scribed for *o*-chlorobenzoic acid. Isolation by the same procedure gave 49 g (88%) of *o*-bromobenzyl alcohol, mp 78–80° (lit.[9] mp 79.5–80°), with ir and nmr spectra in accordance with the assigned structure. Recrystallization from hexane gave 46.4 g of off-white needles, mp 79–80°.

o-**Iodobenzyl Alcohol.** The reduction of 74.5 g (300 mmol) of *o*-iodobenzoic acid was carried out using the procedure described for *o*-chlorobenzoic acid. Following methanolysis, the reaction mixture was concentrated to dryness on a rotary evaporator. The residue contained traces of boron as shown by a flame test. This boron-containing impurity was easily removed by dissolving the solid in 150 ml of methanol and concentrating to dryness on a rotary evaporator.[10] Further drying in a vacuum oven gave 70 g (100%) of *o*-iodobenzyl alcohol, mp 88–89° (lit.[11] mp 91°), with ir and nmr spectra in accordance with the assigned structure.

m-**Hydroxybenzyl Alcohol.** A dry, 1-l. flask equipped with a pressure-equalizing addition funnel, magnetic stirring bar, and reflux condenser was flushed with nitrogen and charged with 100 ml of THF, 100 ml of trimethyl borate, and 44 ml (440 mmol) of BMS. This solution was then stirred in a 20–25° water bath as 41.4 g (300 mmol) of *m*-hydroxybenzoic acid dissolved in 150 ml of THF was added dropwise over a 1-hr period.[12] Instantaneous hydrogen evolution occurred throughout the addition. After stirring for 17 hr at 20–25°, methanol (200 ml) was added dropwise and the solution was filtered *via* nitrogen pressure through a fritted glass funnel charged with diatomaceous earth to remove a minor amount of suspended solid. The clear, light-yellow filtrate was concentrated to dryness on the rotary evaporator, giving a brown oil. This oil was dissolved in 100 ml of methanol, concentrated to dryness, redissolved in 100 ml of methanol, and again concentrated to dryness, giving 36.9 g (99%) of *m*-hydroxybenzyl alcohol as a brown oil, which was free of boron-containing impurities by a flame test. The oil rapidly crystallized at room temperature, giving tan crystals, mp 69–71° (lit.[13] mp 73°), with an ir spectrum identical with that reported for the authentic material.[14]

o-**Aminobenzyl Alcohol.** A dry, 1-l. flask equipped as usual was charged with 41 g (300 mmol) of anthranilic acid, 200 ml of THF, and 40 ml of trimethyl borate. The resulting solution was heated at reflux as 87 ml (870 mmol) of BMS was added dropwise over a 1-hr period. Vigorous hydrogen evolution occurred during the BMS addition. The reaction mixture was maintained at reflux with stirring for an additional 2 hr. After cooling to 20–25°, the light-yellow supernate was removed *via* nitrogen pressure, leaving behind a small amount of black precipitate. Methanol (280 ml) was then added dropwise over a 1-hr period at 20–25°. The reaction mixture was then heated to a gentle reflux for a few minutes with stirring and concentrated on a rotary evaporator to a red oil. This oil was dissolved in 150 ml of ethyl ether and treated with 200 ml of 6 *N* aqueous sodium hydroxide. After heating at reflux for 2 hr and then cooling to 20–25°, the organic layer was removed and the aqueous layer was saturated with potassium carbonate and extracted with ethyl ether (3 × 50 ml). The combined organic layers were dried over anhydrous potassium carbonate, filtered, and concentrated to dryness on a rotary evaporator. Further drying in a vacuum oven gave 34.6 g (94%) of *o*-aminobenzyl alcohol as a light-tan, crystalline solid, mp 81–82° (lit.[13] mp 84°), with an ir spectrum identical with that reported for the authentic material.[15]

p-**Nitrobenzyl Alcohol.** The reduction of 50.2 g (300 mmol) of *p*-nitrobenzoic acid was carried out using the procedure described for *o*-chlorobenzoic acid. However, the THF solution of the acid and trimethyl borate was heated at reflux as 33 ml (330 mmol) of BMS was added dropwise over a 1-hr period. Vigorous hydrogen evolution occurred during the BMS addition. The reaction mixture was then heated at reflux with stirring for an additional 3 hr. Methanolysis and isolation of the product, using the procedure described for *o*-iodobenzyl alcohol, gave 48 g (>100% yield) of a light-yellow, crystalline solid. This solid was washed with hot hexane, filtered, and dried in a vacuum oven, giving 44.8 g (97.6%) of *p*-nitrobenzyl alcohol, mp 93–94.5° (lit.[16] mp 93°), with an ir spectrum identical with that reported for the authentic material.[17]

4,4′-Sulfonyldibenzyl Alcohol. The reduction of 91.8 g (300 mmol) of 4,4′-sulfonyldibenzoic acid with 66 ml (660 mmol) of BMS was carried out using the procedure described for *o*-chlorobenzoic acid. Methanolysis and isolation of the product, using the procedure described for *m*-hydroxybenzyl alcohol, gave 83.3 g (99%) of 4,4′-sulfonyldibenzyl alcohol: mp 133–135°; ir (mineral oil mull) 3401 (s), 3311 (s), 2933 (vs), 2865 (vs), 1597 (w), 1458 (m), 1412 (w), 1376 (w), 1309 (m), 1290 (m), 1267 (w), 1202 (w), 1151 (s), 1103 (m), 1070 (w), 1030 (s), 1012 (m), 986 (w); nmr ($CDCl_3$ plus DMSO-d_6) δ 4.58 (s, 4 H), 5.11 (s, 2 H), 7.47 (d, 4 H), 7.76 (d, 4 H).

Registry No.—BMS, 13292-87-0; trimethyl borate, 121-43-7; hexanoic acid, 142-62-1; benzoic acid, 65-85-0.

References and Notes

(1) Part I: C. F. Lane, *J. Org. Chem.*, **39**, 1437 (1974).
(2) (a) For a recent, excellent review of organic reductions using boron hydrides, see H. C. Brown, "Boranes in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1972, pp 209–251; (b) for a summary of organic reductions using BH_3–THF, see H. C. Brown, P. Heim, and N. M. Yoon, *J. Amer. Chem. Soc.*, **92**, 1637 (1970).
(3) N. M. Yoon, C. S. Pak, H. C. Brown, S. Krishnamurthy, and T. P. Stocky, *J. Org. Chem.*, **38**, 2786 (1973).
(4) A. Pelter, M. G. Hutchings, T. E. Levitt, and K. Smith, *Chem. Commun.*, 347 (1970).
(5) A detailed mechanistic study of the reduction of carboxylic acids with both BH_3–THF and BMS is currently in progress at Purdue University: H. C. Brown and T. P. Stocky, private communication, 1973.
(6) The bulletin "Handling Air-Sensitive Solutions" is available upon request from Aldrich Chemical Co., Milwaukee, Wis.
(7) J. B. Shoesmith and R. H. Slater, *J. Chem. Soc.*, 218 (1926).
(8) C. J. Pouchert, "The Aldrich Library of Infrared Spectra," Aldrich Chemical Co., Milwaukee, Wis., 1970, p 512f.
(9) R. C. Fuson and B. Freedman, *J. Org. Chem.*, **23**, 1161 (1958).
(10) This simple isolation procedure failed to remove boron-containing residues completely in the preparation of *o*-chlorobenzyl alcohol and *o*-bromobenzyl alcohol. In these cases, the washing with aqueous bicarbonate was necessary and may have been due to impurities present in the starting benzoic acid.
(11) R. G. R. Bacon and W. S. Lindsay, *J. Chem. Soc.*, 1375 (1958).
(12) This order of addition was necessary because when BMS was added to a solution of the acid and trimethyl borate in THF an insoluble polymeric intermediate formed.
(13) C. Mettler, *Chem. Ber.*, **38**, 1751 (1905).
(14) Reference 8, p 513a.
(15) Reference 8, p 535f.
(16) B. M. Bogoslovskii and Z. S. Kazakova, *Zh. Prikl. Khim.*, **21**, 1183 (1948); *Chem. Abstr.*, **43**, 6182*a* (1949).
(17) Reference 8, p 600d.

O-Benzylmonoperoxycarbonic Acid. A New Oxygenating Reagent[1]

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Although the peroxycarboxylic acids are a well known and widely used group of oxygenating agents,[3–5] the corresponding peroxycarbonic acids (*e.g.*, **2**) have been little studied. The parent member of this family, monoperoxycarbonic acid (H_2CO_4) has been suggested as a transient intermediate[6] and a number of its metal salts have been reported.[7] Dialkyl esters of monoperoxycarbonic acid ($ROCO_3R'$) have been prepared.[8]

However, there seems to be no mention of an *O*-alkylmonoperoxycarbonic acid ($ROCO_3H$) in the literature, although such compounds would be expected to be reasonably stable and readily prepared by perhydrolysis of the well-known dialkyl peroxydicarbonates.[8,9] It is possible that the active oxidizing agents formed by the reaction of hydrogen peroxide and aryl isocyanates are, in fact, *N*-arylperoxycarbamic acids ($ArNHCO_3H$), nitrogen analogs of *O*-alkylperoxycarbonic acids.[10,11]

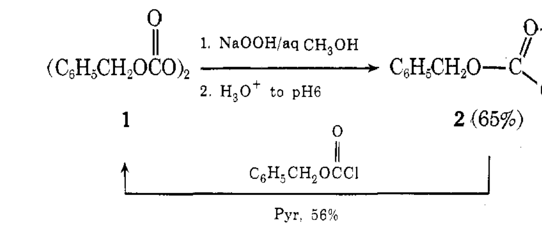
We have prepared *O*-benzylmonoperoxycarbonic acid (**2**) by perhydrolysis[12] of dibenzyl peroxydicarbonate (**1**),[8] a crystalline, relatively stable peroxydicarbonate which is easily obtained from the reaction of benzyl chloroformate and alkaline hydrogen peroxide.[8,13]

The structure of **2** is based upon its reconversion to dibenzyl peroxydicarbonate (**1**) upon reaction with benzyl chloroformate in pyridine, its high peroxide content (>97% of theoretical amount by iodometric titration), its acidic

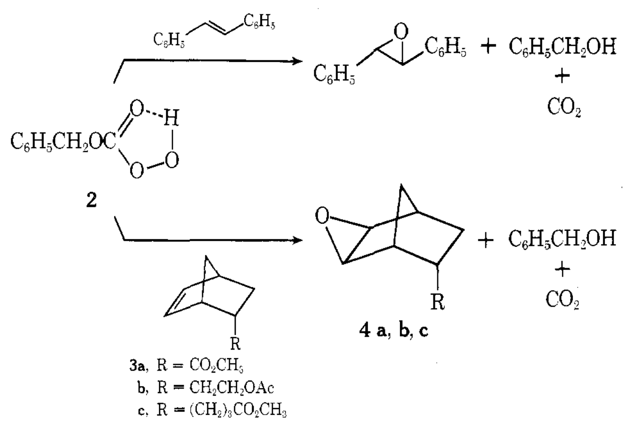
Table I
Comparison of Rates of Epoxidation of *trans*-Stilbene by *O*-Benzylmonoperoxycarbonic Acid (2) and Selected Aromatic Peroxycarboxylic Acids, with the Acidity of the Parent Acid

Peroxy acid	$10^4 k_2^{25°}$, l./mol sec[a]	k_{rel}	pK_a of parent acid[b]	$-\text{Log } k_2/\text{p}K_a$
O-Benzylmonoperoxycarbonic acid (**2**)	7.12 ± 0.04[c]	1.7	3.76[d]	0.84
Peroxybenzoic acid	4.27[e]	(1.0)	4.21	0.80
m-Chloroperoxybenzoic acid	15.0[e]	3.5	3.82	0.74

[a] In benzene solution. [b] Data from ref 15. [c] Average of three separate runs with measured rate constants (10^4k_2) 6.67, 7.00, and 7.68. Error indicates deviation of individual rate constants from the average. [d] pK_a of carbonic acid. [e] Data from ref 14.



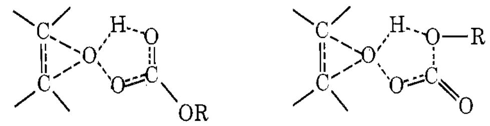
character (extraction of the alkaline reaction mixture prior to acidification affords only a small amount of recovered 1), and its spectral properties [ir (film) ν_{max} 3700–2700 and 1775 (C═O, br) cm^{-1}; nmr (CCl_4, −22°) δ 12.17 (s, 1 H, OCO_3H), 7.25 (s, 5 H, Ar H), and 5.08 (s, 2 H, CH_2)]. *O*-Benzylmonoperoxycarbonic acid (**2**) reacts with olefins to afford moderate to good yields of epoxides and the by-products benzyl alcohol and carbon dioxide (assumed).



O-Benzylmonoperoxycarbonic acid (**2**) could be stored in the cold with relatively little decomposition, *i.e.*, loss in peroxide content according to iodometric titration [approximate decomposition rates: ∼4%/week at −20° (neat); ∼7%/week at 1° (benzene solution)]. The rate of decomposition at room temperature is appreciable (∼50% loss of peroxide content after 2½ days at 23° in benzene solution).

Since the log of the rate of olefin epoxidation (k_2) of various peroxybenzoic acids correlates rather precisely with the σ constant (pK_a) of the corresponding normal acid,[14] it was of interest to determine the rate of epoxidation with *O*-benzylmonoperoxycarbonic acid (**2**). The rate of epoxidation of stilbene with **2** (0.069 *M* in benzene at 25 ± 0.5°) was followed to ∼60% completion by iodometric titration giving a second-order rate constant $k_2 = 7.1 \pm 0.4 \times 10^{-4}$ l./mol sec (average of three runs). Thus, *O*-benzylmonoperoxycarbonic acid (**2**) is a more reactive epoxidizing reagent toward *trans*-stilbene than peroxybenzoic acid but is less reactive than *m*-chloroperoxybenzoic acid (see Table I). Although the acidity of the parent acid, *O*-benzylcarbonic acid, is unknown, it should be approximated by the acidity of carbonic acid (pK_a = 3.76).[15] The data in Table I indicate that the epoxidative reactivity of **2** toward *trans*-stilbene is rather close to, though apparently somewhat less than, that predicted on the basis of the acidity of carbonic acid.

Two alternative transition states (A and B) for olefin epoxidation with an *O*-alkylmonoperoxycarbonic acid may be



A B

considered. The first (A), analogous to that usually suggested for epoxidation with peroxycarboxylic acids,[3,4,16] would initially form an *O*-alkylcarbonic acid which would subsequently collapse to the alcohol and carbon dioxide. The second (B) suggests that epoxidation and decarboxylation may be concerted. Since the epoxidative reactivity of **2** corresponds rather closely to that expected on the basis of the acidity of carbonic acid, we assume that the transition state very likely resembles that for peroxycarboxylic acid epoxidation (A).

O-Benzylmonoperoxycarbonic acid (**2**), as well as other peroxycarbonic acids, should provide a useful alternative reagent to peroxycarboxylic acids for epoxidation and other oxygen transfer reactions. This type of peroxy acid has the potential advantage that the reaction medium remains essentially neutral during the oxidation reaction.[17] Side reactions are sometimes catalyzed by the carboxylic acid formed in the reactions of peroxycarboxylic acids.[3b,4,19] However, for slow reactions self-decomposition of the reagent may become competitive. It is also necessary to be able to separate the desired product from benzyl alcohol.

Experimental Section[20]

***O*-Benzylmonoperoxycarbonic Acid (2).** Dibenzylperoxydicarbonate (1, 5.01 g, 16.6 mmol)[8,13] was suspended in a solution containing 30% hydrogen peroxide (8.03 ml, 75.0 mmol) and magnesium sulfate (heptahydrate, 0.22 g, 0.83 mmol) in alkaline, aqueous methanol [3.00 g (75.0 mmol) of sodium hydroxide, 75 ml of methanol, and 67 ml of distilled water].[12] The mixture was stirred vigorously for 10 min, diluted with 80 ml of cold distilled water, and extracted with cold chloroform (2 × 50 ml) to remove neutral products (<1% recovery of dibenzyl peroxydicarbonate by iodometric titration[21]). Acidification with 10% sulfuric acid (to ∼pH 6) of the aqueous reaction solution and extraction with cold benzene (3 × 50 ml) gave the peroxycarbonic acid **2** in 65% yield (determined by iodometric titration) in benzene solution.

Evaporation (*in vacuo* without heat) of a 5.0-ml aliquot of the cold benzene solution (0.129 *M* in peroxycarbonic acid **2**) gave a clear, colorless oil (111 mg): ir (film) ν_{max} 3700–2700, 1775 (br) cm^{-1}; nmr (100 MHz, CCl_4, −22°) δ 12.17 (s, 1 H, $-OCO_3H$), 7.25 (s, 5 H, Ar H), 5.08 (s, 2 H, CH_2); iodometric titration showed the oil product to contain >97% theoretical peroxide content for peroxycarbonic acid **2**.

In a separate experiment, benzyl chloroformate (0.6100 g, 3.58 mmol) and pyridine (0.2830 g, 3.58 mmol) were placed in a flask and cooled to 5–10°.[22] A benzene solution of peroxycarbonic acid **2** (75 ml of a 4.76 × 10^{-2} *M* solution; 0.6015 g, 3.58 mmol of **2**) was added to the flask, and the resulting solution was stirred for 5 min and placed in a refrigerator (+1°) overnight. The solution was then washed with distilled water (3 × 50 ml), dried ($MgSO_4$), and evaporated to yield 1.268 g of an oily, white precipitate (∼100% peroxide content, according to initial peroxycarbonic acid titer). Recrystallization from acetone–water (−20°) gave dibenzyl peroxydicarbonate **1** in 56% yield as powdery, white crystals: mp 99–100° with gas evolution (lit.[8] mp 101–102° dec); nmr (CCl_4) δ (CH_2) 7.37 (s, 10 H, Ar H), 5.30 (s, 4 H, CH_2); peroxide content 97% of theoretical amount for **1** by iodometric titration.

The peroxycarbonic acid **2** was stored at −20°, with only 4% decomposition after 7 days (by titration). The peroxycarbonic 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 peroxycarbonic 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*-Benzylmonoperoxycarbonic Acid (2). A. Preparative Run.[14] *trans*-Stilbene (~4.4 mmol) was added to a solution of the peroxycarbonic 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 ($MgSO_4$), 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 ($CHCl_3$) 870 cm^{-1}; δ (CCl_4) 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 peroxycarbonic 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 peroxycarbonic acid **2** in benzene solution at room temperature, the values obtained ($k_2 = 6.67 \times 10^{-4}$, 7.68×10^{-4}, and 7.00×10^{-4} l. mol^{-1} sec^{-1}) gave an average rate constant of $k_2 = 7.12 \times 10^{-4}$ l. mol^{-1} sec^{-1}.

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

The olefin was added to a cooled (0–5°) benzene solution containing a 25% excess of peroxycarbonic 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 ($MgSO_4$), 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.

References and Notes

(1) Taken in part from Ph.D. thesis of J. W. W., University of Illinois, 1973.
(2) A. P. Sloan Foundation Fellow, 1971–1973.
(3) D. Swern, Ed., "Organic Peroxides," Wiley-Interscience, New York, N. Y.: (a) Vol. I, 1970, Chapters VI and VII; (b) Vol. II, 197771, Chapter V.
(4) H. O. House, "Modern Synthetic Reactions," Second ed, W. A. Benjamin, Menlo Park, Calif., 1972, Chapter 6.
(5) J. B. Lee and B. C. Uff, *Quart. Rev.*, **21**, 429 (1967).
(6) (a) P. Günther and L. Holzapfel, *Z. Phys. Chem.*, **49**, 303 (1941). (b) K. Schmidt, *Nature*, **187**, 931 (1960). (c) A. Vaskelis and A. Prokopcikas, *Lietuvos TSR Mokslu Akad. Darbai, Ser. B.*, 75 (1963); *Chem. Abstr.*, **60**, 10215 (1964).
(7) (a) J. R. Partington and A. H. Fatballah, *J. Chem. Soc.*, 1934 (1950); (b) M. Gutierrez de Celis and J. R. Masaquer, *Anal. Reale Soc. Espan. Fis. Quim. (Madrid)*, **51B**, 693 (1955); *Chem. Abstr.* **50**, 6237 (1956).
(8) F. Strain, W. E. Bissinger, W. R. Dial, H. Rudoff, B. J. DeWitt, H. C. Stevens, and J. H. Langston, *J. Amer. Chem. Soc.*, **72**, 1254 (1950).
(9) Ref 3: Vol. I, p 68; Vol. II, pp 863–867.
(10) N. Matsumura, N. Sonoda, and S. Tsutsumi, *Tetrahedron Lett.*, 2029 (1970).
(11) Professor J. Rebek, Jr. (Department of Chemistry, University of California, Los Angeles) has kindly informed us that a number of other peroxycarbamic acids have been prepared in his laboratories.
(12) Y. Ogata and Y. Sawaki, *Tetrahedron*, **23**, 3327 (1967); R. N. MacDonald, R. N. Steppel, and J. E. Dorsey, *Org. Syn.*, **50**, 15 (1970).
(13) Dibenzyl peroxydicarbonate is also commercially available from the Pennwalt Co., Lucidol Division.
(14) B. M. Lynch and K. H. Pausacker, *J. Chem. Soc.*, 1525 (1955).
(15) "Lange's Handbook of Chemistry," Eleventh ed., J. A. Dean, Ed., McGraw-Hill, New York, N. Y., 1973.
(16) P. D. Bartlett, *Rec. Chem. Progr.*, **11**, 47 (1950).
(17) Peroxycarboxylic acids have pK_a values in the range of 7–8.[3,18] It is assumed that the lifetime of the intermediate *O*-benzylcarbonic acid is too short to lower the effective pH of the medium appreciably.
(18) A. J. Everett and G. J. Minkoff, *Trans Faraday Soc.*, **49**, 410 (1953).
(19) A. Rosowsky in "Heterocyclic Compounds," Vol. 19, A. Weissberger, Ed., part 1, Chapter 1.
(20) Melting points were taken in open capillary tubes on a Thomas-Hoover melting point apparatus and are uncorrected. Spectra were recorded with the following instruments: Perkin-Elmer Model 137 or 237 B ir spectrophotometers; Varian Associates Model A-60A or HA-100 nmr spectrophotometers. All nmr spectra were determined in deuterated chloroform unless otherwise stated and chemical shifts are reported as δ values using tetramethylsilane as internal standard. Microanalyses were performed in the University of Illinois Microanalytical Laboratory. Gas-liquid phase chromatography (glpc) was performed on a Wilkens Aerograph A-90-P3 instrument using one of the following columns: A (5 ft × ¼ in., 15% FFAP on 60/80 mesh Chromosorb W AW/DMCS) or B (5 ft × ⅜ in., 15% FFAP on 60/80 mesh Chromosorb W AW/DMCS). Purifications by column chromatography were carried out with Brinkman 0.02–0.5 mm silica gel eluting with the solvent(s) indicated.
(21) V. R. Kokatnur and M. Jelling, *J. Amer. Chem. Soc.*, **63**, 1432 (1941).
(22) W. Gerrard and A. M. Thrush, *J. Chem. Soc.*, 2117 (1953).
(23) For the methods of preparation of **3a**, **3b**, and **3c** and characterization of the corresponding epoxides **4a**, **4b**, and **4c**, see the Ph.D. thesis of J. W. W., University of Illinois, Urbana, Ill., 1973.

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

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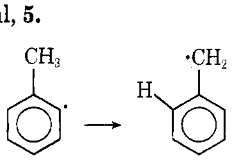
The observation of CIDNP signals in the nmr spectra of solutions in which free-radical reactions occur provides an extremely effective means of probing the mechanisms of such reactions.[1] Since the discovery of CIDNP in the thermolysis of benzoyl peroxide by Bargon and Fischer[2] there have been numerous CIDNP studies of aroyl 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 postulated[4] intramolecular rearrangement of the *o*-toluoyloxy radical, **4**, to the *o*-carboxybenzyl radical, **5**.



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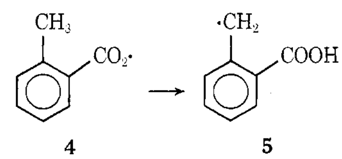

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