

TABLE II

Structure	Rel intensity, parent mass less 58 units
	0.83
	0.35
	0.32
	0.82
	0.88
	0.26
	0.38
	0.82

peak). In the first set, those isomers containing one original C_2H_2S group have relative intensities of 0.32 and 0.35; those with two such groups, 0.82–0.88. In the second set, the isomers containing no original C_2H_2S group have relative intensities of 0.26 and 0.38; the one with two such groups, 0.82.

To gain some further insight into the loss of CHS from condensed ring thiophenic compounds, we attempted to prepare dibenzothiophene specifically labeled with deuterium at C-4. The synthesis did not go exactly according to plan, but gave a product with the isotopic composition 22.3% d_2 , 68.5% d_1 , and 9.2% unlabeled, measured by mass spectrometry at reduced ionizing voltage.¹² The absence of species with more than two deuterium atoms, in light of the equivalence of positions 4 and 6, supports the view that deuterium was introduced at the desired position and that the second atom in the doubly labeled species is at C-6.

Table III shows the parent and parent-less-CHS regions of the spectra of the unlabeled and labeled dibenzothiophenes, corrected for naturally occurring heavy isotopes. Intensity at mass 141, after approximate correction for a small contribution of $C_{11}H_8^+-d$, measures the yield of $C_{11}H_7^+-d_2$ produced by loss of CHS from dibenzothiophene- d_2 . Comparison¹³ with the corresponding data for the unlabeled compound leads to an estimate of 80% for the fraction of $C_{11}H_7^+$ ions retaining both deuterium atoms. Even though the hydrogen atoms on C-4 and C-6 are the closest ones to the sulfur in the original dibenzothiophene molecule, they clearly are not preferentially incorporated into the CHS radical lost from the ionized molecule. In fact, the observed retention agrees well, within the limits of a reasonable isotope effect, with the value of 75% calculated for complete loss of identity of all the hydrogens in the parent ion before decomposition.

(12) D. P. Stevenson and C. D. Wagner, *J. Am. Chem. Soc.*, **72**, 5612 (1950).

(13) H. M. Grubb and S. Meyerson, in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., 1963, Chapter 10.

TABLE III

PARTIAL SPECTRA OF DIBENZOTHIOPHENES^a

Mass	Ion ^b	Unlabeled	Labeled ^c
186		...	22.3
185		...	71.1
184	$C_{12}H_8S^+$	100.0	11.7
183		3.36	1.80
182		2.04	0.53
181		0.11	0.06
180		0.03	0.01
142		...	0.25
141		...	2.97
140		0.76	9.49
139	$C_{11}H_7^+$	13.7	3.36
138		1.79	0.83
137		0.79	0.28
136		0.08	0.19

^a Corrected for contributions of naturally occurring heavy isotopic species. ^b Formulas listed correspond to unlabeled ions of indicated masses. ^c 22.3% d_2 , 68.5% d_1 , and 9.2% unlabeled.

Evidently, the process by which CHS is lost involves some deep-seated reorganization of the molecule.

Experimental Section

Dibenzothiophene was purchased from Aldrich Chemical Co., Milwaukee, Wis., and recrystallized twice from alcohol; mp 99°. A solution of 9.213 g (0.05 mole) of dibenzothiophene in 150 ml of dry ether was refluxed with 100 ml (0.234 mole) of 15% *n*-butyllithium in hexane for 16 hr.¹⁴ The mixture was cooled to 0°, treated with 15 ml (0.75 mole) of deuterium oxide, and refluxed for 4 hr. The solvent was evaporated and the residue crystallized twice from hexane to give dibenzothiophene-4-*d*, 6.9 g, mp 97–98°.

Naphthothiophene was synthesized in 6% yield by the method of Carruthers and Crowder.¹⁵ It melted at 184–185° (lit. mp 186–189°) after purification by gas chromatography.

Mass spectra were measured with 70-v electrons on a modified¹⁶ Consolidated 21-103 instrument with the inlet system at 250°. For the low-voltage measurements used for isotopic analysis, the repellers were maintained at an average potential of 3 v; exact values were selected for maximum sensitivity.

Registry No.—Dibenzothiophene, 80-76-2; naphthothiophene, 268-77-9.

(14) H. Gilman and A. L. Jacoby, *J. Org. Chem.*, **3**, 108 (1938).

(15) W. Carruthers and J. R. Crowder, *J. Chem. Soc.*, 1933 (1957).

(16) H. M. Grubb, C. H. Ehrhardt, R. W. Vander Haar, and W. H. Moeller, 7th Annual Meeting of American Society for Testing Materials Committee E-14 on Mass Spectrometry, Los Angeles, Calif., May, 1959.

The Synthesis and Thermal Decomposition of 3,3-Di-*t*-butyl Diperoxyphthalid¹

NICHOLAS A. MILAS AND RAINER J. KLEIN²

Department of Chemistry,
Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139

Received September 8, 1967

When the symmetrical phthalyl chloride was allowed to undergo solvolysis^{3,4} with *t*-butyl hydroperoxide, a

(1) Paper XL on Organic Peroxides, originally submitted June 30, 1966.

(2) Postdoctoral Research Associate (1962–1964); presently at Hoechst A.G., Frankfurt-Hochst, Germany.

(3) N. A. Milas, R. J. Klein, and D. G. Orphanos, *Chem. Ind. (London)*, 423 (1964).

(4) N. A. Milas, D. G. Orphanos, and R. J. Klein, *J. Org. Chem.*, **29**, 3099 (1964).

mixture of mono-*t*-butyl peroxy hydrogen phthalate (I), di-*t*-butyl diperoxyphthalate (II), and 3,3-di-*t*-butyl diperoxyphthalid (III) was formed which was separated into the pure components by liquid-liquid extraction and column chromatography. Peroxy esters (I and II) have been reported in the literature,^{5,6} while 3,3-di-*t*-butyl diperoxyphthalid (III) is a new isomer of II. The structure of III is based on elemental analysis, infrared and nmr spectra, hydrolysis, and thermal decomposition experiments.

The low yield (13.7%) of the diperoxyphthalid obtained from the symmetrical phthalyl chloride prompted us to try the solvolysis of the unsymmetrical phthalyl chloride.⁷ This produced a mixture of 3,3-di-*t*-butyl diperoxyphthalid and di-*t*-butyl diperoxyphthalate which was separated by column chromatography. When the reaction was carried out under basic conditions,⁶ the symmetrical diperoxy ester (II) was formed exclusively. Even in dioxane, using the potassium salt of *t*-butyl hydroperoxide, the unsymmetrical dichloride yielded a mixture of the acid peroxy ester (I) and diperoxy ester (II) but no peroxyphthalid (III). Similarly, when the symmetrical phthalyl chloride was allowed to react with *t*-butyl hydroperoxide in the presence of a base,⁶ the formation of III was completely suppressed and only II was obtained. The fact that in the absence of alkali the solvolysis of both phthalyl chlorides produces essentially the same mixture of diperoxy products (II and III) may be due to an equilibrium known to exist between the two isomeric phthalyl chlorides.⁸ These reactions are illustrated in Scheme I.

Thermal Decomposition of 3,3-Di-*t*-butyl Diperoxyphthalid

The structure and chemical behavior of the diperoxyphthalid, such as its failure to give a positive test for a peroxy ester,⁹ to undergo hydrolysis with 50% sulfuric acid, or to react with *t*-butyl hydroperoxide, resemble the analogous properties of perketals.^{10,11}

In view of the juxtaposition of the two peroxy groups in the diperoxyphthalid, we became interested in its thermal decomposition. This was carried out under nitrogen in cumene at a temperature of 132°. Under these conditions, 3,3-di-*t*-butyl diperoxyphthalid decomposes to phthalic anhydride, acetone, and *t*-butyl alcohol together with ethylene and ethane as the gaseous products; no oxygen or carbon dioxide was detected in the gaseous products. Dicumyl was also formed as the result of a coupling reaction between cumyl radicals. Table I illustrates the quantitative determination of the decomposition products.

The experimental results, especially the isolation of dicumyl, indicate that the thermal decomposition of 3,3-di-*t*-butyl diperoxyphthalid in cumene seems to proceed *via* homolysis to form phthalic anhydride (IV), *t*-butyl radical (VI), and *t*-butylperoxy radical (VII)

SCHEME I
REACTION OF SYMMETRICAL AND UNSYMMETRICAL PHTHALYL CHLORIDE WITH *t*-BUTYL HYDROPEROXIDE

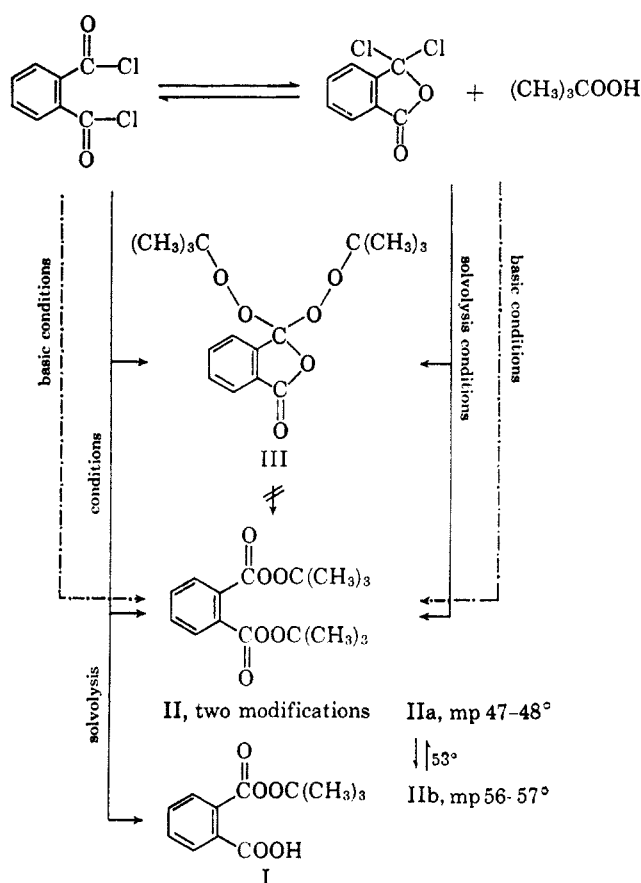


TABLE I

PRODUCTS FORMED IN THE THERMAL DECOMPOSITION OF 3,3-DI-*t*-BUTYL DIPEROXYPHTHALID IN CUMENE AT 132°

Product	Mole × 10 ⁴	Moles/mole of peroxide	Product formed from radicals, %
Ethane ^a	Not determined
Ethylene ^a	Not determined
Phthalic anhydride	4.20	0.83	83.0
Acetone	1.77	0.35	23.0
<i>t</i> -Butyl alcohol	6.05	1.19	77.0
Dicumyl	1.54	0.30	...

^a Analyzed by infrared and mass spectra but not estimated quantitatively.

although the unstable di-*t*-butyl trioxide (V) recently claimed by Milas and Arzoumanidis¹² and Bartlett and Günther¹³ may also be involved in the decomposition. However, according to Benson¹⁴ the trioxide is not expected to remain stable at 132° and would therefore spontaneously go over to *t*-butoxy (VI) and *t*-butylperoxy (VII) radicals¹⁵ both of which can abstract hydrogen atoms from cumene to give *t*-butyl alcohol.

Of the two initial radicals, the *t*-butoxy radical is the least stable¹⁶ and can undergo two competitive reactions: one, the abstraction of hydrogen atoms from cumene to form *t*-butyl alcohol; the other, the decomposition to acetone and methyl radicals which can di-

(5) A. G. Davis, R. V. Foster, and A. M. White, *J. Chem. Soc.*, 1953, 1541.

(6) N. A. Milas and D. G. Surgenor, *J. Am. Chem. Soc.*, **68**, 6426 (1946).

(7) E. Ott, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p 528.

(8) W. Csányi, *Ber.*, **52**, 1792 (1919).

(9) D. Swern and L. S. Silbert, *Anal. Chem.*, **30**, 385 (1958).

(10) F. H. Dickey, F. F. Rust, and W. E. Vaughan, *J. Am. Chem. Soc.*, **71**, 1432 (1949).

(11) F. H. Dickey, *et al.*, *Ind. Eng. Chem.*, **41**, 1673 (1949).

(12) N. A. Milas and G. G. Arzoumanidis, *Chem. Ind. (London)*, 67(1966).

(13) P. D. Bartlett and P. Günther, *J. Am. Chem. Soc.*, **88**, 3288 (1966).

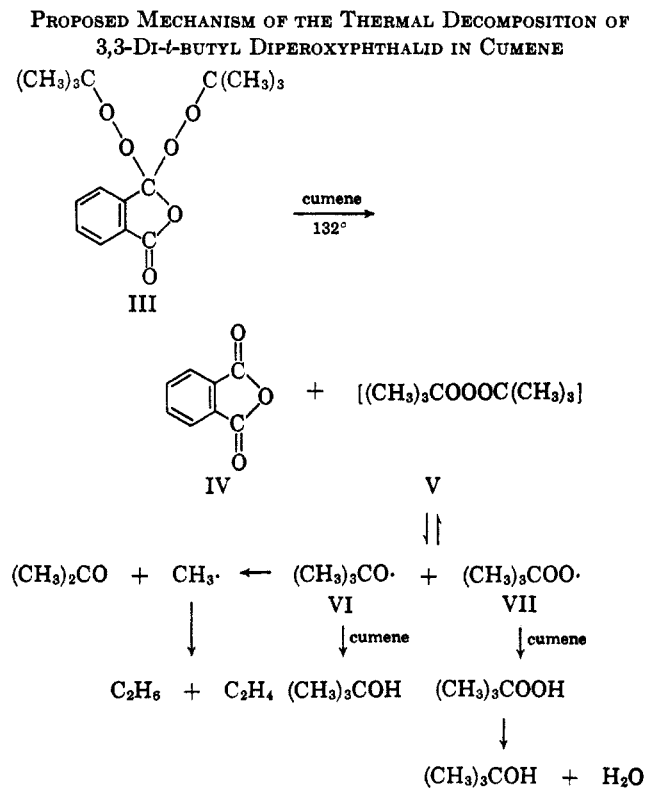
(14) S. W. Benson, *ibid.*, **86**, 3922 (1964).

(15) A. Factor, C. A. Russell, and T. G. Traylor, *ibid.*, **87**, 3692 (1965).

(16) P. Gray and A. Williams, *Chem. Rev.*, **59**, 239 (1959).

merize to form ethane or disproportionate to form ethylene, both of which have been detected in the gaseous products of the decomposition. The preferred hydrogen abstraction of both initial radicals results in the formation of 77% *t*-butyl alcohol and 23% of acetone. Scheme II illustrates the thermal decomposition of 3,3-di-*t*-butyl diperoxyphthalid in cumene.

SCHEME II



Experimental Section

Solvolysis of Symmetrical Phthalyl Chloride with *t*-Butyl Hydroperoxide.—Freshly distilled phthalyl chloride (8.2 g, 0.04 mole) was mixed with *t*-butyl hydroperoxide¹⁷ (9.0 g, 0.10 mole, 99% pure) and the mixture was allowed to stand for 15–20 min, then subjected to a vacuum (60 mm) on a rotary evaporator. The reaction proceeded with strong evolution of heat and gas and as soon as it subsided, the mixture was heated at 50–60° for 3 hr. *t*-Butyl hydroperoxide (6.0 g, 0.067 mole) was then added and the reaction was allowed to continue overnight at room temperature on a rotary vacuum evaporator. The excess hydroperoxide was then removed by subjecting the reaction mixture to a vacuum of 2 mm. A colorless, viscous liquid was obtained which was dissolved in ether and shaken several times with 5% sodium bicarbonate solution. From the bicarbonate layer a solid was recovered, after acidification with 10% sulfuric acid, which was recrystallized from a 70:30 mixture of petroleum ether (bp 30–60°) and ethyl ether [mp 104–105°, yield 4.7 g (49.2%)] identified as mono-*t*-butyl peroxyhydrogen phthalate.⁸ Its infrared spectrum (10% in chloroform) showed the following bands: 3500, 3000, 2898, 1762, 1705, 1598, 1583, 1492, 1448, 1411, 1367, 1238, 1186, 1139, 1102, 1055, 1025, 911, and 833 cm^{-1} .

The ether layer was washed with water, dried over magnesium sulfate, and the solvent removed under vacuum. A colorless, viscous liquid was obtained which failed to crystallize. Its infrared spectrum 10% in carbon tetrachloride showed two carbonyl bands at 1803 and 1772 cm^{-1} indicating that a mixture

of two different peroxy compounds was present. Since we expected one of these to be the *sym*-di-*t*-butyl diperoxyphthalate, we synthesized it by the standard procedure.⁸ Instead of the reported melting point (mp 57–57.5°) the peroxy ester obtained melted sharply at 48°.

Anal. Calcd for $\text{C}_{16}\text{H}_{22}\text{O}_6$: C, 61.92; H, 7.14; O, 10.34. Found: C, 62.09; H, 7.14; O, 10.20.

The infrared spectrum of this peroxy ester (10% in carbon tetrachloride) showed the following bands: 2978, 2922, 1772, 1595, 1577, 1473, 1442, 1390, 1367, 1245, 1183, 1125, 1085, 1022, and 835 cm^{-1} .

The colorless viscous liquid from the original experiment was passed through a silica gel column, employing a mixture of petroleum ether and ether (75:25) as eluent. The first eluate (combination of several fractions) yielded a viscous liquid which crystallized on standing. Recrystallization from a (75:25) mixture of petroleum ether and ethyl ether gave colorless crystals, mp 86–87°, yield 1.7 g (13.7%). This was identified as 3,3-di-*t*-butyl diperoxyphthalid.

Anal. Calcd for $\text{C}_{16}\text{H}_{22}\text{O}_6$ (III): C, 61.92; H, 7.15; O, 10.31; mol wt, 310.34. Found: C, 61.81; H, 7.05; O, 7.42 (HI method); mol wt, 309.0 (cryoscopic in benzene).

The infrared spectrum (10% in carbon tetrachloride) showed the following bands: 2988, 2928, 1803, 1609, 1470, 1392, 1370, 1347, 1286, 1258, 1198, 1139, 1103, 1067, 1047, 1028, 972, 942, 867, and 694 cm^{-1} .

The nmr spectrum (25% in carbon tetrachloride using tetramethyl silane as internal standard) showed aliphatic protons at 1.26 ppm, aromatic protons at 7.71 ppm with splitting at 7.61, 7.68, 7.66, 7.79, and 7.84 ppm. The nmr spectrum, under the same conditions, of the *sym*-di-*t*-butyl diperoxyphthalate showed aliphatic and aromatic protons at 1.36 and 7.86 ppm, respectively, but without splitting.

The second eluate (combination of several fractions) also yielded a viscous liquid which crystallized after several hours on standing. Recrystallization from petroleum ether gave a product which had a melting point of 45–46° and was identified as di-*t*-butyl diperoxyphthalate by infrared spectra, mixture melting point, and a comparison of the R_f value (0.542) on a paper chromatogram with an authentic sample.

The difference between the previous published melting point of di-*t*-butyl diperoxyphthalate⁸ and the one given in the present work was further investigated. It was found that when a weighed amount of the peroxy ester (mp 47°) was heated under reduced pressure (60–70 mm) a few degrees above its melting point, then allowed to crystallize again, the melting point of the crystals was 56–57° without any loss in weight. Similarly when the higher melting peroxy ester was heated under the same conditions above its melting point, the crystals obtained after cooling melted at 47–47.5° again without any loss of weight. Both peroxy esters are identical in their chemical properties but they exist in a different crystalline modification. So far as we know, this phenomenon has not been observed previously in the peroxide field.

Solvolysis of Unsymmetrical Phthalyl Chloride with *t*-Butyl Hydroperoxide.—Unsymmetrical phthalyl chloride was prepared by heating symmetrical phthalyl chloride with aluminum chloride.⁷ Unsymmetrical phthalyl chloride (4.06 g, 0.02 mole) was mixed with *t*-butyl hydroperoxide (14.40 g, 0.16 mole) and the mixture was allowed to stand for 0.5 hr, then subjected to a 60-mm vacuum on a rotary evaporator. The reaction was not exothermic as in the case of the symmetrical phthalyl chloride. As soon as the evolution of gas bubbles diminished, the reaction mixture was heated to 50–60° for 2 hr on the rotary evaporator (60 mm) then allowed to continue overnight at room temperature. The excess of *t*-butyl hydroperoxide was then removed by subjecting the mixture to a vacuum of 2 mm. A colorless liquid was obtained which was passed through a silica gel column, using as eluent a mixture (75:25) of petroleum ether and ethyl ether. The first eluate (combination of several fractions) yielded a viscous liquid which crystallized on standing. The crystals were washed with petroleum ether, dried [mp 86–87°, yield 1.50 g (24.2%)], and identified as 3,3-di-*t*-butyl diperoxyphthalid. The second eluate (combination of several fractions) also yielded a viscous liquid which crystallized on standing over petroleum ether. It was recrystallized from petroleum ether [mp 46–47°, yield 0.44 g (7.10%)] and identified by mixture melting point and R_f as di-*t*-butyl diperoxyphthalate.

Thermal Decomposition of 3,3-Di-*t*-butyl Diperoxyphthalid.—3,3-Di-*t*-butyl diperoxyphthalid (1.60 g, 5.10 mmoles) was

(17) Kindly supplied by Lucidol Division of Wallace and Tiernan, Inc., Buffalo, N. Y.

dissolved in 10 ml of purified cumene¹⁸ and the solution was degassed, while cooled with liquid nitrogen. The reaction mixture was then allowed to warm up to room temperature and gradually heated to 132° under a nitrogen atmosphere and maintained at this temperature for 5 hr. The gases evolved were caught and analyzed in an Orsat apparatus.

When the reaction was finished, the mixture was allowed to cool to room temperature and kept overnight in the refrigerator. Colorless needles separated out and were identified as phthalic anhydride, mp 132°; a mixture melting point with an authentic sample gave no depression, yield 0.543 g (72%). From the filtrate (8.656 g) a vapor phase chromatogram was run showing the presence of acetone and *t*-butyl alcohol (column, polypropylene glycol UC oil LB-550-X; column temperature, 73°). The quantitative amounts of both products were determined from their peak areas of the chromatogram. In addition to the gas chromatographic identification, the formation of acetone and *t*-butyl alcohol was proved by preparing derivatives. The reaction solution was therefore fractionated in order to separate the mixture of acetone and *t*-butyl alcohol from most of the cumene. The distillate was divided into two portions which were treated with 2,4-dinitrophenylhydrazine and 3,5-dinitrobenzoylchloride,¹⁹ respectively. The melting points of the corresponding acetone 2,4-dinitrophenylhydrazone and *t*-butyl-3,5-dinitrobenzoylbenzoate agreed with the literature values. The remaining cumene solution was subjected to a vacuum (2 mm) distillation to remove the cumene; more crystalline product separated. Petroleum ether was added, causing a partial solution of the solid material. This was separated by filtration and identified as additional phthalic anhydride (0.08 g), increasing the total yield of phthalic anhydride to 0.623 g (83%). From the filtrate, the petroleum ether was removed under vacuum and a yellow crystalline compound was obtained which was purified by recrystallization from ethanol and identified as dicumyl, mp 118°, and by a mixture melting point with an authentic sample²⁰ and comparison of the infrared spectra; yield 0.367 g.

Analysis of the gaseous products showed that no oxygen or carbon dioxide had been formed. An infrared spectrum run in a gas cell exhibited the following bands: 3050-2900 (triplet), 1730, 1440, 1340, 1300, 1260-1200, and 890 cm⁻¹. Furthermore, a mass spectrum was run showing absorptions at *m/e* 27 and 29. Both spectra indicate strongly the presence of ethane and ethylene.

Reaction of Unsymmetrical Phthalyl Chloride with *t*-Butyl Hydroperoxide in the Presence of Pyridine.—Unsymmetrical phthalyl chloride (2.03 g, 0.01 mole), dissolved in 10 ml of anhydrous ether, and *t*-butyl hydroperoxide (3.60 g, 0.04 mole), likewise dissolved in 10 ml of anhydrous ether, were dropped simultaneously in the course of 0.5 hr to a solution of dry pyridine (1.58 g, 0.02 mole) in 20 ml of anhydrous ether at 0° with stirring. Pyridine hydrochloride precipitated during the addition. The reaction mixture was then allowed to warm up to room temperature and stirring was continued overnight. After separation of the pyridine hydrochloride by filtration, the ether was removed under reduced pressure leaving a colorless liquid which was subjected to a vacuum of 2 mm to remove the excess *t*-butyl hydroperoxide. An infrared spectrum taken of the final product revealed that di-*t*-butyl diperoxyphthalate was the only peroxidic product present. For further purification, the product was redissolved in ether, and the ether solution was extracted with ice-cold 10% sodium hydroxide, the ether layer was washed with water, dried over magnesium sulfate, filtered, and the ether was removed under reduced pressure, leaving a viscous liquid which crystallized on standing. The crystals were washed with petroleum ether, dried (mp 48°), and identified as di-*t*-butyl diperoxyphthalate by mixture melting point and infrared spectrum; yield 2.28 g (73.6%).

Effect of *t*-Butyl Hydroperoxide on 3,3-Di-*t*-butyl Diperoxyphthalide.—Since the unsymmetric 3,3-di-*t*-butyl diperoxyphthalid contains a γ -lactone ring it was thought advisable to try the effect of *t*-butyl hydroperoxide on this ring. Consequently 0.2 g of 3,3-di-*t*-butyl diperoxyphthalid was heated with stirring at 60-70° with excess *t*-butyl hydroperoxide for 2.5 hr. The excess

t-butyl hydroperoxide was then removed at 2 mm, whereby a slightly yellow viscous liquid was separated which crystallized on standing. When the crystals were washed with petroleum ether and dried, they melted at 86° and were shown by mixture melting point to be identical with the starting material and the recovery was nearly quantitative.

Acid Hydrolysis of 3,3-Di-*t*-butyl Diperoxyphthalide.—Sulfuric acid (1 ml, 50% concentrated) was added to a stirred solution of 3,3-di-*t*-butyl diperoxyphthalid (0.20 g) in 10 ml of ether at 0°. The reaction was allowed to continue for 2 hr, while the mixture was warmed to room temperature. Water was then added and the sulfuric acid was neutralized with magnesium carbonate, the ether layer was separated, dried over magnesium sulfate, filtered, and the ether was removed under reduced pressure. White crystals were separated (mp 84-85°) and identified by mixture melting point as the starting material and the recovery was nearly quantitative. This experiment shows that the acid failed to open the γ -lactone ring.

Basic Hydrolysis of 3,3-Di-*t*-butyl Diperoxyphthalide.—3,3-Di-*t*-butyl diperoxyphthalid (0.10 g, 3.22×10^{-4} mole) was dissolved in 6 ml of ethylene glycol monomethyl ether and to the solution was added 0.8 ml of 10% aqueous sodium hydroxide. The reaction mixture was stirred for 2 hr at 40°, then added to it successively 15 ml of acetic acid, 3 ml of saturated potassium iodide solution, and a piece of Dry Ice. After standing for 0.5 hr at 60°, the iodine liberated was titrated with standard sodium thiosulfate. On the basis of formula III, 86.5% of the expected 2 mole equiv of *t*-butyl hydroperoxide was found. In a separate experiment one of the hydrolysis products (phthalic acid) was isolated by extracting the acidified reaction mixture with ether and evaporating the solvent. A white solid was obtained mp 186-187° and identified as phthalic acid by mixture melting point.

Registry No.—I, 15042-77-0; II, 2155-71-7; III, 15044-23-2.

Acknowledgment.—The authors wish to thank Dr. Nagy for the combustion analyses, Dr. Nancy Wang for assistance in some of the experiments, the Lucidol Division of Wallace and Tierman, Inc., and the Industrial Fund of Massachusetts Institute of Technology for financial support of this investigation.

Reactions of Hydrazines with Esters and Carboxylic Acids

RICHARD F. SMITH¹, ALVIN C. BATES,¹ ANGELLO J. BATTISTI,² PETER G. BYRNES,¹ CHRISTINE T. MROZ,¹ THOMAS J. SMEARING,¹ AND FREDERICK X. ALBRECHT²

Department of Chemistry, State University College at Geneseo, Geneseo, New York 14454, and Department of Chemistry, State University of New York at Albany, Albany, New York

Received August 18, 1967

As part of a continuing study of the thermolytic and photolytic decomposition of amine imides,³ we required large quantities of 1,1-dimethyl-2-acylhydrazines (I) for subsequent conversion to trimethylamine imides. Hinman⁴ has reported that 1,1-dimethylhydrazine reacts with benzoyl chloride to give mixtures of 1,1-dibenzoyl-2,2-dimethylhydrazine and 1-benzoyl-2,2-dimethylhydrazine with the former predominating under

(18) P. D. Bartlett, E. P. Benzinger, and R. E. Pincock, *J. Am. Chem. Soc.*, **82**, 1766 (1960).

(19) R. L. Shriner, R. C. Fuson, "The Systematic Identifications of Organic Compounds," 4th ed, John Wiley and Sons, Inc., New York, N. Y., 1959.

(20) H. Pines, C. N. Pillai, *J. Am. Chem. Soc.*, **82**, 2921 (1960).

(1) Department of Chemistry, State University College at Geneseo, Geneseo, N. Y.

(2) Natural Science Foundation Undergraduate Research Participant, State University of New York at Albany, Albany, N. Y., 1964-1965.

(3) R. F. Smith and P. C. Briggs, *Chem. Commun.*, **7**, 120 (1965).

(4) R. L. Hinman, *J. Am. Chem. Soc.*, **78**, 1645 (1956).