

gas evolution (lit.⁸ mp 101–102° dec); nmr (CCl₄) δ (CH₂) 7.37 (s, 10 H, Ar H), 5.30 (s, 4 H, CH₂); peroxide content 97% of theoretical amount for 1 by iodometric titration.

The peroxydicarbonic acid 2 was stored at –20°, with only 4% decomposition after 7 days (by titration). The peroxydicarbonic acid was determined (by titration) to decompose at a rate of ~7% per week in benzene solution when kept cold (+1°). The half-life of peroxydicarbonic acid 2 in benzene solution at room temperature (~23°) was found, in two independent determinations, to be ~61 hr, with an average rate of decomposition of ~0.09 mg/hr.

Epoxidation of *trans*-Stilbene with *O*-Benzylmonoperoxydicarbonic Acid (2). A. Preparative Run.¹⁴ *trans*-Stilbene (~4.4 mmol) was added to a solution of the peroxydicarbonic acid 2 (~4.8 mmol) in benzene (~80 ml). The reaction mixture was stirred to dissolve the olefin and then allowed to stand at room temperature (23–24°) for 2–3 days. The benzene solution was then extracted with 5% sodium bicarbonate (2 × 50 ml), washed with distilled water (1 × 50 ml), dried (MgSO₄), and evaporated to yield a mixture of benzyl alcohol and *trans*-stilbene epoxide. The solid epoxide was obtained in highest yield (85%) by column chromatography (silica gel, ether–hexane) of the product mixture (benzyl alcohol was also obtained in 66% recovery, based on the initial concentration of 2 in the solution; four other unidentified minor products were obtained, accounting for 11% of the weight of crude product placed on the column). Recrystallization from absolute ethanol gave white crystals: mp 68–69° (lit.¹⁴ mp 69°); ir (CHCl₃) 870 cm⁻¹; δ (CCl₄) 7.25 (s, 10 H, Ar H), 3.70 (s, 2 H, epoxide H). Direct recrystallization of the crude product mixture from absolute ethanol gave the epoxide in ~75% yield.

B. Kinetics.¹⁴ A benzene solution of the peroxydicarbonic acid 2 (~6.9 × 10⁻² M) was brought to temperature equilibrium (25 ± 0.5°) in a water bath. *trans*-Stilbene was then added with stirring to make the solution initially ~5.5 × 10⁻² M in olefin. Aliquots were removed at set intervals and titrated iodometrically, thus following the reaction from 0–60% completion. The rate constant was determined from data obtained in three independent runs, assuming second-order kinetics. After correcting for the decomposition of peroxydicarbonic acid 2 in benzene solution at room temperature, the values obtained (*k*₂ = 6.67 × 10⁻⁴, 7.68 × 10⁻⁴, and 7.00 × 10⁻⁴ l. mol⁻¹ sec⁻¹) gave an average rate constant of *k*₂ = 7.12 × 10⁻⁴ l. mol⁻¹ sec⁻¹.

Epoxidation of Substituted Norbornenes (3a, 3b, and 3c) with *O*-Benzylmonoperoxydicarbonic Acid (2).²³ A typical procedure for the epoxidation of the norbornenes 3a, 3b, and 3c²³ is as follows.

The olefin was added to a cooled (0–5°) benzene solution containing a 25% excess of peroxydicarbonic acid 2 (~4.5 × 10⁻² M in 2). The homogenous solution was then allowed to warm to room temperature and stand for an average of 3 days. The solution was then extracted with 5% sodium bicarbonate solution, washed with distilled water, dried (MgSO₄), and evaporated *in vacuo* to yield a mixture of benzyl alcohol and the epoxide.

Analysis of the crude product mixture by glpc (column A, 155–195°) showed the yields of epoxides to be ~70% in the cases of norbornene analogs 3a and 3c. Preparative glpc (column B, 155–195°) gave the pure epoxides (4a and 4c) in 39% average yield. Column chromatography (silica gel, ether–hexane) of the crude product mixture obtained with the acetate 3b gave the pure epoxide (4b) in 53% yield.

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Registry No.—1, 2144-45-8; 2, 52123-51-0; 3a, 6203-08-3; 3b, 52123-52-1; 3c, 52123-53-2; *trans*-stilbene, 103-30-0.

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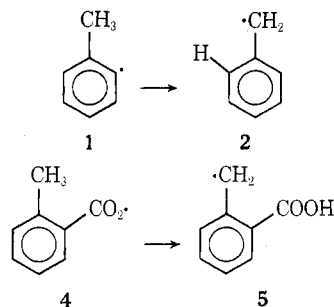
Rearrangement of the *o*-Tolyl Radical to the Benzyl Radical. A CIDNP Study

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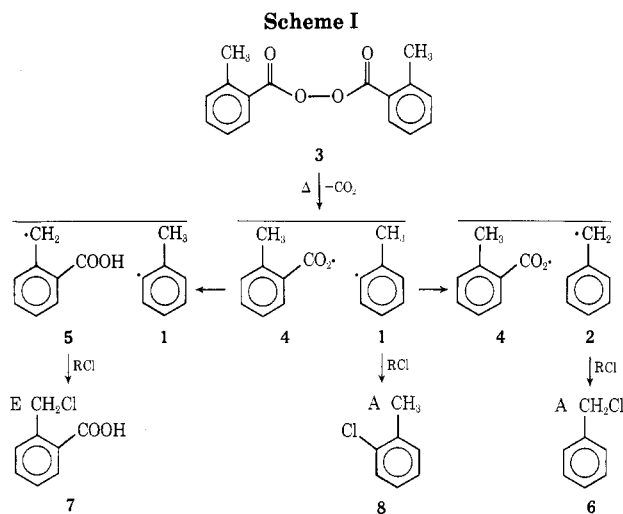
The observation of CIDNP signals in the nmr spectra of solutions in which free-radical reactions occur provides an extremely effective means of probing the mechanisms of such reactions.¹ Since the discovery of CIDNP in the thermolysis of benzoyl peroxide by Bargon and Fischer² there have been numerous CIDNP studies of aryl peroxides.³ We report here the use of CIDNP techniques to detect the rearrangement of the *o*-tolyl radical, 1, to the benzyl radical, 2, during the thermolysis of *o*-toluyl peroxide, 3. In addition, we have confirmed the postulated⁴ intramolecular rearrangement of the *o*-toluoyloxy radical, 4, to the *o*-carboxybenzyl radical, 5.



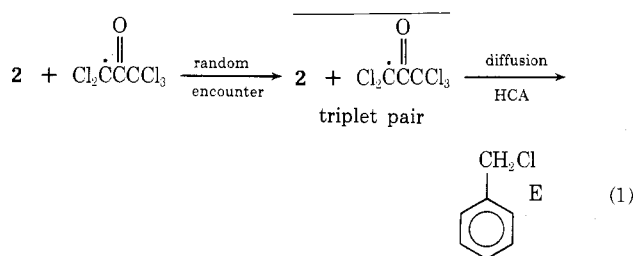
Prior to the discovery of CIDNP, a thorough investigation of the thermal decomposition of **3** was reported by Greene and coworkers.⁴ These authors obtained products resulting from **5** and proposed that rearrangement of **4** to **5** occurs. However, products resulting from **2** were not obtained in sufficient quantity to allow their detection.

If rearrangement to **1** to **2** generates **2** as a member of a radical pair, the high sensitivity of the CIDNP technique should permit the detection of polarized products resulting from **2**. Accordingly, the nmr spectrum recorded during the 115° thermolysis of **3** in hexachloroacetone (HCA) showed a strong enhanced absorption for the methylene protons of benzyl chloride, **6**. The benzyl protons of α -chlorotoluic acid, **7**, exhibited emission while the methyl protons of *o*-chlorotoluene showed enhanced absorption.

These CIDNP results along with their mechanistic interpretation are shown in Scheme I. The formation of polarized benzyl chloride is evidence that rearrangement of **1** to **2** is occurring within the solvent cage. Initial cleavage of the O-O bond in **3**, followed by decarboxylation, would produce the radical pair (**1** + **4**). Extensive studies on the analogous benzoyl peroxide system have confirmed that this process produces a singlet radical pair.³ Rearrangement of **1** to **2** now yields the radical pair (**2** + **4**) also in the singlet state. Hyperfine splitting (hfs) by the methylene protons in **2** should be negative, and the oxygen centered radical **4** should have the higher *g* value. Hence, enhanced absorption is predicted⁵ for the benzyl protons of **6** which arises by diffusion of **2** from the singlet radical pair (**2** + **4**).



An alternative mechanism for the formation of benzyl radicals is *via* hydrogen abstraction from a small amount of toluene produced in the reaction. Benzyl chloride, resulting from **2** generated in this manner, should exhibit polarization only if a random encounter between **2** and a solvent radical (S \cdot) has occurred. Such a random encounter will yield the triplet radical pair (**2** + S \cdot). Diffusion of **2** from this triplet radical pair followed by chlorine abstraction (eq 1) would yield **6** whose benzyl protons would show emission rather enhanced absorption.



In order to test the hypothesis outlined in eq 1, benzyl radicals must be generated in HCA and the polarization of benzyl chloride measured. We have done this by thermally decomposing benzoyl peroxide with a small amount of toluene in HCA solvent. This reaction produces **6** which exhibits strong emission as predicted by eq 1. This experiment shows that the enhanced absorption observed for the benzyl protons of **6** when *o*-toluoyl peroxide is decomposed in HCA cannot be the result of a random encounter between **2** and S \cdot . Such encounters ultimately result in emission rather than enhanced absorption for the methylene protons of **6**. The polarization in **6** must result from the singlet radical pair (**2** + **4**) which is formed by rearrangement of **1** to **2**.

The stability of the benzyl radical as compared to a phenyl radical provides the thermodynamic driving force for this rearrangement. An estimate of the ΔH for the rearrangement, using bond dissociation energies for aromatic and benzyl C-H bonds,⁶ yields -26.5 kcal/mol. Although this rearrangement is thermodynamically favorable, geometric constraints on the transition state undoubtedly decrease its importance relative to intermolecular reactions of **1**. That this rearrangement is a minor pathway is evidenced by the fact that only a trace of benzyl chloride could be detected by nmr at the conclusion of the reaction. The assignment of enhanced absorption to the methylene protons of **6** was confirmed by adding a small amount of benzyl chloride to a hexachloroacetone solution of **3** before heating. Thermolysis of this sample showed the methylene proton singlet of **6** grow in intensity during the reaction and diminish at its conclusion. Benzyl chloride was also detected by gas chromatography.

Greene and coworkers⁴ have presented convincing evidence for the rearrangement of **4** to **5**. When they carried out the thermolysis of **3** in carbon tetrachloride, a major product was *o*-(β,β,β -trichloroethyl)benzoic acid. In the present study, the emission for the benzyl protons of **7** indicates that this rearrangement produces a radical pair consisting of **1** and **5**. If the *g* factor of **5** is greater than that of **1**, diffusion of **5** from the radical pair followed by chlorine abstraction would result in the observed emission. It is likely that the Δg is in this direction as INDO calculations⁷ predict a small amount of unpaired spin density on the oxygens of **5**. Alternately, the polarization in **7** may result from a random encounter of **5** with a solvent radical in the manner outlined in eq 1 for the benzyl radical. Since this process is also expected to result in emission for the benzyl protons in **7**, it cannot be ruled out at this time.

A final point of interest is that the methyl protons of *o*-chlorotoluene, the major product, show enhanced absorption. This result requires that there be hyperfine splitting (hfs) by the methyl protons in **1** and that the sign of this hfs be negative. An esr study of **1** has confirmed that there is hfs by the methyl protons of less than 3 G.⁸ We have carried out INDO molecular orbital calculations⁷ on **1** which predict a value of -1 G for this hfs.

Experimental Section

The *o*-toluoyl peroxide was prepared according to the procedure of Greene and coworkers.⁴ All nmr spectra were recorded with a Varian A-60 spectrometer.

CIDNP Studies of 3. An nmr sample tube containing a 0.56 *M* solution of **3** in HCA was placed in the preheated (115°) probe of the spectrometer. Consecutive spectra were then recorded at a sweep time of 100 sec. After completion of the reaction, a small amount of toluene was added to the hot solution as an internal standard. The positions of the CIDNP signals are reported in ppm downfield from the methyl signals in toluene at 115°. The benzyl protons of **6** exhibited enhanced absorption at 2.27 ppm, the benzyl protons of **7** showed emission at 2.75 ppm, and the methyl peak of *o*-chlorotoluene exhibited enhanced absorption at 0.05 ppm.

The identity of the above signals was established by adding a small amount of each compound to the hot solution and observing the signal grow in intensity. Benzyl chloride and *o*-chlorotoluene were also identified by their gc retention times on a 20% SE-30 on 40/60 Chromosorb W column. In addition to the above CIDNP signals, strong polarizations in the aromatic proton region and weak polarizations in the aryl methyl region were observed.

Thermolysis of Benzoyl Peroxide with Toluene in HCA Solution. CIDNP from an HCA solution of 60 mg of benzoyl peroxide and 25 mg of toluene was measured at 115° in the manner described above. The methylene protons of 6 exhibited strong emission signals in this sample.

Registry No.—1, 22904-44-5; 2, 2154-56-5.

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Ring Opening of Indene Oxide with Benzoic Acid¹

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A stereochemical study on the ring opening of indene oxide with benzoic acid was recently reported by Gagis, Fusco, and Benedict.² We find that in addition to *trans*-1,2-indandiol, *cis*-1,2-indandiol³ is also formed on hydrolysis of the hydroxy benzoates initially produced. A third product, not hitherto reported in this context, is 2-indanone, which is formed concurrently with the hydroxy benzoates and can be isolated directly from the reaction mixture.⁴ This parallels our findings for the reaction of indene oxide with formic acid in chloroform where the *cis* and *trans* esters together with 2-indanone are formed in a ratio of about 2:2:1.⁵ The least equivocal evidence for the simultaneous formation of the *cis* and *trans* benzoates we think lies in the appearance of the nmr doublets at δ 6.32 and 6.17 in the raw reaction mixture. These must almost certainly be assigned to the C₁ proton in the benzoates from the analysis of analogous compounds by Rosen, *et al.*⁶

These results give credence to a carbonium ion or ion-pair mechanism in which positive charge is localized on the benzylic carbon. The formation of both *cis* and *trans* benzoates can be associated with the susceptibility of such a benzylic carbon to attack on either side of the ring. The formation of 2-indanone may be attributed to hydride ion transfer.

Our work supports that of Brewster,⁷ and of Berti and Bottari.⁸

Experimental Section

All melting points were taken on a Mel-Temp apparatus and are uncorrected. Infrared spectra were taken on a Beckman IR-5 spectrophotometer as Nujol mulls. Nmr spectra were obtained on a

Varian A56/60 spectrometer, using tetramethylsilane in CHCl₃ as an external standard.

Preparation of Chloroform.⁹ To remove the ethyl alcohol which is present as a preservative, 250 ml of Fisher certified grade chloroform was washed with three 100-ml portions of concentrated sulfuric acid followed by 100-ml portions of water until the washings were neutral to litmus. The chloroform was dried over anhydrous calcium chloride and distilled. The chloroform was further dried by passing over Linde 4A molecular sieve just before using.

Preparation of Indene Oxide (1). A solution of 100 g of indene bromohydrin (prepared by the method of Suter and Milne)¹⁰ in 900 ml of 95% ethanol was cooled to 5°. To this was added slowly, with stirring, 55 g of 85% potassium hydroxide in 95% ethanol, keeping the temperature below 10°. The reaction mixture was poured over 2000 g of ice and the crude indene oxide was taken up in ~200 ml of diethyl ether, washed twice with water, and dried over anhydrous sodium sulfate. After removal of the ether on a rotary evaporator the crude oxide was sublimed at 5 Torr with a cold-finger temperature of 0-10°: mp 30-31°; ir 1230, 1005, 986 cm⁻¹ (lit.¹¹ mp 31°).

Reaction of Indene Oxide with Benzoic Acid. A solution of 0.037 mol (4.88 g) of 1 and 0.037 mol (4.51 g) of benzoic acid in 60 ml of chloroform was allowed to stand for about 72 hr at room temperature (25°). The solution was washed with 50 ml of 10% sodium bicarbonate twice and with 50 ml of water and dried over anhydrous sodium sulfate. The chloroform was removed on a rotary evaporator at about 50° and the product was transferred to a sublimation apparatus. Sublimation of the viscous liquid at 5 Torr and with a cold-finger temperature of 0-10° gave in about 3 hr 0.4 g of colorless crystals (2) and a residue of 5.3 g of a viscous liquid. Nmr analysis (CCl₄) showed that the separation of indanone was incomplete.

Identification of 2 as 2-Indanone. The nmr spectrum showed only two resonances at δ 7.11 and 3.32 (CCl₄). The melting point was 56-56.5° (lit.¹¹ mp 57-59°); 2,4-dinitrophenylhydrazone mp 196.5-197.5° (lit.⁶ mp 198-198.5°).

Saponification of Benzoate. The 5.3 g of liquid from the reaction of indene oxide with benzoic acid was treated under reflux with 1.3 g of potassium hydroxide in 50 ml of 95% ethanol. The solution quickly turned dark brown and a precipitate gradually formed. After 3 hr the precipitate was removed by filtration,¹² 50 ml of water was added, and the solution was extracted with four 100-ml portions of diethyl ether. The extract was washed with water, dried over anhydrous sodium sulfate, and evaporated to dryness in a rotary evaporator at about 50°. The solid so obtained was recrystallized from benzene, after treatment with Norite, to yield 1.6 g (40.5%) of crystals, mp 156-157°; the ir spectrum was identical with that of *trans*-1,2-indandiol (mp 158-159°) prepared by the method of Rosen, *et al.*⁶ The mother liquor from the recrystallization was evaporated to a viscous liquid which on sublimation at 90° and 5 Torr gave 0.4 g (6.2%) of colorless crystals, mp 92-93°. The ir spectrum of this material was identical with that of authentic sublimed *cis*-1,2-indandiol (mp 93-95°) obtained by the method of Rosen, *et al.*⁶

Nmr Spectrum of Reaction Mixture. A sample of the reaction mixture was withdrawn after about 72 hr and the nmr spectrum (CHCl₃) was obtained on the untreated mixture: δ 8.12 (m, ArH), 7.4 (m, ArH), 6.7 (m), 6.32 (d), 6.17 (d), 5.7-4.5 (m), 3.51 (s), 3.3 (m). The relative intensities of the doublets at δ 6.32 and 6.17 and the singlet at δ 3.51 were estimated from the peak heights and half-widths to be roughly in the ratio 15:115:200, respectively. The overall spectrum was that expected from the work of Rosen, *et al.*⁶

Reaction of Indene Oxide with Benzoic Acid.¹³ A solution of 0.0378 mol (5.0 g) of 1 and 0.0420 mol (5.13 g) of benzoic acid in 60 ml of chloroform (purified only by distillation and passing over Linde 4A molecular sieve) was allowed to stand for 72 hr at room temperature (25°). The solution was washed with a 5% sodium bicarbonate solution and then with water, dried, and concentrated on a rotary evaporator at about 50° to yield 9.21 g of an oily liquid which proved difficult to crystallize. Sublimation of the viscous liquid at 5 Torr with a cold-finger temperature of 0-10°, water-bath temperature of 35-40°, gave in about 3 hr 0.40 g of colorless crystals (2) and a residue of 7.75 g of a viscous liquid.

Reduction of Benzoate. A 250-ml two-necked round-bottomed flask was fitted with a reflux condenser, a dropping funnel, a magnetic stirrer, and a heating mantle. In the flask were placed 2.0 g of pulverized lithium aluminum hydride and 50 ml of tetrahydrofuran which had been dried over lithium aluminum hydride and distilled. A solution of the 7.75 g of residue from the sublimation apparatus in 20 ml of dry tetrahydrofuran was then added slowly