

tion of solvents, there was obtained 6.2 g of crude *N*-benzylidibromoacetamide (39% yield based on acid halide). Upon recrystallization this material had a mp of 133.5–134.5°C.

Anal. Calcd for  $C_9H_9Br_2NO$ : C, 35.21; H, 2.92; N, 4.56; Found: C, 35.45; H, 2.80; N, 4.57.

**Isolation of I in Hexane.**—An 80-ml portion of I reaction solution obtained by dehalogenation as described above containing 3.6 g of I was vigorously stirred while 100 ml of dry hexane was added dropwise under a nitrogen atmosphere. This resulted in the precipitation of the zinc halide. After the addition, the hexane solution was separated from the precipitated zinc halide with a pipet. The ether was removed by distillation to yield 100 ml of a hexane solution containing 3 g of I. This hexane solution was assayed as described previously.<sup>5</sup> An infrared spectrum of this solution showed the characteristic absorption of  $C=C=O$  at  $1970\text{ cm}^{-1}$ .

The ketene could be concentrated in hexane by simply removing some of the hydrocarbon by distillation at reduced pressure. The ketene does not distill with hexane.

**Preparation of I by Dehydrohalogenation.**—A solution containing 11.0 g (0.047 mole) of dibromoacetyl chloride and 25 ml of dry heptane was added with stirring to 100 ml of heptane and 5.0 g (0.05 mole) of triethylamine at 0–5°. This addition was made under nitrogen atmosphere. The acid halide solution was added dropwise over a period of 30 min and stirring was continued in the cold for 1 hr. A solid separated from the reaction solution during the course of addition. This material was separated from the reaction solution by filtration and found to contain 6.5 g of triethylammonium chloride. The remaining material was black and tacky, could not be vacuum distilled, and appeared to be polymeric. The filtrate was treated with an excess of benzylamine. This solution was washed with dilute hydrochloric acid and finally water. Drying and evaporation of the solvent yielded 2 g of solid which upon recrystallization was found to be identical with *N*-benzylidibromoacetamide described above. This corresponds to a yield of 14% based on the acid halide.

**Preparation of 7,7-dibromobicyclo[3.2.0]hept-2-en-6-one, the Cycloadduct of I and Cyclopentadiene.**—A solution containing 14.5 g (0.144 mole) of triethylamine, 75 g (1.15 mole) of cyclopentadiene and 100 ml of dry hexane was cooled to 0–5° under a nitrogen atmosphere. A solution of 29.6 g (0.115 mole) of dibromoacetyl chloride in 25 ml of anhydrous hexane was added dropwise to the cooled solution over a period of 30 min. After the addition, the reaction mixture was allowed to stir for an additional 2 hr. The triethylammonium chloride which precipitated during the addition was removed by filtration. The filtrate was then concentrated on a steam bath. The residue was vacuum distilled. The high boiling portion was fractionated to yield 15.1 g at 71.5–73.5° at 0.3 mm. This corresponds to a 58% yield. This cycloadduct darkened on standing at room temperature: infrared absorption (smear),  $1800\text{ cm}^{-1}$  (s) and  $1600\text{ cm}^{-1}$  (w); nmr spectrum ( $CCl_4$ ), pair of multiplets at 5.9 and 6.2 ( $-CH=CH-$ ), multiplet at 4.3 ( $>CH-$ ), and multiplet at 2.7 ppm (methylene). These peak areas were in the ratio of 1:1:1.

Anal. Calcd for  $C_7H_8Br_2O$ : C, 31.61; H, 2.27; Br, 60.09. Found: C, 31.55; H, 2.35; Br, 59.81; mol wt, 276.

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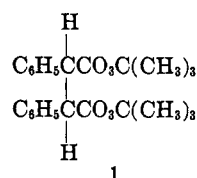
### Peroxy Esters. *meso*-Di-*t*-butylperoxy 2,3-Diphenylsuccinate

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Our continuing interest in peroxy esters and their modes of decomposition has prompted us to prepare *meso*-di-*t*-butylperoxy 2,3-diphenylsuccinate (1).



The simultaneous cleavage of two bonds during the thermal decomposition of many peroxy esters has been well established,<sup>2</sup> and there is evidence that in certain cases three bonds may be breaking in the rate-determining step.<sup>3</sup> Attempts<sup>2,4</sup> have been made to detect concerted four-bond cleavage, but in no case has evidence for such a reaction been found.

The rate constants for the decomposition of 1 in cumene at three temperatures are recorded in Table I. The kinetic plots showed good first-order behavior

TABLE I  
RATE CONSTANTS FOR THE DECOMPOSITION OF  
*meso*-Di-*t*-BUTYLPEROXY 2,3-DIPHENYLSUCCINATE IN CUMENE  
( $\Delta H^* = 30\text{ kcal/mole}$ ;  $\Delta S^* = 12\text{ cal/deg mole}$ )

| Temp.,<br>°C | Concn,<br>mole/l. | $k \times 10^{-6}$<br>sec <sup>-1</sup> |
|--------------|-------------------|---|
| 90.0         | 0.009             | 120                                     |
| 90.0         | 0.09              | 124                                     |
| 79.9         | 0.009             | 32.9                                    |
| 79.9         | 0.09              | 33.6                                    |
| 70.1         | 0.009             | 9.83                                    |
| 70.1         | 0.09              | 9.89                                    |

for >80% of the decomposition. There were only slight changes in the rate constants when the concentration of the peroxy ester was increased tenfold. This strongly suggests, although does not prove, that no induced decomposition is taking place and that the decomposition is truly first order. Activation parameters for this peroxy ester calculated from the rate constants are  $\Delta H^* = 30\text{ kcal/mole}$  and  $\Delta S^* = 12\text{ cal/deg}$ .

The products from the decomposition of 1 in cumene are tabulated in Table II. *cis*-Stilbene and bibenzyl were not found among the nonvolatile products. *cis*-Stilbene is not converted to *trans*-stilbene under the conditions of the experiment.

TABLE II  
PRODUCTS OF DECOMPOSITION OF *meso*-Di-*t*-BUTYLPEROXY  
2,3-DIPHENYLSUCCINATE IN CUMENE AT 80°<sup>a</sup>

| Product                 | Mg                | mmoles | Mole/mole<br>of<br>peroxy ester |
|-------------------------|-------------------|--------|---------------------------------|
| Carbon dioxide          | 82.8 <sup>b</sup> | 1.88   | 1.84                            |
|                         | 83.6 <sup>c</sup> | 1.90   | 1.86                            |
| <i>t</i> -Butyl alcohol | 140.8             | 1.92   | 1.88                            |
| Acetone                 | Trace             |        |                                 |
| <i>trans</i> -Stilbene  | 151.2             | 0.84   | 0.82                            |
| Dicumyl                 | 169               | 0.50   | 0.49                            |
| Unidentified            | 120               |        |                                 |

<sup>a</sup> Peroxy ester: 440 mg, 1.02 mmoles; cumene: 10 ml. <sup>b</sup> By volume. <sup>c</sup> By weight.

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TABLE III  
ACTIVATION PARAMETERS OF PEROXY ESTERS

| Compound 1   | $\Delta H^*$ | $\Delta S^*$ |
|--|--------------|--------------|
| <i>t</i> -Butylperoxy trimethylacetate <sup>a</sup>      | 30           | 12           |
| <i>t</i> -Butylperoxy phenyldimethylacetate <sup>b</sup> | 26.1         | 5.8          |
| <i>t</i> -Butylperoxy phenylacetate <sup>a</sup>         | 28.1         | 2.2          |

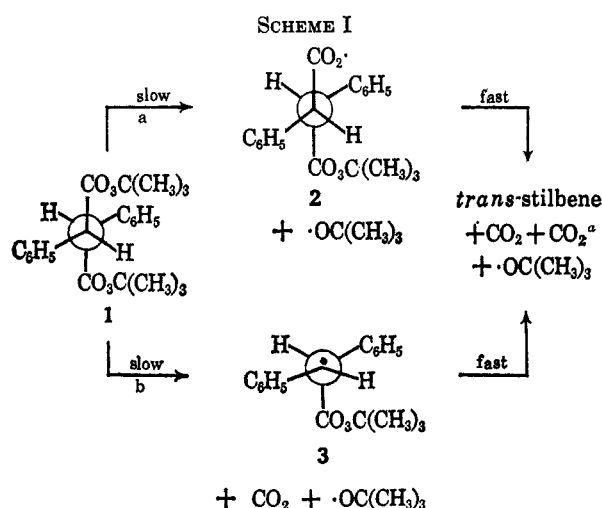
<sup>a</sup> P. D. Bartlett and D. M. Simons, *J. Am. Chem. Soc.*, **82**, 1753 (1960). <sup>b</sup> P. D. Bartlett and R. R. Hiatt, *ibid.*, **80**, 1398 (1958).

A comparison of the activation parameters of **1** with those of other peroxy esters is made in Table III. The relatively high entropy of activation of **1** suggests that (1) all conformations of the molecule are favorable for producing a stabilized radical (two-bond cleavage) or three stable molecules (four-bond cleavage) on decomposition, or (2) the conformation of the molecule in the ground state is frozen and further orientation or reorientation as the transition state is approached is severely restricted. In other words, either the molecule *need not* orient itself, or it *cannot* orient itself.

If all conformations of the molecule are favorable for production of a stabilized radical one would expect the enthalpy of activation for the decomposition of **1** to be lower than that of *t*-butylperoxy phenylacetate (1-phenylethyl radical *vs.* benzyl radical), but it is 2 kcal/mole higher. The enthalpy of activation should also be much lower than observed if all conformations of **1** are favorable for decomposition to three stable molecules.

The fact that both the enthalpy and entropy of activation are so high is evidence for a frozen conformation in the ground state that will not permit the orientation necessary for the maximum stabilization of the incipient radical in the transition state. This does not, however, prevent simultaneous two-bond cleavage but merely raises the energy requirement for it to occur. A space-filling model of **1** demonstrates that rotation is severely limited in the ground state.

These arguments, coupled with the nearly quantitative yield of carbon dioxide and the absence of bibenzyl or *cis*-stilbene in the products, suggest that the decomposition of **1** proceeds through a rate-determining one-bond cleavage followed by a rapid decomposition of the intermediate radical **2** (route a) (Scheme I), or a rate-determining two-bond cleavage



<sup>a</sup> From route a only.

followed by a rapid decomposition of the intermediate radical **3** (route b). No distinction can be made between these two possibilities at the present time.

The failure to observe simultaneous four-bond cleavage may, of course, be due to many factors. In the present case, however, the steric constraint on the system, *i.e.*, the inability of the molecule to assume the most favorable conformation in the transition state, appears to have precluded four-bond cleavage.

#### Experimental Section<sup>6</sup>

**Materials.**—Cumene was purified as described by Bartlett, *et al.*<sup>3a</sup> *t*-Butyl hydroperoxide 70 obtained from the Lucidol Division of Wallace and Tiernan, Inc., was used without further purification. Potassium *t*-butylperoxide was prepared according to the procedure of Kornblum and de la Mare.<sup>6</sup>

**meso-2,3-Diphenylsuccinic Acid.**—This acid was obtained through the hydrolysis of the dinitrile<sup>7</sup> as described by Wawzonek.<sup>8</sup> The acid was purified through its potassium salt. Further purification could be achieved by recrystallization from hot ethyl alcohol. Two melting points were obtained for different batches of the diacid, 229 and 252°, corresponding to data in the literature.<sup>9,10</sup>

**meso-2,3-Diphenylsuccinyl Chloride.**—This acid chloride was prepared using the procedure of McRae and Townsend.<sup>11</sup> *meso*-2,3-Diphenylsuccinic acid (12 g) (45 mmoles) was thoroughly mixed with 22.1 g (106 mmoles) of phosphorus pentachloride. The reaction mixture was warmed over a steam bath and occasionally stirred until it had become a thick paste. Phosphorus oxychloride and excess phosphorus pentachloride were removed under reduced pressure (water aspirator) while the reaction mixture was heated over a steam bath. The residue was dissolved in warm benzene. Cooling the resulting benzene solution yielded 7.5–8 g (55–60%) of acid chloride, mp 190°.

**meso-Di-*t*-butylperoxy 2,3-Diphenylsuccinate.**—To a solution of 1.56 g (5.1 mmoles) of *meso*-2,3-diphenylsuccinyl chloride dissolved in 115–130 ml of ether and cooled to 0° was added 2.88 g (20.4 mmoles) of potassium *t*-butylperoxide suspended in 20 ml of ether. This reaction mixture was stirred for 4 hr at 0–10°. After overnight refrigeration the reaction mixture was poured into ice-water. The ether layer was separated, washed with 25-ml portions of cold 10% Na<sub>2</sub>CO<sub>3</sub>, cold 10% H<sub>2</sub>SO<sub>4</sub>, and cold water, and then dried over sodium sulfate. The ether was removed at reduced pressure and the solid residue was recrystallized from a minimum amount of ether. The yield was 0.7 g (33%), mp 104–105°.

**Anal.** Calcd for C<sub>24</sub>H<sub>30</sub>O<sub>6</sub>: C, 69.56; H, 7.24. Found: C, 69.78; H, 7.24.

**Kinetics Procedure.**—The procedure used for analysis was that described by Bartlett, *et al.*<sup>3a</sup> Calibration curves showed the validity of Beer's Law for the infrared absorption used (5.597  $\mu$ ). Rate constants were calculated with an IBM 1620 computer using the method of least squares.

**Product Studies.**—The general technique used for the analysis of the products was similar to that described by Bartlett, *et al.*<sup>3a</sup> The nonvolatile residue left in the decomposition flask was chromatographed on 100–200 mesh silica gel. The fractions were identified by comparison of their infrared spectra with spectra of authentic samples, and by mixed melting point determinations.

**Stability of *cis*-Stilbene.**—A solution of *cis*-stilbene ( $ca. 3 \times 10^{-6}$  mole/l.) in cumene was sealed under nitrogen and heated at 80° for 345 min. A similar solution containing approximately equal amounts of *cis*-stilbene and benzoyl peroxide was sealed under nitrogen and heated for the same length of time. This length of time corresponds to 10 half-lives of **1** at

(5) A Perkin-Elmer Model 21 spectrophotometer and a Perkin-Elmer infracord were used for infrared spectra. The Model 21 was used for all rate determinations and Beer's Law studies. Analysis was by Schwartzkopf Microanalytical Laboratory, Woodside, N. Y.

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this temperature. The ultraviolet spectra of both solutions from 275 to 310  $m\mu$  were unchanged with respect to the spectra of the unheated samples except for small decreases in absorption. At least 75% of the *cis*-stilbene was still present after heating in both cases. *trans*-Stilbene absorbs much more strongly than *cis*-stilbene in this same ultraviolet region. There was no evidence for any *trans*-stilbene formation in either case.

### A Cyclodehydration Synthesis of 2-Aryl-3-methylindenes<sup>1a,b</sup>

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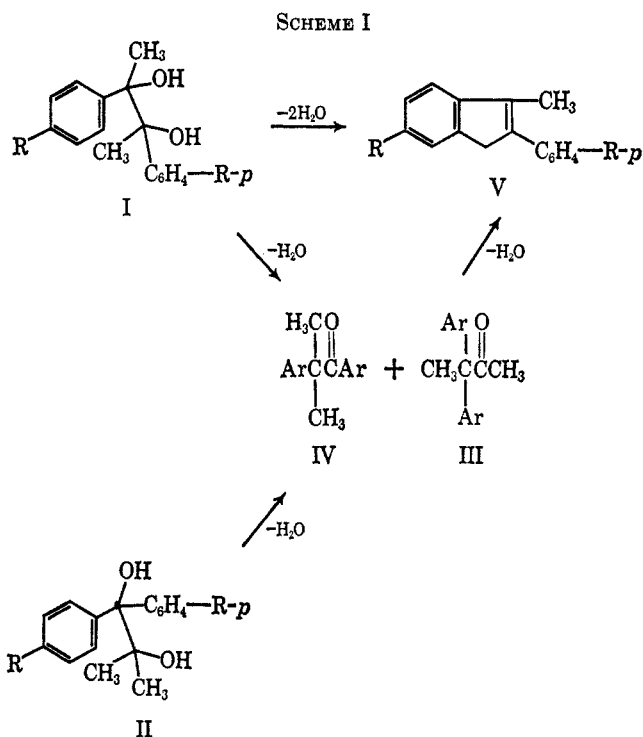
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The double dehydration of symmetrical alkyl aryl pinacols to olefinic hydrocarbons has been reported by numerous workers with a variety of conclusions as to the nature of the products. Various cyclobutenes,<sup>2</sup> anthracenes,<sup>3</sup> butadienes,<sup>4</sup> and indenenes<sup>5</sup> have been claimed. Careful work has established the existence of the butadienes<sup>6</sup> and indenenes<sup>7</sup> and the presumed elimination of anthracenes and cyclobutenes as authentic reaction products.

Activated aryl groups bearing electron-releasing amino, dimethylamino, and hydroxyl substituents in the diaryl dialkyl pinacols have been found to undergo indene cyclodehydration with dilute acid catalysis.<sup>5,8</sup> These substituents presumably enhance the reactivity of the ring to electrophilic alkylation. With pinacols which are phenyl or *p*-tolyl members of the symmetrical diaryl dialkyl ethanediol family, mild acids produce only pinacol-pinacolone rearrangement.<sup>9</sup>

The utilization of polyphosphoric acid at elevated temperatures has provided a convenient synthesis of 2-aryl-3-methylindenes. In this fashion 32–39% yields of the unsubstituted, chloro-, methyl-, and phenyl-6-*R*-3-methyl-2-*p*-*R*-phenylindenes (V) (Scheme I) were obtained. The nmr spectra excluded the possibility of isomeric alternative cyclization products. The indenenes showed characteristic methyl triplets at 2.2–2.5 ppm and methylene quartets ( $J = 2$  cps) at 3.6–3.8 ppm.

It was observed that the identical indenenes were available, although in somewhat poorer yields, by the polyphosphoric acid treatment of the monodehydration



products of pinacols, *i.e.*, pinacolones. Under comparable reaction conditions of time, temperature, and concentration, the parent pinacols were converted in greater percentage to indene product than were the pinacolones. It therefore appears that pinacolones are not obligatory intermediates in the cyclodehydration and that another mechanistic pathway, other than direct cyclization from diols to butadienes to indenenes, as hypothesized by Allen and Corwin,<sup>5</sup> exists for ketonic intermediates.

The observation that  $\beta$ -benzpinacolone, structurally incapable of forming indene products, can undergo rearrangement in strongly acidic medium<sup>10</sup> can be used to support the view that pinacolones can protonate and rearrange. Thus pinacols, such as the symmetrical diaryl dialkyl ethanediols reported here, have the possibility of both a direct and an indirect (through protonated pinacolones) route to indene products.

In the case of the unsymmetrical pinacol, 1,1-di-*p*-tolyl-2-methyl-1,2-propanediol (II,  $R = \text{CH}_3$ ) it appears that there is no appreciable direct closure from diol to indene but that in fact the pinacolone, 3,3-di-*p*-tolyl-2-butanone (III,  $R = \text{CH}_3$ ), is the critical intermediate. See data in Table I.

TABLE I<sup>a</sup>

| Compd,<br>R = CH <sub>3</sub> | Hours of<br>contact | Rel %                    |              |               | %<br>recov-<br>ery <sup>c</sup> |
|-------------------------------|---------------------|--------------------------|--------------|---------------|---------------------------------|
|                               |                     | Indene<br>V <sup>b</sup> | Ketone<br>IV | Ketone<br>III |                                 |
| I                             | 0.25 (200°)         | 2.4                      | 2.2          | 95            | 91                              |
|                               | 3.50                | 39                       | 27           | 31            | 72                              |
| II                            | 0.25                | 3.2                      | 14           | 83            | 73                              |
|                               | 3.50                | 9.0                      | 43           | 48            | 72                              |
| III                           | 6.0                 | 15                       | 18           | 67            | 70                              |
| IV                            | 5.0                 | 1.1                      | 94           | 4.0           | 84                              |

<sup>a</sup> Nonequilibrium conditions; compound mixed with polyphosphoric acid and heated to 245–255° (exception as noted). <sup>b</sup> 3,6-Dimethyl-2-*p*-tolylindene. <sup>c</sup> Based on total moles of material isolated to total moles of starting compound. Polymeric resins were present in each reaction; for similar experiences, see ref. 6.

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