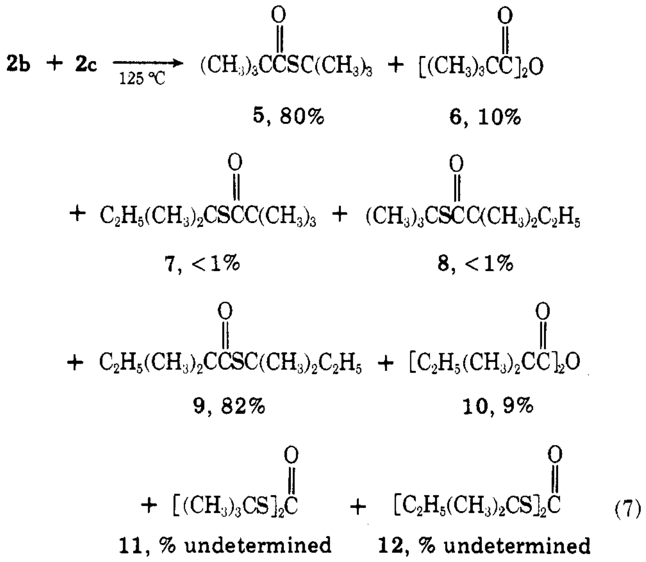
Kinetic Studies of 2a–c. Attempts to measure the rates of decomposition of these compounds were undertaken utilizing IR.[7,12] This method was not possible with **2a** due to the overlap of the carbonyl bands of the starting material and pivalic anhydride, the major product of the decomposition. Further, there was no other IR absorption in **2a** which was suitable to use. However, with the thiolcarbonic anhydrides **2b** and **2c**, carboxylic acid anhydride formation is minor, and through 80% reaction, interference is minimal. A detailed study of **2b** was undertaken to verify kinetic and thermodynamic similarity to previously studied thiolcarbonic anhydrides.[7] The results of this study can be found in Tables II and III.

Although a detailed study of **2c** was not undertaken, a rate determination was carried out at 125 °C, the temperature at

Table I. Measurement of CO_2 Evolution

Compd	Weight decomposed	Weight of CO_2 collected	% of 1 eq.
 $(CH_3)_3C\overset{O}{\overset{\Vert}{C}}O\overset{O}{\overset{\Vert}{C}}OC(CH_3)_3$ **2a**	1.2464	0.1719	63
	0.5604	0.0741	61
			Av 62 (60)[a]
 $(CH_3)_3C\overset{O}{\overset{\Vert}{C}}O\overset{O}{\overset{\Vert}{C}}SC(CH_3)_3$ **2b**	0.1904	0.0319	83
	0.4334[b]	0.0905	103
	0.2313	0.0445	95
	0.1155	0.0207	89
	0.1823	0.0305	83
	0.2049	0.0421	102
			Av 92 (94)[a]
 $C_2H_5(CH_3)_2C\overset{O}{\overset{\Vert}{C}}O\overset{O}{\overset{\Vert}{C}}SC(CH_3)_2C_2H_5$ **2c**	0.3723	0.0600	90 (89)[a]
2b + **2c**	0.3235, 0.4172	0.1066	76
	0.9745, 0.2040[b]	0.2850	75
			Av 76 (92)[a]

[a] These numbers represent the predicted amount of CO_2 on the basis of VPC analysis of residue comparing ester to anhydride ratio. [b] These reactions were carried out in chlorobenzene, while all others were carried out without solvent.



which the crossover experiment was run. At this temperature a 0.4515 M solution of **2c** in chlorobenzene had a first-order rate constant of $4.05 \times 10^{-4}\ s^{-1}$ and a 0.3795 M solution had a rate constant of $3.95 \times 10^{-4}\ s^{-1}$. Interpolation of the Arrhenius plot for pivalic *tert*-butylthiolcarbonic anhydride (**2b**) yielded a rate constant of $11.0 \times 10^{-4}\ s^{-1}$ at this same temperature.

Discussion

In this study we have examined carboxylic carbonic anhydrides, in which the carboxylic portions of the molecules are derived from aliphatic acids with an adjacent tertiary group and not from aromatic acids as in earlier studies.[5-7] Further, we have contrasted the reactivity of two of these mixed anhydrides, which differ only with respect to whether they contain oxygen or sulfur in the carbonic moiety (X = O in **2a** and X = S in **2b**), and we have decomposed two similar mixed anhydrides, **2b** and **2c**, simultaneously in the same reaction vessel to determine if products expected from an ionic chain decomposition are formed.

The reaction of these dually hindered anhydrides with a primary amine led to an interesting observation. Although there is an increased yield of the corresponding carbamate, the reaction was far from being selective, with the major product still the amide for **2a, 2b,** and **2c.** Whether this change in product ratios is due to steric or electronic effects has not been answered.

Although the aliphatic carboxylic thiolcarbonic anhydrides **2b** and **2c** do decompose more readily than corresponding aromatic carboxylic thiolcarbonic anhydrides, decomposition kinetics are still first order and the product ratios are essentially the same. The oxygen analogue **2a** seems to differ very little both in ease of decomposition and in the range and variability of products formed from the corresponding aromatic system.[5] It seems that **2a** decomposes by one mechanism, while **2b** and **2c** decompose by another. That this may be the case is likely when one considers the much greater propensity for carbon–oxygen cleavage as opposed to carbon–sulfur cleavage in tertiary systems[13,14] and the greater nucleophilicity of sulfur as compared to oxygen.

Since earlier suggestions[5,6] of an ionic chain mechanism for

Table II. Reaction Rates for Pivalic *tert*-Butylthiolcarbonic Anhydride (2b)

Concn, M	Solvent	Temp, °C	First-order $k \times 10^4$ s
0.040 88	Decalin	118.5	2.96
0.121 2		118.5	2.79
0.083 52		125.9	5.25
0.040 09		138.6	14.6
0.040 62	Chlorobenzene	108.2	2.06
0.040 62		118.5	5.33
0.040 62		133.6	17.8

Table III. Activation Parameters for Decomposition of Pivalic *tert*-Butylthiolcarbonic Anhydride

Temp, ±0.1 °C	$k \times 10^4$ s	Concn, M	E_a, kcal/mol	ΔH, kcal/mol	ΔS, eu
		In Decalin			
118.5	2.96	0.040 88	25.5	24.7	−12.0
125.9	5.25	0.083 52			
138.6	14.6	0.040 09			
		In Chlorobenzene			
108.2	2.06	0.04062			
118.5	5.33	0.040 62	26.2	25.4	−9.1
133.6	17.8	0.040 62			

oxygen anhydrides similar to **2a** seem to explain the results quite well, we decided to carry out a crossover experiment to determine if we could rule out an ionic chain mechanism for the decomposition of the corresponding thiol anhydrides **2b** and **2c** with some degree of certainty. Comparison of the individual decomposition rates of **2b** and **2c** at the temperature at which the crossover study was run showed that **2b** decomposed slightly less than three times as fast as **2c**. On the basis of earlier work,[15] this new rate seems reasonable and one would expect not too much difference in the reactivity of **2b** and **2c**. If the compounds decompose via an ionic chain, reasonably one could expect at least 10–15% of the crossover products **7** and **8**. The results given in eq 7 clearly show that this is not the case. When coupled with the relatively small change in rate constants with a change in polarity of solvents, a result which has been noted previously with the aromatic carboxylic thiolcarbonic anhydrides,[7] this experiment virtually rules out the ionic chain. However, the formation of even trace amounts of these compounds, as well as larger fractions of symmetrical acid anhydrides and thiolcarbonates, is not consistent with a completely intramolecular process. That these compounds might arise from a relatively slow biomolecular process is a possibility, but there is not evidence for this.

Experimental Section

General. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. All melting and boiling points are uncorrected. The IR spectra for qualitative work were recorded on a Beckmann IR-10 or a Perkin-Elmer 727 spectrometer in solution or neat as indicated for each compound. Quantitative IR spectra were recorded in solution on a Perkin-Elmer 621 spectrometer. The NMR spectra were recorded on a Jeol MH-100 instrument under the conditions indicated. For kinetic experiments the temperature was controlled by an E. H. Sargent Co. mercury capillary thermoregulator, which maintained temperatures at ±0.1 °C of the stated values, which have been corrected by calibration against a Dymec Model DY-2801A quartz thermometer (Hewlett-Packard, Dymec Division, Palo Alto, Calif.).

Preparation of Pivalic *tert*-Butylcarbonic Anhydride (2a). A slight modification of the published method[5] was used to prepare the title compound. Potassium *tert*-butoxide (6.0 g, 0.054 mol) was first carbonated in 50 mL of THF, and then treated with freshly distilled pivaloyl chloride (6.2 g, 0.052 mol) in 20 mL of THF over a 3-h period, giving 6.0 g (58%), which appeared to be the desired product from its IR spectrum. Subsequent vacuum distillation at 80–82 °C (12 mm) led to 4.6 g (44%) of a viscous material, which had a neat proton NMR spectrum[16] of equivalent singlets at 1.60 and 1.31 ppm and an IR spectrum (CCl_4) with carbonyl absorption at 1800 and 1745 cm^{-1}. The pure material had mp 21–23 °C.

Anal. Calcd for $C_{10}H_{18}O_4$: C, 59.39; H, 8.97. Found: C, 59.25; H, 8.96.

Preparation of *tert*-Butyl Pivalate. Equimolar quantities of pivaloyl chloride and triethylamine with a twofold excess of *tert*-butyl alcohol in THF were refluxed for 40 h. After a standard workup on the reaction mixture, distillation gave the ester: bp 134.5–137 °C, NMR spectrum in chlorobenzene of equivalent singlets at 1.39 and 1.12 ppm, and neat IR spectrum with a single carbonyl absorption at 1720 cm^{-1}.

Preparation of Pivalic Anhydride (6). Reaction of equimolar quantities of pivaloyl chloride, pivalic acid, and triethylamine in refluxing THF led to the production of a material whose bp was 192–194 °C and whose IR spectrum (CCl_4) showed carbonyl absorption at 1810 and 1735 cm^{-1}. The NMR spectrum consisted of a singlet at 1.14 ppm in chlorobenzene, and VPC indicated only one compound was present.

Preparation of *tert*-Butylthiol Chlorocarbonate (3b). The following is a modification of the procedure[17] of Tarbell and Parasaran and is due primarily to the unpublished work of Dr. Yutaka Yamamoto. An excess of phosgene (18 g, 0.18 mol) was collected in 50 mL of benzene (an increase in volume of 1 mL is equal to 1.2 g) and then added to an ice–salt cooled 250-mL three-neck round-bottomed flask equipped with nitrogen inlet, mechanical stirrer, and addition funnel. Via the addition funnel a solution of *tert*-butyl mercaptan (14.4 g, 0.16 mol) and pyridine (12.0 g, 0.15 mol) in about 40 mL of benzene was introduced over a period of 30 min and stirred for another hour at ice bath temperature under a nitrogen atmosphere. After the solution was allowed to rise to room temperature over 3 h, insoluble material was removed by suction filtration through a medium-fritted filter while under a dry nitrogen atmosphere, and solvent was removed in vacuo. This provided a crude yield of 17.6 g (75%) of the desired chlorocarbonate as a cloudy solution which exhibited a very characteristic neat IR spectrum with broad absorption centered at 1755 (s) and 1625 cm^{-1} (w). In this case, the thiol chlorocarbonate was used without further purification, although one can readily purify the crude material by distillation at 43 °C (12 mm). The thiol chlorocarbonate appears relatively stable and can be stored in the refrigerator for several weeks without any apparent decomposition.

Preparation of *tert*-Amylthiol Chlorocarbonate (3c). The reaction of *tert*-amyl mercaptan (10.4 g, 0.10 mol) and pyridine (8.0 g, 0.10 mol) with phosgene (6.0 g, 0.60 mol) in benzene, as described previously for **3b**, yielded 11.7 g (70%) of crude product. Subsequent distillation at 30 °C (1 mm) led to 11.2 g (67%) of product with an IR spectrum quite similar to that of **3b**. This material is relatively stable, as evidenced by its unchanged IR spectrum, after storage in the refrigerator for 1 month.

Preparation of 2,2-Dimethylbutyric Acid.[18] The modified procedure[19,20] of Puntambeker and Zollner was used to prepare the title compound from carbon dioxide and *tert*-amyl chloride, which was first prepared from *tert*-amyl alcohol by the procedure[21] of Norris and Olmstead. Distillation at 74 °C (0.5 mm) led to the desired product.

Preparation of Pivalic *tert*-Butylthiolcarbonic Anhydride (2b). The preparation of the title compound was effected by modification of published procedures.[4,17] First, **3b** was prepared as described earlier and was used as the crude product without further purification. A solution of **3b** (17.6 g, 0.12 mol) in 20 mL of benzene was added dropwise to a magnetically stirred solution of pivalic acid (11.8 g, 0.12 mol) and pyridine (9.2 g, 0.12 mol) in 40 mL of benzene at ice bath temperature over a period of 30 min. After the solution was allowed to warm to room temperature over a 3-h period, it was filtered by suction through a medium-fritted funnel under a nitrogen atmosphere. The filtrate was then washed with three 40-mL portions of a 10% sodium carbonate solution, followed by three 40-mL portions of water and dried. Filtration and removal of solvent in vacuo led to **2b** as a white wax which melted from 62.5 to 64.5 °C (lit.[10] mp 57–59 °C). The IR spectrum agreed with the previous report and the NMR spectrum[16] showed equivalent singlets at 1.34 and 1.09 ppm in chlorobenzene.

Preparation of 2,2-Dimethylbutyric *tert*-Amylthiolcarbonic Anhydride (2c). The preparation of the title compound was effected in the same manner in which **2b** was prepared. Reaction of 2,2-dimethylbutyric acid (5.8 g, 0.05 mol) and **3c** (8.3 g, 0.05 mol) in benzene with 1 equiv of pyridine led to 8.0 g (65%) of the title compound. The IR spectrum (CCl_4) showed carbonyl absorptions at 1795 and 1730 cm^{-1}; the NMR (CCl_4) consisted of a multiplet at 1.71 ppm (4 H), a singlet at 1.47 ppm (6 H), a singlet at 1.19 ppm (6 H), and a quartet at 0.95 ppm (6 H); and the compound boiled at 75–76 °C (0.02 mm).

Anal. Calcd for $C_{12}H_{22}O_3S$: C, 58.50; H, 9.00. Found: C, 58.77; H, 9.13.

Preparation of *tert*-Butyl Thiolpivalate (5). Freshly distilled pivaloyl chloride (6.0 g, 0.05 mol) was added dropwise over a 30-min period to a solution of *tert*-butyl mercaptan (6.8 g, 0.075 mol) in 50 mL of dry pyridine and refluxed for 4 h. After the addition of 100 mL of ether, the solution was washed successively with 100 mL in three portions each of water, 5% aqueous hydrochloric acid, and 5% sodium carbonate solution. The resulting ethereal solution was dried, filtered, reduced in vacuo, and distilled in 174–175 °C to yield 4.8 g (55%) of a constant boiling material. Analysis by VPC indicated only one compound was present, and mass spectroscopy showed a parent ion at 174. The IR spectrum (CCl_4) had a strong absorption at 1680 cm^{-1} and the NMR[16] showed two equivalent singlets at 1.19 and 1.47 ppm in chlorobenzene.

Anal. Calcd for $C_{10}H_{18}O_4$: C, 59.39; H, 8.97. Found: C, 59.25; H, 8.96.

Preparation of Di-*tert*-butyl Dithiolcarbonate (11). The method[7] of Wei and Tarbell was used to prepare the title compound in a crude yield of 61% from sodium *tert*-butyl mercaptide and *tert*-butylthiol chlorocarbonate. Spectra and physical properties were in agreement with the previous report.

Preparation of *tert*-Amyl Thiolpivalate (7). Attempted preparation of *tert*-amyl thiolpivalate in the same manner in which *tert*-butyl thiolpivalate was formed resulted in the formation of a mixture of compounds. From IR and VPC results, the mixture appears to be primarily the desired compound and pivalic anhydride. Attempts to separate the mixture by distillation and column chromatography on silica gel were unsuccessful. The compound was then isolated by VPC and its identify was confirmed by its mass spectrum, which exhibited a peak at *m/e* 188 that corresponds to the molecular ion, a base peak at *m/e* 85 that corresponds to the acyl ion $(CH_3)_3CC^+{=}O$, and a prominent peak at *m/e* 119 that corresponds to the "McLafferty +1" product[22] $(CH_3)_3CC({=}SH^+)OH$. The IR spectrum (CCl_4) contained a carbonyl absorption at 1670 cm^{-1}.

Product Studies. Analysis for carbon dioxide, which was evolved during the thermal decomposition of the various carbonates, was carried out by collecting the carbon dioxide on Ascarite. The apparatus consisted of a two-neck flask equipped with a nitrogen inlet and an upright condenser, which was connected in series to a dry-ice trap containing Drierite, a U-shaped tube filled with Ascarite, and finally a sulfuric acid trap which was placed directly after the condenser. The nitrogen inlet consisted of an adapter, with a stopcock, connected in series to two Ascarite filled tubes, a sulfuric acid trap, and a tank of prepurified nitrogen. The stopcock was open only when the system was under a positive pressure from the tank. The decompositions were usually effected either neat or in solution by placing the two-neck flask in a stirred oil bath heated between 100 and 175 °C. With the adapter stopcock closed, the flask was heated for 3 h, then removed from the bath, and allowed to cool for 5 min. At this time the stopcock was opened and the system was flushed for 15 min with nitrogen before the U-shaped Ascarite tube was weighed. This procedure was repeated at 1-h intervals until a constant weight was obtained for the U-shaped Ascarite tube.

Analysis for other products was usually effected with VPC and IR. The chromatography was carried out on 5 ft × ¼ in. column of 5% SE 30 on Chromosorb W or 5% Ucon on Chromosorb W at injection port temperatures ranging from 170 to 220 °C and column temperatures ranging from 100 to 150 °C. Usually compounds were identified on the basis of their retention times, although in some cases compounds were identified by either coinjection techniques or by collection and analysis of IR and NMR spectra. Samples were usually analyzed at two different column temperatures for comparative purposes. Retention times for the compounds on the Ucon column at an injection port temperature of 210 °C, column temperature of 145 °C, and flow rate of 60 mL/min were 2.64 min for *tert*-butyl thiolpivalate (**5**), 3.06 min for pivalic anhydride (**6**), 3.74 min for *tert*-amyl thiolpivalate (**7**), 4.33 min for what is assumed to be *tert*-butylthiol 2,2-dimethylbutyrate (**8**), 5.81 min for *tert*-amylthiol 2,2-dimethylbutyrate (**9**), and 6.74 min for 2,2-dimethylbutyric anhydride (**10**). It should be noted that the identity of *tert*-amylthiol 2,2-dimethylbutyrate (**9**) was confirmed by collection followed by mass spectral analysis. Th compound gave a peak at *m/e* 202 which corresponds to the molecular ion, a base peak at 99 which corresponds to the acyl ion $C_2H_5(CH_3)_2CC^+{=}O$, and a peak at 133 which corresponds to the "McLafferty +1" ion $C_2H_5(CH_3)_2C({=}SH^+)OH$.

Reaction of Mixed Anhydrides 2a–c with *p*-Toluidine. A. Pivalic *tert*-Butylcarbonic Anhydride. To a solution of pivalic *tert*-butylcarbonic anhydride (4.1 g, 0.02 mol) in 25 mL of dry THF was added a solution of *p*-toluidine (2.5 g, 0.023 mol) in 25 mL of THF. After refluxing for 40 m the THF was removed in vacuo to leave a solid mixture with a wide melting range beginning at 65 °C. Addition of 15 mL of anhydrous ether, resulting in partial solution of the mixture, and subsequent filtration yielded a white crystalline substance whose IR ($CHCl_3$) showed a carbonyl absorption at 1670 cm^{-1}; whose NMR ($CHCl_3$) showed a singlet at 1.25 (9 H) and 2.23 ppm (3 H), and multiplet from 6.88 to 7.27 ppm (5 H); and whose melting range was 119–121 °C. All of this information is consistent with this compound being the *N*-pivaloyl derivative of *p*-toluidine, which was reported by Davis and Hickinbottom[23] to have a melting point of 120 °C.

The ethereal solution was then shown to contain two major components. Removal of ether in vacuo was followed by the addition of 10 mL of hexane, which once again led to only partial solution. Filtration gave more of the white crystals. Next the yellowish brown hexane solution was chromatographed on 50 g of silica gel by elution in succession with 550 mL of hexane, 200 mL of 5% ether–hexane, 200 mL of 10% ether–hexane, 200 mL of 20% ether–hexane, 200 mL of 50% ether–hexane, and 200 mL of chloroform to yield two major fractions. The second fraction which came off was more of the *N*-pivaloyl derivative and when added to the previously collected fractions amounted to 2.5 g (66%). The first fraction had an IR spectrum ($CHCl_3$) which showed a carbonyl maximum at 1718 cm^{-1}, and an NMR spectrum ($CDCl_3$) which displayed a singlet at 1.46 ppm (9 H), a singlet at 2.24 ppm (3 H), and a multiplet from 6.28 to 7.00 ppm (5 H). This information coupled with the fact that its melting range was 91–93 °C indicated that this compound was *N*-*tert*-butoxycarbonyl-*p*-toluidine, which was reported by Choppin and Rogers[9] to have a melting range of 92–92.8 °C. The yield of this compound was 1.3 g (32%).

B. Pivalic *tert*-Butylthiolcarbonic Anhydride (2b). Next, **2b** was reacted with *p*-toluidine in the same fashion as its oxygen homologue. Its IR once again indicated the presence of two types of carbonyl absorptions and TLC also indicated two different major components. However, an attempt to purify this mixture by chromatography on silica gel proved unsuccessful. Comparison of the IR spectrum of this mixture with authentically prepared *N*-thiol-BoC derivative of *p*-toluidine and the pivalamide indicated that the thiol derivative was the minor component.

Preparation of *N*-Thiol-Boc of *p*-Toluidine. To a solution of *p*-toluidine (2.4 g) in 10 mL of chloroform was added **3b** (1.75 g) in 15 mL of chloroform over a 20-min period. After stirring overnight the solution was filtered to remove insoluble material and the solvent was removed in vacuo to give 2.1 g (85%) of a crude solid which melted from 99 to 105 °C. Recrystallization from CCl_4 led to a white crystalline solid which melted from 104.5 to 106 °C. The IR spectrum (CCl_4) showed a strong absorption at 1690 cm^{-1} and the NMR spectrum (CCl_4) a singlet at 1.48 ppm (9 H), a singlet at 2.22 ppm (3 H), and a multiplet from 6.62 to 7.11 ppm (5 H).

Anal. Calcd for $C_{12}H_{17}NOS$: C, 64.53; H, 7.67. Found: C, 64.39; H, 7.80.

C. 2,2-Dimethylbutyric *tert*-Amylthiolcarbonic Anhydride. Reaction once again led to the production of two major components by TLC and two different carbonyl absorptions in the IR. No attempt was made to purify these products.

Kinetic Studies. The kinetic studies were performed using the procedure[12] of Dean, Tarbell, and Friederang with one major exception. Rate constants were determined by computer utilizing a program[24] which yielded a least-squares fit for the data. Also, the activation parameters were determined by computer in order to obtain a least-squares fit.

Acknowledgment. We are indebted to Grant GP-7874 from the National Science Foundation for support of this work.

Registry No.—**2a,** 39982-01-9; **2b,** 28058-95-9; **2c,** 63528-31-4; **3b,** 13889-95-7; **3c,** 63528-32-5; **4a** [R = $C(CH_3)_3$], 21354-40-5; **4b** [R = $C(CH_3)_3$], 14618-59-8; **5,** 28058-96-0; **6,** 1538-75-6; **7,** 63528-33-6; **9,** 63528-34-7; **11,** 16118-32-4; potassium *tert*-butoxide, 865-74-4; pivaloyl chloride, 3282-30-2; *tert*-butyl pivalate, 16474-43-4; pivalic acid, 75-98-9; phosgene, 75-44-5; *tert*-butyl mercaptan, 75-66-1; *tert*-amyl mercaptan, 1679-09-0; *tert*-amyl chloride, 594-36-5; 2,2-dimethylbutyric acid, 595-37-9; *p*-toluidine, 106-49-0; *p*-toluidine *N*-thiol-BoC derivative, 63528-35-8.

References and Notes

(1) (a) Taken from the Ph.D. Thesis of R. L. Stanley, Vanderbilt University, 1976. (b) Present address: School of Pharmacy, Ferris State College, Big Rapids, Michigan 49307.
(2) For a review of pertinent literature, see D. S. Tarbell, *Acc. Chem. Res.*, **2**, 296 (1969).
(3) D. S. Tarbell and N. A. Leister, *J. Org. Chem.*, **23**, 1149 (1958).
(4) D. S. Tarbell and E. J. Longosz, *J. Org. Chem.*, **24**, 774 (1959).
(5) C. J. Michejda and D. S. Tarbell, *J. Org. Chem.*, **29**, 1168 (1964).
(6) R. C. L. Chow and D. S. Tarbell, *J. Org. Chem.*, **32**, 2188 (1967).
(7) L. Wei and D. S. Tarbell, *J. Org. Chem.*, **33**, 1884 (1968).
(8) We are indebted to Dr. T. M. Harris for suggesting this experiment.
(9) A. R. Choppin and J. W. Rogers, *J. Am. Chem. Soc.*, **70**, 2967 (1948).
(10) C. S. Dean and D. S. Tarbell, *J. Org. Chem.*, **36**, 1180 (1971).
(11) N. A. Leister and D. S. Tarbell, *J. Org. Chem.*, **23**, 1152 (1958).
(12) C. S. Dean, D. S. Tarbell, and A. W. Friederang, *J. Org. Chem.*, **35**, 3393 (1970).
(13) S. G. Cohn and A. Schneider, *J. Am. Chem. Soc.*, **63**, 3382 (1941).
(14) P. N. Rylander and D. S. Tarbell, *J. Am. Chem. Soc.*, **72**, 3021 (1950).
(15) M. S. Newman, *J. Am. Chem. Soc.*, **72**, 4783 (1950).
(16) For ^{13}C NMR spectrum, see Y. Yamamoto, D. S. Tarbell, J. R. Fehler, and B. M. Pope, *J. Org. Chem.*, **38**, 2524 (1973).
(17) D. S. Tarbell and T. Parasaran, *J. Org. Chem.*, **29**, 2471 (1964).
(18) We are indebted to Mr. J. V. Bonnet for his assistance in the preparation of this compound.
(19) S. V. Puntambeker and E. A. Zollner, "Organic Syntheses", Collect. Vol. 1, Wiley, New York, N.Y., 1930, p 524.
(20) F. C. Witmore and A. L. Houk, *J. Am. Chem. Soc.*, **54**, 3716 (1932).
(21) J. F. Norris and A. W. Olmstead, "Organic Syntheses", Collect. Vol. 1, Wiley, New York, N.Y., 1930, p 144.
(22) F. W. McLafferty, "Interpretation of Mass Spectra", 2nd ed, W. A. Benjamin, Reading, Mass., 1973, p 68.
(23) M. A. Davis and W. J. Hickinbottom, *J. Chem. Soc.*, 2207 (1958).
(24) We thank Dr. B. A. Hess for kindly supplying the computer programs.