Attempted Crossover Experiment.—An intimate mixture of 1.4 g of **4** and 1.6 g of **22** was heated at 125° for 75 min. The residual oil was refluxed with 30 ml of cyclohexane. On cooling a solid separated and was filtered and triturated with 80 ml of boiling cyclohexane. After cooling a solid separated which had mp 145–147°. Recrystallization gave 1.0 g of **19**, mp 147–148°. The infrared spectrum of the crude solid was identical with that of pure **19**.

The combined cyclohexane filtrates were evaporated. The residual oil was taken up in hot methylcyclohexane. On cooling 1.4 g of a solid, mp 90.5–91.5° was obtained. The infrared spectrum of this material was identical with that of pure **23**, mp 94–95°. No evidence for the presence of either **24** or **25** was observed.

Registry No.—**4,** 6158-51-6; **7,** 15982-16-8; **8,** 15982-30-6; **9,** 15982-17-9; **10,** 15982-35-1; **11,** 15982-37-3; **12,** 15982-36-2; **13,** 15982-18-0; **13** dinitrophenylhydrazone, 15982-19-1; **14,** 1518-20-3; **14** dinitrophenylhydrazone, 16031-68-8; **15,** 15982-20-4; **16,** 15982-21-5; **18,** 15982-22-6; **19,** 13369-55-6; **21,** 13369-57-8; **22,** 15982-25-9; **23,** 15982-26-0; **24,** 15982-27-1; **25,** 15982-28-2; **27,** 15982-29-3; **31,** 15982-31-7; **33,** 15982-32-8; *cis*-1-carboxy-2-cyclopropanecarboxamide, 15982-33-9; *cis*-2-benzoyl-1-cyclopropanecarboxamide, 15982-34-0.

The Mechanism of Decomposition of Some Carboxylic Thiolcarbonic Anhydrides[1]

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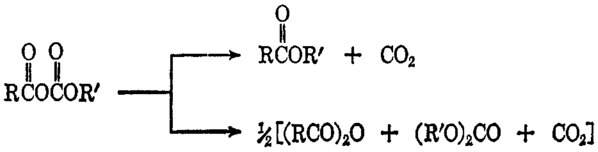
p-Nitrobenzoic *t*-butylthiolcarbonic anhydride IIa decomposes solely by acyl–sulfur cleavage to yield the corresponding thiol ester and carbon dioxide, in contrast to its oxygen analog. The analogous isopropylthiolcarbonic (IIb), the benzylthiolcarbonic (IIc), and the phenylthiolcarbonic anhydrides (IId) give also only carbon dioxide and the thiol ester. Kinetic studies on the decomposition of the *t*-butylthiol and the isopropylthiol compounds, following the reaction by infrared spectroscopy, showed that in *o*-dichlorobenzene both decompositions were strictly first order; the activation parameters ($\Delta H^{\ddagger}$ about 30 kcal/mol and $\Delta S^{\ddagger}$ about -5 eu) were similar. The *t*-butyl compound showed in decalin a very similar rate, with $\Delta H^{\ddagger}$ 30 kcal/mol and $\Delta S^{\ddagger}$ about -7 eu. In benzonitrile, $\Delta H^{\ddagger}$ was 22 kcal/mol and $\Delta S^{\ddagger}$ much more negative, -24 eu. The relatively slight effect on the rate of changes in polarity of the solvent indicates that the transition state is more covalent than ionic in character. The rate of reaction of the *t*-butyl compound was markedly catalyzed by nucleophiles; in *o*-dichlorobenzene, tetra-*n*-butylammonium iodide increased the rate proportionally to its concentration, the reaction products were the same as in the absence of the iodide, and, for the first 40–50% of the reaction, the rate was first order in the iodide and in the anhydride. The results are discussed in the light of some covalent and ion-pair decomposition reactions.

In earlier papers,[3] decomposition of mixed carboxylic carbonic anhydrides (eq 1) was shown to lead to two types of products: (A) ester and carbon dioxide and (B) symmetrical acid anhydride and carbonate ester.

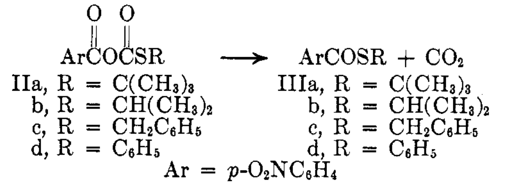


$$\mathrm{R\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}OR'} \longrightarrow \begin{cases} \mathrm{R\overset{O}{\overset{\|}{C}}OR' + CO_2} \\ \tfrac{1}{2}[\mathrm{(RCO)_2O + (R'O)_2CO + CO_2}] \end{cases} \qquad (1)$$

Stereochemical[3] and ^{18}O studies[4] show that, when R′ was a *sec*-alkyl group, there was no evidence for alkyl–oxygen cleavage. With R′ = *p*-methoxybenzyl,[5] alkyl–oxygen cleavage does occur under some, but not all, conditions. With R′ = *t*-butyl (I),[6] the main path of decomposition, which occurs rapidly at about 100°, is alkyl–oxygen fission to the *t*-butyl carbonium ion. With the thiol analog[7] IIa of I, there was no fission of

$$\mathrm{ArCOOCOOC(CH_3)_3 \longrightarrow ArCOOCOO^- + {}^{+}C(CH_3)_3}$$
$$\mathrm{I,\ Ar = \mathit{p}\text{-}NO_2C_6H_4}$$

the *t*-butyl–S linkage, and a temperature of 150° was required for a reasonable rate of reaction. The contrast between the behavior of the analogous sulfur

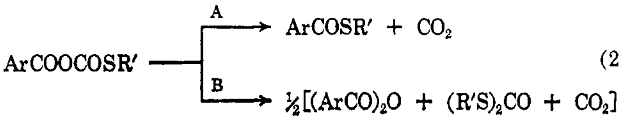


$$\mathrm{Ar\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}SR \longrightarrow ArCOSR + CO_2}$$

$$\begin{array}{ll} \mathrm{IIa,\ R = C(CH_3)_3} & \mathrm{IIIa,\ R = C(CH_3)_3} \\ \mathrm{b,\ R = CH(CH_3)_2} & \mathrm{b,\ R = CH(CH_3)_2} \\ \mathrm{c,\ R = CH_2C_6H_5} & \mathrm{c,\ R = CH_2C_6H_5} \\ \mathrm{d,\ R = C_6H_5} & \mathrm{d,\ R = C_6H_5} \end{array}$$
$$\mathrm{Ar = \mathit{p}\text{-}O_2NC_6H_4}$$

and oxygen systems was discussed,[7] and this contrast, which has been of interest to us in many cases, led to the present kinetic study of the conversion of the *t*-butyl and the isopropyl compounds IIa and IIb into the corresponding thiol esters IIIa and IIIb. The benzyl and phenyl compounds were characterized, but could not be obtained in yields high enough to allow detailed kinetic study.

Decomposition Products from the Anhydrides IIa–d.—The data in Table I shows that the decomposition of the anhydrides IIa–d follows path A predominantly (eq 2).



$$\mathrm{ArCOOCOSR'} \longrightarrow \begin{cases} \xrightarrow{\mathrm{A}} \mathrm{ArCOSR' + CO_2} \\ \xrightarrow{\mathrm{B}} \tfrac{1}{2}[\mathrm{(ArCO)_2O + (R'S)_2CO + CO_2}] \end{cases} \qquad (2)$$

The gaseous products from the *t*-butyl compound IIa were analyzed by the mass spectrometer, and less than 0.2% of carbonyl sulfide was found,[8] indicating a

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[1] Supported by Grant GP-4961 from the National Science Foundation.

[2] To whom inquiries should be addressed: the Department of Chemistry, Vanderbilt University, Nashville, Tenn. 37203.

[3] (a) D. S. Tarbell and E. J. Longosz, *J. Org. Chem.*, **24**, 774 (1959); (b) *ibid.*, **26**, 2161 (1961).

[4] C. J. Michejda, D. S. Tarbell, and W. H. Saunders, Jr., *J. Amer. Chem. Soc.*, **84**, 4113 (1962).

[5] R. C. L. Chow and D. S. Tarbell, *J. Org. Chem.*, **32**, 2188 (1967).

[6] C. J. Michejda and D. S. Tarbell, *ibid.*, **29**, 1168 (1964); V. Boellert, G. Fritz, and H. Schnell [German Patent 1,133,727; *Chem. Abstr.*, **58**, 6752 (1963)] report the synthesis of $C_6H_5COOCOOC(CH_3)_3$, mp 72°, from sodium benzoate and $ClCOOC(CH_3)_3$ in aqueous solution with tertiary amine in the presence of methylene chloride.

[7] D. S. Tarbell and T. Parasaran, *J. Org. Chem.*, **29**, 2471 (1964).

[8] This figure is based on the ratio of the *m/e* 60 peak to the *m/e* 44 peak; in spite of the obvious assumptions being made here, it is clear that no appreciable amount of carbonyl sulfide was present.

TABLE I

THERMAL DECOMPOSITION OF *p*-NITROBENZOIC THIOLCARBONIC ANHYDRIDES (p-$NO_2C_6H_4COOCOSR'$) IN THE ABSENCE OF SOLVENT

R,	Temp, °C	% CO_2	% thiol ester[a]	% symmetrical anhydride[b]
t-C_4H_9	150 ± 5	100 ± 5	90 ± 4	3–5
i-C_3H_7	140 ± 5	99 ± 5	89 ± 4	4–5
$C_6H_5CH_2$	140 ± 2	~94	86	~4
C_6H_5	110	~92	80	. . .

[a] % thiol ester is the % yield of the recrystallized sample. [b] % symmetric anhydride is the % yield of the isolated sample without further recrystallization.

negligible amount of alkyl–sulfur cleavage. The thiol esters were separated from the highly insoluble symmetrical *p*-nitrobenzoic anhydride and identified by mixture melting point determination and spectroscopic comparison with synthetic samples. The small amounts of dithiolcarbonates present were identified by tlc or vpc comparisons with known samples because actual isolation of the small amounts was difficult.

The possibility that the thiol ester resulted from reaction of the symmetrical anhydride and the dithiolcarbonate was eliminated by heating equimolar amounts of *p*-nitrobenzoic anhydride and di-*t*-butyl dithiolcarbonate at 160° for 6 hr; no thiol ester was formed, as indicated by the absence of its characteristic carbonyl absorption at 1666 cm^{-1}.

$$(ArCO)_2O + (R'S)_2CO \not\longrightarrow 2ArCOSR' + CO_2$$
$$Ar = p\text{-}NO_2C_6H_4;\ R' = C(CH_3)_3$$

It has been found[3,5] that the decomposition of mixed anhydrides is strongly catalyzed by nucleophiles, such as halide ions, 1,4-diazabicyclo[2.2.2]octane (DABCO) and other bases. The data in Table II shows that the presence of a nucleophile did not affect particularly the proportion of thiol ester formed, although the rate of decomposition was greatly accelerated. Thus, IIa showed only very slight reaction after refluxing for 60 hr in benzene or cyclohexane, but the addition of 6 mol % of N-methylpiperidine gave complete reaction within 7 hr.

TABLE II

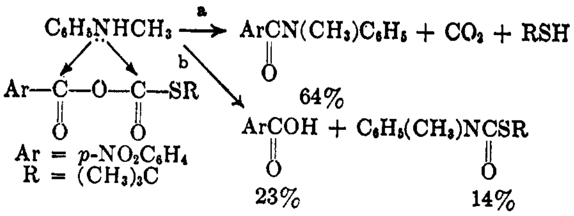
DECOMPOSITION OF *p*-NITROBENZOIC *t*-BUTYLTHIOLCARBONIC (IIa) ANHYDRIDE IN THE PRESENCE OF NUCLEOPHILES

Additive	Concn, mol %	Temp, °C	Solvent	% CO_2	% thiol ester[a]
DABCO	21	105 ± 1	*o*-$C_6H_4Cl_2$	99	86
(n-$C_4H_9)_4NI$	22	105 ± 1	*o*-$C_6H_4Cl_2$	98	90
(n-$C_4H_9)_4NI$	1	81	C_6H_{12}	. . .	95
$C_5H_{10}NCH_3$[b]	6	80	C_6H_6	94	85
$C_5H_{10}NCH_3$	100	98	C_7H_{16}	. . .	82

[a] *p*-Nitrobenzoic anhydride was isolated in minor amounts in all cases. [b] N-Methylpiperidine.

Reaction of the anhydride IIa with N-methylaniline gave the products and yields indicated in Scheme I. The carboxyl carbonyl was attacked preferentially compared to the carbonate carbonyl; this is due to the electron-withdrawing effect of the *p*-nitrophenyl group, as well as the steric effect of the *t*-butyl group.

SCHEME I



Kinetic Studies of the Thermal Decomposition of the *t*-Butyl and Isopropylthiolcarbonic Anhydrides (IIa and IIb).—The reaction could be followed satisfactorily by measuring the decrease in absorption of the anhydride carbonyl band at 1787 cm^{-1}; in a few runs, the rate was followed by measuring the *increase* in the thiol ester absorption at 1666 cm^{-1}. The results from the two methods were in agreement.

The rate of decomposition of the mixed anhydride IIa was measured in *o*-dichlorobenzene at five temperatures over a range of 110–151°. The reaction gave good first-order constants up to 70–85% completion, and the first-order constants were unchanged by a fivefold increase in concentration. The rate of the reaction was unaffected by the presence (at the beginning of a run) of 30 mol % of the product, the thiol ester.

Equally good rate constants were obtained in benzonitrile and decalin (Table III). The reaction was slightly faster in the more polar solvents (Table IV). The Arrhenius plots gave good straight lines.

TABLE III

RATES OF DECOMPOSITION OF *p*-NITROBENZOIC *t*-BUTYLTHIOLCARBONIC ANHYDRIDE

Temp, °C	Concn × 10^2M	$k_1 \times 10^5$ sec^{-1}
	(a) In *o*-Dichlorobenzene	
110.2 ± 0.1	3.40	0.34 ± 0.01
120.3 ± 0.1	3.58	0.85 ± 0.02
130.5 ± 0.1	4.08	2.36 ± 0.02
	2.98	2.35 ± 0.02
	3.40	2.56 ± 0.04
140.7 ± 0.1	3.57	6.89 ± 0.03
	19.4	6.61 ± 0.03
151.3 ± 0.1	2.98	16.1 ± 0.06
	(b) In Benzonitrile	
120.3 ± 0.01	3.40	2.90 ± 0.07
	3.14	2.80 ± 0.07
130.5 ± 0.01	4.15	5.70 ± 0.06
	3.40	6.29 ± 0.02
	3.58	6.10 ± 0.06
140.7 ± 0.1	2.56	12.4 ± 0.12
	2.35	12.3 ± 0.20
151.3 ± 0.1	3.58	29.1 ± 0.19
	3.58	29.1 ± 0.15
	(c) In Decalin	
130.4 ± 0.1	1.38	1.33 ± 0.02
	1.89	1.27 ± 0.02
139.6 ± 0.2	1.52	3.23 ± 0.02
140.7 ± 0.1	1.89	3.26 ± 0.02
151.3 ± 0.1	1.56	8.67 ± 0.13
160.1 ± 0.2	1.63	18.0 ± 0.19

TABLE IV

EFFECT OF THE SOLVENT ON THE RATES OF DECOMPOSITION OF *p*-NITROBENZOIC *t*-BUTYLTHIOLCARBONIC ANHYDRIDE (IIa) AT 140.7°

Solvent	Dielectric constant	Dipole moment (D)	Relative rate
Decalin	2.0	0	1
o-Dichlorobenzene	9.9	2.26	2
Benzonitrile	25.1	4.05	4

The isopropyl anhydride IIb decomposition was studied in *o*-dichlorobenzene as solvent at three temperatures from 120 to 140°; the reaction was again accurately first order. The rate constant at 140° was about 1.3 times greater than that for the *t*-butyl compound under the same conditions. The rate data is given in Table V, and the activation parameters for both the isopropyl and *t*-butyl compounds are in Table VI.

Table V

Rates of the Decomposition of *p*-Nitrobenzoic Isopropylthiolcarbonic Anhydride (IIb) in *o*-Dichlorobenzene

Temp, °C	Concn × $10^2 M$	$k_1 \times 10^5$ sec^{-1}
120.3 ± 0.1	3.41	1.21 ± 0.02
	4.16	1.15 ± 0.02
	3.95	1.26 ± 0.02
130.5 ± 0.1	2.98	3.23 ± 0.03
	3.35	3.06 ± 0.04
	2.76	3.20 ± 0.04
140.7 ± 0.1	3.42	8.35 ± 0.13
	3.95	8.97 ± 0.28

Table VI

Activation Parameters of Decomposition of *p*-Nitrobenzoic *t*-Butyl- and Isopropylthiolcarbonic Anhydrides (IIa and IIb)

Compd	Solvent	$\Delta H^\ddagger$ kcal/mol	$\Delta S^\ddagger$ eu
IIa	Decalin	30.0 ± 0.5	−7.0 ± 0.9
IIa	*o*-Dichlorobenzene	30.3 ± 0.5	−5.1 ± 1.1
IIa	Benzonitrile	22.0 ± 0.5	−23.9 ± 1.1
IIb	*o*-Dichlorobenzene	30.6 ± 0.5	−3.7 ± 1.2

The effect of an added nucleophile, tetra-*n*-butylammonium iodide, on the decomposition rate of the *t*-butyl compound was studied at concentrations of nucleophile ranging from 0.5 to 8 mol %. In most runs, the decomposition was found to be first order with respect to the mixed anhydride up to *ca.* 50% completion of the decomposition. A decrease in rate as the reaction proceeded was usually observed after the 50% reaction. The apparent first-order rate constant, k_{app}, calculated from the initial 50% decomposition, showed a dependence on the concentration of the nucleophile, B. A plot of the apparent first-order constant, k_{app} *vs.* the nucleophile concentration indicated their linear relationship. Extrapolating to zero nucleophile concentration gave essentially the same value of k_1 as obtained in the uncatalyzed decomposition. Therefore, to a first approximation, the following equation was valid.

$$k_{\mathrm{app}} = k_1 + k_2(\mathrm{B})$$

Table VII lists the k_{app} and the k_2 calculated according to this equation; these data are less accurate than those reported for the uncatalyzed reaction.

Discussion of Results

The accelerating effect of nucleophiles, such as the quaternary iodide and DABCO, on the decomposition of IIa is doubtless due to the initiation of ionic chain reactions by the attack of the nucleophile on one of the carbonyls of the anhydride, as described earlier.[3,5]

Table VII

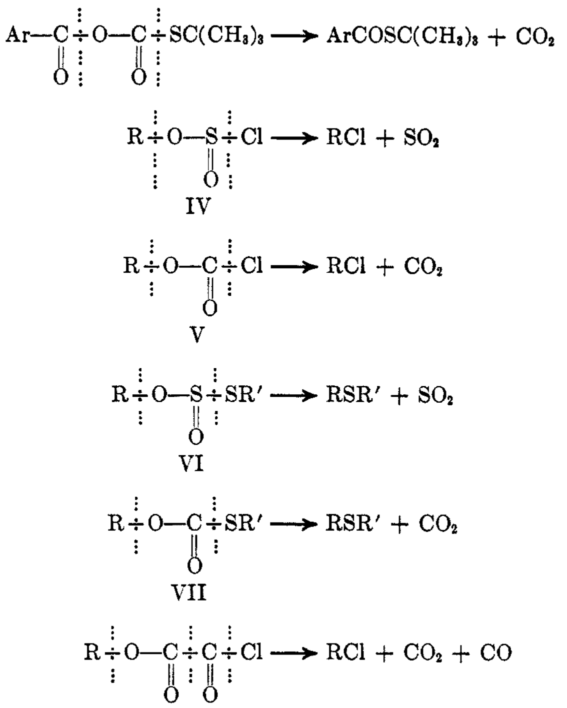
Rates of the Decomposition of *p*-Nitrobenzoic *t*-Butylthiolcarbonic Anhydride (IIa) in *o*-Dichlorobenzene in the Presence of Tetra-*n*-butylammonium Iodide

Temp, °C	k_1, sec^{-1}	Concn$_A$, $10^2 M$[a]	Concn$_I$, $10^4 M$ (mol %)	$k_{\mathrm{app}} \times 10^5$, sec^{-1}	k_2, M^{-1} sec^{-1}
110.2 ± 0.1°	3.4×10^{-6}	3.40	13.8 (4.06)	9.6 ± 0.8	0.069
		3.40	20.8 (6.12)	16 ± 1.0	0.078
		3.40	27.7 (8.15)	23 ± 2.0	0.081
120.3 ± 0.1	8.5×10^{-6}	3.58	2.12 (0.59)	3.7 ± 0.2	0.13
		3.75	4.24 (1.13)	6.0 ± 0.2	0.12
		7.50	4.24 (0.56)	5.5 ± 0.4	0.11
130.5 ± 0.1	2.4×10^{-5}	4.08	2.12 (0.52)	5.6 ± 0.4	0.16
		4.08	6.36 (1.56)	15 ± 1.0	0.18
		4.08	10.6 (2.60)	22 ± 1.2	0.19
		3.40	8.32 (2.45)	17 ± 1.1	0.17
		3.40	13.9 (4.09)	29 ± 1.0	0.19

[a] Concn$_A$ = initial concentration of the mixed anhydride. [b] Concn$_I$ = initial concentration of tetra-*n*-butylammonium iodide.

The formal similarity between the present decomposition and a number of other carefully studied reactions can be indicated as shown in Scheme II.

Scheme II



The alkyl chlorosulfites[9] decompose by a mechanism involving ion pairs, shown by the great increase of rate in solvents of higher ionizing power. The same is true of the chlorocarbonates[10] (V). The thermal decomposition of thiolsulfonates[11] and thiolcarbonates[12] (VI and VII) evidently lies near the ion pair end of the mechanistic spectrum, but is definitely less ionic than the chlorosulfite and chlorocarbonate decompositions.

In pronounced contrast to other chlorosulfite and chlorocarbonate decompositions, α-trifluoromethylallyl

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(9) D. J. Cram, *J. Amer. Chem. Soc.*, **75**, 332 (1953); E. S. Lewis and C. E. Boozer, *ibid.*, **74**, 308 (1952); **75**, 3182 (1953); S. H. Sharman, F. F. Caserio, R. F. Nystrom, J. C. Leak, and W. G. Young, *ibid.*, **80**, 5965 (1958).

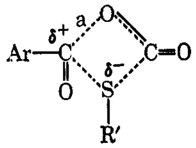
(10) K. B. Wiberg and T. B. Shryne, *ibid.*, **77**, 2774 (1955); K. L. Oliver and W. G. Young, *ibid.*, **81**, 5811 (1959).

(11) J. L. Kice, F. M. Parham, and R. M. Simons, *ibid.*, **82**, 834, 6168 (1960); J. L. Kice and R. H. Engebrecht, *J. Org. Chem.*, **27**, 4654 (1962).

(12) J. L. Kice, R. A. Bartsch, M. A. Dankleff, and S. L. Schwartz, *J. Amer. Chem. Soc.*, **87**, 1734 (1965).

chlorosulfite[13] decomposes only seven times faster in nitrobenzene than in decane, indicating that the decomposition involves a covalent rather than an ion-pair process. The decomposition of chloroglyoxalates[14] (VIII) is similar in showing a slight rate increase in nitrobenzene compared to tetralin; this, coupled with the large negative entropy of activation, suggests that the rate-determining process is a concerted one.

The anhydride IIa showed only a fourfold rate increase going from decalin to benzonitrile. One explanation is that the rate-determining step in the decomposition of the carboxylic thiolcarbonic anhydrides involves much less ionic character than that for the chlorosulfites, chlorocarbonates, thiolsulfonates, and thiolcarbonates. The transition state may be pictured as IX, with a partial negative charge on the sulfur and a partial positive charge on the carboxyl carbon.



IX

There may be a lesser degree of formation of the new C–S bond than dissociation of the "a" and "b" bonds. In the more polar solvent benzonitrile, the anhydride in the ground state may exist in various (solvated) conformations quite different from the quasi-ring which forms the basis for the transition state IX; thus, in going from the ground state to the transition state IX, a relatively large loss in degrees of freedom would occur. This would be consistent with the $\Delta S^{\ddagger}$ of −23.9 eu (Table VI) observed in this solvent.

The marked change in activation parameters, in going from decalin to benzonitrile, should be emphasized; these counteract each other, and hence the overall rate is very similar in the two solvents.

Experimental Section[15]

***p*-Nitrobenzoic *t*-butylthiolcarbonic anhydride (IIa)**[7] was prepared from *p*-nitrobenzoic acid, *t*-butyl thiochlorocarbonate, and triethylamine in 32% yield; with sublimed DABCO as base, the yield of product in THF was 85%. The recrystallized material melted at 83–84.5°, and its ultraviolet spectrum in cyclohexane showed a band at λ_{max} 254 mμ (ϵ_{max} 1.69 × 10^4). (This figure represents a correction of that published earlier,[7] 2.69 × 10^4, which may have been a misprint.) The nmr spectrum in deuteriochloroform showed a 9 H singlet at 8.42, and a 4 H unsymmetrical doublet centered at 1.72.

The *t*-butyl compound IIa was also prepared from the thiol by the carbonation procedure[6] as follows.

To a slurry of 5.0 g (0.1 mol) of sodium hydride (51% in mineral oil) in 50 ml of THF was added dropwise with mechanical stirring 9.0 g (0.1 mol) of *t*-butyl mercaptan under nitrogen. The mixture was refluxed on steam bath for 2 to 4 hr until a thick white slurry was obtained. Dry and oxygen-free carbon dioxide was passed into the reaction mixture for 15 to 20 min. Carbon dioxide from Dry Ice was passed through four gas washing bottles, two containing chromous sulfate,[16] one containing water, and the other containing concentrated sulfuric acid.

The thick white slurry changed to a gel. It was then cooled in a Dry Ice–acetone bath, and the addition of carbon dioxide was continued for another hour. To the gel was added dropwise 18.6 g (0.1 mol) of *p*-nitrobenzoyl chloride in 250 ml of THF, with vigorous stirring for 3 hr. The solution became less viscous as the reaction proceeded. Stirring was continued for another 30 min, and the bath was gradually warmed to *ca.* −30°. The mixture was then suction filtered through celite; the filtrate was cooled with a Dry Ice–acetone bath during the filtration. To the filtrate was added 500 ml of ether, and the product was quickly worked up by washing three times with a total volume of 300 ml of 2% sodium bicarbonate solution and with water, followed by drying over magnesium sulfate in an ice box. Removal of the solvent at room temperature under reduced pressure yielded 22.7 g of the crude mixed anhydride as a pale yellow crystalline solid, mp 71–78°. Three recrystallizations from carbon tetrachloride–petroleum ether (60–80°) gave 14.1 g (48% yield) of pale straw-colored flat needles, mp 83–84.5° (lit.[7] mp 86.5–87°). The infrared spectra of IIa prepared by both methods were identical; the mixture melting point was not depressed. Small amounts of *p*-nitrobenzoic anhydride, *p*-nitrobenzoic acid, and *t*-butyl *p*-nitrothiolbenzoate were isolated.

***p*-Nitrobenzoic isopropylthiolcarbonic anhydride (IIb)** was prepared from *p*-nitrobenzoic acid (3.34 g) and isopropyl thiolchlorocarbonate (2.78 g) with triethylamine (2.5 g); the reaction mixture was cooled with a Dry Ice–chloroform bath at −50 to −40°. Removal of the solvent under reduced pressure at room temperature gave 3.56 g of shining pale straw-colored flakes, mp 67–72°. After three recrystallizations from carbon tetrachloride–petroleum ether, 2.50 g (46% yield of IIb) was obtained as colorless shining flakes, mp 73.5–75°. The infrared spectrum in carbon tetrachloride was characterized by the following peaks (cm^{-1}): 3110–3050 w, 2960, 2920, 2860, 1787 s, 1727, 1606, 1525, 1450 w, 1349 s, 1320 w, 1250 s, 1237, 970, 870 w, 845, 710. The nmr spectrum in carbon tetrachloride showed a 6 H unsymmetrical doublet centered at τ 8.56 (J = 7 cps), a 1 H multiplet centered at 6.35 (J = 7 cps), and a 4 H singlet at 1.74.

Anal. Calcd for $C_{11}H_{11}NO_5S$: C, 49.06; H, 4.12; N, 5.20; S, 11.91. Found: C, 49.01; H, 4.13; N, 5.17; S, 11.91.

p-Nitrobenzoic anhydride, isopropyl *p*-nitrothiolbenzoate, and *p*-nitrobenzoic acid were also isolated in minor amounts.

The carbonation procedure was applied to 2.0 g of isopropyl mercaptan, and 1.0 g of sodium hydride, in a 1:1 mixture of THF–ether, and 3.72 g of *p*-nitrobenzoyl chloride. After two crystallizations from carbon tetrachloride–petroleum ether, 2.7 g (50%), mp 73.5–75°, was obtained, identical with that obtained above from the chlorothiolcarbonate process.

***p*-Nitrobenzoic benzylthiolcarbonic anhydride (IIc)** was prepared from *p*-nitrobenzoic acid (1.67 g) and benzyl thiolchlorocarbonate (1.87 g) with DABCO (1.12 g). Three recrystallizations from chloroform–petroleum ether yielded 0.66 g (21% yield) of IIc as colorless long needles, mp 66–68°. When triethylamine was used as catalyst instead of DABCO, IIc was obtained in *ca.* 10% yield. The infrared spectrum in carbon tetrachloride was characterized by the following peaks (cm^{-1}): 3100 w, 3080 w, 3060 w, 2940, 1789 s, 1730, 1605, 1525, 1348 s, 1320, 1250, 1237, 990, 850, 710.

Anal. Calcd for $C_{15}H_{11}NO_5S$: C, 56.77; H, 3.50; N, 4.41; S, 11.10. Found: C, 56.82; H, 3.53; N, 4.61; S, 11.30.

It was also prepared in about 10% yield from benzyl mercaptan, sodium hydride, carbon dioxide, and *p*-nitrobenzoyl chloride.

***p*-Nitrobenzoic Phenylthiolcarbonic Anhydride (IId).**—The same procedure was followed to prepare IId from phenyl thiolchlorocarbonate (1.73 g) and *p*-nitrobenzoic acid (1.67 g) In comparison with its alkyl analogs it was much harder to obtain in a pure form. Several tertiary amines, triethylamine, N-methylpiperidine, tri-*n*-butylamine, and DABCO, were tried; various solvent systems, reaction temperatures, and reaction times were used.

The run which gave the highest yield of the mixed anhydride (*ca.* 15%) was carried out at −20 to −40° in THF with triethylamine as the catalyst. The product was obtained as colorless needles (from chloroform–petroleum ether), and melted at 90–92° and decomposed at 105–110°. The other mixed anhydrides started to decompose at 140–150°. The infrared spectrum

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[13] J. A. Pegolotti and W. G. Young, *J. Amer. Chem. Soc.*, **83**, 3251 (1961).

[14] S. J. Rhoads and R. E. Michel, *ibid.*, **85**, 585 (1963).

[15] All melting points were uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 421 recording spectrophotometer, and ultraviolet spectra were taken on a Cary Model 11 recording spectrophotometer. Nuclear magnetic resonance spectra, reported in τ values, were recorded on a Varian A-60 spectrometer under the direction of Dr. L. D. Colebrook. Vapor phase chromatographic analyses were done on a Wilkins Aerograph Model A-90-P instrument using a 15-ft SF-96 or a 15-ft di-*n*-decylphthalate column. Microanalyses were by Micro-Tech Laboratories, Skokie, Ill.

[16] Prepared according to C. E. Castro, *ibid.*, **83**, 3262 (1961).

in chloroform was characterized by the following peaks (cm^{-1}): 3110–3000 w, 1788 s, 1730, 1606, 1520, 1455 w, 1346 s, 1315, 1245–1195, 985, 845. The ultraviolet spectrum in cyclohexane showed an absorption at λ_{max} 2.54 mμ (ϵ_{max} 2.11 × 10^4). The nmr spectrum in deuteriochloroform showed a 5 H unresolved multiplet at τ 2.75 and a 4 H unsymmetrical doublet centered at 2.0.

Anal. Calcd for $C_{14}H_9O_5NS$: C, 55.44; H, 2.99; N, 4.62; S, 10.57. Found: C, 54.90; H, 3.06; N, 4.92; S, 10.59.

In all runs, phenyl *p*-nitrothiolbenzoate, mp 158–159° (lit.[17] mp 157–158°) was isolated as the major product.

All attempts to prepare IId by the carbonation procedure resulted in the formation of the ester, phenyl *p*-nitrothiolbenzoate, as the major product with a very slight amount of the mixed anhydride.

Thermal Decompositions of Anhydrides without Solvent. (Table I).—These were carried out as described previously.[3] In one run 879 mg of IIa yielded 137.5 mg (100.6%) of carbon dioxide; the solid residue (740 mg) melted at 63–68°. To 370 mg of this was added 10 ml of carbon tetrachloride; filtration gave *ca.* 15 mg of material melting at 182–188°. Its infrared spectrum in KBr was practically identical with that of *p*-nitrobenzoic anhydride. The product collected from several runs was recrystallized from benzene, and was shown to be identical with a known sample of *p*-nitrobenzoic anhydride; the yield was *ca.* 3%.

Removal of solvent from the filtrate gave 350 mg of a pale yellow solid, mp 69–72°. It was recrystallized from methanol–water to give 320 mg of yellow needles which melted at 73–75°. The infrared spectrum in carbon tetrachloride was identical with that of *t*-butyl *p*-nitrothiolbenzoate. The mixture melting point with the authentic sample showed no depression (lit.[7] mp 74.5–75°). The yield of the thiol ester was 87% (640 mg).

Vapor phase chromatographic analysis of the carbon tetrachloride solution of the other half of the solid residue, from which *p*-nitrobenzoic anhydride had been filtered off, showed the presence of a minor quantity of di-*t*-butyl dithiolcarbonate. This new dithiolcarbonate has been prepared and characterized below.

In another run, the gaseous decomposition product was collected, degassed, and analyzed by mass spectrometry; the ratio of the 44 peak (carbon dioxide) to the 60 peak (carbonyl sulfide) was 820:1. Decomposition of IIa in *o*-dichlorobenzene in the presence of tetra-*n*-butylammonium iodide, DABCO, N-methylpiperidine, or triethylamine gave similar proportions of products.

Decomposition of the anhydrides IIb–d were carried out and the products were identified in a similar fashion.

Isopropyl *p*-nitrothiolbenzoate (IIb) was prepared from *p*-nitrobenzoyl chloride, isopropyl mercaptan, and triethylamine in benzene solution. Recrystallization from methanol–water gave 1.7 g (75%) of isopropyl *p*-nitrothiolbenzoate as shining colorless flakes, mp 66–68°. The infrared spectrum in carbon tetrachloride was characterized by the following peaks (cm^{-1}): 3110–3050 w, 2960–2920, 2860, 1665 s, 1606, 1520, 1450, 1390 w, 1375 w, 1350 s, 1315 w, 1195 s, 1155, 1108, 1060 w, 920 s, 862, 845, 695. The nmr spectrum in carbon tetrachloride showed a 6 H doublet at τ 8.58 (J = 7 cps), a 1 H septuplet centered at 6.17 (J = 7 cps), and a 4 H multiplet centered at 1.84.

Anal. Calcd for $C_{10}H_{11}NO_3S$: 53.31; H, 4.92; N, 6.22; S, 14.23. Found: C, 53.43; H, 4.85; N, 6.30; S, 14.15.

Preparation of Di-*t*-Butyl Dithiolcarbonate. A.—To a THF solution of sodium *t*-butyl mercaptide (0.2 mol) was added dropwise 30 g (0.20 mol) of *t*-butyl thiolchlorocarbonate with vigorous stirring over a period of 1 hr, with cooling in an ice bath. Stirring was continued for additional 2 hr at room temperature. Ether (300 ml) was added, the solution was washed with water and dried, and the solvent was removed to give 25.0 g of colorless crystalline solid which melted at 50–55°. Two recrystallizations from methanol–water yielded 21.0 g (50% yield) of di-*t*-butyl dithiolcarbonate as colorless needles, mp 58–59°. The infrared spectrum in carbon tetrachloride was characterized by the following peaks (cm^{-1}): 3000 w, 2970 s, 2920, 2900, 2860 w, 1710, 1637 s, 1475, 1455, 1365 s, 1162, 1020 w, 930 w, 845 s. The nmr spectrum in carbon tetrachloride showed a single peak at τ 8.53. The ultraviolet absorption showed a band at λ_{max} 257 mμ (ϵ 7.03 × 10^3).

Anal. Calcd for $C_9H_{18}OS_2$: C, 52.38; H, 8.79; S, 31.07. Found: C, 52.19; H, 8.91; S, 31.38.

B.—Diisopropyl dithiolcarbonate was also prepared from isopropyl mercaptan (4.6 g) and isopropyl thiolchlorocarbonate (8.3 g) in *ca.* 40% yield. The reaction mixture after removal of solvent was purified by vpc on an SF-96 column. A colorless liquid was obtained. The infrared spectrum (liquid film) showed the characteristic carbonyl absorption at 1640 cm^{-1}, and the other absorption peaks were at 2960, 2920, 2860, 1725 w, 1445, 1375, 1365, 1305, 1240, 1155, 1050, 855 cm^{-1}. The nmr spectrum in carbon tetrachloride showed a 6 H doublet centered at τ 8.68 (J = 7 cps) and a 2 H septet centered at 6.26 (J = 7 cps).

Anal. Calcd for $C_7H_{14}OS_2$: C, 47.15; H, 7.91. Found: C, 46.93; H, 7.84.

Thermal Stability of *t*-Butyl *p*-Nitrothiolbenzoate. *t*-Butyl *p*-nitrothiolbenzoate (2.37 g) was heated in the thermal decomposition vessel previously described[3] at 150° for 4 hr. At the end of the heating, no increase in the weight of the absorption tubes was detected. A pale yellow solid, 2.3 g, was obtained, mp 72–74°. The infrared spectra of the sample before and after the heating were essentially the same.

In another run 0.27 g of the *t*-butyl *p*-nitrothiolbenzoate in 10 ml of methanol was refluxed for 4 hr. Removal of solvent left 0.26 g of a pale yellow solid which melted at 70–73°. The infrared spectra of the sample before and after the refluxing were the same. Recrystallization from ethanol and water gave the pure thiol ester, mp 73–75°.

Thermal Stability of Di-*t*-butyl Dithiolcarbonate.—The dithiolcarbonate was also heated at 145–150° for 4 hr. It was virtually unchanged. The infrared spectra of the sample before and after the heating were the same.

A mixture of *p*-nitrobenzoic anhydride (0.32 g) and di-*t*-butyl dithiolcarbonate (0.21 g) was heated at 160° for 6 hr. The infrared spectra (in potassium bromide) of the mixture before and after the heating were essentially the same; the characteristic carbonyl absorption of *t*-butyl *p*-nitrothiolbenzoate at 1666 cm^{-1} was not observed.

Reactions of *p*-Nitrobenzoic *t*-Butylcarbonic Anhydride with N-Methylaniline. Preparation of N-Methyl-N-phenyl *t*-Butylthiolcarbamate.—To 1.897 g of the *t*-butylthiocarbonic anhydride in 50 ml of anhydrous ether was added dropwise with rapid stirring 0.745 g of N-methylaniline, freshly distilled from zinc dust, in 15 ml of ether. The reaction mixture was cooled with a Dry Ice–carbon tetrachloride bath at −26 to −23°. Stirring was continued for 40 hr and the solution was gradually warmed to room temperature. It was extracted four times with a total volume of 55 ml of 5% sodium bicarbonate solution. The aqueous layer was withdrawn and acidified with concentrated hydrochloric acid to give a pale yellow precipitate. This suspension, after addition of sodium chloride, was extracted with 50 ml of ether and then with 10 ml of saturated sodium chloride solution and was dried. Removal of ether gave 261 mg (23% yield) of *p*-nitrobenzoic acid. The original ether layer was extracted with 15 ml of 5% hydrochloric acid. The aqueous layer was withdrawn and made basic with sodium hydroxide solution. It was extracted with ether and dried; removal of the ether gave no detectable amount of N-methylaniline. The ether layer, after the acid and base extraction, was washed with 25 ml of saturated sodium chloride and dried. Removal of ether left 1.46 g of a colorless crystalline solid. It was chromatographed on 42 g of silica gel, using the following eluents (benzene, benzene–chloroform, chloroform, chloroform–ether, ether) successively to give 0.27 g of a colorless crystalline solid, mp 56–57°, which was identified as a new thiolurethan, N-methyl-N-phenyl *t*-butylthiolcarbamate. Its infrared spectrum was superimposable upon that of the authentic sample prepared below, and the mixture melting point was not depressed. A second colorless solid, 0.98 g, was eluted by ether, and melted at 108–109.5°. It was identified as N-(*p*-nitrobenzoyl)-N-methylaniline (lit.[18] mp 113°). The mixture melting point with an authentic sample showed no depression, and their infrared spectra were identical.

N-Methyl-N-phenyl *t*-Butylthiolcarbamate.—To 7.7 g of *t*-butyl thiolchlorocarbonate in 10 ml of absolute methanol, cooled with an ice bath, was added dropwise 5.5 g of N-methylaniline with rapid stirring. Stirring was continued for 17 hr at room temperature; the mixture was poured with vigorous stirring into 5 g of ice water mixture to give 6.5 g of a white solid, mp 50–55°. Recrystallization from methanol–water yielded 5.1 g (46% yield) of colorless flakes, mp 56–57°. The infrared spec-

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(17) G. F. Grillot, P. M. Levin, R. Green, and R. I. Bashford, *J. Amer. Chem. Soc.*, **72**, 1863 (1950).

(18) P. Grammaticakis, *Bull. Soc. Chim. Fr.*, **27**, 1966 (1960).

trum in carbon tetrachloride exhibited the following peaks (cm^{-1}): 3053 w, 3024 w, 2992 w, 2958, 2911, 1659 s, 1650 s, 1595, 1497, 1479, 1455, 1362, 1337 s, 1266, 1161, 1107, 871, 696.

Anal. Calcd for $C_{12}H_{17}NOS$: C, 64.53; H, 7.67; N, 6.27; S, 14.37. Found: C, 64.35; H, 7.51; N, 6.08; S, 14.46.

Kinetic Studies of the Thermal Decomposition of *p*-Nitrobenzoic *t*-Butyl and Isopropylthiolcarbonic Anhydrides. Purification of Solvents and Additives. A. Decahydronaphthalene.—The Eastman Kodak White Label sample, containing less than 0.01% tetralin, was used, $n^{20.8}$D 1.4761, (lit.[19] *cis* isomer, n^{20}°D 1.4811; *trans* isomer, n^{20}D 1.4697).

B.—*o*-Dichlorobenzene was twice fractionally distilled through a 38-cm Vigreux column under reduced pressure. The middle fraction was used: bp 34–36° (1 mm); $n^{26.4}$D 1.5483 (lit.[20] n^{25}D 1.5491).

C. Benzonitrile.—A commercial grade was steam distilled. The distillate was extracted with ether, washed with dilute sodium carbonate solution, and dried over calcium chloride. The ether was removed, and the remaining liquid was twice fractionally distilled through a 38-cm Vigreux column under reduced pressure. The middle fraction which boiled at 40–42° (0.4–0.5 mm), $n^{26.4}$D 1.5253 (lit.[21] n^{20}D 1.5282), was used.

D. Tetra-*n*-butylammonium Iodide.—An Eastman Kodak White Label sample was recrystallized from benzene and dried at *ca.* 110° for 10 hr, mp 144.5–145° (lit.[22] mp 144–145°).

Kinetic runs were carried out in a constant-temperature bath controlled within ± 0.1°.

Pyrex tubes of 8-mm i.d. were cleaned thoroughly by soaking in sodium dichromate cleaning solution for 30 min and then rinsing with water, dilute aqueous ammonium hydroxide, water, and distilled water. Tubes of 20-cm length were drawn out and pulled thin at 16-cm length for convenient sealing in the degassing process. The tubes were dried in an oven at *ca.* 110° for at least 10 hr.

A stock solution of the *p*-nitrobenzoic thiolcarbonic anhydride which had been recrystallized prior to the kinetic runs and always had a melting point range of less than 2°, was prepared from a weighed sample. Stock solutions of additives were prepared similarly and mixed in the required proportions.

Into each tube 1 ml of the stock solution was transferred with a syringe having a 6-in.-long needle; the tubes were then connected to a glass manifold, and the solution was degassed by freezing the tubes in liquid nitrogen under 0.1–0.3 mm of pressure. The tubes were sealed under this pressure and frozen in a Dry Ice–acetone bath until the carrying out of the kinetic runs. 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 wax bath (each tube was immersed up to 13 cm). It usually took 1.5 to 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 sample. The other tubes were withdrawn at suitable time intervals in the same way. The last tube usually was removed after three half-lives of the reaction. The tubes were frozen in the Dry Ice–acetone bath until infrared analyses were carried out.

Analyses of Kinetic Runs by Infrared Spectrophotometry and Treatment of Data.—The rate of the thermal decomposition was followed by measuring the decrease in absorbance of the carbonyl peak of the mixed anhydride, using a Perkin-Elmer Model 421 infrared spectrophotometer[23] 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 mixed anhydride was less than 4×10^{-2} *M*.

The spectrum was scanned two to three times at a speed of 70 cm^{-1}/min in the region of 1850–1650 cm^{-1}. In some runs after finding the carbonyl maximum of the mixed anhydride, the scanning mechanism was disconnected and the drum was allowed to move at this speed for 3–5 min. Both methods were found to be satisfactory. Essentially the same procedure of analysis was used for all the kinetic runs, except that, in decalin, the slit width was opened at a constant value of 250 μ, whereas in *o*-dichlorobenzene and benzonitrile it was at 500 μ because of the absorption of the latter two solvents in this region. Zero and one hundred per cent transmittance (T_o and T_{100}) were adjusted at the carbonyl maximum when both cells were filled with pure solvent or with the solvent containing the same concentration of additive. To avoid the possibility of setting the pen against the mechanical stop, zero transmittance was set at 0–5% and one hundred per cent transmittance was set at 90–95%. The true per cent transmittance, T_x, of a sample was thus calculated from the observed transmittance, T_{obsd}, $T_x = (T_{obsd} - T_o)/(T_{100} - T_o)$. Each time the sample cell was cleaned with analytical grade acetone, dried under a slow stream of nitrogen, and rinsed four or five 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% transmittance. Therefore, the mixed anhydride solutions were made up at (or uniformly diluted to) such a concentration that the zero time transmittance would be around 20–30% and thus the two to three half-lives transmittance would be around 80%.

From the per cent transmittance, the optical density at time *t* was obtained, and the first-order rate constants were determined from the slope of the first-order plots of log OD_t/OD_0 *vs.* time. The activation parameters were calculated from the Eyring equation in the usual way.[24] The enthalpy of activation, $\Delta H^{\ddagger}$, was determined from the least-squares slope through the points on a plot of ln (k_1/T) *vs.* $1/T$. The entropy of activation, $\Delta S^{\ddagger}$, was calculated from the intercept of the plot. All the least squares analyses were done by Mr. C. A Whiteman, Jr., on the IBM 650 of General Railway Signal Co.

Registry No.—IIa, 16118-27-7; IIb, 16118-28-8; IIc, 16118-29-9; IId, 16118-30-2; isopropyl *p*-nitrothiolbenzoate, 16118-31-3; di-*t*-butyl dithiolcarbonate, 16118-32-4; di-isopropyl dithiolcarbonate, 16118-33-5; *t*-butyl *p*-nitrothiolbenzoate, 16118-34-6; N-methyl-N-phenyl *t*-butylthiolcarbamate, 16118-35-7.

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