

Mechanisms of Induced Decomposition. II. Reactivity of Di-*tert*-butylperoxy Phthalate¹

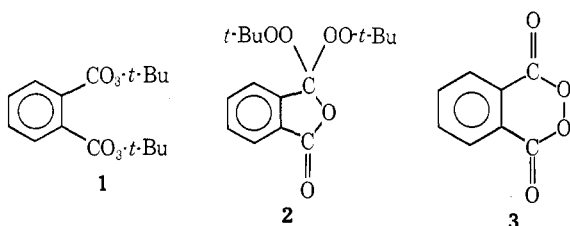
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The reactivity of di-*tert*-butylperoxy phthalate (1) in cumene solution has been examined. The rate of disappearance of 1 ($k_1 = 4.68 \times 10^{-5} \text{ sec}^{-1}$ at 115°) and the activation parameters for this process ($\Delta H^* = 33.6 \text{ kcal/mol}$, $\Delta S^* = 7.8 \text{ eu}$) are consistent with an initial one-bond cleavage at one of the peroxy groups and formation of the *o*-(carbo-*tert*-butylperoxy)benzoate radical (11). The products at 115° include CO₂, methane, acetone, *tert*-butyl alcohol, benzene, phthalic anhydride, phthalic acid, benzoic acid, bicumyl, *o*-cumylbenzoic acids 4-6, and *o*-cumylbenzenes 7-9. The potential reaction product *tert*-butylperoxy hydrogen phthalate (12) is thermally unstable at 80° and gives phthalic anhydride and *tert*-butyl hydroperoxide by a nonradical process. A mechanism for the reaction of 1 is proposed involving initial formation of 11, which either abstracts hydrogen to form 12 or decarboxylates to form the *o*-(carbo-*tert*-butylperoxy)phenyl radical (13). The observed products are then formed by further reaction of 12 and 13. *o*-Carbomethoxy-*o*'-isopropylbiphenyl (10), prepared by methylation of 4, displays nonequivalent diastereotopic isopropyl methyl groups in the nmr owing to restricted rotation around the aryl-aryl bond at room temperature. This nonequivalence is greatly enhanced by the addition of tris-(dipivalomethanato)europium. The methyls remain nonequivalent below at least 105° in the noncomplexed case and 150° in the presence of the shift reagent.

Di-*tert*-butylperoxy phthalate (1) is a commercially available free-radical initiator with close structural similarities to 3,3-di-*tert*-butylperoxy phthalide (2)



and phthalyl peroxide (3). There has recently been great interest in the preparation and reactivity of 1,^{3a} 2,³ and 3,⁴ as well as other difunctional peresters and acyl peroxides, both cyclic⁵ and noncyclic.⁶ This investigation of 1 is part of a program in these laboratories to investigate intramolecular interactions between radicals and peroxides.¹

There has been a brief report⁷ on the kinetics of thermal decomposition of 1 in di-*n*-butyl phthalate solution measured by iodometric titration. We have mea-

sured the rate of reaction of 1 in cumene solution by observing the disappearance of the carbonyl band at 1770 cm⁻¹ in the infrared. During the reaction new bands appear around 1790 (due to phthalic anhydride) and 1700 cm⁻¹ (due to phthalic and benzoic acids) but satisfactory first-order kinetics for the disappearance of 1 were obtained using the absorption at 1770 cm⁻¹ for up to one half-life. Rate constants and derived activation parameters obtained in this way are given in Table I, along with suitable data for comparison.^{8,9}

Products for the decomposition of 1 in cumene were determined at 115° and are listed in Table II. After removal of gaseous and volatile products the residue was treated with KOH in ethanol and extracted with base, and the basic extract was acidified and treated with diazomethane. Analysis of the resulting material by vpc gave the yields of benzoic acid and the *o*-cumylbenzoic acids 4-6 (as their methyl esters), phthalic acid (as dimethyl phthalate), and phthalic anhydride (as methyl ethyl phthalate). The neutral residue from the base extraction was shown by vpc to consist of a number of minor products, of which the *o*-, *m*-, and *p*-cumylbenzenes (7-9) were identified.

o-Carbomethoxy-*o*'-isopropylbiphenyl (10), derived from methylation of the corresponding acid 4, was identified by its unique nmr spectrum which shows nonequivalent isopropyl methyl groups at room temperature which coalesce near 110° (Figure 1). At 60 or 100 MHz methyl doublets ($J = 7.0 \text{ Hz}$) appeared at δ 1.06 and 1.08; these methyl groups are rendered diastereotopic by the slow rotation around the aryl-aryl bond. However, the coalescence behavior of these peaks is somewhat anomalous, in that the signals appear to merge smoothly without prior line broadening. This may be due to the small chemical shift difference between signals causing the broadening to be imperceptible, or it may mean that the observed coalescence is an accidental equivalence caused by the temperature dependence of the solvation. The latter explanation is probably correct, because the observed coalescence temperature between 105 and 110° is

(1) Presented at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971, Abstracts ORGN 137. For part I, see A. I. Dalton and T. T. Tidwell, *J. Org. Chem.*, **37**, 1504 (1972). Supported by the U. S. Army Research Office—Durham.

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(3) (a) N. A. Milas and R. J. Klein, *J. Org. Chem.*, **36**, 2900 (1971); (b) N. A. Milas and R. J. Klein, *ibid.*, **33**, 848 (1968).

(4) M. Jones, Jr., and M. R. De Camp, *ibid.*, **36**, 1536 (1971).

(5) (a) W. Adam and R. Rucktäschel, *J. Amer. Chem. Soc.*, **93**, 557 (1971); (b) O. L. Chapman, P. W. Wojtkowski, W. Adam, O. Rodriguez, and R. Rucktäschel, *ibid.*, **94**, 1365 (1972); (c) J. M. King, Ph.D. Thesis, University of Michigan, 1965; *Diss. Abstr.*, **27**, 411-B (1966).

(6) (a) E. N. Cain, R. Vukov, and S. Masamune, *Chem. Commun.*, 98 (1969). (b) L. M. Bobroff, L. B. Gortler, D. J. Sahn, and H. Wiland, *J. Org. Chem.*, **31**, 2678 (1966). (c) L. B. Gortler and M. D. Saltzman, *ibid.*, **31**, 3821 (1966). (d) S. S. Ivanchev, and A. I. Prisyazhnyuk, *Dokl. Akad. Nauk SSSR*, **179**, 858 (1968); *Chem. Abstr.*, **69**, 10161s (1968). (e) V. I. Galibei, T. A. Tolpygina and S. S. Ivanchev, *Zh. Org. Khim.*, **6**, 1585 (1970); *Chem. Abstr.*, **73**, 98252p (1970). (f) S. G. Erigova, A. I. Prisyazhnyuk, and S. S. Ivanchev, *Zh. Obshch. Khim.*, **38**, 2416 (1968); *Chem. Abstr.*, **70**, 67296q (1969). (g) Yu. A. Od'dekop, G. S. Bylina, and Zh. I. Bulovichik, *Zh. Org. Khim.*, **4**, 429 (1968); *Chem. Abstr.*, **68**, 104676v (1968). (h) Yu. A. Od'dekop, G. S. Bylina, and M. Matveentseva, *Zh. Org. Khim.*, **4**, 585 (1968); *Chem. Abstr.*, **69**, 2638n (1968). (i) L. Gortler and R. Hom, Abstracts, 163rd National Meeting of the American Chemical Society, Boston, Mass., April 1972, ORGN 61.

(7) D. F. Doehnert and O. L. Mageli, *Ann. Techn. Management Conf., Reinforced Plastics Div., Soc. Plastics Ind., Inc.*, **13**, Sect. 1-B, 1 (1958); *Chem. Abstr.*, **31**, 18534i (1959); *Lucidol Product Bulletins* 6.301 and 30.30.

(8) A. T. Blomquist and A. F. Ferris, *J. Amer. Chem. Soc.*, **73**, 3408 3412 (1951).

(9) W. G. Bentrude and J. C. Martin, *ibid.*, **84**, 1561 (1962).

TABLE I
 RATE OF THERMAL DECOMPOSITION OF PERESTERS

Perester	Solvent	T, °C	$k_1, \text{sec}^{-1} \times 10^5$	$\Delta H^*, \text{kcal/mol}$	$\Delta S^*, \text{eu}$	Ref
1	Cumene	130.1	26.0	33.6	7.8	
	Cumene	115.0	4.68			
	Cumene	99.9	0.834			
1	Di- <i>n</i> -butyl phthalate	130	48	37.0 ^a	17.6 ^a	7
		115	7.8			
		100	1.08			
XPhCO ₂ - <i>t</i> -Bu						
X = H	<i>p</i> -MePhCl	100	0.98 ^b	33.6 ^b	8.2 ^b	8
X = <i>o</i> - <i>t</i> -Bu	PhCl	100	3.81	34.2	12.5	9

^a Calculated from data in ref 7. ^b Calculated from data in ref 8.

 TABLE II
 PRODUCTS FROM THE THERMAL DECOMPOSITION OF
 DI-*tert*-BUTYLPEROXY PHTHALATE (1) AT 115° IN CUMENE

Product	Mole/mole of perester ^a
CO ₂	1.15
CH ₄	0.26
Acetone	0.27
<i>t</i> -BuOH	1.45
Benzene	0.26
Phthalic anhydride	0.11
Phthalic acid	0.03
Benzoic acid	0.04
Bicumyl	1.04
<i>o</i> -Cumylbenzoic acids 4-6	0.42 ^b
<i>o</i> -Cumylbenzenes 7-9	~0.1 ^c

^a Yields of volatile products varied less than $\pm 10\%$ on duplicate runs, and other yields are estimated to be accurate to $\pm 10\%$, except for the totals of 4-9, which may vary by ± 0.1 mol/mol. ^b 35% ortho, 40% meta, 25% para. ^c 17% ortho, 57% meta, 26% para.

lower than what would be expected on the basis of the known coalescence temperatures of *o,o'*-di(acetoxy-methyl)biphenyl (94-127°)¹⁰ and *o,o'*-diisopropylbiphenyl (>200°).^{11,12}

This interpretation received support from experiments using the shift reagent tris(divalomethanato)-europium [Eu(DPM)₃]. Addition of this reagent caused each of the methyl doublets to shift downfield, although the doublet originally at higher field was shifted more strongly and became the lower field absorption. At the highest concentration of Eu(DPM)₃ used, the pair of methyl doublets ($J = 7$ Hz) appeared at δ 1.72 and 2.15, respectively (Figure 2). When this solution of 10 and Eu(DPM)₃ was heated, the shift difference between the pair of doublets gradually decreased (analogous to the results of other studies of the temperature effect on lanthanide-induced chemical shifts).¹³ However, above 100° the resolution obtainable rapidly deteriorated so that 150° was the highest temperature at which usable spectra could be obtained. At this temperature the pair of doublets had still not coalesced. This result indicates that the rotation around the aryl-aryl bond is still slow at this temperature, which is reasonable in view of the results cited above on analogous compounds.

(10) W. L. Meyer and R. B. Meyer, *J. Amer. Chem. Soc.*, **85**, 2170 (1963).

(11) H. Kessler, *Angew. Chem., Int. Ed. Eng.*, **9**, 219 (1970).

(12) We thank Professors M. Raban and T. H. Siddall, III, for helpful discussions regarding this point.

(13) (a) D. L. Rabenstein, *Anal. Chem.*, **43**, 1599 (1971); (b) R. R. Fraser, M. A. Petit, and J. K. Saunders, *Chem. Commun.*, 1450 (1971); (c) R. D. Bennett and R. E. Schuster, *Tetrahedron Lett.*, 673 (1972); (d) C. Beauté, S. Cornuel, D. Lelandais, N. Thoai, and Z. W. Wolkowski, *ibid.*, 1099 (1972).

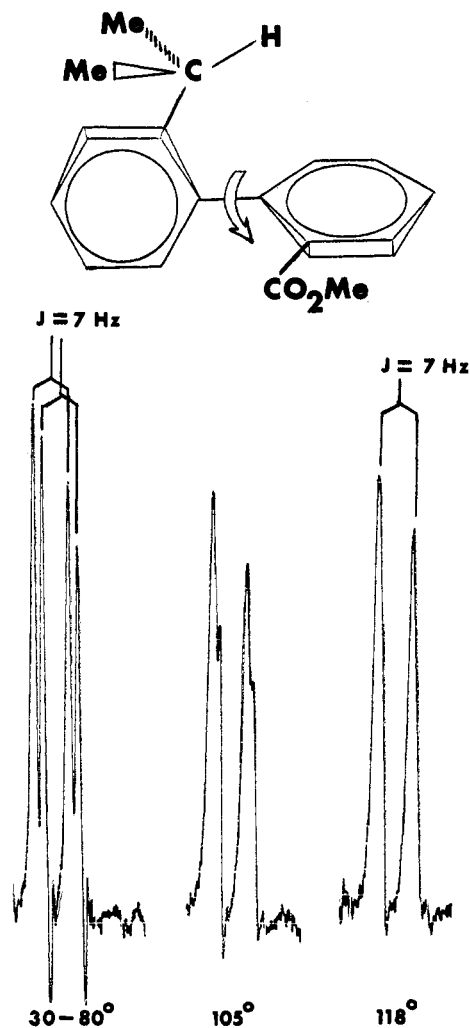


Figure 1.—Isopropyl portion of the nmr spectrum of *o*-carbomethoxy-*o'*-isopropylbiphenyl (10) at 60 MHz.

A mechanism to account for the rate data and the formation of the observed products is shown in Scheme I. The rate of disappearance of 1 is consistent with a normal one-bond homolysis leading to the *o*-(carbomethoxy)benzoate radical (11), without any rate acceleration due to participation by one perester grouping in the reaction of the other. Abstraction of hydrogen by 11 would lead to *tert*-butylperoxy hydrogen phthalate (12). This compound was shown in a separate experiment at 80° to undergo rapid transformation to the anhydride and *tert*-butyl hydroperoxide and would thus not be observed under the conditions used for the product study of 1. Phthalic acid was

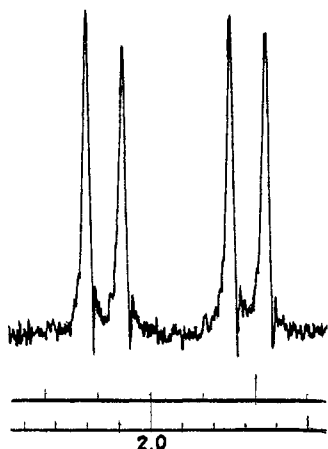
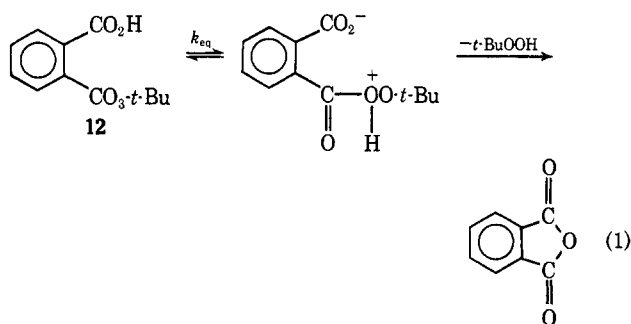


Figure 2.—Isopropyl portion of the nmr spectrum of *o*-carbomethoxy-*o'*-isopropylbiphenyl (10) with $\text{Eu}(\text{DPM})_3$ at 60 MHz and 35° .

shown not to give formation of phthalic anhydride under the conditions of the product study. The formation of anhydride from the thermal reaction of 12 is consistent with the known thermal formation of phthalic anhydride from nonperoxidic half-esters of phthalic acid.¹⁴ Several mechanisms have been considered for the latter process,¹⁴ and a possible route for 12 is shown in eq 1.¹⁵



The product studies of the half-perester 12 at 80 and 115° (Table III) show the presence of small amounts

TABLE III
PRODUCTS FROM THE THERMAL DECOMPOSITION OF
tert-BUTYLPEROXY HYDROGEN PHTHALATE (12) IN CUMENE

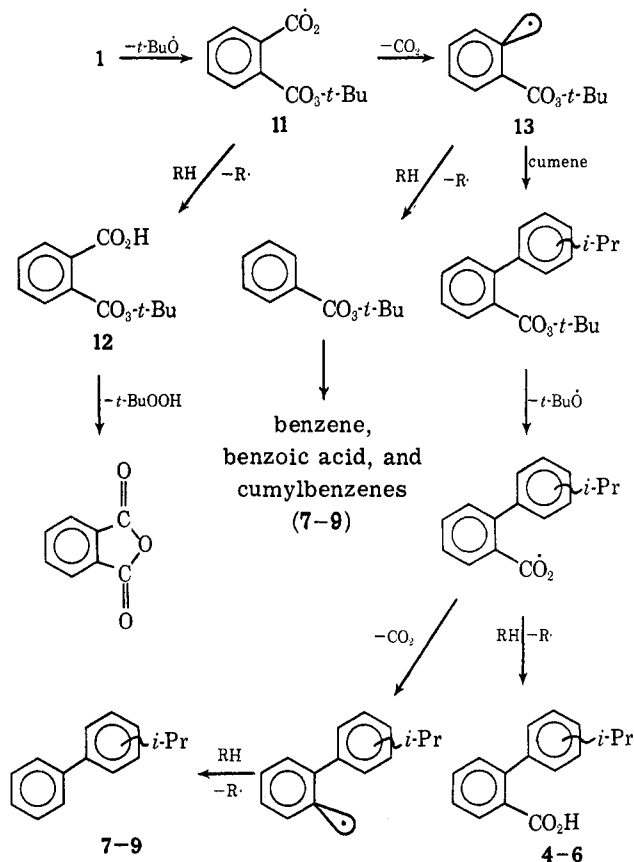
Product	—Mole/mole of perester—	
	115° , 48 hr	80° , 4 hr
CO_2	0.02	0.01
CH_4	0.01	<i>a</i>
Acetone	Trace	<i>a</i>
<i>t</i> -BuOH	Trace	<i>a</i>
<i>t</i> -BuOOH	<i>a</i>	0.73
Phthalic anhydride	0.71	~ 1.0
Bicumyl	0.35	None
Phthalic acid	<i>b</i>	None

^a Not examined. ^b Apparently present as shown by ir. All yields estimated $\pm 10\%$.

of products derived from free-radical reactions. These products may indicate a small amount of homolytic dissociation of 12, or may derive from an induced de-

(14) J. W. Thanassi and T. C. Bruice, *J. Amer. Chem. Soc.*, **88**, 747 (1966).
(15) The formation of phthalic anhydride and *tert*-butyl hydroperoxide from 12 was discovered by T. D. Manly and D. R. Dixon and was cited by R. C. P. Cubbon, *Progr. React. Kinet.*, **5**, 29 (1970). We thank Dr. D. R. Dixon, ICI Ltd., Runcorn, Cheshire, for private communication of his results.

SCHEME I
THERMAL DECOMPOSITION OF
DI-*tert*-BUTYLPEROXY PHTHALATE (1)



composition route involving *tert*-butyl hydroperoxide. The latter compound undergoes slow reaction at 100° , and is itself subject to induced chain reaction.¹⁶ The formation of phthalic acid from 12 at 115° indicates that 12 is the precursor of at least part of the phthalic acid observed in the reaction of 1.

The formation of biphenyls in the reaction of 1 is in accord with results for the thermal decomposition of benzoyl peroxide in cumene. Two separate groups investigated the reactivity of phenyl radicals formed in this way. One group reported 60% abstraction and 40% ring substitution to give the isomeric isopropylbiphenyls in the ratio of 31% ortho, 42% meta, and 27% para,^{17a} and the other group reported 47% abstraction with 53% ring substitution in the ratio 10% ortho, 60% meta, and 30% para.^{17b} The difference between these analyses is presumably due to the inaccurate analytical techniques available at that time.

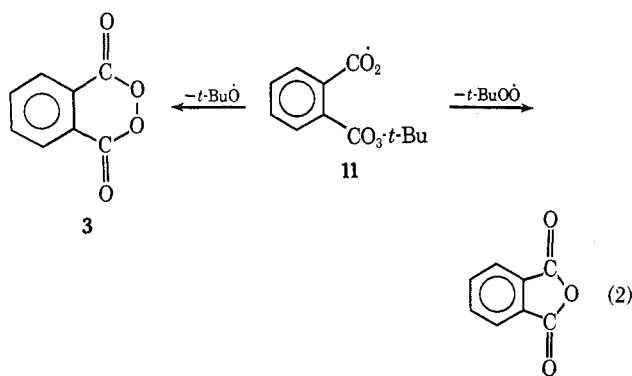
Other minor peaks were noticed in the gas chromatograms, and there are a variety of other products that could conceivably be formed in this reaction. Any of these products would constitute only a few per cent of the total, however.

Two conceivable SH_2 displacement reactions of 11 are shown in eq 2, but neither is required to explain the observed results. Phthalyl peroxide (3) is known¹⁸

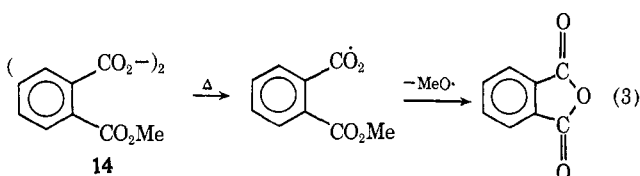
(16) R. Hiatt and K. C. Irwin, *J. Org. Chem.*, **33**, 1436 (1968).

(17) (a) D. H. Hey, B. W. Pengilly, and G. H. Williams, *J. Chem. Soc.*, 1463 (1956); (b) R. L. Dannley and B. Zaremsky, *J. Amer. Chem. Soc.*, **77**, 1588 (1955).

(18) (a) K. E. Russell, *ibid.*, **77**, 4814 (1955). (b) F. D. Greene, *ibid.*, **78**, 2246 (1956); **81**, 1503 (1959).



to be reactive under the conditions of our experiments and would probably not be detected even if it did occur. The SH2 reaction shown in eq 3 has been suggested¹⁹ to occur in the reaction of *o,o'*-dicarbomethoxybenzoyl peroxide (14), but an alternative mechanism¹⁹ involving



hydrogen abstraction and a nonradical cyclization to phthalic anhydride (analogous to eq 1) seems preferable.

Experimental Section

Di-*tert*-butylperoxy phthalate (1) (named in *Chemical Abstracts* as peroxyphthalic acid, di-*tert*-butyl ester) was prepared by the reaction of phthalyl chloride, potassium hydroxide, and *tert*-butyl hydroperoxide²⁰ and was purified by recrystallization from 2:1 pentane-ether at 0°, mp 48.5–49° (lit.²⁰ mp 47–47.5°). The other crystal form,²¹ mp 57–57.5°, was also observed.

***tert*-Butylperoxy hydrogen phthalate (12)** was prepared by the reaction of phthalic anhydride, *tert*-butyl hydroperoxide, and pyridine²¹ and was purified by recrystallization from 4:1 ether-pentane at 0°, mp 105–105.5° (lit.²¹ mp 104–104.5°). The equivalent weight of the acid as determined by base titration was 236 (theory 238) and iodometric titration²² indicated a purity of 96%.

Cumene was purified by washing with sulfuric acid until no further discoloration appeared, washing with water and sodium bicarbonate, drying over calcium chloride, and distillation under nitrogen from sodium at 148–148.5°.

Kinetic Method.—Rate runs were carried out by the ir method.²³ Sample tubes were washed first with nitric acid, then ammonium hydroxide and distilled water, and were thoroughly dried. In each tube was placed 0.5 ml of a 0.06 *M* solution of perester in cumene and the tubes were sealed without degassing. Tubes were placed in the constant-temperature bath and, after 5 min to equilibrate, were removed at intervals. The transmittance of each sample between 1900 and 1650 cm^{-1} was scanned using a Perkin-Elmer 621 spectrophotometer and 0.1-mm sodium chloride cells. Rate constants were calculated from the disappearance of the absorption at 1770 cm^{-1} . During the reaction other absorptions ascribed to phthalic anhydride and acids appeared, but good linear first-order rate plots were obtained during

the period calculated to be the first half-life. At least two runs were made at each temperature, with a maximum deviation of $\pm 3\%$.

Product Studies. I. Di-*tert*-butylperoxy Phthalate (1).—Product studies were carried out by the general procedure of Bartlett and Hiatt.²³ In a typical determination, 1.00 g (0.0034 mol) of perester was dissolved in 10 ml of purified cumene in a glass tube, degassed, and sealed. The sample was heated at 115° for 40 hr. (10 half-lives), cooled, and attached to a vacuum line. The tube was opened to the line *via* a break-seal and the carbon dioxide was absorbed on Ascarite. The amount of methane was determined from the residual pressure after the carbon dioxide had been absorbed. The identification was confirmed by mass spectrometry.

After determination of the gases, the material which was distillable at 25° (0.5 Torr) and trapped by a Dry Ice-isopropyl alcohol bath was removed. A weighed amount of cyclohexane was added as an internal standard, and the amounts of *tert*-butyl alcohol, acetone, and benzene were determined by vpc (10 ft \times 1/8 in. 5% Carbowax 20M on 60/70 Chromosorb G). Identification was confirmed by isolation and spectral comparison with authentic samples.

The residual material was dissolved in hot absolute ethanol. On cooling bicumyl precipitated and was filtered, dried, and weighed. A 0.1 *N* solution of KOH in absolute ethanol was added to the filtrate and the solution was concentrated to a small volume *in vacuo*; water was added and the solution was extracted with chloroform.

The aqueous layer was acidified and extracted with ether (first by shaking and then by continuous extraction for 1 week). The combined ether fractions were dried (MgSO_4), concentrated, and treated with diazomethane in ether. A weighed amount of diethyl phthalate was added as an internal standard and the amounts of ethyl methyl phthalate (from phthalic anhydride) and dimethyl phthalate and methyl benzoate (from their respective acids) were determined by analytical vpc (10 ft \times 1/8 in. 5% SE-30 on Chromosorb W). Identification was confirmed by isolation (preparative vpc on 10 ft \times 1/8 in. 30% SE-30 on Chromosorb W) and spectral comparison with authentic samples. A control experiment with authentic phthalic anhydride gave a 95% conversion to ethyl methyl phthalate and 5% dimethyl phthalate.

Three other esters were also isolated from the reaction product and were identified as the three isomeric isopropyl-*o*-carbomethoxybiphenyls (from the corresponding acids 4–6) by their distinctive nmr spectra. The *o'*-isopropyl isomer (the first eluted) showed a pair of doublets for the diastereotopic isopropyl methyls resulting from slow rotation around the aryl-aryl bond. The yield of these isomers was taken as the difference in weight between the total weight of the acid residue and the combined weights of benzoic and phthalic acids and phthalic anhydride. The ratios of the separate isomers were determined by vpc integration.

The chloroform extract was dried (MgSO_4), filtered, and concentrated *in vacuo*. Preparative vpc (10 ft. \times 3/8 in. 30% SE-30) gave numerous peaks, and the four major ones were isolated. The main fraction was shown to be bicumyl by comparison with authentic material. The three remaining components were identified as the isomeric cumylbenzenes (7–9) by their nmr spectra and comparison of their ir absorptions (ortho at 750, meta at 810, and para at 842 cm^{-1}) with those reported^{17a} for these compounds.

The formation of phthalic anhydride was further confirmed by vpc isolation from material sublimed from the original solid reaction product and comparison with authentic material. Control experiments showed that the phthalic acid did not lead to phthalic anhydride under the reaction and work-up conditions.

II. *tert*-Butylperoxy Hydrogen Phthalate (12).—The volatile products [gases and material distillable at 25° (0.5 Torr)] from reaction at 115° were analyzed by the same procedure as the products of 1. Analysis of the residue by ir showed that phthalic anhydride was the major product, along with traces of acid and bicumyl. The residue was dissolved in warm chloroform and extracted with base. The chloroform layer was dried (CaSO_4) and concentrated *in vacuo* to afford a pale yellow solid. The major component of this solid (over 90%) was identified as bicumyl by vpc and spectral comparison with an authentic sample. The basic extract was acidified and extracted with ether. The ether fraction was dried (CaSO_4) and concentrated *in vacuo* to afford a white solid which was identified as phthalic acid by spectral comparison.

(19) G. I. Nikishin, E. K. Starostin, and B. A. Golovin, *Izv. Akad. Nauk SSSR, Ser. Khim.* 946 (1971), 327 (1972); *Chem. Abstr.*, **75**, 75920c (1971), **77**, 48104z (1972).

(20) N. A. Milas and D. M. Surgenor, *J. Amer. Chem. Soc.*, **68**, 642 (1946).

(21) A. G. Davies, R. V. Foster, and A. M. White, *J. Chem. Soc.*, 1541 (1952).

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

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

When the decomposition of **12** (0.512 g in 20 ml of cumene) was run at 80° for 4 hr, several modifications of the above procedure were used. The volatile liquids were distilled at 25° (0.5 Torr), collected in a Dry Ice-isopropyl alcohol trap, and made up to 25 ml with toluene. A 5-ml aliquot was subjected to iodometric titration. The peroxide content corresponded to a 73% yield of

tert-butyl hydroperoxide. The solid residue from the distillation was shown by ir to be phthalic anhydride, with no detectable bicumyl or acids present.

Registry No.—**1**, 2155-71-7; **10**, 35356-77-5; **11**, 35356-78-6; **12**, 15042-77-0.

Ion Radicals. XXVI. Reaction of Perylene Perchlorate with Cyanide Ion¹

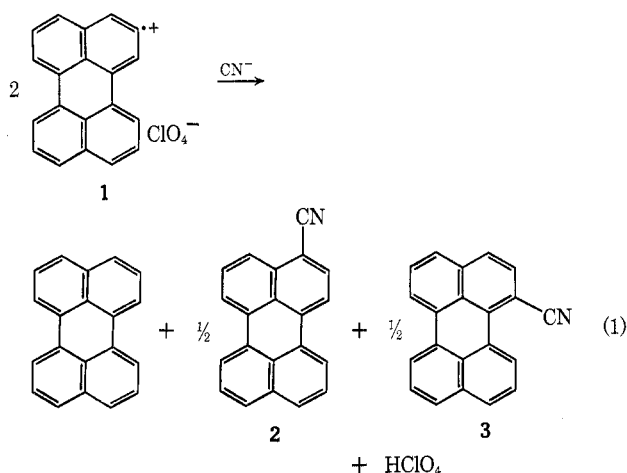
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Reaction of perylene perchlorate (**1**) with potassium cyanide in acetonitrile gave both 3- (**2**) and 1-cyanoperylene (**3**), each in 13% yield. The structure of **3** was deduced from hydrolysis to the carboxylic acid and from reaction with LiAlH₄. Whereas reduction of **2** with LiAlH₄ led to 3-formylperylene, reaction of **3** with LiAlH₄ gave perylene-1-*d* (**4**) and 1'-aza-1,12-benzoperylene-2'-*d* (**5**). The reaction of **1** with cyanide ion is the first we have encountered of substitution in the 1 as well as 3 position of **1**. This is attributed to the high nucleophilicity, small size, and linearity of the cyanide ion.

In previous papers we have shown that perylene perchlorate (**1**) reacts with nucleophiles (NO₂⁻, OAc⁻, Bz⁻, H₂O, pyridine) in the 3 position.^{3,4} Charge densities in the perylene cation radical, according to the simple Hückel MO calculations,⁵ are in accord with this, although one would anticipate that substitution in the 1 position ($q = 0.084$) might occur as well as in the 3 position ($q = 0.110$). This has now been achieved in reaction of **1** with cyanide ion. In addition to the anticipated perylene (eq 1) and 3-cyanoperylene (**2**),



a third product was formed which we deduce from its analysis, parent-peak mass number (277), and reactions to be 1-cyanoperylene (**3**). We believe the stoichiometry^{3,4} of reaction to be as shown in eq 1, according to which the yields of **2** and **3** were each 26% of those anticipated, while the yield of perylene was greater than 100%, signifying that perylene was formed also by another reaction, *e.g.*, reduction by cyanide ion.

Compound **2** is known, having been made *via* the

sequence perylene → 3-formylperylene → 3-formylperylene oxime → **2**.⁶ We confirmed the structure of our **2** by hydrolysis to perylene-3-carboxylic acid,^{6,7} by reduction with lithium aluminum hydride to 3-formylperylene,⁶ and by oxidation of the 3-formylperylene to perylene-3-carboxylic acid, as well as by the direct synthesis of authentic **2**.⁶

As far as we are aware, compound **3** is new. Very few 1-substituted perylenes are known,⁸⁻¹⁰ and we have deduced the structure in the following ways.

Hydrolysis of **3** gave a carboxylic acid, mp 395°. The only known perylenecarboxylic acids are perylene-3- (mp 335°) and perylene-2-carboxylic acid (mp 342°).⁹ The acid with mp 395° had an ultraviolet spectrum similar to but not identical with the spectra of the known acids. The electronic spectra of perylene and its derivatives (alkyl,¹⁰ acyl,⁷ and carboxyl⁷) have numerous bands, and our acid, believed to be perylene-1-carboxylic acid, is no exception.

Zieger attempted to synthesize perylene-1-carboxylic acid by two routes starting with 1-bromohexahydroperylene, but was unsuccessful.⁷ We also were unsuccessful in our attempts to prepare an authentic sample of the acid by oxidation of 1-methylperylene⁸ with aqueous chromic acid, chromium trioxide in acetic acid, and potassium permanganate in acetone. We were unable to isolate products of oxidation, and it is perhaps possible that the perylene ring itself is too susceptible to oxidation to permit alkyl-group oxidation only. We were also unable to reduce **3** to 1-methylperylene by the technique of boiling with limonene over 5% palladium on charcoal.¹¹

Further evidence for the structure of **3** was obtained by reduction with lithium aluminum deuteride (LiAlD₄). Reduction of **2** with LiAlH₄ led to 3-formylperylene easily. Reduction of **3** with LiAlH₄ gave perylene and another compound, isomeric with **3**, whose structure is discussed later. The course of reduction was discerned by use of LiAlD₄. This gave

(1) Part XXV: H. J. Shine, J. J. Silber, R. J. Bussey, and T. Okuyama, *J. Org. Chem.*, **37**, 2691 (1972). Supported by the National Science Foundation, Grant No. GP-25989X.

(2) Postdoctoral Fellow, 1970-1971, supported by a grant from Texas Tech University, no. 191-4719.

(3) C. V. Ristagno and H. J. Shine, *J. Amer. Chem. Soc.*, **93**, 1811 (1971).

(4) C. V. Ristagno and H. J. Shine, *J. Org. Chem.*, **36**, 4050 (1971).

(5) C. A. Coulson and A. Streitwieser, Jr., "Dictionary of π -Electron Calculations," Pergamon Press, New York, N. Y., 1965.

(6) N. P. Buu-Hoi and C. T. Long, *Recl. Trav. Chim. Pays-Bas*, **75**, 1221 (1956).

(7) H. E. Zieger, Ph.D. Dissertation, Pennsylvania State University, 1961.

(8) H. E. Zieger and E. M. Laski, *Tetrahedron Lett.*, 3801 (1966).

(9) H. E. Zieger, *J. Org. Chem.*, **21**, 2977 (1966).

(10) H. E. Zieger and J. E. Rosenkranz, *J. Org. Chem.*, **29**, 2469 (1964).

(11) K. Kindler and K. Luhrs, *Ber.*, **99**, 227 (1966).