Further Aspects of the Assisted Thermal Decomposition of Mixed Carbonic Anhydrides[1]

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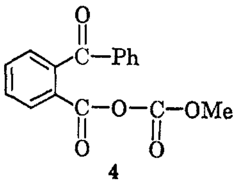
The thermal decomposition of the *cis*- and *trans*-2-benzoylcyclopropanecarboxylic acidethylcarbonic anhydrides (**7** and **8**) was investigated. The *trans* isomer decomposed readily by the normal reaction process. The ratio of products obtained was independent of the decomposition temperature. The decomposition of the *cis* isomer (**7**), however, was much more complex. At 100° the reaction proceeded much slower than did the decomposition of **8**, and little keto group participation was observed. At 140° the ψ ester (**15**) was the primary product establishing that participation was occurring at this temperature but at 160° normal ester (**13**) formation predominated. It was indicated that formation of **15** did not occur by way of an intramolecular process as was shown to be taking place in the decomposition of the mixed anhydride of *o*-benzoylbenzoic acid (**4**). It is proposed that the difference between the observed modes of reaction of **7** and **4** is probably the result of the difference in carbonyl group conformation required for conjugation with a cyclopropane and a benzene ring.

Mixed carbonic anhydrides (**1**) have been shown to rearrange when heated to give the corresponding esters (**2**) and symmetrical anhydrides (**3**).[4] Rather extensive investigations of this reaction[4-7] showed that (1) the product ratio obtained is markedly dependent on the relative size of the acyl and alkoxy portions of **1**; (2) the reaction is facilitated by the presence of nucleophilic agents; (3) the product composition is independent of the presence of these nucleophiles as well as of concentration and solvent effects; (4) alkyl oxygen bond cleavage does not normally occur;[8] and (5) the reaction is not a free-radical process. These factors led to the formulation of the mechanism shown in Scheme I for this reaction.[6]

More recently it has been shown that the carbonyl group of *o*-benzoylbenzoic acid methyl carbonic anhydride (**4**) takes part in the decomposition to give the ψ ester **5** as the product.[9] It was proposed that this product was obtained by way of a concerted process taking place through the [3.2.1] transition state, **6**.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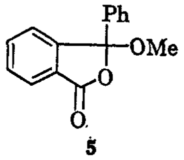
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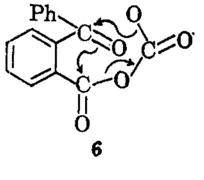
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Prior to this publication[9] we had embarked on a study of the decomposition of the mixed carbonic anhydrides of *cis*- and *trans*-2-benzoyl-1-cyclopropanecarboxylic acids (**7** and **8**) in an attempt to delineate the extent to which the keto group would assist the reaction. With the *trans* isomer serving as a model for the nonparticipation reaction it was felt that a comparison of the data obtained from the decomposition of both isomers would lead to a more definitive picture of the participation reaction. Since the results of this investigation led to conclusions different from those arrived at from the decomposition of **4**[9] they are presented here in an effort to give a more general understanding of the factors involved in neighboring carbonyl group participation.

Results

The *cis*- and *trans*-2-benzoyl-1-cyclopropanecarboxylic acids (**9** and **10**) were prepared as outlined in Schemes II and III. Treatment of either **9** or **10** with ethyl chloroformate and triethylamine resulted in the formation of the mixed (**7** or **8**) and symmetrical anhydrides (**11** or **12**). In both series the symmetrical anhydrides were separated from the mixture by precipitation from cold ether. Treatment of the mixed anhydrides with sodium ethoxide at 0° gave the normal ethyl esters (**13** or **14**) as the sole products.

The nmr spectra of these compounds were quite characteristic (see Experimental Section). In each case the aromatic proton peaks were split into two multiplets integrating for two and three protons as anticipated for the presence of phenyl ketones.[10] The cyclopropyl proton peaks showed different splitting patterns for the isomeric compounds. In each case the *trans* isomer showed an A_2XY spectrum while the *cis* isomer exhibited an ABXY splitting pattern. In the infrared the carbonyl stretching frequencies of the *cis* isomers were at higher wave numbers than the corresponding *trans* compound as found for other carbonyl-substituted cyclopropanes.[11] Interestingly, the Nujol mull spectra of the symmetrical anhydrides (**11** and **12**) did not show

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[3] American Cyanamid Educational Award recipient, 1964-1966. This work was taken, in part, from the Ph.D. Dissertation submitted by F. G. P. to Seton Hall University, 1966.

[4] D. S. Tarbell and E. J. Longosz, *J. Org. Chem.*, **24**, 774 (1959).

[5] T. B. Windholz, *ibid.*, **25**, 1703 (1960).

[6] E. J. Longosz and D. S. Tarbell, *ibid.*, **26**, 2161 (1961).

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

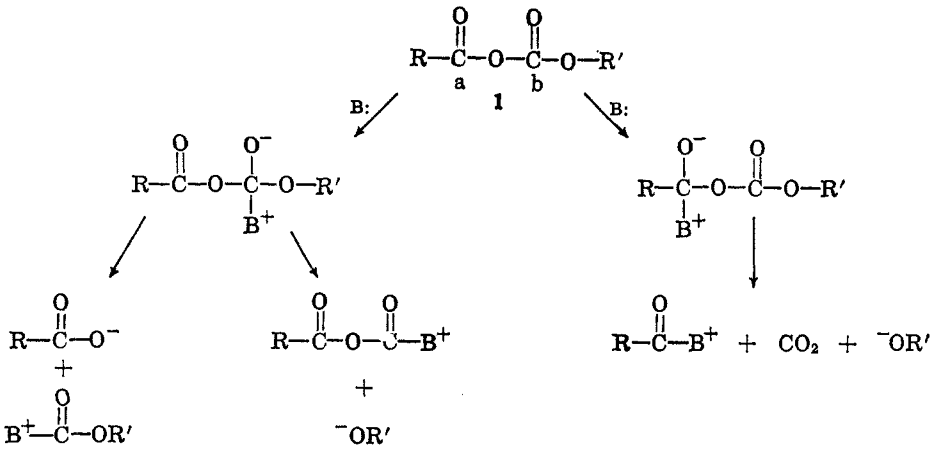
[8] In those cases in which the alkyl group can readily form a carbonium ion, *e.g.*, a *t*-butyl group, some products arising from alkyl oxygen bond cleavage have been observed: C. J. Michejda, Ph.D. Dissertation, University of Rochester, Rochester, N. Y., 1964.

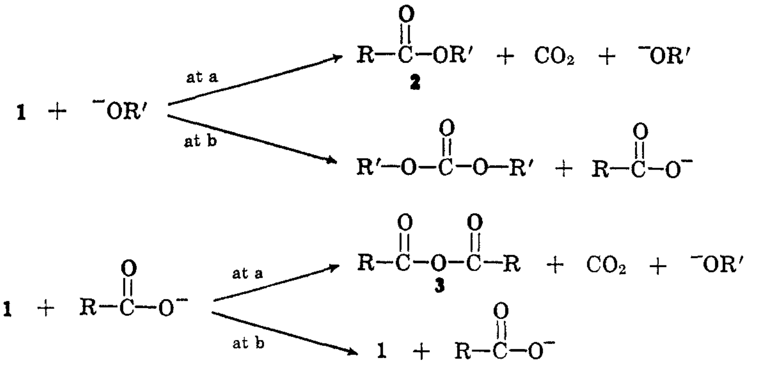
[9] M. S. Newman and C. Courduvelis, *J. Amer. Chem. Soc.*, **88**, 781 (1966).

[10] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1962.

[11] R. J. Mohrbacher and N. H. Cromwell, *J. Amer. Chem. Soc.*, **79**, 401 (1957).

Scheme I





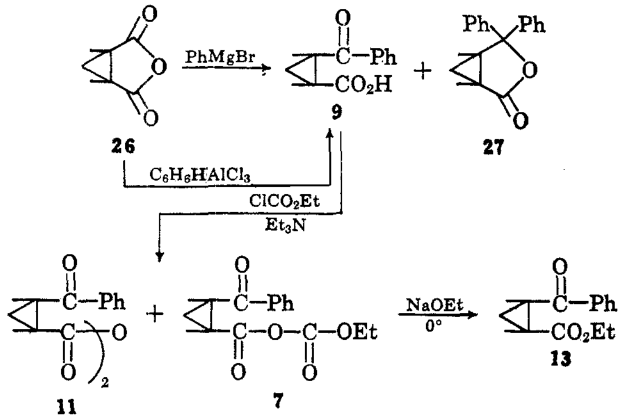
$$1 + {}^{-}OR' \xrightarrow{\text{at a}} R{-}\overset{O}{\overset{\|}{C}}{-}OR' \;(\mathbf{2}) + CO_2 + {}^{-}OR' \quad (1)$$

$$1 + {}^{-}OR' \xrightarrow{\text{at b}} R'{-}O{-}\overset{O}{\overset{\|}{C}}{-}O{-}R' + R{-}\overset{O}{\overset{\|}{C}}{-}O^{-} \quad (2)$$

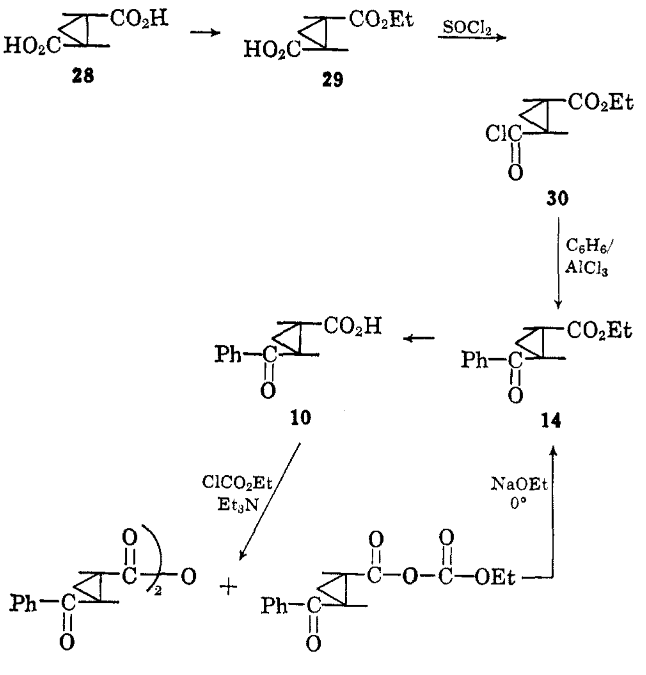
$$1 + R{-}\overset{O}{\overset{\|}{C}}{-}O^{-} \xrightarrow{\text{at a}} R{-}\overset{O}{\overset{\|}{C}}{-}O{-}\overset{O}{\overset{\|}{C}}{-}R \;(\mathbf{3}) + CO_2 + {}^{-}OR' \quad (3)$$

$$1 + R{-}\overset{O}{\overset{\|}{C}}{-}O^{-} \xrightarrow{\text{at b}} 1 + R{-}\overset{O}{\overset{\|}{C}}{-}O^{-} \quad (4)$$

Scheme II



Scheme III



the doublet characteristic of the anhydride group.[12] We have found no mention of a similar finding in the literature. These doublets were present, however, in the solution spectra of these compounds.

Distillative decomposition of **7** led to the formation of two volatile components, the normal ester **13** and the ψ ester **15**. The structure of **15** was inferred from its elemental analysis by the presence of a single carbonyl peak at 1785 cm^{-1} (γ lactone) in its infrared spectrum and by the singlet aromatic proton adsorption in the nmr indicating the loss of the phenyl ketone moiety. With all of the products expected from the decomposition of **7** and **8** isolated and characterized, analysis of the product mixtures obtained from the decomposition run under different conditions was considerably simplified.

The mixed anhydrides (**7** and **8**) were decomposed by refluxing 3% solutions of these materials in hydrocarbon solvents. The solvents used were chosen to provide a sufficiently wide range of reaction temperatures: methylcyclohexane (100°), xylene (140°), and mesitylene (160°). The time required for complete decomposition was determined in preliminary runs by the spectral analysis of aliquots taken at periodic intervals. When there was no change in the infrared spectra of successive aliquots the reaction was considered to be complete. By use of this technique it was found that the decomposition of **7** at 100° was extremely slow and that, even on prolonged heating, considerable quantities of the

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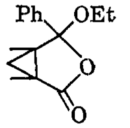
[12] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958.

starting anhydride were still present in the reaction mixture. This led to considerable errors in product analysis since **7** was decomposed on vpc analysis to give predominantly the normal ester **13**. In this reaction, therefore, it was necessary to estimate the amount of **13** in the reaction mixture by the intensity of its characteristic carbonyl adsorption frequency at 1733 cm^{-1}. The determination of the amount of **15** present by vpc analysis, however, was not influenced by the presence of **7**. In all other runs, decomposition was complete.

After the various reaction mixtures had been heated for the required time the solvent was removed under reduced pressure; the symmetrical anhydrides were separated by triturating the residue with cold ether. Only **12** was obtained from **8** but on heating **7** a mixture of **11**, **12**, and **16** was obtained. The *cis,trans* isomer, **16**, was the major component of this mixture. Refluxing a solution of **11** in methylcyclohexane resulted in the precipitation of **16** from the hot solution. Thus, **16** is probably not a primary decomposition product but, instead, is formed by the thermal rearrangement of **11**.



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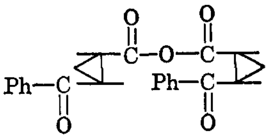

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The oils left after separation of the symmetrical anhydrides were analyzed by vpc with the products identified by comparison of their retention time and spectral properties with those of authentic samples. Whereas the presence of diethyl carbonate was detected in some of the reaction mixtures, no attempt was made to determine the amount of this material present since its volatility would make such determination prone to large errors. The data obtained from the decomposition of **7** and **8** at different temperatures are given in Table I. The product composition is estimated to be accurate to ±5%.

TABLE I

PERCENTAGE OF PRODUCTS OBTAINED FROM THE THERMAL DECOMPOSITION OF 2-BENZOYL-1-CYCLOPROPANECARBOXYLIC ETHYLCARBONIC ANHYDRIDES

cis Isomer **7**

Temperature, °C (time, hr)	Pseudo ester **15**, %		Normal ester **13**, %		Symmetrical anhydride, %
100 (40)	20		5[a]		40
140 (6)	70		10		5
160 (4)	20		50		10
	Ethyl (**15**)	Benzyl (**18**)	Ethyl (**13**)	Benzyl (**31**)	
140 (2) with benzyl alcohol	5	55	5	20	...

trans Isomer **8**

Temperature, °C (time, hr)	Ester **14**, %	Symmetrical anhydride, **12**, %
100 (17)	80	15
140 (6)	75	15

[a] There still remained about 20% of **7** undecomposed in the reaction mixture. The amount of normal ester present was estimated from the infrared spectrum of the reaction mixture.

Discussion

As can be seen from the data in Table I the modes of decomposition of the two isomeric mixed anhydrides **7** and **8** are considerably different. The decomposition of **8** follows the general mechanism proposed by Tarbell[6] and shown in Scheme I. This reaction took place readily at both 100 and 140° and gave essentially the same product ratio at both temperatures.

The decomposition of **7**, however, was more complex. As mentioned previously, this reaction took place very slowly at 100° in contrast to the decomposition of the *trans* isomer (**8**) which occurred readily at this temperature. The symmetrical anhydride was the primary product obtained from heating **7** at 100°, but at 140° formation of the ψ ester (**15**) predominated. At higher temperatures (160°), however, normal ester (**13**) formation was favored. In order to determine whether this normal ester formation was the result of a secondary reaction of **15** at the higher temperatures, a mixture of 15% of **13** and 85% of **15** was refluxed in mesitylene for 4 hr in the presence of a 20% molar concentration of sodium ethoxide.[13] A mixture of 45% of **13** and 55% of **15** was obtained from this reaction. Thus, although these results do indicate that a secondary conversion of the ψ ester **15** into the normal ester **13** is possible, the formation of considerably less of **13** in this reaction than is obtained from the high temperature decomposition of **7** indicates that most of the normal ester obtained in this latter reaction is formed directly from the mixed anhydride.[14]

These results are consistent with the presence of two competing reaction pathways for the decomposition of **7**, the normal decomposition route[6] (Scheme I) and a process involving participation of the keto carbonyl group. At 100° the normal route is favored. The presence of the *cis* benzoyl group hinders attack at the acyl carbonyl group[4,5] [a in **1** (Scheme I)] and thus attack by a nucleophile would be expected to occur primarily at the alkoxy carbonyl [b in **1** (Scheme I)]. This latter reaction would generate a carboxylate anion as the chain carrying species but attack of this entity at b only regenerates starting material (eq 4, Scheme I). Since the formation of products can take place only by the reaction of ethoxide ion (eq 1) or carboxylate ion (eq 3) at a, the preferred attack at b results in the observed slow formation of normal products from this reaction.

Since little ψ-ester formation was observed, carbonyl group participation can be occurring only slightly at this low temperature. This is entirely unexpected since neighboring group participation in general[15] or in particular of a keto group on halide solvolysis[16] results in a marked increase in reaction rate when compared to the unassisted reaction. The opposite is observed here. Consideration of the preferred conformation of **7**, how-

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(13) Since ethoxide ion can be formed during the decomposition of **7** its presence in this test reaction mixture was essential. The amount of ethoxide ion present in a decomposition mixture is not known but, since these reactions were run in hydrocarbon solvents, it was felt that it would be considerably lower than the amount added to the test reaction.

(14) It has also been reported that ester formation results from the high temperature reaction between symmetrical anhydrides and dialkylcarbonates.[5] However, heating the sterically more accessible *trans* anhydride (**12**) with diethyl carbonate at 160° for 4 hr gave none of the ester. Only starting materials were recovered.

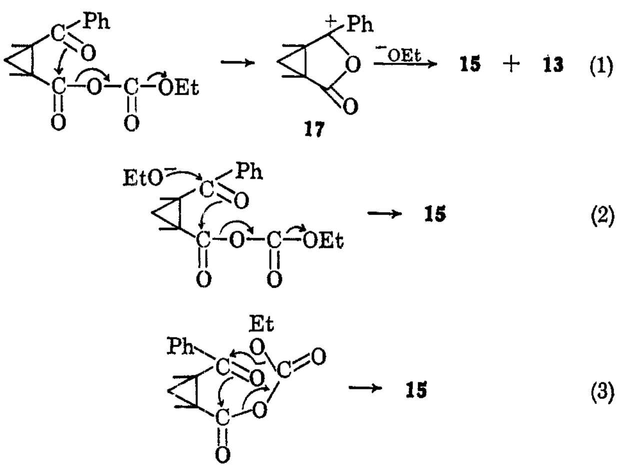
(15) B. C. Capon, *Quart. Rev.* (London), 45 (1964).

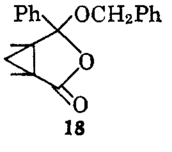
(16) D. J. Pasto and M. P. Serve, *J. Amer. Chem. Soc.*, **87**, 1515 (1965).

ever, can resolve this apparent difficulty. It has been shown that for maximum interaction to occur between a cyclopropane ring and a keto[17] or an aldehydic[18] group this carbonyl group must be perpendicular to the plane of the ring. Thus, in **7** the two carbonyl groups must be parallel to each other in the ground state and any participation by the keto group would require it to be rotated out of conjugation with the cyclopropane ring. Therefore, at lower temperatures such participation would not be favorable.

However, at higher temperatures (140°) this reorientation becomes more facile and a product (**15**) arising from carbonyl group participation was obtained. This participation can be pictured as taking place in one of three ways: (1) direct assistance by the keto group to give the carbonium ion intermediate **17**[19] which then reacts with ethoxide to give the ψ ester (**15**) and, possibly, some of the normal ester (**13**) (eq 1, Scheme IV); (2) a nucleophile-promoted decomposition similar to that proposed for the normal decomposition of mixed carbonic anhydrides[6] but which would involve attack by ethoxide ion at the keto carbonyl group to give the ψ ester (**15**) directly, a process which is analogous to that followed in the base hydrolysis of appropriately substituted keto esters[20] (eq 2, Scheme IV); or (3) rearrangement by a concerted process proceeding through a bicyclic [3.2.1] transition state as proposed for the thermal decomposition of **4**[9] (eq 3, Scheme IV).

SCHEME IV





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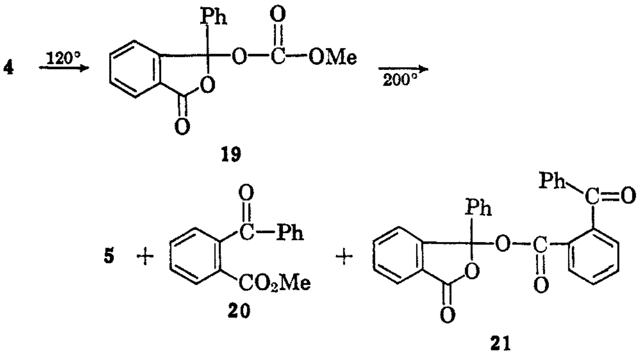
If this latter process were operative in the decomposition of **7** it would be expected that little or no incorporation of an added nucleophile would be observed. However, when the decomposition of **7** was run in xylene containing benzyl alcohol the major product obtained was the ψ benzyl ester **18** (Table I). That this material was a primary product of the decomposition and did not result from a secondary reaction of a benzyloxy ion on **15** was shown by refluxing a mixture of 85% of **15** and 15% of **13** in benzyl alcohol containing a small amount of sodium ethoxide[13] for the time required for the decomposition of **7**. Under these condition only 10% of **18** was formed, much less than was obtained from the decomposition run. Although these results tend to eliminate from consideration any concerted intramolecular process for the decomposition of **7**, one cannot state unequivocally that this is the case. For instance, the incorporation of the benzyloxy group into ψ ester could be the result of an initial transesterification of **7** followed by a concerted rearrangement. It is obvious then that further work is necesssary to determine the exact process utilized in the formation of **15** from **7**.

Even with this lack it is quite apparent that the results found here for the decomposition of **7** are quite different from those reported for the decomposition of **4**.[9] The thermal reactions of **4** were, therefore, reexamined in an attempt to obtain more information with which to resolve this problem. Compound **4** was prepared and purified by the same procedure used to prepare **7**. When **4** was heated at 120–135° either neat or in solution no carbon dioxide was evolved and nearly quantitative amounts of the ψ mixed anhydride (**19**) were formed. The structure of **19** was determined primarily from its infrared spectrum with absorption at 1754 and 1736 cm^{-1} (γ lactone) but no benzoyl carbonyl absorption. When **19** was heated to 190–220°, carbon dioxide evolution was observed and the ψ ester (**5**), the normal ester (**20**), and the ψ symmetrical anhydride (**21**) were obtained in yields of 25, 25, and 50%, respectively.[21,22] Similar transformations have been reported to occur on heating *o*-(α,α-dimethylphenacyl)benzoic acid methyl carbonate mixed anhydride.[23]



In order to determine unequivocally the process by which **4** is converted into **19** an equimolar mixture of **4** and *p*-toluoylbenzoic ethylcarbonic mixed anhydride (**22**) was heated at 125° for 75 min. The only products obtained were the mixed ψ anhydrides **19** and **23**. Neither **24** nor **25**, which would result from an intermolecular reaction, was found in the reaction mixture. Thus, this rearrangement does indeed occur *via* an intramolecular process. The mechanism of the further breakdown of these materials was not investigated.

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(17) E. M. Kosower and M. Ito, *Proc. Chem. Soc.* (London), 25 (1962).

(18) L. S. Bartell, B. C. Carroll, and J. P. Guillory, *Tetrahedron Lett.*, 705 (1964).

(19) The direct observation of a carbonium ion intermediate in carbonyl-assisted solvolysis has recently been reported: H. R. Ward and P. D. Sherman, Jr., *J. Amer. Chem. Soc.*, **89**, 4222 (1967).

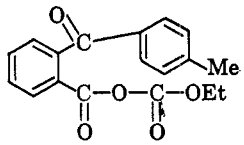
(20) C. Djerassi and A. E. Lippman, *ibid.*, **77**, 1825 (1955); M. S. Newman and S. Hishida, *ibid.*, **84**, 3582 (1962); U. R. Ghatak and J. Chakravarty, *Chem. Commun.*, 184 (1966).

(21) Another reinvestigation of the decomposition of **4** has also been made.[22] Essentially the same products and product ratios were obtained as well as evidence substantiating the unimolecular nature of the reaction. We wish to thank Professor Newman for making these results available to us prior to their publication.

(22) M. S. Newman and L. K. Lala, *J. Org. Chem.*, **32**, 3225 (1967).

(23) M. S. Newman and S. Mladenovic, *J. Amer. Chem. Soc.*, **88**, 4523 (1966).

It can be seen, then, that the thermal reactions of **4** and related compounds[22] differ considerably from those observed for **7**. At no time during the studies on the decomposition of **7** was there indication of the formation of any ψ mixed or ψ normal anhydrides. It appears, then, that the difference in reactivity between **7** and the other keto mixed anhydrides lies primarily in the ground-state geometry of the carbonyl groups in the various compounds. The spectral properties of **4** and related materials[9] show that the carbonyl groups are conjugated with and parallel to the benzene ring and thus are in position for facile intramolecular participation. However, as discussed previously, the carbonyl groups of **7** are perpendicular to the plane of the cyclopropane ring and not in position for a ready participation by the keto group in the reaction. Further work is underway to determine the extent to which this factor influences other participation reactions in carbonyl substituted cyclopropanes.



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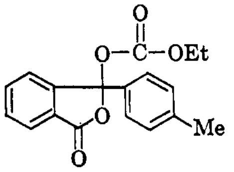

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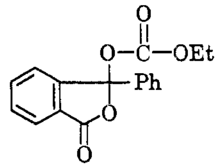

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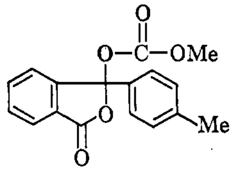

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Experimental Section[24]

cis-**1,2-Cyclopropanedicarboxylic acid anhydride** (**26**) was prepared as described,[25] mp 58–60° (lit.[26] mp 58–60°); the nmr spectrum showed cyclopropyl CH at δ 2.83 (m 2) and 1.77 (m 2).

cis-**1-Carboxy-2-cyclopropanecarboxamide** was prepared by reaction of **26** with ammonium hydroxide, mp 178–179.5° (ethanol).

Anal. Calcd for $C_5H_7NO_3$: C, 46.51; H, 5.43; N, 10.85. Found: C, 46.48; H, 5.36; N, 11.01.

Preparation of *cis*-**2-Benzoyl-1-cyclopropanecarboxylic Acid** (**9**). **Method A. Friedel-Crafts Reaction.**—A solution of 53.8 g (0.48 mol) of **26** in 200 ml of dry benzene was added slowly to a suspension of 156 g (1.18 mol) of powdered anhydrous aluminum chloride in 600 ml of dry benzene. Hydrogen chloride gas was rapidly evolved. The reaction mixture was stirred overnight at room temperature and then refluxed, with stirring, for an additional 3 hr. The cooled suspension was poured into cold dilute hydrochloric acid. The resulting solid was filtered, washed thoroughly with cold water, and dried in a Büchner funnel. Recrystallization from acetonitrile afforded 60.5 g (66%) of **9** as a white solid, mp 144–145° (lit.[26] mp 146°). The infrared spectrum (Nujol) showed COOH absorption at 1709 and a PhC=O band at 1675 cm^{-1}. The nmr spectrum had bands for a carboxylic H at δ 10.37 (s 0.7), aromatic CH at 7.98 (m 2) and 7.40 (m 3), and cyclopropyl CH at 2.87 (m 1), 2.25 (m 1), 1.90 (m 1), and 1.43 (m 1).

Anal. Calcd for $C_{11}H_{10}O_3$: C, 69.46; H, 5.30. Found: C, 69.60; H, 5.41.

Method B. Grignard Reaction.—Phenylmagnesium bromide was prepared in the usual manner from 80 g (0.51 mol) of bromobenzene, 13 g (0.53 g-atom) of magnesium turnings, and 175 ml of anhydrous ether. This solution was added over a 3-hr period to a solution of 51.5 g (0.53 mol) of **26** in 400 ml of tetrahydrofuran (previously distilled from lithium aluminum hydride). The addition was carried out at −30°. The reaction mixture was allowed to warm to room temperature after addition was completed and then poured into ice water. The aqueous layer was separated and extracted with ether. Acidification of the aqueous solution with concentrated hydrochloric acid gave 45.5 g (53%) of **9** which was identical with the product obtained by method A.

cis-**2-Diphenylhydroxymethylcyclopropanecarboxylic Acid Lactone** (**27**).—The ether extracts from the above work-up were combined, dried over anhydrous sodium sufate, and then concentrated to give 13.4 g of a solid which was recrystallized from acetonitrile. The resulting material melted at 146–147.5°. The infrared spectrum (Nujol) had absorption bands for a strained γ lactone at 1785 cm^{-1}, and the nmr spectrum showed peaks for aromatic CH at δ 7.30 (m 10) and cyclopropyl CH at 2.75 (m 1), 2.23 (m 1), 1.28 (m 1), and 0.85 (m 1).

Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.60; H, 5.60. Found: C, 81.59; H, 5.54.

trans-**Ethyl Hydrogen Cyclopropane-1,2-dicarboxylate** (**29**).—*trans*-1,2-Cyclopropanedicarboxylic acid (**28**) was obtained as a by-product in the preparation of **26**,[25] mp 177–178° (lit.[25] mp 177–177.5°).

Compound **28** was converted into the half ethyl ester **29** as described by Wiberg,[27] bp 90–93° (0.03 mm) [lit.[27] bp 130–134° (1.5 mm)].

Ethyl *trans*-**2-Benzoyl-1-cyclopropanecarboxylate** (**14**).—To a solution of 50 ml of thionyl chloride in 20 ml of dry benzene was added 22.4 g (0.142 mol) of **29** in 50 ml of benzene. The resulting solution was refluxed for 3 hr and then distilled, first at atmospheric pressure to remove the benzene and excess thionyl chloride and finally at reduced pressure to obtain the desired acid chloride (**30**) (20.8 g, 83%), bp 50° (0.02 mm).

To a suspension of 26.6 g (0.20 mol) of powdered aluminum chloride in 200 ml of dry benzene was added a solution of 17.7 g (0.10 mol) of **30** in 110 ml of dry benzene. Hydrogen chloride was slowly evolved. The mixtue was refluxed for 5 hr, stirred overnight at room temperature, poured into cold dilute hydrochloric acid, and extracted with ether. The ether extracts were washed with dilute sodium bicarbonate solution, dried over magnesium sulfate, filtered, and distilled to give 21.8 g (82%) of **14**, bp 110–113° (0.08 mm). The infrared spectrum (film) had bands for $COOC_2H_5$ at 1730 and PhC=O at 1675 cm^{-1}. The nmr spectrum showed aromatic CH at δ 7.75 (m 2) and 7.33 (m 3), ethyl CH_2 at 4.06 (q 2), cyclopropyl CH at 3.08 (m 1), 2.28 (m 1), and 1.47 (m 2), and ethyl CH_3 at 1.17 (t 3).

Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.56; H, 6.42. Found: C, 71.41; H, 6.34.

The **2,4-dinitrophenylhydrazone** melted at 174–176° (ethanol).

Anal. Calcd for $C_{19}H_{18}N_4O_6$: C, 57.29; H, 4.52; N, 14.07. Found: C, 57.07; H, 4.65; N, 14.01.

trans-**2-Benzoyl-1-cyclopropanecarboxylic Acid** (**10**).—To a solution of 6 g (0.15 mol) of sodium hydroxide in 150 ml of water was added 21.8 g (0.118 mol) of **14**. The mixture was stirred overnight at room temperature and acidified with dilute hydrochloric acid, and the resulting white solid was filtered. Recrystallization from benzene gave 14.5 g (76%) of **10**, mp 120.5–122°. The infrared spectrum (Nujol) showed peaks for COOH at 1692 and PhC=O at 1665 cm^{-1}. The nmr spectrum had bands for carboxylic H at δ 11.90 (s 0.6), aromatic CH at 7.97 (m 2) and 7.42 (m 3), and cyclopropyl CH at 3.22 (m 1), 2.38 (m 1), and 1.63 (m 2).

Anal. Calcd for $C_{11}H_{10}O_3$: C, 69.47; H, 5.26. Found: C, 69.36; H, 5.29.

cis-**2-Benzoyl-1-cyclopropanecarboxylic Ethylcarbonic Anhydride** (**7**).—A solution of 28.3 g (0.26 mol) of ethyl chloroformate in 300 ml of anhydrous ether was slowly added to a solution of 26.5 g (0.26 mol) of triethylamine in 800 ml of ether at 0°. To the resulting suspension was slowly added, at 0°, a solution con-

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[24] Boiling points and melting points are uncorrected. Infrared spectra were obtained on a Beckman IR-10 recording double-beam infrared spectrophotometer. Nuclear magnetic resonance (nmr) spectra were obtained in deuteriochloroform on a Varian Associates Model A-60A spectrometer using tetramethylsilane as the internal standard. The spectral data are reported in units of δ and the multiplicity of the resonance signal and the number of protons integrated for by the peak are given in parentheses. Vapor phase chromatographic analyses were made with an F & M Model 609 flame ionization gas chromatograph using a helium flow rate of 60 cc/min.

[25] L. L. McCoy, *J. Amer. Chem. Soc.*, **80**, 6568 (1958).

[26] G. Maier, *Angew. Chem.*, **75**, 920 (1963).

[27] K. B. Wiberg, R. K. Barnes, and J. Albin, *J. Amer. Chem. Soc.*, **79**, 4994 (1957).

taining 45.0 g (0.237 mol) of **9** in 200 ml of acetone. The reaction mixture was stirred for 1 hr at 0° and then filtered to give 28 g (85.8%) of triethylamine hydrochloride.

The filtrate was diluted with 200 ml of methylene chloride and then washed successively with cold dilute hydrochloric acid, dilute sodium bicarbonate solution, and finally with a saturated solution of sodium chloride. The organic solution was dried over magnesium sulfate and then concentrated at room temperature under reduced pressure to give 57.8 g of a liquid residue. This was treated with 200 ml of dry ether and refrigerated overnight to give, as a precipitate, 19 g (22.6%) of ***cis,cis*-2-benzoyl-1-cyclopropanecarboxylic anhydride** (**11**), which recrystallized as a white solid from cold acetone and water, mp 108–109°. The infrared spectrum in Nujol showed anhydride C=O absorption at 1810 and PhC=O absorption at 1682 cm^{-1} whereas in CH_2Cl_2 the spectrum showed bands for anhydride C=O at 1815 and 1750 and PhC=O at 1680 cm^{-1}. In the nmr spectrum absorption was found for aromatic CH at δ 7.92 (m 4) and 7.42 (m 6), and cyclopropyl CH at 2.90 (m 2), 2.32 (m 2), 1.85 (m 2), and 1.42 (m 2).

Anal. Calcd for $C_{22}H_{18}O_5$: C, 72.92; H, 5.01. Found: C, 72.88; H, 5.22.

The ether filtrate from the precipitation of the symmetrical anhydride **11** was concentrated under reduced pressure to give 36 g (58%) of **7** as a liquid residue. The infrared spectrum (CH_2Cl_2) had bands for anhydride C=O at 1818 and 1755 and PhC=O at 1680 cm^{-1}. The nmr spectrum showed peaks for aromatic CH at δ 7.89 (m 2) and 7.13 (m 3), ethyl CH_2 at 4.03 (q 2), cyclopropyl CH at 2.88 (m 1), 2.25 (m 1), 1.63 (m 1), and about 0.83 (multiplet partially buried under the ethyl CH_3 signal, 1), and ethyl CH_3 at 1.20 (t 3).

Anal. Calcd for $C_{14}H_{14}O_5$: C, 64.12; H, 5.38. Found: C, 64.08; H, 5.28.

A small sample of this mixed anhydride was converted into the amide by the addition of concentrated ammonium hydroxide to a cold ether solution of **7**. The white precipitate of ***cis*-2-benzoyl-1-cyclopropanecarboxamide** was filtered and recrystallized from benzene, mp 117.5–119°. The infrared spectrum (Nujol) had absorption bands for NH at 3490 and 3810, PhC=O at 1675, $CONH_2$ at 1660, and at 1620 cm^{-1}. The nmr spectrum showed the presence of aromatic CH at δ 7.98 (m 2) and 7.48 (m 3), NH at 6.03 (broad 0.4), and cyclopropyl CH at 2.87 (m 1), 2.28 (m 1), 1.85 (m 1), and 1.37 (m 1).

Anal. Calcd for $C_{11}H_{11}NO_2$: C, 69.83; H, 5.86; N, 7.40. Found: C, 70.01; H, 5.95; N, 7.23.

On distillation **7** decomposed to give a mixture, bp 112° (0.2 mm). One component was identified by comparison of its vpc[28] retention time with that of a known sample of **13**.

The mixture was redistilled and a fraction collected at 104° (0.05 mm). Its infrared spectrum (film) showed lactonic C=O absorption at 1785 cm^{-1} while its nmr spectrum had bands for aromatic CH at δ 7.40 (s 5), ethyl CH_2 at 3.47 (m 2), cyclopropyl CH at 2.65 (m 1), 2.27 (m 1), and about 0.67 (m 1), and ethyl CH_3 at 1.17 (t 3). One cyclopropyl CH is buried beneath the ethyl CH_3 signal.

These spectral properties are consistent with those expected of the pseudo ethyl ester of ***cis*-2-benzoyl-1-cyclopropanecarboxylic acid, 15**.

Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.21; H, 6.83.

Attempts to purify **7** by passing samples through columns containing neutral or acid washed alumina or silica gel also resulted in decomposition.

The residual oil, **7**, after removal of the symmetrical anhydride **11** was used directly in the decomposition experiments.

***trans*-2-Benzoyl-1-cyclopropanecarboxylic Ethylcarbonic Anhydride (8)**.—To a solution of 4.15 g (0.22 mol) of **10** and 2.65 g (0.026 mol) of triethylamine in 250 ml of methylene chloride was slowly added, at 0°, a solution of 2.83 g (0.026 mol) of ethyl chloroformate in 50 ml of methylene chloride. The resulting solution was stirred at 0° for 1.5 hr and then extracted with cold water, dilute hydrochloric acid, dilute sodium bicarbonate, and a saturated sodium chloride solution. The organic solution was dried over magnesium sulfate and then concentrated in a rotary evaporator under reduced pressure. The oily residue weighed 4.85 g (86%). The infrared spectrum (film) had bands for anhydride C=O at 1815 and 1755 and PhC=O at 1675 cm^{-1} while the nmr spectrum showed the presence of aromatic CH at δ 7.85 (m 2) and 7.38 (m 3), ethyl CH_2 at 4.17 (q 2), cyclopropyl CH at 3.18 (m 1), 2.32 (m 1), and 1.58 (t 2), and ethyl CH_3 at 1.20 (t 3).

Anal. Calcd for $C_{14}H_{14}O_5$: C, 64.12; H, 5.38. Found: C, 64.54; H, 5.45.

No solid, as was obtained in the preparation of the *cis* isomer **7**, was obtained when the oily residue, in ether, was refrigerated overnight.

***trans,trans*-2-Benzoyl-1-cyclopropanecarboxylic Anhydride (12)**.—The procedure used to prepare the mixed anhydride **10** was followed using acetone instead of methylene chloride as the solvent. The reaction mixture was drowned in cold water, extracted with methylene chloride and the organic solution worked up as before. The residue, after the removal of solvent, consisted of a mixture of a solid and an oil. This mixture was treated with a small amount of ether and refrigerated overnight. The precipitate was filtered from the ether solution of **8** to give 28% of a white solid which was recrystallized by dissolving it in cold acetone and adding water until a permanent turbidity was produced. Cooling afforded **12** as white needles which melted at 118–119°. The infrared spectrum in Nujol showed absorption for anhydride C=O at 1800 and PhC=O at 1675 cm^{-1}, whereas in methyl cyclohexane the spectrum showed bands for anhydride C=O at 1810 and 1745 and PhC=O at 1675 cm^{-1}. The nmr spectrum showed aromatic CH at δ 7.98 (m 4) and 7.48 (m 6) and cyclopropyl CH at 3.27 (septet 2), 2.47 (sextet 2), and 1.72 (t 4).

Anal. Calcd for $C_{22}H_{18}O_5$: C, 72.92; H, 5.01. Found: C, 72.78; H, 4.81.

***cis,trans*-2-Benzoyl-1-cyclopropanecarboxylic Anhydride (16)**.—A 0.5-g sample of **11** was refluxed in 30 ml of dry methylcyclohexane for 20 hr. A solid crystallized during the heating period and was isolated by decanting the supernatant liquid while still hot. The solid residue was recrystallized from benzene to give 0.1 g of **16** melting at 149–151°. The infrared spectrum (Nujol) had bands for anhydride C=O at 1805 and 1745 and PhC=O at 1680 cm^{-1} while the nmr spectrum showed aromatic CH at δ 8.00 (m 4) and 7.38 (m 6), and cyclopropyl CH at 2.90 (m 2), 2.38 (m 2), 1.97 (m 1), 1.30 (m 2), and 0.70 (m 1).

Anal. Calcd for $C_{22}H_{18}O_5$: C, 72.92; H, 5.01. Found: C, 72.71; H, 5.12.

Ethyl *cis*-2-Benzoyl-1-cyclopropanecarboxylate (13).—To a solution of 5.5 g of **7** in 20 ml of absolute ethanol was slowly added, at 0°, a solution of 0.5 g of sodium in 10 ml of ethanol. After 30 min the reaction mixture was poured into cold water and extracted with ether. The ether solution was dried over magnesium sulfate and filtered, and the ether was removed to give about 3.0 g of a residue which distilled at 113–114° (0.05 mm). The infrared spectrum (film) showed absorption for $COOC_2H_5$ at 1733 at PhC=O at 1678 cm^{-1}. The nmr spectrum had absorption bands for aromatic CH at δ 7.97 (m 2) and 7.40 (m 3), ethyl CH_2 at 3.92 (q 2), cyclopropyl CH at 2.53 (m 1), 2.17 (m 1), 1.78 (m 1), and 1.30 (m 1), and ethyl CH_3 at 1.00 (t 3).

Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.32; H, 6.28.

The 2,4-dinitrophenylhydrazone melted at 173–174° (from ethanol). This was depressed to 140–155° when admixed with the 2,4-dinitrophenylhydrazone obtained from the *trans* isomer, **14**.

Anal. Calcd for $C_{19}H_{18}N_4O_6$: C, 57.29; H, 4.55; N, 14.06. Found: C, 57.46; H, 4.75; N, 14.31.

Benzyl *cis*-2-Benzoyl-1-cyclopropanecarboxylate (31).—To a solution of 2.8 g of **7** in 15 ml of benzyl alcohol was added a solution of 0.42 g of sodium in 20 ml of benzyl alcohol at 0°. After stirring for 30 min the solution was poured into cold water and extracted with ether. The ether solution was dried over magnesium sulfate, filtered, and distilled to give 2.0 g of **31**, bp 160–161° (0.05 mm). The infrared spectrum (film) showed absorption for $COOCH_2Ph$ at 1730 and PhC=O at 1675 cm^{-1} while the nmr spectrum showed aromatic CH at δ 7.85 (m 2) and 7.18 (m 8), benzyl CH_2 at 4.77 (m 2), and cyclopropyl CH at 2.87 (m 1), 2.23 (m 1), 1.72 (m 1), and 1.20 (m 1).

Anal. Calcd for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 77.31; H, 5.61.

Thermal Decomposition of 7. A. At 100°.—An 0.8-g sample of **7** in 30 ml of dry methylcyclohexane was immersed in an oil bath preheated to 120°. The solution was allowed to reflux for 17 hr and was then concentrated under reduced pressure to give an oily residue. This residue was dissolved in methylene chloride, dried over magnesium sulfate and then concentrated under

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[28] Stainless steel column (6 ft, 0.25-in. o.d.) packed with 3% SE 30 on Chromosorb W, programmed at 2.3°/min from 125 to 250°.

reduced pressure to give 0.67 g of a liquid residue. On standing overnight, 0.17 g of a solid which melted at 133–138° precipitated from the residue. The solid was washed with cold ether and was shown by its infrared spectrum to be **16**, probably contaminated with some of the *cis,cis* and/or *trans,trans* isomers

The residual oil was anlyzed by vapor phase chromatography[28] as well as by its infrared spectrum and was found to contain 25% of the pseudo ethyl ester (**15**) and 75% of undecomposed **7** by comparison of the retention time with those of known samples. No normal ester was detected by use of the infrared spectrum.

The oily mixture (0.43 g) was again refluxed in 15 ml of dry methylcyclohexane for an additional 23 hr and then worked up as before. The residual oil weighed 0.3 g. On standing, an additional 0.03 g of **16**, mp 134–138°, precipitated from the oil. The remainder of the oil was shown by its infrared spectrum to contain a small amount of the normal ester **13**. Vapor phase chromatography indicated the presence of 40% of the pseudo ethyl ester (**15**) and 60% of a mixture of normal ethyl ester (**13**), and undecomposed **7**. From the infrared spectrum it was estimated that the latter mixture contained about 10% of **13**.

The over-all reaction yielded 40% of **16**, 20% of **15**, 5% of **13**, and 20% of undecomposed **7**.

B. At 140°.—A 2.0-g sample of **7** in 60 ml of dry xylene was immersed in an oil bath preheated to 160°. The solution was refluxed for 6 hr and then worked up as described in the previous experiment. The residual oil weighed 1.4 g and was shown by its infrared spectrum and vapor phase chromatogram to contain 85% of the pseudo ethyl ester (**15**), 10% of the normal ethyl ester (**13**), and about 5% of the symmetrical anhydride (**16**). The reaction yielded 70% of **15**, 10% of **13**, and 5% of **16**.

C. At 160°.—A 2.0-g sample of **7** in 60 ml of dry mesitylene was immersed in an oil bath preheated to 175°. The solution was refluxed for 4 hr and then worked up as previously described. The oily residue weighed 1.35 g and yielded 0.16 g of **16** which melted at 134–137°. The residual oil was analyzed by its infrared spectrum and vapor phase chromatogram and was found to be a mixture of 30% of **15** and 70% of **13**. The reaction yield was 50% of **13**, 20% of **15**, and 10% of **16**.

D. In Benzyl Alcohol at 140°.—A 2.0-g sample of **7** in a mixture of 25 ml of dry xylene and 15 ml of dry benzyl alcohol was immersed in an oil bath preheated to 160°. The solution was refluxed for 2 hr and the solvents were removed by vacuum distillation at 50° (0.1 mm). The residue solidified on standing and was treated with cold absolute ethanol and filtered to give 0.7 g of **pseudo-benzyl *cis*-2-benzoyl-1-cyclopropanecarboxylate** (**18**). This was recrystallized from 95% ethanol and melted at 110–111°. The infrared spectrum (Nujol) showed lactone (C=O absorption at 1783 cm^{-1}. The nmr spectrum had peaks for aromatic CH at δ 7.30 (m 10), benzyl CH$_2$ at 4.37 (four triplets 2), and cyclopropyl CH at 2.68 (m 1), 2.23 (m 1), 1.13 (m 1), and 0.70 (m 1).

Anal. Calcd for $C_{18}H_{16}O_3$: C, 77.14; H, 5.71; mol wt, 280. Found: C, 77.29; H, 5.83; mol wt, 290.

The above ethanolic filtrate was concentrated to give 1.0 g of an oil which was found, by its infrared spectrum and vapor phase chromatogram,[28] to be a mixture of 5% of **15**, 5% of **13**, 45% of **18**, and 45% of **31**. The reaction yield was 5% of **15**, 5% of **13**, 55% of **18**, and 20% of **31**.

Thermal Decomposition of 8. A. At 100°.—A 2.0-g sample of **8** was refluxed for 17 hr in 60 ml of dry methylcyclohexane. The reaction mixture was worked up as described for the *cis* isomer (**7**) and gave 1.55 g of a residual oil. This, on standing, afforded 0.2 g of a solid which melted at 97–102° and which had an infrared spectrum identical with that of the *trans,trans* symmetrical anhydride (**12**).

The remaining oil was shown by its infrared spectrum and vapor phase chromatogram[28] to be **14** by comparison of its properties with those of an authentic sample. The reaction yielded 15% of **12** and 80% of **14**.

B. At 140°.—A 2.0-g sample of **8** was refluxed for 6 hr in 60 ml of dry xylene. This gave 1.45 g of a residue from which was obtained 0.2 g of **12**. The remaining oil was found to have an identical infrared spectrum and vapor phase chromatogram with those from an authentic sample of **14**. The reaction yield was 15% of **12** and 75% of **14**.

Stability of the Pseudo Ester 15.—A 0.4-g sample containing a mixture of 85% of **15** and 15% of **13** was refluxed for 4 hr in dry mesitylene at 160° in the presence of 0.035 ml of a 10% sodium ethoxide solution in ethanol (about 20% molar amount). The solvent was removed under reduced pressure and the residue was analyzed by vapor phase chromatography. The mixture contained 55% of **15** and 45% of **13**.

Reaction of 15 with Benzyl Alcohol.—A 0.67-g sample containing 85% of **15** and 15% of **13** was refluxed for 2.5 hr in a mixture of 15 ml of dry xylene, 10 ml of benzyl alcohol, and 0.035 ml of a 5% sodium ethoxide solution in ethanol. The solvents were removed under reduced pressure at 60° (0.1 mm) and the residue was analyzed by vapor phase chromatography. The reaction mixture consisted of 50% of **15**, 15% of **13**, 10% of **18**, and 25% of **31**.

***o*-Benzoylbenzoic methylcarbonic anhydride** (**4**) was prepared from *o*-benzoylbenzoic acid, triethylamine, and methyl chloroformate using the procedure described for the synthesis of **7**, mp 69–71° (lit. mp 66–68°,[9] 70–71°[22]). The infrared spectrum (Nujol) showed absorption for PhC=O at 1672 and anhydride at 1745 and 1811 cm^{-1} while the nmr spectrum showed aromatic H at δ 8.27–7.17 (m 9.5) and OCH$_3$ at 3.75 (s 3).

***o*-Toluoylbenzoic ethylcarbonic anhydride** (**22**) was prepared from *o*-toluoylbenzoic acid, ethyl chloroformate and triethylamine using the procedure described for the preparation of **7**, mp 60–61°. The infrared spectrum showed absorption for PhC=O at 1667 and anhydride at 1745 and 1815 cm^{-1}.

Anal. Calcd for $C_{18}H_{16}O_5$: C, 69.23; H, 5.13. Found: C, 69.20; H, 4.88.

Decomposition of 4.—A 2-g sample of **4** was added to 20 ml of refluxing xylene and the resulting solution was refluxed for 4 hr. After cooling, petroleum ether was added and on further cooling 1.55 g of a white solid, mp 141–143°, precipitated. Recrystallization from benzene gave pure **19**, mp 147–148° (lit.[22] mp 148–149°). The infrared spectrum had lactone absorption at 1792 and carbonate absorption at 1760 cm^{-1}.

Anal. Calcd for $C_{16}H_{12}O_5$: C, 67.61; H, 4.22. Found: C, 67.66; H, 4.16.

Compound **19** was also obtained in 90–95% yield on heating **4** neat at 120°.

On heating 2.0 g of **4** at 220°, carbon dioxide evolution was noted almost immediately and continued for about 10 min. The mixture was cooled and the residual oil (1.5 g) was dissolved in benzene. The resulting solution was diluted with heptane until turbid and on cooling 0.75 g of the ψ symmetrical anhydride (**21**) was obtained, mp 140–141.5° (benzene–heptane) (lit.[9] mp 140–141°). The infrared spectrum had bands for PhC=O at 1665, ester at 1748, and lactone at 1785 cm^{-1}.

Anal. Calcd for $C_{28}H_{18}O_5$: C, 77.42; H, 4.15. Found: C, 77.61; H, 4.02.

Evaporation of the filtrate from the isolation of **21** gave 0.75 g of an oil which was shown by vpc analysis to be equal amounts of the normal ester **20** and the ψ ester **5**. The reaction yield was 22% of **5**, 22% of **20**, and 50% of **21**. On heating preformed **19** to 220°, carbon dioxide evolution was noted and **5**, **20**, and **21** were obtained in 25, 25, and 50% yields, respectively.

The rearrangment of 22 was done at a temperature of 140° using the same procedure that produced **19** from **4**. The ψ mixed anhydride (**23**) was obtained in 80–90% yield, mp 94–95°. The infrared spectrum showed the presence of lactone at 1801 and carbonate at 1773 cm^{-1}.

Anal. Calcd for $C_{18}H_{16}O_5$: C, 69.23; H, 5.13. Found: C, 69.57; H, 5.28.

***o*-Benzoylbenzoic ethylcarbonic mixed anhydride** (**32**) was prepared as described for the preparation of **7**, mp 49–50°. The infrared spectrum had bands for PhC=O at 1672 and anhydride at 1745 and 1810 cm^{-1}.

Anal. Calcd for $C_{17}N_{14}O_5$: C, 68.46; N, 4.70. Found: C, 68.42; H, 4.45.

Heating **32** at 120° gave the ψ mixed anhydride (**24**), mp 104.5–105.5°. The infrared spectrum had absorption for lactone at 1785 and carbonate at 1769 cm^{-1}.

Anal. Calcd for $C_{17}H_{14}O_5$: C, 68.46; H, 4.70. Found: C, 68.46; H, 4.73.

***o*-Toluoylbenzoic methylcarbonic mixed anhydride** (**33**) was prepared as described for the preparation of **7**, mp 77–79°. The infrared spectrum showed the presence of PhC=O at 1665 and anhydride at 1740 and 1815 cm^{-1}.

Anal. Calcd for $C_{17}H_{14}O_5$: C, 68.46; H, 4.70. Found: C, 68.51; H, 4.65.

Heating **33** at 120° gave the ψ mixed anhydride (**25**), mp 114–115°. The infrared spectrum had bands for lactone at 1785 and carbonate at 1755 cm^{-1}.

Anal. Calcd for $C_{17}H_{14}O_5$: C, 68.46; H, 4.70. Found: C, 68.54; H, 5.07.

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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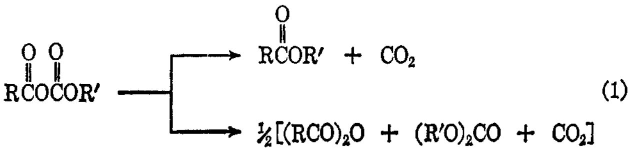
p-Nitrobenzoic *t*-butylthiolcarbonic anhydride IIa decomposes solely by acyl–sulfur cleavage to yield the corresponding thiol ester and carbon dioxide, in contrast to its oxygen analog. The analogous isopropylthiolcarbonic (IIb), the benzylthiolcarbonic (IIc), and the phenylthiolcarbonic anhydrides (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.

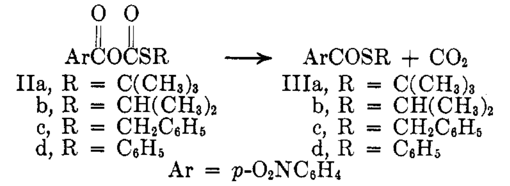


$$\mathrm{R\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}OR'} \longrightarrow \begin{cases} \mathrm{R\overset{O}{\overset{\|}{C}}OR'} + \mathrm{CO_2} \\ \tfrac{1}{2}[\mathrm{(RCO)_2O} + \mathrm{(R'O)_2CO} + \mathrm{CO_2}] \end{cases} \qquad (1)$$

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

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

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

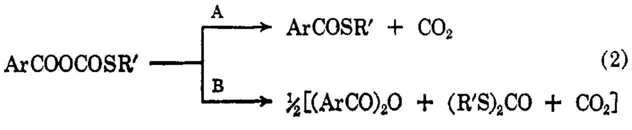


$$\mathrm{Ar\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}SR} \longrightarrow \mathrm{ArCOSR} + \mathrm{CO_2}$$

IIa, R = $\mathrm{C(CH_3)_3}$ IIIa, R = $\mathrm{C(CH_3)_3}$
b, R = $\mathrm{CH(CH_3)_2}$ b, R = $\mathrm{CH(CH_3)_2}$
c, R = $\mathrm{CH_2C_6H_5}$ c, R = $\mathrm{CH_2C_6H_5}$
d, R = $\mathrm{C_6H_5}$ d, R = $\mathrm{C_6H_5}$
Ar = p-$\mathrm{O_2NC_6H_4}$

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).



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

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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[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 $\mathrm{C_6H_5COOCOOC(CH_3)_3}$, mp 72°, from sodium benzoate and $\mathrm{ClCOOC(CH_3)_3}$ 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.