

Thermal Decomposition of *exo*- and *endo*-Norborylcarbonic-*p*-Nitrobenzoic Anhydrides

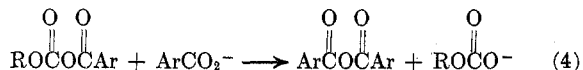
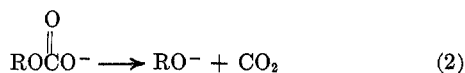
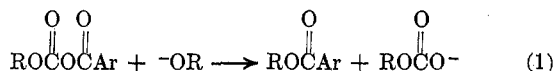
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The ability of the norbornyl system to stabilize a positive charge prompted the study of the mechanism of the thermal decomposition of *exo*-norborylcarbonic-*p*-nitrobenzoic anhydride 1 and its *endo* isomer 2. Anhydrides 1 and 2 were prepared from the corresponding oxygen-18-labeled norborneols and 1 was also prepared from optically active norborneol. When the thermal decomposition was carried out in nitrobenzene or acetonitrile at 130–140°, 1 decomposed with approximately 20% alkyl-oxygen cleavage. The alkyl-oxygen cleavage could be quenched by addition of triethylamine. The decomposition of 1 in xylene and 2 in all three solvents proceeded exclusively by acyl-oxygen cleavage. Semiquantitative analysis of the products of the decompositions indicated large differences in product distributions when the decompositions were carried out in xylene as compared to acetonitrile. The product distribution in xylene could be altered by addition of catalytic amounts of triethylamine. The rate measurements were not very reproducible but indicated that the rate differences between the decomposition of 1 in xylene and nitrobenzene were very small. The decomposition of 2 was actually faster in xylene than in nitrobenzene. The data lead to a conclusion that in polar solvents 1 decomposes partly by a unimolecular process, which leads to the formation of the norbornyl cation, but the bulk of the decomposition proceeds by an ionic chain mechanism. Anhydride 2 decomposes exclusively by the ionic chain mechanism in nitrobenzene and acetonitrile. In xylene both anhydrides decompose by a cyclic S_Ni-like mechanism which leads to the formation of the respective norbornyl esters and carbon dioxide as the principal products.

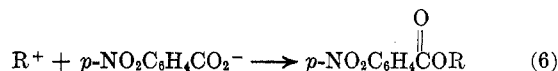
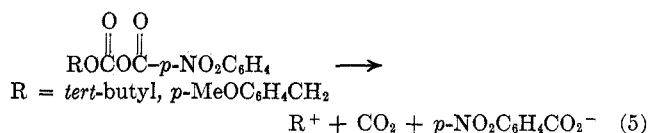
The thermal decomposition of mixed carboxylic-carbonic anhydrides has been studied exhaustively by Tarbell and his coworkers.¹ These workers found that, when the mixed anhydride was derived from a primary or secondary alcohol, the decomposition proceeded by an ionic chain mechanism in which the alkoxide ion was the chain carrier. The products of the



reaction were the ester (produced in step 1), the symmetrical carbonate and the symmetrical anhydride (produced in steps 3 and 4, respectively), and carbon dioxide. The ratios of the products formed were an invariant property of each anhydride and depended on the structure of R and Ar. One feature of this mechanism was that the alkyl-oxygen bond remained intact throughout the reaction.^{2,3}

A different situation exists if the group R is capable of stabilizing a carbonium ion. Thus it was found that, when R was *tert*-butyl and Ar was *p*-nitrophenyl, the anhydride decomposed mainly by alkyl-oxygen cleavage.⁴ The same was true when the mixed anhydride was derived from *p*-methoxybenzyl alcohol and *p*-nitrobenzoic acid,⁵ although here the course of the reaction depended on the conditions. Thus, a second mechanism may be written (eq 5 and 6 or 7),

which takes the alkyl-oxygen cleavage into account. It must be added that the ionic chain mechanism, as



outlined, competes with unimolecular cleavage in all the cases studied.

In view of these data a study of the decomposition of the mixed anhydrides derived from *exo*- and *endo*-norborneols was undertaken. The unusual stability of the norbornyl cation is well known. The participation of the 1,6-σ bond in solvolysis reactions is well documented, although that concept is not without its opposition.⁶ The study reported here sought to test the effect of the norbornyl system on the mechanism of the thermal decomposition of mixed anhydrides derived from it.

Results

Synthesis.—The mixed anhydrides 1 and 2 were prepared by the conventional procedure⁷ from *exo*- and *endo*-norboryl chloroformates, respectively, and *p*-nitrobenzoic acid, using triethylamine as the base. The chloroformates were prepared from *exo*- and *endo*-norborneols and phosgene, using standard procedures.

The oxygen-18-labeled anhydrides were prepared from the corresponding oxygen-18-labeled chloroformates, which were prepared, in turn, from the labeled norborneols. These preparations were carried out according to Schemes I and II.

The details of the preparation are given in the Experimental Section. The amount of labeling in each

(1) For a recent review of that work see D. S. Tarbell, *Accounts Chem. Res.* **2**, 296 (1969).

(2) E. J. Longosz and D. S. Tarbell, *J. Org. Chem.*, **26**, 2161 (1961).

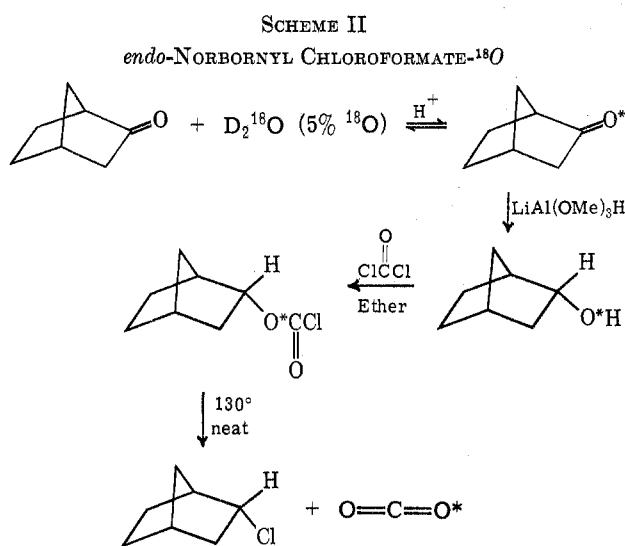
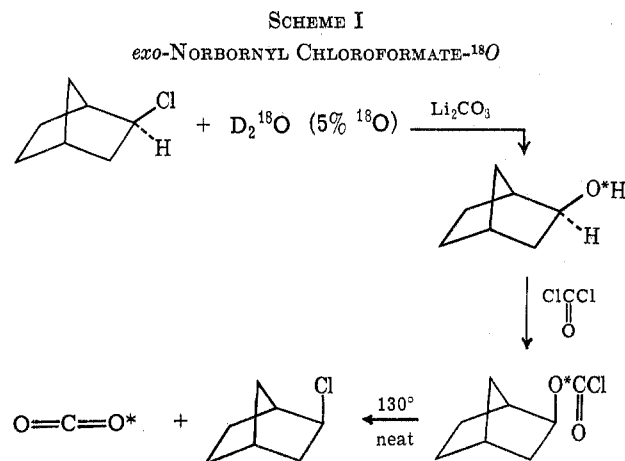
(3) C. J. Michejda, D. S. Tarbell, and W. H. Saunders, Jr., *J. Amer. Chem. Soc.*, **84**, 4113 (1962).

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

(5) R. C. L. Chow and D. S. Tarbell, *ibid.*, **32**, 2188 (1967).

(6) Cf. P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, New York, N. Y., 1965.

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



chloroformate was determined by heating the neat chloroformate at 130° or in the presence of quinoline at 80°. The former procedure gave more reproducible results. The carbon dioxide from each decomposition was trapped in a liquid N₂ trap. The carbon dioxide samples were then distilled on a vacuum line and, after degassing, were subjected to mass spectroscopic analysis. The ratio of *m/e* 46 to *m/e* 44 of the experimental sample, compared with this ratio for natural carbon dioxide, gave the amount of labeling. These results are tabulated in Table I. The labeled chloroformates were then converted to the labeled mixed anhydrides.

The optically active *exo*-norbornylcarbonic-*p*-nitrobenzoic anhydride was prepared from the optically active *exo*-norborneol. The latter was resolved by the procedure of Winstein and Trifan.⁸ *exo*-Norborneol was converted to the acid phthalate by heating the alcohol with phthalic anhydride in pyridine. The acid phthalate was resolved using cinchonidine as the resolving agent. After four crystallizations the acid phthalate was liberated from the alkaloid. The mother liquors were also worked up. It was found, as in the original resolution, that the mother liquors contained the more highly resolved material. The resolved acid phthalate used in subsequent work had $[\alpha]_D^{27} - 8.68^\circ$.

(8) S. Winstein and D. Trifan, *J. Amer. Chem. Soc.*, **74**, 1154 (1952).

TABLE I
OXYGEN-18-LABELING DATA

Origin of CO ₂	(<i>m/e</i> 46/ <i>m/e</i> 44) × 100	Average (<i>m/e</i> 46/ <i>m/e</i> 44) × 100	Relative average per cent enrichment
Natural (from tank)	0.55 0.48 0.58	0.54 ± 0.04	0
<i>exo</i> -Norbornyl chloroformate	5.16 5.21 5.05	5.14 ± 0.06	100.00
Exo anhydride 1			
In acetonitrile	0.98 1.12 1.43 2.69 1.02	1.45 ± 0.49	19.7
In xylene	0.58 0.51	0.54 ± 0.04	0
In nitrobenzene	1.79 1.25 1.21	1.42 ± 0.25	19.1
With trace of Et ₃ N	0.65	0.71 ± 0.06	3.7
In acetonitrile	0.77		
Neat	0.71 0.52	0.62 ± 0.09	1.7
Unlabeled exo anhydride (1)			
In nitrobenzene	0.59	0.59	
<i>endo</i> -Norbornyl chloroformate	4.35 4.30 4.38	4.34 ± 0.03	100.00
Endo anhydride 2			
In acetonitrile	0.58 0.47 0.55	0.53 ± 0.04	0
In xylene	0.50	0.50	0
In nitrobenzene	0.53	0.53	0
Neat	0.49	0.49	0

This material was hydrolyzed with sodium hydroxide to give the optically active norborneol. The norborneol was immediately converted to the chloroformate which, in turn, was converted to the mixed anhydride, which had $[\alpha]_D^{27} - 5.593^\circ$ (*c* 5.68).

Part of the optically active norborneol was converted to *exo*-norbornyl *p*-nitrobenzoate. This material had $[\alpha]_D^{27} - 8.23^\circ$ (*c* 9.677).

Decomposition of Oxygen-18-Labeled Anhydrides.—The mixed anhydrides were decomposed by two different methods, which are described in the Experimental Section. The carbon dioxide samples were collected in liquid nitrogen traps. At the end of a run the carbon dioxide was distilled on a vacuum line and degassed. The samples were analyzed mass spectroscopically. Measurements were made of the parent peak at *m/e* 44 and the isotope peak at *m/e* 46. Each sample was scanned 15–20 times and the ratio of *m/e* 46 to *m/e* 44 was recorded. These data are presented in Table I. It is readily apparent from the table that the decomposition of *exo*-norbornylcarbonic-*p*-nitrobenzoic anhydride (1) proceeds with about 20% alkyl-oxygen cleavage when the decomposition is carried out in acetonitrile and nitrobenzene.

There is no alkyl-oxygen cleavage during the decomposition of 1 in xylene, and there is a significant decrease in the amount of alkyl-oxygen cleavage when

the reaction is carried out in the presence of the nucleophile triethylamine or in the absence of solvent. In contrast the endo anhydride 2 decomposes without any alkyl-oxygen cleavage under all the conditions studied.

Decomposition of Optically Active Exo Anhydride 1.

—The anhydride was decomposed in acetonitrile, nitrobenzene, and xylene. After being heated for 10 hr at 130–140° the solvent was removed and the *exo*-norbornyl *p*-nitrobenzoate was extracted and purified. Samples of the ester were analyzed polarimetrically. The ester was shown to be configurationally stable under the reaction conditions. The data are presented in Table II.

TABLE II

DECOMPOSITION OF OPTICALLY ACTIVE <i>exo</i> -NORBORNLYCARBONIC- <i>p</i> -NITROBENZOIC ANHYDRIDE (1) ^a AS A FUNCTION OF SOLVENT, ^b TEMPERATURE 130–140°		
Source of <i>exo</i> -Norbornyl <i>p</i> -nitrobenzoate	Specific rotation, [α] ²⁵ _D , deg	% racemization
Original active norborneol ^c	−8.23	0
Decomposition of 1 in acetonitrile	−7.50	17.8
Decomposition of 1 in nitrobenzene	−7.85	9.2
Decomposition of 1 in xylene	−8.23	0
Decomposition of 1 in acetonitrile in the presence of triethylamine ^d	−8.17	1.6

^a The specific rotation of the anhydride 1 was −5.39°. ^b The concentration of the anhydride 1 in the solvents used was approximately 0.3 M. ^c Preparation is given in the Experimental Section. ^d The concentration of the triethylamine was approximately 0.07 M.

Although the polarimetric data do not mirror the labeling data exactly, particularly in the case of the decomposition of 1 in nitrobenzene, the correlation between the two sets of data is gratifying.

Products of Decomposition of Anhydrides 1 and 2.—The mixed anhydrides were heated in acetonitrile and xylene for 11–13 hr at 130–140° to effect complete decomposition. Table III gives the products as

TABLE III

PRODUCTS ^a OF DECOMPOSITION OF 1 AND 2 AS FUNCTIONS OF SOLVENT, TEMPERATURE 130–140°			
Anhydride in solvent	Ester ^b	Anhydride ^b	Carbonate ^{b,d}
1 in acetonitrile	0.80	0.17	~0.1
	0.79 ^c	0.25	
1 in xylene	0.82	0	0-trace
2 in acetonitrile	0.38	0.42	~0.15
	0.40		
2 in xylene	0.89	0.03	~0.02

^a The product yields are expressed as mol of product/mol of mixed anhydride. ^b Ester is *exo*-norbornyl *p*-nitrobenzoate from 1 and the endo isomer from 2; anhydride is *p*-nitrobenzoic anhydride; carbonate is dinorbornyl carbonate (exo from 1, endo from 2). ^c Isolated yield. ^d The carbonate yields are very approximate and should be treated as a lower limit.

functions of solvent. The products were determined by a variety of methods, which are described in the Experimental Section. Most difficulty was encountered in the analysis for *p*-nitrobenzoic acid and *p*-nitrobenzoic anhydride in the presence of each other. The products from the decomposition in nitrobenzene were not analyzed quantitatively because of the difficulty of removing the last traces of the solvent. The

major products from 1 and 2 in nitrobenzene, however, were the corresponding *exo* and *endo* esters. The yields of carbon dioxide produced in the reactions were not determined quantitatively, but it is obvious from the data in Table III that they were better than 90%.

Varying amounts of *p*-nitrobenzoic acid and norborneol were also found. These products were probably secondary, formed during the manipulation of the decomposition mixtures. In most cases only small amounts were found to be present.

The effect of added triethylamine on the thermal decomposition of 1 and 2 in xylene was very instructive. These data are presented in Table IV. It should be

TABLE IV

EFFECT OF TRIETHYLAMINE ^a ON THE PRODUCTS FROM 1 AND 2				
Anhydride	Decomposition medium	Products (mol of product/mol of anhydride)		
		Ester	Symmetrical anhydride	Carbonate
1	Xylene	0.82	0.00	0-trace
	Xylene + Et ₃ N	0.75	0.17	~0.12
2	Xylene	0.89	0.03	~0.02
	Xylene + Et ₃ N	0.27	0.37	~0.1

^a Triethylamine concentration = 0.2 mol/mol of anhydride. Temperature of decomposition, 138°.

noted that the products of decomposition in the presence of triethylamine show virtually identical distributions with those found in the decomposition of the respective anhydrides in acetonitrile. This suggests that the presence of the nucleophilic catalyst in xylene causes the anhydrides to decompose in a similar manner as in the polar solvent.

Rates of Decomposition of 1 and 2.—An attempt was made to study the kinetics of the decomposition reactions in nitrobenzene and xylene. The rates were followed using the disappearance of the strong infrared carbonyl bands (1808 cm⁻¹) of the mixed anhydrides, according to the procedure of Bartlett and Hiatt.⁹

In some runs the reaction showed an induction period (up to 30 min at 138°) but then followed reasonably clean first-order kinetics. The rate constants, however, were not reproducible. For example, duplicate runs for the *exo* anhydride 1 at 138.5° in nitrobenzene were 2.7 × 10⁻⁴ sec⁻¹ and 4.1 × 10⁻⁴ sec⁻¹. The rates of decomposition of *endo* anhydride 2 in nitrobenzene at the same temperature were approximately an order of magnitude slower than the rate of 1. The rate data are shown in Table V. Although it must be stressed

TABLE V

RATES OF DECOMPOSITION OF ANHYDRIDES 1 AND 2 ^a		
Anhydride	Solvent	k × 10 ⁶ sec ⁻¹
1	Nitrobenzene	40.7, 27.4 ^b
	Xylene	16.3
2	Nitrobenzene	4.96, 2.07 ^b
	Xylene	14.5

^a Decomposition temperature, 138.5°. ^b Duplicate runs.

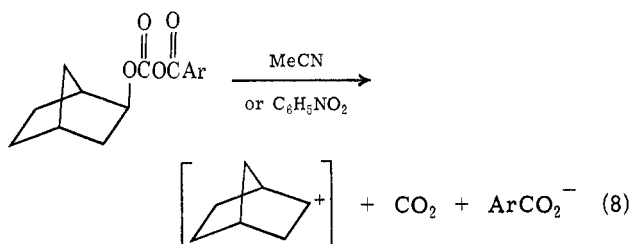
that the individual rate constants are suspect, Table V does show some startling results. There is remarkably little effect on the rate of decomposition of 1 in going from the highly polar nitrobenzene to the nonpolar xylene. Perhaps even more startling is the result

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

that the decomposition of **2** in xylene is actually faster than in nitrobenzene.

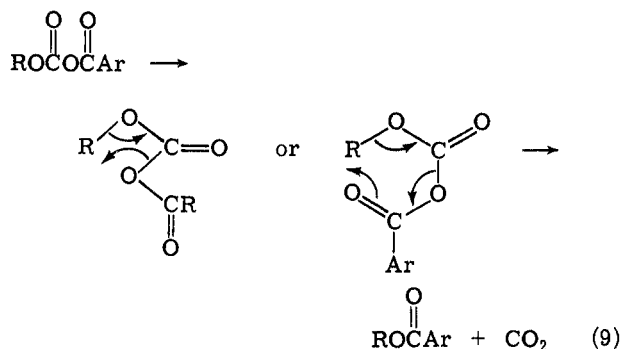
Discussion

Decomposition in Polar Solvents.—It is clear from the oxygen-18-labeling data and the stereochemical experiment in the case of anhydride **1** that approximately 20% of the decomposition of **1** proceeds with alkyl-oxygen cleavage. An attractive explanation of this result is that, at least 20% of the time, the anhydride decomposes to give a norbornyl cation, carbon dioxide, and the *p*-nitrobenzoate ion. The cation and the anion then collapse to give the exo ester. It is



significant that no norbornene was ever found among the products. This may mean that the ester is formed rapidly by the collapse of an ion pair and that the cation never really gets free. This suggestion is supported by the fact that no dinorbornyl ether was ever found. The latter product could have arisen from the reaction of the cation with the anion of norborneol. The alkoxide ion is undoubtedly present in a steady state concentration during the reaction because the remaining 80% of the reaction, which occurs with retention of the alkyl-oxygen bonds, must proceed by the ionic chain mechanism discussed in the first part of this article. In that mechanism the alkoxide ion is the chain-carrying species. Thus, the decomposition of **1** in acetonitrile and nitrobenzene appears to be similar to the decomposition of *tert*-butylcarbonic-*p*-nitrobenzoic anhydride,⁴ although the percentage of alkyl-oxygen cleavage in the case of **1** appears to be lower. This is consistent with the generally recognized lower stability of the norbornyl cation relative to the *tert*-butyl cation. It is interesting to note that this is the first example of a mixed anhydride derived from a nonbenzylic secondary alcohol which decomposes, at least in part, by alkyl-oxygen cleavage. This formation of the norbornyl cation, under nonsolvolytic conditions, points again to the extraordinary stability of this system. The alkyl-oxygen cleavage can be quenched, however, by addition of small amounts of triethylamine. The presence of the nucleophilic catalyst evidently speeds up the chain mechanism at the expense of the unimolecular cleavage. It could be argued on the basis of the oxygen-18-labeling data that the alkyl-oxygen cleavage in the decomposition of **1** was the result of cyclic processes such as the one shown in eq 9. Such a mechanism would require retention of configuration of the norbornyl system. Our stereochemical data indicate, however, that racemization roughly parallels the amount of alkyl-oxygen cleavage.

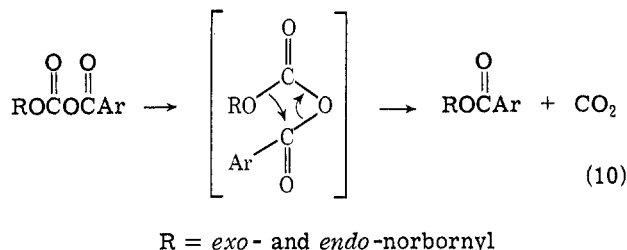
The decomposition of the mixed anhydride **2** in acetonitrile and nitrobenzene seems to proceed exclusively by the ionic chain mechanism. There is also



lutely no alkyl-oxygen cleavage, as shown by the labeling data. It is interesting to note that the rate of decomposition of the endo anhydride **2** is an order of magnitude slower in nitrobenzene than the rate of the exo anhydride **1** (Table V).

Decomposition in Xylene.—Even a casual perusal of the data suggests that the decomposition of both **1** and **2** in xylene is completely different from the reaction in more polar solvents. The oxygen-18-labeling data and the stereochemical data show that the alkyl-oxygen bond remains unbroken in the decompositions of both **1** and **2** in xylene. Examination of the products of the decomposition indicates that the respective esters are, for all intents, the exclusive products in both anhydrides. The rates of the decompositions in xylene are remarkably similar to one another, and there is very little rate depression in going from the polar nitrobenzene to the nonpolar xylene. The kinetic data suggest strongly that the reactions do not involve ionic intermediates. Finally, the data shown in Table IV indicate that the reaction in xylene can be forced to behave in the manner of the reactions in polar solvents by the addition of the nucleophile triethylamine to the decomposition mixture.

These data lead us to conclude that the decomposition of both **1** and **2** in xylene and, by implication, in other nonpolar solvents, proceeds by yet another mechanism. We propose that this reaction is a unimolecular cyclic process that leads to the ester and carbon dioxide directly. Such a mechanism accounts



for the retention of the alkyl-oxygen bond, the retention of configuration in **1**, the relatively fast rate of decomposition, and the overwhelming preponderance of the ester in the products of both anhydrides. The small amounts of the symmetrical anhydride and carbonate observed in the decomposition of **2** were probably due to the presence of small amounts of adventitious nucleophiles, which directed part of the reaction *via* the chain decomposition route. The role of the added triethylamine was to force the reaction to proceed by the chain mechanism; hence we have the product distribution so similar to the one observed in acetonitrile.

The reaction, as indicated in eq 10, is favored by the presence of a nitro group on the aromatic ring, which makes the carbon of the carboxyl carbonyl more electron deficient. The substitution of a strongly electron donating group, such as a methoxyl, on the aromatic ring could be expected to produce the opposite effect and hence the reaction might be found to follow a more orthodox path. To test this hypothesis both the *exo*- and *endo*-norbornylcarbonic-*p*-methoxybenzoic anhydrides were prepared. It was gratifying to find that in the case of the *endo* anhydride the decomposition products in xylene and acetonitrile were very similar; almost exclusively, the symmetrical anhydride and the carbonate were found. The decomposition of the *exo* anhydride was examined in xylene only. Both ester and the symmetrical anhydride were formed. These data, however, are not so conclusive as they might appear. The reason for this is that the product ratios of the decomposition of the anhydrides derived from *p*-methoxybenzoic acid can be changed by addition of triethylamine. The reason for this unexpected result is still not clear.

The cyclic mechanism indicated in eq 10 has not been observed before in the decomposition carboxylic-carbonic anhydrides. One might ask whether all the carboxylic-carbonic anhydrides derived from primary and secondary alcohols might not decompose by that mechanism in very nonpolar solvents. Recently, Wei and Tarbell¹⁰ proposed a similar mechanism for the decomposition of *p*-nitrobenzoic-*tert*-butylthiocarbonic anhydride. That substance, however, seemed to decompose by the cyclic mechanism over a wide range of solvent polarities.

Experimental Section

Melting points are uncorrected. Infrared spectra were taken on Perkin-Elmer Models 21, 621, and 237 spectrophotometers. Proton magnetic resonance spectra were obtained on Varian Models A-60 and T-60. Mass spectra were obtained on a Perkin-Elmer Hitachi Model RMU6D double-focusing instrument. Varian Aerograph Models 1520 and A90P3 were used for the gas chromatography. Polarimetric measurements were carried out on a Perkin-Elmer Model 241M automatic polarimeter. Microanalyses were performed by A. Bernhardt, Elbach-uber-Engelskirchen, West Germany.

Purification of Solvents.—Xylene was heated at reflux over sodium and distilled from sodium. Nitrobenzene was chromatographed through alumina, then crystallized from ethanol, and finally distilled through a fractionating column. Acetonitrile was heated at reflux over P₂O₅ and then distilled.

Preparation of *exo*-Norborneol.—This compound was prepared by Schleyer's method¹¹ from norbornene and formic acid. The resulting formate ester was hydrolyzed with potassium hydroxide to *exo*-norborneol, mp 127–128 (lit.¹¹ 127–128°). The yield, based on norbornene, was 60%.

Preparation of *endo*-Norborneol.—The procedure of Schleyer was used to oxidize *exo*-norbornyl formate with chromic acid to give a 60% yield of norcamphor (mp 93°, lit.¹² 93–94°). The ketone was reduced with lithium aluminum trimethoxy hydride.¹³ The hydride was prepared by the dropwise addition of 24 ml (0.6 mol) of dry methanol to 8.25 g (0.217 mol) of lithium aluminum hydride in 405 ml of dry tetrahydrofuran at 0°. To this mixture was added dropwise 15.0 g (0.136 mol) of norcamphor in tetrahydrofuran. After 1 hr of stirring, the excess hydride was

decomposed with water. Ether was added and the mixture was treated with a saturated solution of sodium potassium tartrate. The organic layer was separated and dried. Evaporation of the solvent *in vacuo* and sublimation [40° (1.5 mm)] of the crude residue afforded 10.9 g (72% yield) of *endo*-norborneol, mp 150–151° (lit.¹² 152–153°).

Preparation of *exo*- and *endo*-Norbornyl Chloroformates.—The procedure for both compounds was identical. The preparation of the *exo* isomer will be described.

Into a 250-ml three-necked flask fitted with an addition funnel and a Dry Ice condenser and equipped with a magnetic stirrer was condensed 15 ml (0.2 mol) of phosgene. This was dissolved in 75 ml of dry ether. The solution was chilled in an ice bath and 15 g (0.134 mol) of *exo*-norborneol in a little ether was added dropwise with stirring. After the addition was complete the mixture was stirred at room temperature for about 3 hr. The excess phosgene and the ether were removed *in vacuo* to yield a clear, somewhat viscous liquid. No attempt was made to purify the product. The yield was virtually quantitative. Both isomeric chloroformates exhibited a strong band in the infrared spectrum at 1775 cm⁻¹ (CCl₄).

Preparation of Anhydrides 1 and 2.—Again the procedures were virtually identical. The preparation of 1 will be described.

To a solution of 6.2 g (0.035 mol) of *exo*-norbornyl chloroformate and 5.0 g (0.035 mol) of *p*-nitrobenzoic acid in 200 ml of dry ether was added 3.8 g (0.038 mol) of dry triethylamine. After the dropwise addition was complete, the mixture was stirred for an additional 2.5 hr. The precipitated amine hydrochloride was filtered off and the ether solution was washed successively with dilute hydrochloric acid, sodium bicarbonate solution, and water. The solution was then dried over magnesium sulfate and the ether was evaporated *in vacuo* to give 7.25 g (67%) of *exo*-norbornylcarbonic-*p*-nitrobenzoic anhydride, mp 63.8–64°.

Anal. Calcd for C₁₅H₁₅NO₆: C, 59.01; H, 4.95; N, 4.59. Found: C, 59.06; H, 5.08; N, 4.48.

The *endo* isomer 2 was prepared in 64% yield, mp 71–72°.

Anal. Calcd for C₁₅H₁₅NO₆: C, 59.01; H, 4.95; N, 4.59. Found: C, 59.03; H, 4.91; N, 4.44.

Both anhydrides exhibited the characteristic strong double carbonyl bands at 1808 and 1748 cm⁻¹ (CCl₄).

Preparation of *exo*- and *endo*-Norbornyl *p*-Nitrobenzoates.—Both the optically active and inactive esters were prepared in an identical fashion.

In a 100-ml three-necked flask equipped with an addition funnel, condenser, and a magnetic stirrer was placed 1.2 g (0.0065 mol) of *p*-nitrobenzoyl chloride and 0.67 g (0.006 mol) of *exo*-norborneol in approximately 40 ml of dry ether. To this solution was added dropwise over a 10-min period 0.47 g (0.006 mol) of pyridine in about 10 ml of ether. The mixture was stirred for 3 hr. The pyridine hydrochloride was filtered off and the ether solution was washed successively with dilute hydrochloric acid, sodium bicarbonate solution, and water. After drying, the ether was removed *in vacuo* to afford 0.95 g (37%) of *exo*-norbornyl *p*-nitrobenzoate, mp 83–84° (lit.¹⁴ mp 84–85°) after recrystallization from hexane.

The *endo*-norbornyl-*p*-nitrobenzoate was prepared in 74% yield, mp 80° (lit.¹⁴ mp 81°).

Preparation of *exo*-Norbornyl Carbonate.—Into a 250-ml flask was placed 4.0 g (0.036 mol) of *exo*-norborneol in 30 ml of pyridine. To this solution was added dropwise with stirring, at 0°, 6.3 g (0.036 mol) of *exo*-norbornyl chloroformate. The reaction was stirred for 1 hr at 0°, followed by stirring at room temperature for 6 hr. Ether was added to the mixture and the amine hydrochloride was filtered off. The ether solution was washed thoroughly with dilute hydrochloric acid and then water. After drying, the solvent was removed *in vacuo* to yield a yellow oily residue. This material was purified by chromatography on a Florisil column and was eluted by Skellysolve B (light petroleum ether). The product was a white waxy solid, mp 57–59°. The yield was 6.1 g (73%). The compound's infrared spectrum showed a strong carbonyl band at 1730 cm⁻¹.

Anal. Calcd for C₁₅H₂₂O₃: C, 70.55; H, 9.31. Found: C, 70.74; H, 9.17.

Preparation of *endo*-Norbornyl Carbonate.—This compound was prepared in similar manner to *exo*-norbornyl carbonate described above. Using 2.1 g (0.019 mol) of *endo*-norborneol and 3.4 g (0.020 mol) of *endo*-norbornyl chloroformate in 16 ml of

(10) L. Wei and D. S. Tarbell, *J. Org. Chem.*, **33**, 1884 (1968).

(11) P. v. R. Schleyer, *Org. Syn.*, **42**, 79 (1962).

(12) "Dictionary of Organic Compounds," Vol. IV, Oxford University Press, New York, N. Y., 1965.

(13) H. C. Brown and P. M. Weissman, *J. Amer. Chem. Soc.*, **87**, 5614 (1965).

(14) N. J. Toivonen and K. Ojala, *Makromol. Chem.*, **18/19**, 414 (1956).

dry pyridine and the work-up described above, the crude product was obtained, yield 4.6 g (95%). An analytical sample was purified by sublimation at mp 165–166° (110°/2 mm).

The infrared spectrum (CCl₄) showed a carbonyl band at 1730 cm⁻¹.

Anal. Calcd for C₁₅H₂₂O₃: C, 70.55; H, 9.31. Found: C, 70.68; H, 9.21.

Preparation of Norbornyl Chloride.—The method of Schmerling¹⁵ was used for the preparation of this compound. Into a flask fitted with a stirrer and gas bubbler was placed 25.0 g (0.265 mol) of norbornene in 95 ml of pentane. The flask was cooled in a Dry Ice–acetone bath and HCl was bubbled through for 20 min. The mixture was allowed to stand for several hours at room temperature. The pentane was removed by distillation, and the product was distilled at reduced pressure to yield 28.5 g (82%) of norbornyl chloride, bp 71° (20 mm) [lit.¹⁵ bp 52° (11 mm)].

Preparation of *exo*-Norborneol-¹⁸O.—A mixture of 21.3 g (0.162 mol) of *exo*-norbornyl chloride, 13.0 g (0.194 mol) of lithium carbonate, and 40 ml of D₂¹⁸O (Diaprep, ¹⁸O 5.0%) was heated at reflux for 41 hr. The mixture was extracted with ether. The ether extracts were dried over anhydrous magnesium sulfate and evaporated to yield 17.6 g (97%) of *exo*-norborneol-¹⁸O, mp 127–128°.

Preparation of Norcamphor-¹⁸O.—To a mixture of 20 g (0.182 mol) of norcamphor and 25 ml of D₂¹⁸O (Diaprep, ¹⁸O 5.0%) was added three drops of concentrated H₂SO₄. The mixture was heated at reflux for 4.5 hr. After cooling a small amount of potassium carbonate was added. The mixture was extracted with ether. The ether was dried over magnesium sulfate and evaporated to yield 18.0 g (90% recovery) of norcamphor-¹⁸O.

Preparation of *endo*-Norborneol-¹⁸O.—The reduction of norcamphor-¹⁸O to *endo*-norborneol-¹⁸O was carried out in the same manner described for the unlabeled compound, using lithium aluminum trimethoxy hydride in THF, mp 149–150°.

Preparation of *exo*- and *endo*-Norbornyl Chlorocarbonates-¹⁸O.—The preparation of both the *exo*- and *endo*-norbornyl chlorocarbonates-¹⁸O was carried out in the same manner as the unlabeled compounds described above.

Preparation of *exo*- and *endo*-Norbornylcarbonic-*p*-Nitrobenzoic Anhydrides-¹⁸O.—The preparation of both the *exo*- and *endo*-norbornylcarbonic-*p*-nitrobenzoic anhydrides-¹⁸O was carried out in the same manner as the unlabeled compounds, using the corresponding oxygen-18-labeled chlorocarbonates.

Decomposition of the Labeled Mixed Anhydrides and Collection of the Carbon Dioxide for Mass Spectral Analysis.—The oxygen-18 content of the mixed anhydrides was determined by comparison with the corresponding labeled chlorocarbonates. Decomposition of the chlorocarbonates was carried out either neat at 130° or in the presence of an equimolar quantity of quinoline at 80°. The CO₂ evolved was subjected to mass spectral analysis. The mixed anhydrides were decomposed in solutions at 140 ± 5° and the carbon dioxide was collected for mass spectral analysis. The decompositions were carried out by one of the two following procedures.

A.—A 0.3-g sample of the anhydride in the appropriate solvent was decomposed in a 50-ml round-bottomed flask heated in an oil bath. The flask was equipped with a reflux condenser and a side arm for admission of a stream of dry nitrogen. The top of the condenser was connected to a U trap cooled with Dry Ice–acetone; this trap was connected in turn to a U trap cooled by liquid nitrogen. The liquid nitrogen trap was fitted with inlet and outlet stopcocks and standard taper joints. When sufficient carbon dioxide was condensed in the trap the stopcocks were closed, the N₂ flushing was stopped, and the sample of carbon dioxide was degassed and distilled. The ratio of *m/e* 46 to *m/e* 44 was then determined by mass spectral analysis.

B.—A 0.3-g sample of the anhydride in the appropriate solvent was placed in a thick-walled tube fitted with a vacuum stopcock and a standard taper joint. The sample was degassed on a vacuum line and the stopcock on the evacuated tube was closed. The tube was heated in an oil bath. Heating time varied from 1 to 3 hr. The tube was then connected to the vacuum line and the carbon dioxide was distilled out. The ratio of *m/e* 46 to *m/e* 44 was then determined by mass spectral analysis.

Mass Spectral Measurements.—The mass peaks used for the measurements were the parent peak at *m/e* 44 and the isotope parent peak at *m/e* 46. Each sample was repeatedly scanned

over this region 15–20 times and the ratio of *m/e* 46 to *m/e* 44 was then calculated as an average of these scans.

Preparation of Optically Active 1.—The procedure of Winstein and Trifan⁸ was followed for the resolution of norborneols. Starting with 168.0 g (1.5 mol) of *exo*-norborneol and 223 g (1.5 mol) of phthalic anhydride, there was obtained 255 g (65%) of *exo*-norbornyl acid phthalate, mp 97–99° (lit.⁸ mp 98.6–99.7°). The acid phthalate was resolved by forming the diastereomeric mixture with cinchonidine. The resolved *exo*-norbornyl acid phthalate was obtained from the CHCl₃ mother liquors and crystallized from an ether–petroleum ether solution to yield 14.4 g of product, [α]_D²⁰ –8.68° (lit.⁸ [α]_D²⁴ –8.49°), mp 89–90° (lit.⁸ mp 89.3–90.3). The active ester was hydrolyzed by aqueous NaOH (25 g/100 ml) to give a yield of 6.1 g (98.3%) of the active norborneol, mp 126° (lit.⁸ mp 126–226.6°). The optically active alcohol was immediately converted to *exo*-norbornyl *p*-nitrobenzoate, mp 77–78°, [α]_D²⁰ –8.23°, and to the optically active mixed anhydride 1, mp 53.5–55, [α]_D²⁰ –5.39°.

Decomposition of Optically Active 1.—Approximately 1-g samples of the optically active mixed anhydride, dissolved in the appropriate solvent, were decomposed at 130–140° in sealed tubes. After 10 hr of heating the tubes were opened, the solvent was removed under reduced pressure, and the *exo*-norbornyl *p*-nitrobenzoate was extracted and recrystallized from hexane. The optical activity of the *exo*-norbornyl *p*-nitrobenzoate thus obtained was measured.

Polarimetric Measurements.—The specific rotations of optically active compounds were determined on a Perkin-Elmer Model 141M polarimeter. The path length of the cell used was 1 dm. The cell was thermostated at 27° during the runs. Chloroform was used as the solvent.

Kinetic Procedure.—The rate of the thermal decompositions of both the *exo*- and *endo*-norbornylcarbonic-*p*-nitrobenzoic anhydrides in xylene and nitrobenzene was followed by observing the decrease of the infrared anhydride carbonyl band at 1808 cm⁻¹. For each solvent and anhydride, a standard curve of known concentrations of anhydride vs. per cent transmittance was determined. A typical run is described.

Into a large test tube fitted with a serum cap was placed 0.6099 g of *exo*-norbornylcarbonic-*p*-nitrobenzoic anhydride in 20 ml of freshly distilled nitrobenzene. The tube was lowered into an oil bath at 138.5° ± 0.1° and after 2 min a sample was withdrawn with a syringe; this time was marked as zero time. Samples were then collected at regular intervals and frozen. When all the samples for a run were collected, the intensity of the infrared band at 1808 cm⁻¹ was determined for each sample. Typically, 11 points were measured.

The rate constants were calculated using a linear least-squares fit of the integrated form of the first-order rate equation.

Quantitative Analysis of the Decomposition Products.—The appropriate mixed anhydride was decomposed in solution in a thick-walled tube fitted with a vacuum stopcock. The sample was degassed prior to heating. The samples were heated at a temperature of 130–140° for a period of 11–13 hr to effect complete decomposition.

***p*-Nitrobenzoic Anhydride, Acid, and Norbornyl Ester.**—The analytical procedure developed by Lukashovich¹⁶ was used. The decomposition mixture was divided into two equal portions. The solvent was removed from each, under reduced pressure. Portion A was dissolved in 20 ml of dry methanol and 10 ml of dry pyridine, and was left to stand for 30 min. Portion B was dissolved in 10 ml of pyridine and 10 ml of water; this sample was immediately titrated with 0.098 *N* sodium hydroxide to the phenolphthalein end point. After 30 min, portion A was also titrated with 0.098 *N* sodium hydroxide. The titer of portion B was equivalent to all the free acid and two equivalents of acid per mole of anhydride. The titer of portion A yielded the acidity due to the free acid and one equivalent of acid per mole of anhydride. The amount of ester in the mixture was then determined by difference.

***exo*- and *endo*-Norbornyl Carbonates and Norborneol.**—These compounds were analyzed by glc, using a 6 ft × 1/4 in. glass column packed with 5% Carbowax 20M coated on Chromosorb W. The estimates were made by comparison of the glc peaks with those of appropriate standards.

(16) V. D. Lukashovich, *Khim. Prom. Moscow*, **8**, 1086 (1931), as quoted in C. W. Hammond, "Organic Analysis," Vol. III, Interscience, New York, N. Y., 1956, p 106.

Preparation of *endo*-Norborylcarbonic-*p*-Methoxybenzoic Anhydride.—To a mixture of 3 g (0.017 mol) of *endo*-norboryl chlorocarbonate and 2.61 g (0.017 mol) of *p*-anisic acid in 100 ml of dry ether at 0° was added, dropwise with stirring, 1.73 g (0.017 mol) of triethylamine in dry ether. The reaction mixture was stirred for 1 hr. The amine hydrochloride was filtered off and the ether solution was washed with dilute HCl, NaHCO₃, and water, and then dried over anhydrous magnesium sulfate. Upon evaporation of the ether an oil was obtained. Attempts to induce the oil to crystallize met with failure.

Anal. Calcd for C₁₆H₁₈O₅: C, 66.19; H, 6.25. Found: C, 66.04; H, 6.38.

The infrared spectrum (CCl₄) showed a double carbonyl band at 1805 and 1745 cm⁻¹, a separation of 60 cm⁻¹.

Preparation of *exo*-Norborylcarbonic-*p*-Methoxybenzoic Anhydride.—This compound was prepared in the same manner as the *endo* isomer described above. An oil was obtained from the reaction mixture which crystallized upon cooling, mp 50.5–51.5°, yield, 94%.

Anal. Calcd for C₁₆H₁₈O₅: C, 66.19; H, 6.25. Found: C, 66.03; H, 6.36.

The infrared spectrum (CCl₄) showed a double carbonyl band at 1785 and 1727 cm⁻¹.

Registry No.—1 (*exo*), 35042-30-9; 2 (*endo*), 35042-31-0; *exo*-norboryl carbonate, 35042-32-1; *endo*-norboryl carbonate, 35042-33-2; *exo*-norboryl *p*-nitrobenzoate, 10472-43-2; *endo*-norborylcarbonic-*p*-methoxybenzoic anhydride, 35042-35-4; *exo*-norborylcarbonic-*p*-methoxybenzoic anhydride, 35042-36-5.

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Azaindolizines. 2. N-5 and C-1 and C-3 Protonation of 1,3-Disubstituted 5-Azaindolizines

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1,2,3,6-Tetramethyl-5-azaindolizine (**2e**) and 1,3,6-trimethyl-2-phenyl-5-azaindolizine (**2f**) have been shown by pmr studies in trifluoroacetic acid to protonate solely at C-3. The di-5-azaindolizynlmethane (**6**) in trifluoroacetic acid diprotonates to give the di C-3 cation (**7**, 32%) and the C-3/N-5' dication (**8**, 68%). The perchlorates of **2e** and **2f**, when examined in trifluoroacetic acid, show protonation at N-5. Equilibration in solution leads to the formation of the 1-H (**4c** and **4d**) and 3-H cations (**3c** and **3d**) at the expense of the N-5 cations (**5a** and **5b**). The 3-H cation, initially observed in low concentration is eventually the sole cation established in solution.

Carbon protonation of heteroaromatic systems containing a π -equivalent nitrogen is exceptional and is shown solely by the 2*H*-cyclopenta[*d*]pyridazine and 5-azaindolizine structures **1a–c**¹ and **2a–d**.² Both these systems can be considered to be nitrogen heteroanologs of azulene which contain a π -excessive and a π -equivalent nitrogen.³ Protonation of these compounds occurs at carbon with the establishment of a 6- π cation in the six-membered ring; other similarly structured nitrogen heteroanologs of azulene do not protonate at carbon but at the π -equivalent nitrogen with the formation of a 10- π cation.^{2,4,5}

Previous pmr studies of 5-azaindolizines (**2a–d**) and their perchlorates⁶ showed protonation of **2a** and **2b** to occur at C-3 to give the 3-H cations **3a** and **3b** whereas their corresponding 3-methyl derivatives **2c** and **2d** protonated solely and predominantly at C-1 to give the 1-H cations **4a** and **4b**. This suggests that the 3-methyl group sterically inhibits protonation at C-3 in a manner akin to that found in 3-alkylindolizines.^{7,8} None of the 5-azaindolizines (**2a–d**) or their perchlorates in trifluoroacetic acid⁹ showed signals which could be attributed to the presence of a N-5 protonated cation.

This suggests that if the N-5 cation is formed it is either too transient or in concentrations too low to be detected by pmr spectroscopy. 1,3-Disubstituted 5-azaindolizines (**2e**, **2f**, and **6**) were synthesized to test whether this steric factor would sufficiently suppress C-1 and or C-3 protonation to cause protonation at the π -equivalent N-5 site with the formation of the corresponding 10- π cations.

Results

The pmr spectra of 1,3-dimethyl-5-azaindolizines (**2e** and **2f**) in trifluoroacetic acid¹⁰ showed them to protonate solely at the C-3 position to give the corresponding 6- π 3-H cations **3c** and **3d**. However, the pmr spectra of the isolated perchlorates of **2e** and **2f**, prepared by the addition of perchloric acid to an ethyl acetate solution of **2e** and **2f**, gave, when dissolved in trifluoroacetic acid, spectra which differed from the corresponding spectra of the 3-H cations **3c** and **3d**. These first recorded spectra of the perchlorates¹⁰ are considered to arise from protonation of **2e** and **2f** at the respective N-5 sites to give the 10- π cations **5a** and **5b**. The spectra of the cations **5a** and **5b** gradually became more complex with time. After approximately 6 hr at 25° or 1

(1) A. Anderson and D. Forky, *J. Amer. Chem. Soc.*, **91**, 924 (1969).

(2) M. Fraser, *J. Org. Chem.*, **36**, 3087 (1971).

(3) A π equivalent heteroatom provides one electron and a π -excessive heteroatom provides two electrons to the π structure.

(4) K. Hofner and M. Kreuder, *Angew. Chem.*, **73**, 657 (1961).

(5) W. Armarego, *J. Chem. Soc.*, 4226 (1964).

(6) Perchlorates of (**2a–d**) were prepared originally from ethanol; subsequently better yields were obtained using ethyl acetate as solvent.

(7) M. Fraser, S. McKenzie, and D. Reid, *J. Chem. Soc. B*, 44 (1966).

(8) W. Armarego, *ibid.*, 191 (1966).

(9) Spectra of the perchlorates of (**2a–f**) in (CD₃)₂SO were identical in pattern with the spectra of (**2a–f**) in CDCl₃ due to the loss of perchloric acid.

(10) Pmr spectra of **2e** in CF₃CO₂H (cation **3c**), **2e** HClO₄ in CF₃CO₂H (cation **5a**), **2e** HClO₄ in CF₃CO₂H after 15 min (**5a**, **3c**, and **4c**), and **6** in CF₃CO₂H (cations **7** and **8**), and ir spectra of **2a** HClO₄ and **2e** HClO₄ will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JOC-37-3027. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.