

**1,2,3,4-Dibenzo-9,10-dihydrophenanthrene (III).**—The crude oxide was dissolved in 45 cc. of acetic acid, 30 cc. of 34% hydrobromic acid added and the mixture refluxed for twenty-four hours. At the end of this period, the solution was diluted and the product taken up in benzene. The benzene solution was freed from acid and then evaporated. Upon vacuum distillation of the residue, a pale yellow resin was obtained. This material could not be crystallized and so was used directly in the dehydrogenation reaction. A sample of the dihydro compound was converted to the picrate in acetic acid solution giving dark red needles, m. p. 135–136°.

*Anal.* Calcd. for  $C_{28}H_{18}N_3O_7$ : N, 8.25. Found: N, 8.16.

**1,2,3,4-Dibenzophenanthrene (IV).**—The crude cyclization product was heated at 200–220° for thirty minutes with 0.4 g. of sulfur and then at 250° for an additional one and one-half hours. A pinch of zinc dust was added and the mixture heated for fifteen minutes longer. At the

end of this heating, the product was vacuum-distilled directly from the reaction flask. The distillate, once recrystallized from acetic acid gave 1.93 g. (51% calculated from the dihydronaphthalene) of yellow crystals, m. p. 111.5–114°. Recrystallized, the product melted at 115–116° (Hewett<sup>4</sup> 114.5–115°).

*Anal.* Calcd. for  $C_{22}H_{14}$ : C, 94.93; H, 5.07. Found: C, 95.26; H, 4.96.

The hydrocarbon formed a red picrate, m. p. 139.5–140.5° (Hewett<sup>4</sup> 140–140.5°).

Oxidation with sodium dichromate gave a red quinone, m. p. 238–240° (Hewett<sup>4</sup> 237–238°).

### Summary

The olefin oxide type of cyclization has been found to afford a simple and convenient method for the preparation of 1,2,3,4-dibenzophenanthrene.

DURHAM, N. C.

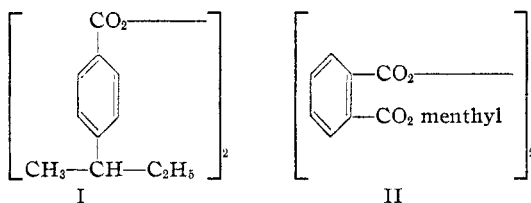
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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

## Optically Active Acyl Peroxides. Preparation, Decomposition, and Use as Catalysts for Vinyl Polymerization<sup>1</sup>

BY C. S. MARVEL, ROBERT L. FRANK<sup>2</sup> AND ERHARD PRILL<sup>3</sup>

This work on optically active acyl peroxides was undertaken in order, (1) to make use of their optical activity in following the kinetics of their thermal decomposition, and (2) to see if asymmetric polymerization of vinyl monomers could be accomplished to yield optically active polymers. Two optically active acyl peroxides, *l-p-s*-butylbenzoyl peroxide (I) and *l-o*-carbomenthoxybenzoyl peroxide (II), have been synthesized for



these studies from the corresponding acid chlorides by treatment with aqueous sodium peroxide.

*p-s*-Butylbenzoic acid was prepared by two methods both starting with *p*-bromo-*s*-butylbenzene. It was obtained in 56% yield by reaction of the Grignard reagent with carbon dioxide and in 64.6% yield by the Rosenmund-von Braun

method using cuprous cyanide,<sup>4</sup> with subsequent hydrolysis of the *p-s*-butylbenzonitrile.

The resolution of *p-s*-butylbenzoic acid was accomplished, after considerable experimentation, through the quinine salt. An acid with a specific rotation of  $-23.5^\circ$  was recovered from the quinine salt after repeated recrystallization from methanol. Regeneration of the acid from the salt obtained by concentrating the mother liquors yielded an acid of specific rotation  $+18.2^\circ$ . Attempted resolutions by means of the salts with brucine, cinchonidine and strychnine all gave poor results.

*l*-Menthyl acid phthalate was prepared according to the method of Pickard and Littlebury.<sup>5</sup>

The kinetics of the thermal decomposition of acyl peroxides in solution has been the object of a number of investigations.<sup>6–10</sup> In each instance the change in peroxide concentration was followed by iodometric determination of the remaining per-

(1) This is the fifteenth communication on vinyl polymers. For the fourteenth see *THIS JOURNAL*, **64**, 2356 (1942).

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(3) Du Pont Post-Doctorate Research Assistant, University of Illinois, 1941–1942.

(4) von Braun and Manz, *Ann.*, **488**, 111 (1931).

(5) Pickard and Littlebury, *J. Chem. Soc.*, **101**, 113 (1912).

(6) Walker and Wild, *ibid.*, 1132 (1937).

(7) Berezovskaya, Semikhatova and Ostrer, *Ber. Inst. physik. Chem. Akad. Wiss. Ukr. S. S. R.*, **9**, 3–16 (1938); *C. A.*, **34**, 2688 (1940).

(8) Berezovskaya and Semikhatova, *ibid.*, **11**, 51–9 (1938); *C. A.*, **34**, 3571 (1940).

(9) D. J. Brown, *THIS JOURNAL*, **62**, 2657 (1940).

(10) Kamenskaya and Medvedev, *Acta Physicochim. U. R. S. S.*, **13**, 565 (1940).

oxide. Walker and Wild<sup>6</sup> found that the thermal decomposition of acetyl peroxide in toluene solution was a first-order reaction with respect to the peroxide. Berezovskaya, Semikhatova and Osterer<sup>7</sup> studied the thermal decomposition of benzoyl peroxide and its *m*- and *p*-nitro derivatives. They found that the order of the reaction in acetone solution was not definite. However, in 30% acetic acid containing sodium acetate, the decomposition followed first-order kinetics. Kamenskaya and Medvedev<sup>10</sup> followed the decomposition of benzoyl peroxide in benzene solution and found that it was a first-order reaction. Recently, Brown<sup>9</sup> studied the decomposition of benzoyl peroxide in benzene and proposed that parallel first- and second-order reactions were involved.

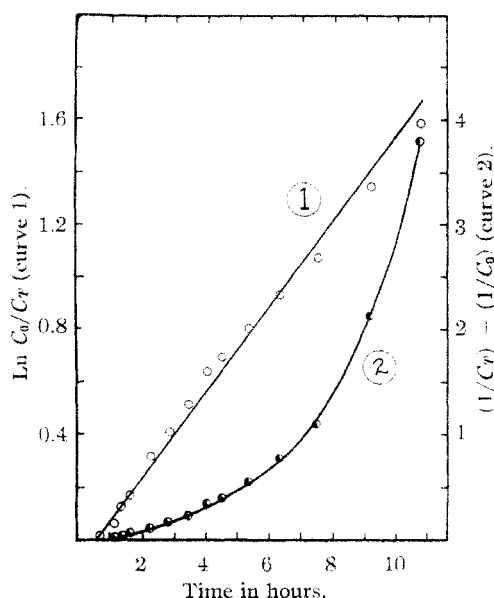


Fig. 1.

In the present work the thermal decomposition studies on *l-p-s*-butylbenzoyl peroxide (I) and *l-o*-carbomenthoxybenzoyl peroxide (II) were carried out in dioxane solution at 55° and the rates of these reactions were followed by changes in the optical rotations of the solutions. The change in concentration of the peroxide was calculated from the equation

$$C_T = \frac{C_0(\gamma_T - \gamma_d)}{\gamma_p - \gamma_d}$$

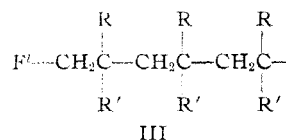
in which  $C_T$  is the concentration of peroxide at time  $T$  (in grams per 100 cc.),  $C_0$  is the initial concentration, and  $\gamma_T$ ,  $\gamma_p$ , and  $\gamma_d$  are the specific rotations of the solution at time  $T$ , the peroxide and the decomposition products, respectively.

The decomposition of *l-p-s*-butylbenzoyl peroxide was carried out at two different concentrations but in neither of these was the change in rotation sufficiently large to give accurate kinetic data. The total rotation changes are recorded in the experimental part.

The decomposition of *l-o*-carbomenthoxybenzoyl peroxide was carried out in dioxane solution at 55° and the data are presented in Fig. 1. The decomposition follows first-order kinetics (Fig. 1, curve 1) for 90% of the reaction. The first-order constant obtained from the graph is  $11.5 \times 10^{-3}$  sec.<sup>-1</sup> and the half life is 1.75 hours. The data also have been considered for second-order kinetics but do not fit (Fig. 1, curve 2).

After completion of the decomposition, the contents of the polarimeter tubes were examined. From the decomposition of *l-p-s*-butylbenzoyl peroxide, the corresponding acid was obtained in 70 and 49% yields. A sample of *dl-p-s*-butylbenzoyl peroxide was decomposed using the same conditions as were used with the active peroxides and a 79% yield of *p-s*-butylbenzoic acid was obtained. No crystalline products could be isolated from the decomposition of *l-o*-carbomenthoxybenzoyl peroxide.

The asymmetric polymerization experiments were carried out with *l-p-s*-butylbenzoyl peroxide (I) using styrene, methyl methacrylate and acrylonitrile. The work of Price, Kell and Krebs<sup>11</sup> has shown that in peroxide-catalyzed vinyl polymerization a fragment of the catalyst is attached at one end of the polymer chain and it was thought possible that if this fragment ( $F^I$  in III) were optically active the resulting polymer (III) might not be as complex a mixture of racemic materials as would be the case in normal polymerizations. This hope was apparently not



realized as polymers produced from the three monomers mentioned above using the optically active peroxide as catalyst could not be distinguished from polymers produced from these monomers under similar conditions using the racemic peroxide or even benzoyl peroxide as catalyst.

(11) Price and Kell, *THIS JOURNAL*, **63**, 2798 (1941); Price, Kell and Krebs, *ibid.*, **64**, 1103 (1942).

### Experimental

***dl-p-s-Butylbenzoic Acid* (from *dl-p-Bromo-s-butylbenzene*).—**Eleven and four-tenths grams of magnesium shavings was placed in a 500-cc. round-bottomed three-necked flask equipped with a stirrer, a reflux condenser and a dropping funnel. This was covered with a small amount of a solution of 98 g. (0.46 mole) of *p-s*-butylbromobenzene<sup>12</sup> in 207 cc. of anhydrous ether. The mixture was warmed slightly for a few minutes until the reaction began, after which the remainder of the solution was added over a period of two hours at a rate sufficient to cause gentle refluxing. The mixture was stirred vigorously during this time. It was then refluxed for five additional hours.

The solution was poured with stirring onto approximately 150 g. of solid carbon dioxide in freshly broken lumps. The material soon set to a nearly solid mass. As soon as the dry-ice had all evaporated, 300 g. of ice, 150 cc. of water and 45 cc. of concentrated hydrochloric acid were added, which decomposed the mass. Solid white material, the desired acid, separated from the mixture. This was dissolved by the addition of 150 cc. of ether. The water layer was drawn off, extracted with three 25-cc. portions of ether, and then discarded. The ether extract was added to the main yellow ether layer. This was washed with 4% hydrochloric acid and was then extracted with four portions of 10% sodium carbonate solution. Two grams of "Norite" was added and the mixture was stirred and filtered by suction, after which the filtrate was acidified with 150 cc. of concentrated hydrochloric acid. A pure white precipitate resulted which was separated by suction filtration and recrystallized from 3400 cc. of 40% aqueous alcohol. The yield was 45.9 g. (56%) of *dl-p-s*-butylbenzoic acid melting at 91–92°.

*Anal.*<sup>13</sup> Calcd. for  $C_{11}H_{14}O_2$ : C, 74.13; H, 7.92. Found: C, 74.50; H, 8.09.

***dl-p-s-Butylbenzonitrile*.**—This was prepared according to the directions of Newman<sup>14</sup> from 102 g. (0.48 mole) of *dl-p-bromo-s-butylbenzene*<sup>9</sup> and 61.0 g. (0.67 mole) of cuprous cyanide.<sup>15</sup> The product was a colorless liquid boiling at 78–80° (4 mm.);  $d_{20}^4$  0.926;  $n_D^{20}$  1.5310. The yield was 64.2 g. (84%).

*Anal.* Calcd. for  $C_{11}H_{13}N$ : N, 8.80. Found: N, 8.75.

***dl-p-s-Butylbenzoic Acid* (from *dl-p-s-Butylbenzonitrile*).—**In a 500-cc. round-bottomed three-necked flask equipped with a stirrer, a dropping funnel and a condenser was placed 250 g. of 75% sulfuric acid. The temperature of the flask was raised to 150° by means of an oil-bath and 64.2 g. (0.404 mole) of *dl-p-s*-butylbenzonitrile was added through a dropping funnel over a period of two hours. The mixture was stirred at 150° for an additional two hours and the temperature was then raised to 190° for another hour.

The black contents of the flask solidified on cooling.

(12) Copenhagen, Roy and Marvel, *THIS JOURNAL* **57**, 1311 (1935).

(13) The analyses reported in this paper are microanalyses and were carried out by Mr. L. G. Fauble, Miss Margaret McCarthy and Miss Theta Spoor.

(14) Newman, *THIS JOURNAL*, **59**, 2472 (1937).

(15) Supniewski and Salzberg, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., second edition, 1941, p. 46.

The material was placed in ice water and the black solid removed by filtration. It was dissolved in 10% sodium hydroxide solution and reprecipitated with excess dilute sulfuric acid. The precipitate, still black, was separated by filtration. It was then dissolved in 500 cc. of benzene and heated with 8 g. of "Darco." The filtered solution was brown in color, and this was not altered by a second treatment with "Darco." The benzene solution was concentrated on a steam-bath and the solid crystalline precipitate obtained on cooling was removed by filtration. It was recrystallized from 400 cc. of 70% aqueous methanol and melted at 93.5–94°. A mixed melting point with the acid previously obtained by the Grignard reaction showed no depression. The acid, weighing 57.8 g., was still slightly brown in color, but one additional crystallization from 70% aqueous methanol gave a white product of the same melting point which weighed 49.7 g. The mother liquors yielded an additional 5.4 g. of pure product. The total yield was 55.1 g. (76.7%).

**Resolution of *p-s*-Butylbenzoic Acid by Means of Quinine.**—Fifty and seven-tenths grams (0.285 mole) of *p-s*-butylbenzoic acid and 92.4 g. (0.285 mole) of anhydrous quinine were placed in a 2-liter Erlenmeyer flask with 1250 cc. of methanol. The material dissolved on heating and the solution was filtered using a hot-water funnel. The filter was washed with 100 cc. of methanol. The solution was placed in the icebox for two days and yielded after this time 83.1 g. of crystals. These were recrystallized from 500 cc. of methanol and yielded 63.4 g. of crystalline salt,  $[\alpha]_D^{25} -129.0^\circ$  (0.1168 g. in 5 cc. of methanol solution). This salt was recrystallized from 300 cc. of methanol and 40.5 g. of crystalline product was obtained,  $[\alpha]_D^{25} -134.2^\circ$  (0.1001 g. in 5 cc. methanol solution).

The quinine salt was then decomposed by solution in 100 cc. of glacial acetic acid. The addition of 500 cc. of water precipitated the regenerated *p-s*-butylbenzoic acid from the solution. It was removed by filtration and recrystallized from 70% aqueous methanol. The yield was 15 g. (59.2%), m. p. 89–90°. An additional recrystallization gave a product melting at 90.5–91.5°,  $[\alpha]_D^{25} -12.53^\circ$  (0.0998 g. in 5 cc. methanol solution).

The 15 g. of *p-s*-butylbenzoic acid obtained by the above partial resolution was reconverted to the quinine salt (27.0 g. of quinine) and the salt was recrystallized three times from 250 cc. of methanol,  $[\alpha]_D^{25} -138.4^\circ$  (0.1032 g. in 5 cc. methanol solution). It melted at 184–185°.

*Anal.* Calcd. for  $C_{31}H_{39}N_2O_4$ : C, 74.10; H, 7.62. Found: C, 74.14; H, 7.67.

The salt was decomposed in 100 cc. of 20% hydrochloric acid, the mixture was cooled in ice, and the acid separated by filtration. It was then recrystallized from 70% aqueous methanol. The yield was 5.0 g. (19.7%), melting at 88.5–89°,  $[\alpha]_D^{25} -23.5^\circ$  (0.1031 g. in 5 cc. methanol solution).

*Anal.* Calcd. for  $C_{11}H_{14}O_2$ : C, 74.13; H, 7.92. Found: C, 74.02; H, 7.95.

The resolution was repeated several times and in most of these trials the specific rotations of the products approached  $-23.5^\circ$ .

By a series of concentrations of the mother liquors from

the above resolution and removal of the less-soluble crops of crystals, it was possible to isolate a sample of the quinine salt of  $[\alpha]^{27D} -121.5^\circ$  (0.1025 g. in 5 cc. methanol solution). The acid recovered from this had a positive rotation,  $[\alpha]^{30D} + 18.2^\circ$  (0.1059 g. in 5 cc. methanol solution).

**Attempted Resolutions of *p*-s-Butylbenzoic Acid by Means of Brucine, Cinchonidine and Strychnine.**—Equimolar amounts of the acid and brucine yielded a crystalline salt after solution in 66% aqueous methanol. This was recrystallized six times from the same solvent to yield a salt which melted at 105–115° with decomposition,  $[\alpha]^{25D} -22.2^\circ$  (0.1033 g. in 5 cc. methanol solution). The acid was regenerated by means of hydrochloric acid and, recrystallized from 70% aqueous methanol, melted at 93–94°,  $[\alpha]^{25D} -6.0^\circ$  (0.0755 g. in 5 cc. methanol solution).

*p*-s-Butylbenzoic acid was treated in a similar fashion with cinchonidine and with strychnine. The cinchonidine salt, after three recrystallizations from methanol, ( $[\alpha]^{25D} -83.8^\circ$  (0.1006 g. in 5 cc. methanol solution)) yielded on treatment with hydrochloric acid an active acid, m. p. 92°;  $[\alpha]^{25D} -8.2^\circ$  (0.1019 g. in 5 cc. methanol solution). The strychnine salt, recrystallized from 66% aqueous methanol, showed the following rotation:  $[\alpha]^{25D} -15.3^\circ$  (0.1034 g. in 5 cc. methanol solution). The regenerated acid, three times recrystallized from 70% aqueous methanol, melted at 90.5–91°,  $[\alpha]^{25D} 0.0^\circ$  (0.1023 g. in 5 cc. methanol solution).

***dl*- and *l*-*p*-s-Butylbenzoyl Chlorides.**—A mixture of 15 g. (0.084 mole) of *dl*-*p*-s-butylbenzoic acid, 20 g. (0.168 mole) of thionyl chloride and a few drops of pyridine was kept at room temperature for two days. It was then refluxed for one hour and distilled to give 14.7 g. (89%) of the acid chloride, which boiled at 152–154° (28 mm.) (135–137° (15 mm.)).

*Anal.* Calcd. for  $C_{11}H_{13}ClO$ : Cl, 18.03. Found: Cl, 18.12.

*l*-*p*-s-Butylbenzoyl chloride was prepared in the same manner from 4.17 g. (0.0234 mole) of the *l*-acid and 11.1 g. (0.093 mole) of thionyl chloride. The yield was 4.24 g. (92%) of the acid chloride, b. p. 143–144° (20 mm.).

*Anal.* Calcd. for  $C_{11}H_{13}ClO$ : Cl, 18.03. Found: Cl, 18.13.

***dl*- and *l*-*p*-s-Butylbenzoyl Peroxides.**—A solution of 10.0 g. (0.051 mole) of *dl*-*p*-s-butylbenzoyl chloride in 10 cc. of dry benzene was added dropwise over a period of fifteen minutes to a stirred solution of 5.0 g. (0.064 mole) of sodium peroxide in 40 cc. of water kept at 0°. Stirring was continued for seven hours. Ether was then added and the layers were separated after shaking. The ether extract was washed once with water and dried over sodium sulfate. The ether was then evaporated from the dried solution and the residue (9.0 g.) was crystallized from 40 cc. of methanol to yield 7.2 g. of needles which melted at 45–47°. The mother liquor was concentrated and a second crop of crystals (0.8 g.) separated which melted at 38–40°. The second crop, on recrystallization from methanol, yielded 0.51 g. of the peroxide melting at 45–46°. The 7.2-g. and 0.51-g. crops were combined and recrystallized to give 7.6 g. (84%) of *dl*-*p*-s-butylbenzoyl peroxide melting at 47.5–49°. The melting point could be raised by further recrystallization to 49–50°.

*Anal.* Calcd. for  $C_{22}H_{26}O_4$ : C, 74.63; H, 7.40. Found: C, 74.71; H, 7.57.

An analysis for peroxide content by the method of Liebafsky and Sharkey<sup>16</sup> gave a value of 99.0% (0.0215 g. peroxide; 11.68 cc. of 0.0103 *N* sodium thiosulfate).

*l*-*p*-s-Butylbenzoyl peroxide was prepared in a similar manner using 4.24 g. (0.0216 mole) of *l*-*p*-s-butylbenzoyl chloride in 6 cc. of dry benzene and 2.5 g. (0.032 mole) of sodium peroxide in 20 cc. of water. The yield was 1.70 g. which melted at 48–49°. The residue from the mother liquors could not be crystallized (the active peroxide was consistently more difficult to purify than the racemic form). Therefore, the solvent was removed and the semi-solid mass was treated with cold, dilute sodium hydroxide solution. The insoluble material (0.44 g.) was removed by filtration and crystallized from methanol to give 0.36 g. of the peroxide which melted at 45.5–47°. The total yield was 2.06 g. (55.0%),  $[\alpha]^{27D} -29.0^\circ$  (0.0483 g. in 5 cc. dioxane solution).

*Anal.* Calcd. for  $C_{22}H_{26}O_4$ : C, 74.63; H, 7.40. Found: C, 74.72; H, 7.63.

An analysis for peroxide content by the method of Liebafsky and Sharkey<sup>13</sup> gave a value of 98.4% (0.0219 g. peroxide; 11.82 cc. of 0.0103 *N* sodium thiosulfate).

The alkaline extract from the treatment above and the aqueous layer from the original reaction mixture were acidified to give 1.51 g. (39.3%) of *l*-*p*-s-butylbenzoic acid which melted at 87.5–89°.

***l*-Menthyl Acid Phthalate.**—The procedure used by Pickard and Littlebury<sup>3</sup> to isolate *l*-menthol as its acid phthalate from a mixture of menthols and menthones was adapted to the preparation of this compound. A mixture of phthalic anhydride (20.0 g.) and *l*-menthol (20.0 g.) was heated in an oil-bath kept at 120–125° for twelve hours. While still warm, the reaction mixture was poured into 800 ml. of 2% sodium carbonate. A taffy-like material was formed which dissolved on standing overnight. The solution was extracted with two portions of ether to remove any methanol and dimethyl phthalate. After acidification, the solution was extracted with three portions of chloroform. The residue remaining after removal of the chloroform was crystallized from dilute acetic acid. Fine white needles (34.0 g., 87%) were obtained which melted at 108.5–110°.

***l*-o-Carbomethoxybenzoyl Peroxide.**—A mixture of *l*-menthyl acid phthalate (10.0 g.), thionyl chloride (10 ml.) and one drop of pyridine was kept at room temperature for three hours. The excess thionyl chloride was then removed under diminished pressure at 40° followed by the addition and removal of two portions of dry benzene. A solution of the acid chloride in dry benzene (10 ml.) was then added over a period of twenty minutes to a stirred solution of sodium peroxide (5.0 g.) in water (40 ml.) kept at 0°. The stirring was continued for three hours. Ether was added to the reaction mixture and the organic layer was washed once with water and dried over anhydrous sodium sulfate. Most of the ether was removed on the steam-bath and the remainder was removed under diminished pressure. The solid residue was crystallized from chloroform-methanol mixture and colorless cubes (4.60 g., 46%) were obtained which melted at 117–118°.

(16) Liebafsky and Sharkey, *THIS JOURNAL*, **62**, 190 (1940).

with decomposition;  $[\alpha]^{27D} -91.6^\circ$  (0.0472 g. made up to 5 cc. with dioxane,  $\alpha -1.73^\circ$ ).

*Anal.* Calcd. for  $C_{10}H_{12}O_4$ : C, 71.26; H, 7.64. Found: C, 71.52, 71.52; H, 7.94, 7.82.

**Kinetic Studies on the Decomposition of Optically Active Peroxides.**—Special water-jacketed 1-dm. polarimeter tubes of Pyrex glass made by the Macalaster Bicknell Company of Cambridge, Massachusetts, were used for the decomposition studies. During a run the tube was kept in a constant temperature bath at  $55^\circ$  and while the polarimeter readings were taken water from the bath was circulated through the jacket of the tube by means of a small centrifugal pump.

In the first experiment, 0.5031 g. of *l-p-s*-butylbenzoyl peroxide was dissolved in purified dioxane and diluted to 10 cc. with the same solvent. The observed rotation of the solution at  $30^\circ$  was  $-1.49^\circ$ ;  $[\alpha]^{30D} -29.6^\circ$ . The polarimeter tube was placed in the constant temperature bath and the reading was taken when the contents of the tube had reached  $55^\circ$  (about fifteen minutes). The initial value of the observed rotation at  $55^\circ$  was  $-1.37^\circ$ . After twenty-four hours the rotation remained constant at  $-1.17^\circ$ .

The contents of the polarimeter tube was concentrated to an oil using a stream of air and the residue was subjected to steam distillation from an alkaline solution. Only a trace of hydrocarbon (detected by its odor) was present in the distillate. The residue from the steam distillation was acidified to give 0.35 g. of *l-p-s*-butylbenzoic acid which melted at  $86-87.6^\circ$  after crystallization from 70% methanol;  $[\alpha]^{25D} -24.1^\circ$  (0.1007 g. made up to 5 cc. with methanol,  $\alpha -0.97^\circ$ ).

The decomposition was repeated using 1.0001 g. of *l-p-s*-butylbenzoyl peroxide dissolved in sufficient purified dioxane to make 5 cc. of solution. The observed rotation of the solution at  $30^\circ$  was  $-4.84^\circ$ ;  $[\alpha]^{30D} -24.2^\circ$ .<sup>17</sup> The initial observed rotation at  $55^\circ$  was  $-4.51^\circ$  and after thirty-three hours the rotation remained constant at  $-3.84^\circ$ .

The contents of the polarimeter tube was added to a large volume of ether and the dioxane was washed out of the resulting solution with water. After drying the ether solution over anhydrous sodium sulfate, the ether was removed and the residue was crystallized from 70% methanol to give 0.49 g. of *l-p-s*-butylbenzoic acid which melted at  $84-86^\circ$ ;  $[\alpha]^{25D} -18.6^\circ$  (0.1074 g. made up to 5 cc. with methanol,  $\alpha -0.80^\circ$ ).

A solution of *dl-p-s*-butylbenzoyl peroxide (3.0 g.) in purified dioxane (60 ml.) was heated at  $55^\circ$  for four days. The dioxane was removed at  $40^\circ$  with a stream of air under slightly diminished pressure. Dilute sodium hydroxide was added to the nearly solid residue and the mixture was subjected to steam distillation. Only a trace of steam-volatile material was obtained. The residue from the steam distillation was acidified and the precipitated solid was removed by filtration. The crude *dl-p-s*-butylbenzoic acid (2.38 g., 79%) melted at  $90-91^\circ$  after two crystallizations from 70% methanol.

(17) The specific rotation of the peroxide is low in this case because, due to the limited supply of active *p-s*-butylbenzoic acid, a less completely resolved sample of the acid was used for the preparation of this sample of peroxide.

A thermal decomposition experiment was carried out using 0.9869 g. of *l-o*-carbomethoxybenzoyl peroxide made up to 10 cc. with purified dioxane. The observed rotation of the solution at  $25^\circ$  was  $-9.17^\circ$ ;  $[\alpha]^{25D} -92.9^\circ$ . The initial reading at  $55^\circ$ , which was  $-8.88^\circ$ , was made after about fifteen minutes. An average of three polarimeter readings was taken for each observation. After twenty-four hours the rotation remained constant at  $-7.35^\circ$ . These results are plotted in Fig. 1. No crystalline decomposition products could be isolated from the contents of the polarimeter tube.

**Preparation of Polymers.**—Freshly-distilled methyl methacrylate was caused to polymerize according to the directions of Strain.<sup>18</sup> Twenty grams of methyl methacrylate, 40 g. of water and 40 g. of methanol were placed in a 125-cc. Erlenmeyer flask with 0.0196 g. of benzoyl peroxide (Lucidol recrystallized once from methanol) and the flask was placed in a constant temperature bath for five days. Two similar flasks were prepared, one containing 0.0291 g. of *dl-p-s*-butylbenzoyl peroxide in place of benzoyl peroxide, the other containing 0.0289 g. of *l-p-s*-butylbenzoyl peroxide. The polymers precipitated as fine powders from the solutions and were removed by filtration, washed with methanol and air dried. The yields were 16.1–18.5 g.

Three mixtures of 20 g. of freshly-distilled styrene and 80 g. of dioxane each were heated at  $50^\circ$  for five days with 0.0202 g. of benzoyl peroxide and 0.0289 g. each of *dl*- and *l-p-s*-butylbenzoyl peroxides. At the end of this time the solutions were cooled in ice water and poured with stirring into 300 cc. of cold alcohol. The resultant precipitates were removed by filtration, air dried and powdered. The yields ranged from 2.1 g. to 4.5 g.

Polycrylonitrile was prepared in the same manner as polystyrene from 9 cc. of freshly-distilled acrylonitrile in 41 g. of dioxane. The amounts of peroxides were the same as with styrene. This polymer precipitated directly in the reaction flask as a fine powder which was removed and dried in an oven at  $65^\circ$ . The yields were 3.7–4.7 g.

**Optical Rotation of the Polymers.**—No rotation at  $30^\circ$  was shown by 0.0527 g. in 5 cc. of dioxane solution of polymethyl methacrylate which had been prepared by *l-p-s*-butylbenzoyl peroxide catalyst.

Likewise, 0.0578 g. of polystyrene formed by *l*-peroxide catalysis showed no rotation at  $30^\circ$  in 5 cc. of dioxane solution.

The polyacrylonitrile polymer was insoluble in dioxane, chloroform and *N*-dimethylacetamide; its rotation was, therefore, not determined.

## Summary

1. The preparation of two optically active acyl peroxides, *l-p-s*-butylbenzoyl peroxide and *l-o*-carbomethoxybenzoyl peroxide, has been described.

2. The thermal decomposition of *l-o*-carbomethoxybenzoyl peroxide has been followed by optical methods and found to follow first-order kinetics.

(18) Strain, U. S. Patent 2,121,839 (June 28, 1938).

3. No evidence that use of an optically active peroxide will cause an asymmetric synthe-

sis in vinyl polymerization has been obtained.  
URBANA, ILLINOIS

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## NOTES

### Trimolecular Acetone Peroxide in Isopropyl Ether

BY FRED ACREE, JR., AND H. L. HALLER

During the past few years several notes have appeared in the literature citing explosions of isopropyl ether.<sup>1</sup> In all cases the ether had stood for several years and the explosion hazard was attributed to the formation of peroxides. So far as we have been able to learn, the responsible peroxide has not been isolated or described.

Recently, while an organic compound was being crystallized from isopropyl ether,<sup>2</sup> the mother liquor was evaporated on the steam-bath with the aid of a stream of air to about one-third of its original volume. On standing at room temperature, a crop of crystals, resembling common salt, separated. They melted at 94°. On recrystallization from methyl alcohol the melting point was 98°. The compound sublimed readily at room temperature, liberated iodine from potassium iodide solution, and exploded on percussion or when heated on a platinum spatula. A molecular weight determination by the Signer method as modified by Clark<sup>3</sup> gave a value of 221. The compound possessed all the properties of trimolecular acetone peroxide,<sup>4</sup> and a mixture melting point determination of the unknown peroxide with an authentic sample of trimolecular acetone peroxide showed them to be identical.

Trimolecular acetone peroxide was readily obtained in crystalline form from four out of five lots of isopropyl ether, all of which gave qualitative tests for peroxides, when the ether was evaporated to one-third of its original volume on the steam-bath with a stream of air. The fifth

lot gave a viscous sirup from which no crystals of the trimolecular acetone peroxide were obtained.

It is of interest to note that Radulesco<sup>5</sup> found that the photochemical oxidation of isopropyl ether was slightly autocatalytic and produced acetone, water, peroxides, acids, and gum; and that Brown<sup>6</sup> has shown the formation of acetone when the ether mixed with oxygen is passed over a silver catalyst. Whether other peroxides are also present in isopropyl ether has not been determined. Trimolecular acetone peroxide is possibly responsible for the peroxide test found by Redemann<sup>7</sup> with isopropanol.

(5) G. Radulesco, *Ann. combustible liquides*, **13**, 1071 (1938).

(6) R. L. Brown, U. S. Patent 2,246,569, June 24, 1941.

(7) C. E. Redemann, *THIS JOURNAL*, **64**, 3049 (1942).

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### Some Fluorinated Compounds of Possible Chemotherapeutical Interest

BY E. BOGRACHOV

In the course of experiments on lipophilic chemotherapeuticals<sup>1</sup> an investigation of fluorinated compounds was undertaken. As these experiments cannot be continued at present, a brief description of three of the new substances prepared may be permitted. They were obtained in well-crystallized and undoubtedly pure form. While the hydrogen and nitrogen analyses (Dumas) were satisfactory, the carbon values were throughout too low, most probably due to the formation of the volatile, stable carbon tetrafluoride.<sup>2</sup>

**N-(*o*-Fluorobenzoyl)-1-amino-4-(benzene-azo)-naphthalene.**—4-(Benzeneazo)-1-naphthylamine (12.3 g.) was dissolved in dry chloroform (100 cc.), and the solution, after addition of pyridine (4 g.), cooled to 0°. At this tempera-

(1) Bergmann, *et al.*, *THIS JOURNAL*, **63**, 2243, 2245 (1941).

(2) Satisfactory values can be obtained only by combustion with lead chromate and silver, not with the method usually applied in microcombustion analysis. Wallach and Heusler, *Ann.*, **248**, 243 (1888); Schiemann and Bolstad, *Ber.*, **61**, 1407 (1928).

(1) (a) E. F. Degering, *J. Chem. Ed.*, **13**, 494 (1936); (b) B. L. Herrington, *Ind. Eng. Chem., News Ed.*, **20**, 1458 (1942); (c) G. T. Morgan and R. H. Pickard, *Chem. and Ind.*, **55**, 421 (1936); (d) E. C. Williams, *J. Soc. Chem. Ind.*, **55**, 580 (1936).

(2) The ether was a commercial grade that had stood in the laboratory in clear glass bottles for at least five years. It was not purified before use.

(3) E. P. Clark, *Ind. Eng. Chem., Anal. Ed.*, **13**, 820 (1941).

(4) R. Wolfenstein, *Ber.*, **28**, 2265 (1895).