The Synthesis and Thermal Decomposition of *p*-Nitrobenzoic *t*-Butylcarbonic Anhydride[1]

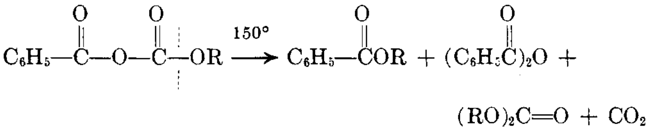
C. J. MICHEJDA[2] AND D. STANLEY TARBELL

Department of Chemistry, University of Rochester, Rochester 27, New York 14620

Received November 27, 1963

The crystalline *p*-nitrobenzoic *t*-butylcarbonic anhydride has been made by two methods: the action of *t*-butyl chlorocarbonate on *p*-nitrobenzoic acid (27% yield) and the action of *p*-nitrobenzoyl chloride on potassium *t*-butyl carbonate (64% yield). Decomposition of *p*-nitrobenzoic *t*-butylcarbonic anhydride at 100° yielded carbon dioxide (90%), isobutene (61%), *p*-nitrobenzoic anhydride (52–84%), *p*-nitrobenzoic acid (7–34%), *t*-butyl *p*-nitrobenzoate (*ca.* 5%), *t*-butyl alcohol (*ca.* 25%), and *t*-butyl carbonate (*ca.* 10%). The reaction thus proceeds mainly by alkyl–oxygen cleavage, and possible mechanisms are discussed.

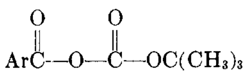
Previous work has made it probable that the decomposition of benzoic alkylcarbonic anhydrides, derived from primary and secondary alcohols, is an ionic chain reaction proceeding by acyl–oxygen cleavage. This conclusion was based on the kinetic characteristics of the reaction,[3] the retention of configuration during the reaction when R was an optically active *s*-octyl group,[4] and the result of an oxygen-18 labeling study which showed that the alkyl–oxygen bond was left intact during the decomposition.[5]



$$C_6H_5-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-OR \xrightarrow{150^\circ} C_6H_5-\overset{O}{\overset{\|}{C}}OR + (C_6H_5\overset{O}{\overset{\|}{C}})_2O + (RO)_2C{=}O + CO_2$$

It is well-known that both the base- and the acid-catalyzed hydrolysis of carboxylic acid esters, derived from primary and secondary alcohols, usually proceeds by acyl–oxygen cleavage.[6] The acid-catalyzed hydrolysis of esters derived from tertiary alcohols, however, involves the cleavage of the alkyl–oxygen bond.[7] The present work was undertaken to prepare a mixed carboxylic–carbonic anhydride with a *t*-alkyl group, and to determine the mode of its thermal decomposition; it has been found that alkyl–oxygen cleavage is predominant over acyl–oxygen cleavage.

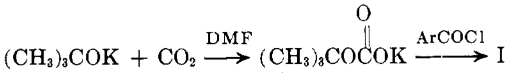
Treatment of the rather unstable *t*-butyl chlorocarbonate[8] with benzoic acid and triethylamine in the usual way[9] yielded an oil which had the two expected anhydride bands in the carbonyl region,[9] but it did not give a satisfactory elementary analysis and could not be purified. The use of *p*-nitrobenzoic acid in this procedure yielded the crystalline *p*-nitrobenzoic *t*-butylcarbonic anhydride (I), m.p. 92–93°



$$Ar\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-OC(CH_3)_3$$

I, Ar = $p\text{-}O_2NC_6H_4$

The mixed anhydride I was prepared more readily and in better yield by another method, using potassium *t*-butyl carbonate.[10] Potassium *t*-butyl carbonate in dimethylformamide (DMF) was treated dropwise with a solution of *p*-nitrobenzoyl chloride in DMF. The carbonate salt was made by passing carbon dioxide through a solution of potassium *t*-butoxide in DMF. The yield of the mixed anhydride I was 64%. After one recrystallization from chloroform and petroleum ether, the product had m.p. 92–93°, undepressed by mixture with the product prepared by the chlorocarbonate method. The infrared spectra of the samples of the anhydride prepared by both methods were identical, exhibiting the characteristic anhydride doublet at 1803 and 1743 cm.$^{-1}$ (carbon tetrachloride solution).[9]



$$(CH_3)_3COK + CO_2 \xrightarrow{DMF} (CH_3)_3CO\overset{O}{\overset{\|}{C}}OK \xrightarrow{ArCOCl} I$$

The decomposition of the mixed anhydride was carried out on neat samples at 100°. The products and their yields are listed in Table I.

TABLE I

PRODUCTS OF DECOMPOSITION OF AR $COCOOC(CH_3)_3$ AT 100°
(Ar = $p\text{-}O_2NC_6H_4$)

Product	Yield, %	Number of runs
CO_2	90 ± 5	12
$CH_2{=}C(CH_3)_2$	61 ± 4	7
$(ArCO)_2O$	52–84	4
ArCOOH	7–34	4
$AcCOOC(CH_3)_3$	2–9	4
$(CH_3)_3COH$	23–28	2
$[(CH_3)_3CO]_2CO$	6–12	2

The large variation in yield of *p*-nitrobenzoic anhydride and of the corresponding acid is probably due to the fact that these products are the result of several competing reactions: the decompositions were carried out without solvent, and minor variations in conditions or the amount of catalytic impurities[3] could affect markedly the relative rates of competing reactions.

The most interesting product from the standpoint of the original purpose of this work was isobutene. The possibility that this compound arose from the decomposition of *t*-butyl *p*-nitrobenzoate was eliminated by the demonstration that the ester was completely stable under the reaction conditions, both in the presence and absence of *p*-nitrobenzoic acid. The value obtained for isobutene (Table I) in seven runs suggests that the compound arose from a unimolecular process

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[1] (a) A preliminary account appeared in *Chem. Ind.* (London), 369 (1964); (b) aided by Grant G-11240 from the National Science Foundation.

[2] Esso Education Foundation Fellow, 1961–1962.

[3] E. G. Longosz and D. S. Tarbell, *J. Org. Chem.*, **26**, 2161 (1961).

[4] D. S. Tarbell and E. G. Longosz, *ibid.*, **24**, 744 (1959).

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

[6] M. Polanyi and A. L. Szabo, *Trans. Faraday Soc.*, **30**, 508 (1934); S. C. Datta, J. N. E. Day, and C. K. Ingold, *J. Chem. Soc.*, 838 (1939); I. Roberts and H. C. Urey, *J. Am. Chem. Soc.*, **60**, 2391 (1938).

[7] S. G. Cohen and A. Schneider, *ibid.*, **63**, 3382 (1941); P. N. Rylander and D. S. Tarbell, *ibid.*, **72**, 3021 (1950); C. A. Bunton and J. L. Wood, *J. Chem. Soc.*, 1522 (1955).

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

[9] D. S. Tarbell and N. A. Leister, *J. Org. Chem.*, **23**, 1149 (1958).

[10] L. A. Carpino, *J. Am. Chem. Soc.*, **82**, 2725 (1960).

which was largely independent of the medium. An attractive mechanism for the formation of isobutene is a concerted cleavage of the mixed anhydride I to yield the *p*-nitrobenzoate ion, carbon dioxide, and the *t*-butyl carbonium ion. The carbonium ion would be expected to lose a proton rapidly to form isobutene.

$$\mathrm{I} \longrightarrow \mathrm{ArCOO^-} + \mathrm{CO_2} + \mathrm{(CH_3)_3C^+}$$

The *p*-nitrobenzoate ion could then react with the unchanged mixed anhydride, leading to the other products as shown below.

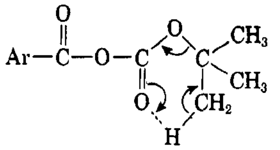
$$\underset{\mathrm{I}}{\mathrm{Ar{-}COO{-}COOC(CH_3)_3}} + \mathrm{Ar{-}COO^-} \longrightarrow \mathrm{(Ar\,CO)_2O} + \mathrm{\bar{O}COOC(CH_3)_3}$$

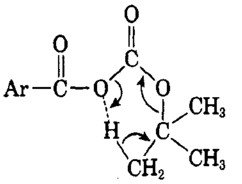
$$\mathrm{\bar{O}COOC(CH_3)_3} \longrightarrow \mathrm{\bar{O}C(CH_3)_3} + \mathrm{CO_2} \xrightarrow{\mathrm{H^+}} \mathrm{HOC(CH_3)_3}$$

$$\mathrm{\bar{O}C(CH_3)_3} + \mathrm{I} \left\{ \begin{array}{l} \longrightarrow \mathrm{Ar\,COOC(CH_3)_3} + \mathrm{\bar{O}COOC(CH_3)_3} \\ \longrightarrow \mathrm{Ar\,COO^-} + \mathrm{[(CH_3)_3CO]_2CO} \end{array} \right.$$

$$\mathrm{Ar\,COO^-} + \mathrm{H^+} \longrightarrow \mathrm{Ar\,COOH}$$

The yield of isobutene indicates that the decomposition of the mixed anhydride I thus proceeds mainly by alkyl–oxygen cleavage. This mode of decomposition is probably the direct result of the stability of the *t*-butyl carbonium ion. The possibility that the alkyl–oxygen cleavage involves transition states such as II or III cannot be excluded on the present evidence.


II


III

Experimental[11]

Preparation of *p*-Nitrobenzoic *t*-Butylcarbonic Anhydride. A. Chlorocarbonate Method.—*t*-Butyl chlorocarbonate was prepared many times essentially by the method of Choppin and Rogers.[8] Phosgene (50 g., large excess) was condensed in a flask which was equipped with a stirrer and a Dry Ice condenser and was chilled by a Dry Ice–acetone bath. Dry ether (200 ml.) was added, followed by 33.6 g. (0.3 mole) of potassium *t*-butoxide,[12] which was added to the rapidly stirred reaction in portions, over a period of 1 hr. The reaction was allowed to stir for an additional 5 hr.; at the end of that time, it was filtered rapidly by suction. The excess phosgene and the ether were removed *in vacuo*, without allowing the solution to warm above 0°. The residue then was distilled, bulb to bulb, at 0.1 mm., to give 13.4 g. (33%) of *t*-butyl chlorocarbonate. The carbamate derivative had the m.p. 107–108°; the reported value[8] is 108–108.5°.

In a flask, equipped with a stirrer and an addition funnel, was placed 300 ml. of dry ether. The ether was chilled to −15° by an ice–salt bath; then 10.8 g. (0.065 mole) of *p*-nitrobenzoic acid and 8.8 g. (0.065 mole) of *t*-butyl chlorocarbonate were added in one portion. The solution was stirred, and 6.5 g. (0.065 mole) of triethylamine in 10 ml. of ether was added dropwise over a period of 1 hr. Stirring was continued for an additional hour and the mixture was allowed to come to room temperature. The amine hydrochloride was filtered off, and the filtrate was washed thoroughly with dilute hydrochloric acid, dilute sodium bicarbonate, and water, and dried over magnesium sulfate. The ether was evaporated at reduced pressure to yield 7.2 g. (27%) of pale yellow crystals which had a melting point of 92–93°. Recrystallization from chloroform and petroleum ether failed to change the melting point.

Anal. Calcd. for $C_{12}H_{13}NO_6$: C, 53.93; H, 4.90. Found: C, 54.19; H, 4.86.

B. **Potassium *t*-Butyl Carbonate Method.**—In a flask equipped with a stirrer, an addition funnel, and a gas dispersion tube was placed a solution of 13 g. (slightly more than 0.1 mole) of potassium *t*-butoxide in 100 ml. of carefully purified[13] DMF. Dry carbon dioxide was passed into the reaction flask for 0.5 hr. The mixture required cooling because the reaction was exothermic. At the end of the addition of carbon dioxide, the reaction mixture was a thick gel. A solution of 18.5 g. (0.1 mole) of *p*-nitrobenzoyl chloride in 50 ml. of DMF was added dropwise to the mixture over a period of 45 min. Stirring was continued for an additional 2 hr. The mixture then was diluted with 100 ml. of ether and filtered to yield a clear filtrate and a water soluble, nearly neutral residue. The filtrate was extracted very thoroughly with water and dried over magnesium sulfate and potassium carbonate. Removal of the solvent yielded 17.2 g. (64%) of crude product, which on one recrystallization from chloroform and petroleum ether had m.p. 92–93°. The infrared spectrum of this product was identical with that of the product prepared by the chlorocarbonate procedure. The mixture melting point was not depressed.

Decomposition of *p*-Nitrobenzoic *t*-Butylcarbonic Anhydride.—The mixed anhydride was decomposed without solvent at 100°. The decomposition apparatus consisted of a 5-ml. flask equipped with a side arm for the admission of prepurified nitrogen and a short (10-cm.) condenser. The top of the condenser was connected to a U-trap cooled to −42° (chlorobenzene slurry). The U-trap in turn was connected to an Ascarite-filled gas absorption tower. The Ascarite tower was attached to a spiral trap cooled to −196° (liquid nitrogen). This trap vented into the atmosphere through a mercury bubbler.

In a typical run, the apparatus was cleaned and flushed thoroughly with prepurified nitrogen. A sample of *p*-nitrobenzoic *t*-butylcarbonic anhydride was weighed (0.1–0.2 g.) into the decomposition vessel, the Ascarite tower was weighed, and the system again was flushed with nitrogen. The decomposition vessel then was heated with an oil bath maintained at 100–110°. The anhydride first melted and then bubbled vigorously. After *ca.* 15 min. of heating, the material in the vessel solidified; heating was continued for an additional 15–30 min. During the decomposition a slow stream of prepurified nitrogen was passed through the system. At the end of the decomposition, the Ascarite tower was disconnected for immediate weighing. The increase in weight corresponded to the amount of carbon dioxide evolved during the reaction. The contents of the spiral trap were shown to be almost pure isobutene by comparison of its mass spectrum with that of a known sample. The amount of isobutene was determined manometrically.

The solid residue from the decomposition was analyzed by the method of Lukoshevich.[14] One portion of the residue was dissolved in dry methanol and pyridine (2:1) and another portion was dissolved in water and pyridine (1:1). The two solutions were titrated with 0.1 *N* sodium hydroxide to the phenolphthalein end point. The first portion yielded the acidity due to the free acid and one equivalent of acid per mole of anhydride. The second portion yielded the acidity due to the free acid plus two equivalents of acid per mole of anhydride. From the two titers the per cent of the anhydride and the acid in the residue could be calculated readily. The ester was obtained by difference.

The amounts of *t*-butyl alcohol and *t*-butyl carbonate were estimated by vapor phase chromatography.

Stability of *t*-Butyl *p*-Nitrobenzoate.—An authentic sample of the ester was subjected to the mixed anhydride decomposition conditions, both in the presence and absence of *p*-nitrobenzoic acid. Heating of the acid and the ester overnight at 100 ± 10° produced no decrease in the weight of the mixture. The infrared spectra of the mixture before and after heating were identical. No isobutylene was detected in any of these experiments.

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[11] We are indebted to J. Souto, Joanne Worosez, and Robert Labarge for preliminary work on this problem.

[12] The commercial material, obtained from the MSA Corp., was used.

[13] DMF was purified by heating under reflux overnight with barium oxide and then distilling from that reagent at atmospheric pressure. The distillate then was redistilled from phosphorus pentoxide at reduced pressure.

[14] C. W. Hammond, "Organic Analysis," Vol. III, Interscience Publishers Inc., New York, N. Y., 1956, p. 106.