**Reaction of the Epoxyether with Benzoic Acid.**—In a 6-in. test-tube was placed 0.6 g. of I and 0.6 g. of benzoic acid. The solids were pulverized and mixed and then heated over a Bunsen burner to 225°. The melt was cooled and then extracted with ethyl ether, after which the ether solution was washed with sodium carbonate solution. The ether was evaporated and the residue recrystallized from ligroin to give 0.52 g. (70%) of α-hydroxy-α,α-diphenylacetophenone benzoate (VII), m.p. 151–152°.

*Anal.* Calcd. for $C_{27}H_{20}O_3$: C, 82.63; H, 5.14. Found: C, 82.82; H, 5.23.

The ketobenzoate VII was prepared independently from 2 g. of α-hydroxyketone (V), 12 g. of benzoyl chloride and 30 ml. of dry pyridine. After the reaction mixture had refluxed for four days, the excess benzoyl chloride was decomposed by the addition of ice and water to the cooled solution. Dilute hydrochloric acid was added and the organic material extracted with ether. The ethereal solution was washed with sodium carbonate solution, dried and the ether evaporated. Recrystallization of the residue from a benzene-ligroin mixture gave 0.6 g. (23%) of the ketobenzoate VII, m.p. 150–151°. A mixture melting point with VII from the epoxyether was not depressed.

**Rearrangement of the Epoxyether (I).**—Dry hydrogen chloride was bubbled into 25 ml. of cold methanol until the alcohol was saturated and then 0.55 g. of epoxyether was added and the solution heated to reflux for five hours. The reaction was acidic to litmus after this time. The solution was cooled in an ice-bath and the resulting solid separated by filtration. The solid proved to be α-methoxy-α.α-diphenylacetophenone (III) and amounted to 0.4 g. (80%), m.p. 90–91°. A mixture melting point with authentic III was not depressed.

**Reaction of the Epoxyether with Acetic Acid.**—A solution of 0.45 g. of epoxyether I in 15 ml. of acetic acid and 10 ml. of acetic anhydride was heated to the reflux temperature for eight hours. After the solution had cooled, aqueous sodium carbonate was added and the organic material was extracted with ether. The ether solution was concentrated and the residue dissolved in ligroin from which 0.45 g. (70%) of α-hydroxy-α,α-diphenylacetophenone acetate (VIII), m.p. 145–146°, could be isolated.

An authentic sample of ketoacetate VIII was prepared by acetylation of the hydroxyketone V. A solution of 4 g. of V and 75 ml. of acetic anhydride was heated at the reflux temperature for 14 hours, after which time the mixture was poured onto ice. The solid that formed was filtered and recrystallized from ligroin to give 2.3 g. (66%) of the ketoacetate,[9] m.p. 143–144°. A mixture melting point with VIII from the epoxyether was not depressed.

In another experiment 1.0 g. of the epoxyether, 15 ml. of acetic acid and 10 ml. of acetic anhydride were heated to the reflux temperature for only three hours. The reaction was then poured onto a mixture of ice and potassium carbonate solution, after which the organic material was extracted with ether. The ether solution was concentrated and the residue dissolved in hot ligroin. After the ligroin solution had cooled, 0.25 g. (24%) of α-hydroxy-α,α-diphenylacetophenoneacetate, m.p. 141–142°, was obtained. Recrystallization from ligroin raised the melting point to 146–147° and the identity of the compound was proved by a mixture melting point determination with an authentic sample.

The initial ligroin mother liquor was concentrated to give 0.5 g. (50%) of α-methoxy-α,α-diphenylacetophenone (III), m.p. 86–90°. The compound caused no depression of melting point when mixed with authentic III.

Solvolysis of **α-Methoxy-α,α-diphenylacetophenone.**—Pure α-methoxyketone III, m.p. 90–92° (1.5 g.) was dissolved in 15 ml. of acetic acid and 10 ml. of acetic anhydride and heated to reflux for a total of 16 hours. The product was isolated by the same procedure as given above and proved to be the ketoacetate VIII, 1.1 g. (78%), m.p. 146–148°.

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[9] M. M. Delacre, *Bull. soc. chim. France*, [3] **13**, 857 (1895), reported a melting point of 144–145°.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE COLLEGE OF ARTS AND SCIENCES OF THE UNIVERSITY OF LOUISVILLE]

# Sulfostyrenes.[1] Preparation and Polymerization of Potassium p-Vinylbenzenesulfonate[2]

BY RICHARD H. WILEY, NEWTON R. SMITH AND C. C. KETTERER[3]

RECEIVED SEPTEMBER 25, 1953

*p*-Vinylbenzenesulfonic acid (sulfostyrene) has been prepared by dehydrohalogenation of β-bromoethylbenzenesulfonyl chloride, isolated as its toluidine and potassium salts, and characterized. The potassium salt has been polymerized to high viscosity polymers. The reduced viscosities ($\eta_{sp}/c$) for these polymers are non-linear functions of concentration ($c$) and show a marked increase as the concentration decreases (Fig. 1). A previously developed relation (equation 2) involving reciprocal reduced viscosity and concentration, but not square root of the concentration (Fig. 2), gives a linear plot (Fig. 3), as does also a log–log plot of reduced viscosity and concentration (Fig. 4). Both of these linear plots have finite intercepts roughly proportional to the specific viscosities of the polymers. The intercepts of the log–log plots are multiples of the $D$ factors of equation 2 for these polysulfostyrenes and are, to the extent that the $D$ factors are also, related to the intrinsic viscosity of the polymer.

Polysulfostyrenes are useful cation exchange resins but, prior to the studies reported herein, they have been available only by the sulfonation of polystyrene. This method of preparation limits the capacity of the polymer to that degree of sulfonation obtainable without excessive decomposition of the polymer or sulfone formation[4,5] and raises a question as to the homogeneous distribution of the sulfo groups amongst the phenyl radicals. Preparation of polysulfostyrenes by polymerization of suitable monomers offers a means of avoiding both of these problems. In this paper we wish to describe the first preparation of monomeric salts of *p*-vinylbenzenesulfonic acid and some characteristics of the polymers obtained on polymerization of the potassium salt.

In our previous work we have described the results obtained in studying various synthetic routes to a sulfostyrene or derivatives thereof. Syntheses starting with *p*-ethylbenzenesulfonyl chloride, a readily available intermediate, involving bromination at the α-position of the ethyl group and subsequent dehydrohalogenation have been

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[1] Previous papers in this series: (a) R. H. Wiley and C. C. Ketterer, THIS JOURNAL, **75**, 4519 (1953); (b) R. H. Wiley, R. P. Davis and N. R. Smith, *J. Org. Chem.*, **18**, 1372 (1953); (c) R. H. Wiley and R. P. Davis, THIS JOURNAL, **74**, 6142 (1952).

[2] This research was supported under Contract AT-(40-1)-229 between the Atomic Energy Commission and the University of Louisville.

[3] Predoctoral research assistant.

[4] R. Signer and A. Demagistri, *J. chim. phys.*, **47**, 704 (1950).

[5] W. C. Baumann and J. Eichhorn, THIS JOURNAL, **69**, 2830 (1947).

uniformly unsuccessful. A variety of replacement reactions are encountered in attempted dehydrohalogenation under different conditions.[1b] Recently we have successfully prepared *p*-sulfonamidostyrene by dehydrohalogenation of $\beta$-bromoethylbenzenesulfonamide.[1a] This amide was prepared from *p*-$\beta$-bromoethylbenzenesulfonyl chloride, an intermediate which we have now successfully converted to salts of the related *p*-vinylbenzenesulfonic acid. The sulfonyl chloride, on treatment with potassium hydroxide in methanol, is hydrolyzed and dehydrohalogenated. *p*-Vinylbenzenesulfonic acid has been separated from the inorganic salts and characterized as the toluidine salt using a procedure previously developed in our laboratories.[1b] The toluidine salt, on neutralization with potassium hydroxide and separation from the toluidine, is converted to the analytically pure potassium *p*-vinylbenzenesulfonate in an over-all yield of 42.8%. Conversion to the known *p*-carboxybenzenesulfonamide establishes the position of the vinyl group as para to the sulfo group.

The polymers obtained from potassium *p*-vinylbenzenesulfonate are hygroscopic and resemble gelatin. The thoroughly dry polymers have the unusual characteristic of decrepitating on absorption of water. Their specific viscosities vary from 0.453 to 2.63 at a concentration of 1.0 g. per 100 cc. The data are summarized in Table I. Plots of the reduced viscosity ($\eta_{sp}/c$) against concentration are non-linear. The reduced viscosity rises markedly at low concentrations (Fig. 1). This behavior is characteristic of various polyelectrolytes in the absence of added electrolyte[6] and is attributed to an uncoiling of the chains caused by charge repulsion. Several different relations have been proposed for obtaining linear relations between these variables. The equation 1 of Fuoss and Strauss[7] with our data gives non-linear plots with

$$\eta_{sp}/c = A/(1 + B\sqrt{c}) \qquad (1)$$

increased deviation from linearity particularly noticeable for low viscosity polymers in concentrated solutions (Fig. 2). Others[8] have reported similar deviations and suggested another equation 2. As seen in Fig. 3, our data give linear plots when $1/(Z - D)$ is plotted against $c$. The values

$$Z = \eta_{sp}/c = A/(1 + Bc) + D \qquad (2)$$

of $D$, given in Table I, are directly proportional to

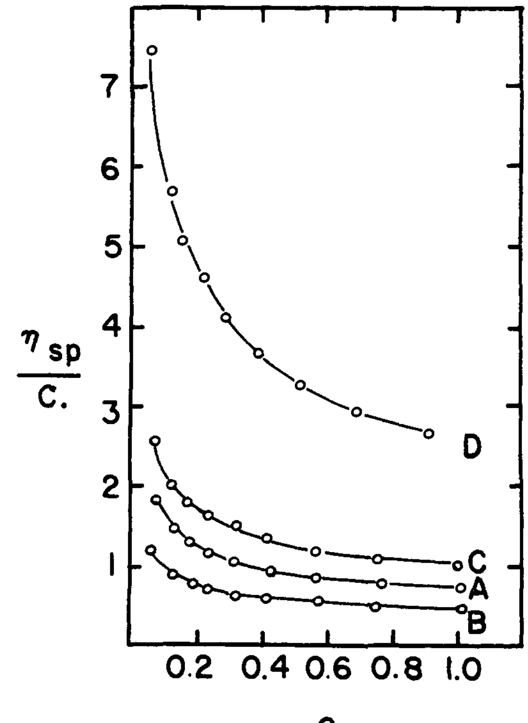

Fig. 1.—Plot of the reduced viscosity against the concentration for potassium *p*-vinylbenzenesulfonate polymers.

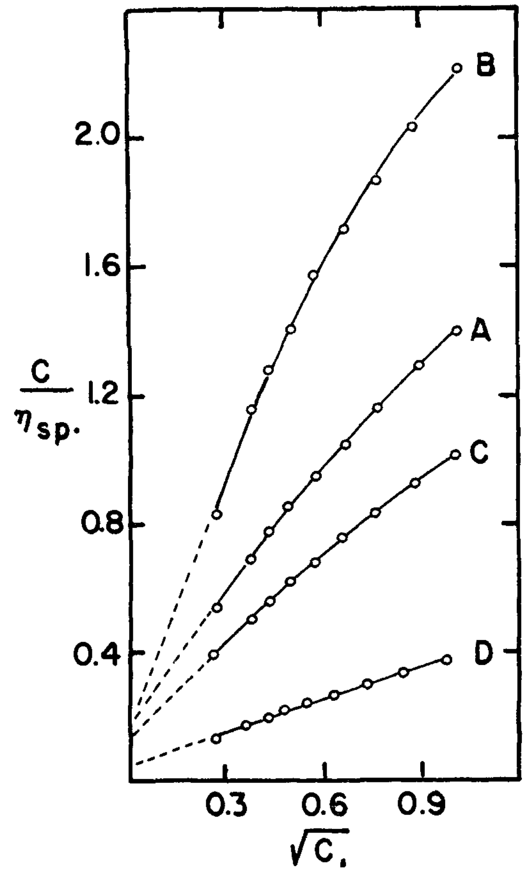

Fig. 2.—Plot of the reciprocal reduced viscosity against the square root of the concentration for potassium *p*-vinylbenzenesulfonate polymers (equation 1).

TABLE I

VISCOSITY CHARACTERISTICS OF POTASSIUM *p*-VINYLBENZENESULFONATE POLYMERS

| Polymer | $\eta_{sp}$[a] | $D$[b] | $a$[c] | $b$[c] |
|---|---|---|---|---|
| A | 0.731 | 0.534 | 0.708 | −0.356 |
| B | .453 | .330 | .446 | − .324 |
| C | .999 | .735 | .987 | − .351 |
| D | 2.62 | 1.88 | 2.58 | − .380 |

[a] At 1.0 g. per 100 cc. [b] Of equation 2. [c] Of equation 3.

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(6) P. Doty and G. Ehrlich, *Ann. Rev. Phys. Chem.*, **3**, 93 (1952).

(7) R. M. Fuoss and U. P. Strauss, *J. Polymer Sci.*, **3**, 246 (1948); *Ann. N. Y. Acad. Sci.*, **51**, 836 (1949).

(8) J. R. Schaefgen and C. F. Trivisonno, THIS JOURNAL, **74**, 2715 (1952).

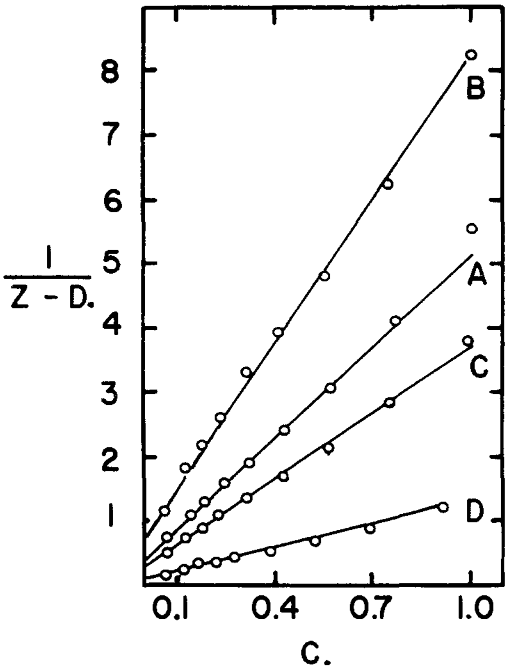

Fig. 3.—Graph of equation 2 for potassium *p*-vinylbenzenesulfonate polymers.

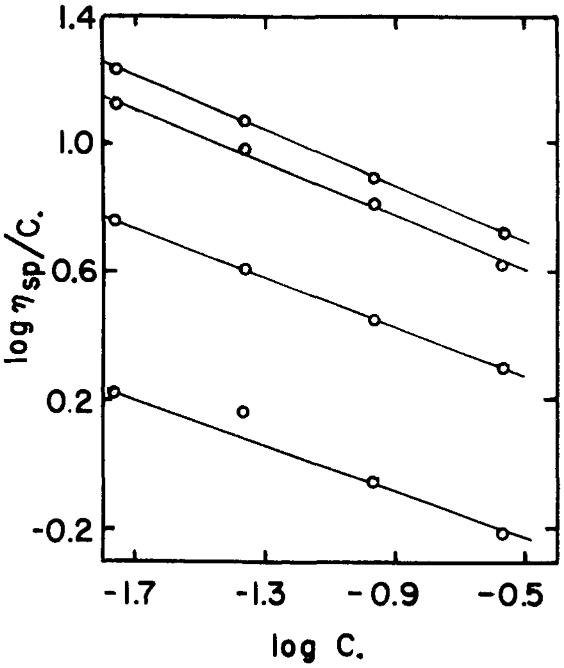

Fig. 5.—Log–log plot of the reduced viscosity against concentration for methacrylic acid polymers of reference 9.

the viscosities of the polymers. We have also obtained linear plots as shown in Fig. 4 from our data plotting log $\eta_{sp}/c$ against log $c$. This indicates that the relation between viscosity and concentration is given by equation 3

$$\eta_{sp}/c = ac^b \qquad (3)$$

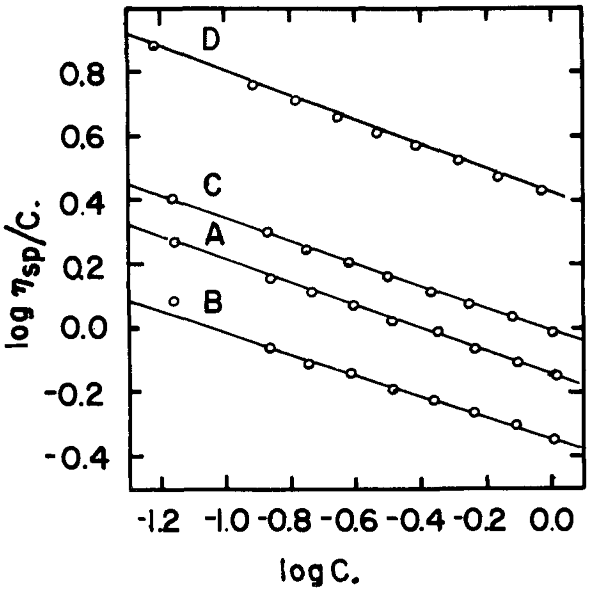

Fig. 4.—Log–log plot of the reduced viscosity against concentration for potassium *p*-vinylbenzenesulfonate polymers.

The values of $a$ and $b$ obtained by the method of least squares from the data given in Fig. 1 are listed in Table I. The slope factors ($b$) are within the range $-0.324$ to $-0.380$. The intercept factors ($a$) are simple multiples ($a = 1.34D$) of the $D$ constants of equation 2 and are thus, to the extent that the $D$ constants are also, related to the intrinsic viscosity of the polyion in its most extended form. Figure 5 is a log–log plot of the data for polymethacrylic acid previously reported[9] and shows that linear log–log relations are not an exclusive feature of the *p*-vinylbenzenesulfonic acid polymers. Data for establishing further the relation between $a$ and $D$, especially for other types of polyelectrolytes, have been collected and will be reported elsewhere. Because the $a$ factor of equation 3 is much more readily obtained from viscosity data than is the $D$ factor of equation 2, it provides a convenient term for comparing the intrinsic viscosity behavior, and thus the chain geometry, of polyelectrolyte molecules.

## Experimental

**Toluidine Salt of *p*-Vinylbenzenesulfonic Acid.**—To 32.6 ml. (0.5 mole) of chlorosulfonic acid cooled to 10° in a three-neck flask equipped with a dropping funnel, stirrer, and acid gas trap was added 13.8 ml. (0.1 mole) of β-bromoethylbenzene slowly. The temperature was held between 10 and 20°. After one hour at room temperature, the reaction mixture was poured onto chopped ice with vigorous stirring. This mixture was extracted with one 100-ml. and two 50-ml. portions of ether. The ether extract was washed with water and with dilute sodium bicarbonate solution and filtered through anhydrous sodium sulfate. The ether was removed under a vacuum leaving the crude sulfonyl chloride. This chloride was placed in a three-neck flask equipped with stirrer, dropping funnel, and condenser and to it was added 70 ml. of methanol. The solution was cooled with an ice-bath while 100 ml. of methanol containing 22.4 g. (0.4 mole) of potassium hydroxide was added slowly. After refluxing for 1 hour the mixture was cooled to −20°. If cooled only with an ice-bath to between 0–5°, the yield of pure salt is lower. The precipitated solids were collected and dried for 5 hours under vacuum to give 54 g. of a mixture of salts. This mixture was dissolved in 150 ml. of water (30°), treated with Norit, and filtered. To the filtrate, cooled in an ice-bath, was added 48 ml. of a mixture of equal volumes of water and concd. hydrochloric acid con-

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[9] A. Oth and P. Doty, *J. Phys. Chem.*, **56**, 43 (1952).

taining 10 g. of *p*-toluidine. The solution was cooled to 8° and filtered. The precipitate was taken up in 100 ml. of warm water and an additional 24 ml. of the water–hydrochloric acid solution containing 5 g. of *p*-toluidine was added. The solution was warmed until all was in solution, treated with Norit filtered hot, and cooled to 8° to precipitate the *p*-toluidine salt of *p*-vinylbenzenesulfonic acid, m.p. 177–182°. After recrystallization from 75 ml. of hot water, there was obtained 8.0 g., 27.5% of the theoretical amount, of the pure toluidine salt of *p*-vinylbenzenesulfonic acid, m.p. 182–183°. This recrystallized salt was used in all of the following experiments.

*Anal.* Calcd. for $C_{15}H_{17}NO_3S$: C, 61.80; H, 5.88; S, 11.0; neut. equiv., 291.35. Found: C, 61.90; H, 5.99; S, 11.12; neut. equiv., 289.

**Potassium *p*-Vinylbenzenesulfonate.**—Five grams of the dry *p*-toluidine salt of *p*-vinylbenzenesulfonic acid, m.p. 182–183°, was dissolved in 30 ml. of water and 14.25 ml. of 1.2 *N* potassium hydroxide. This solution was extracted with three 50-ml. portions of ether and evaporated to dryness. The crude salt thus obtained was dissolved in 1–1 methanol–water and cooled to −20° to precipitate 1.35 g., 42.8% of the theoretical amount, of dry potassium *p*-vinylbenzenesulfonate. Salt thus obtained was used in the preparation of polymers B, C and D.

*Anal.* Calcd. for $C_8H_7KO_3S$: C, 43.22; H, 3.18. Found: C, 43.07; H, 3.25.

A 1.0-g. sample of potassium *p*-vinylbenzenesulfonate was oxidized with potassium permanganate and converted to the sulfonamide. The product was hydrolyzed with alkali to remove any carboxamide. There resulted 0.16 g., 17% of the theoretical amount, of *p*-carboxybenzenesulfonamide, m.p. 276–277° dec.; reported m.p. 280° dec.[1a]

Attempts to isolate the barium and lead salt and the free acid have thus far been unsuccessful.

**Polymerization of Potassium *p*-Vinylbenzenesulfonate.**—Polymer A was prepared by polymerization of a solution of the potassium salt obtained by neutralization of the toluidine salt and extraction of the toluidine. To 3.5 g. of the dry *p*-toluidine salt was added 10 ml. of 1.2 *N* potassium hydroxide. This solution was extracted three times with 50-ml. portions of ether. Seventeen ml. of water was added and the extraction repeated. To this solution were added 0.06 g. of potassium persulfate (2.7% based on monomer) and 0.03 g. of sodium bisulfite (1.33% based on monomer). After 5 hours at 45° under oxygen-free nitrogen the solution was neutralized and evaporated to dryness. The polymer was dried under vacuum for 24 hours.

Polymers B, C and D were prepared from recrystallized potassium *p*-vinylbenzenesulfonate with different concentrations of the monomer in water and different amounts of initiator. Polymer D was prepared from a 25.3% solution of 1.35 g. of the salt in 3 ml. of water. This solution was placed in a flask fitted with a stirrer and flushed with oxygen-free nitrogen. A solution of 0.018 g. of potassium persulfate (1.33% based on monomer) and 0.009 g. (0.67% based on monomer) of sodium bisulfite in one ml. of water was added as initiator. This solution (*p*H 7–8) was stirred under nitrogen for five hours. The *p*H, now 4–5, was adjusted to 7–8 by adding a few drops of dilute potassium hydroxide solution. The solution was evaporated to dryness and dried in a vacuum. Polymer C was prepared following this procedure using twice as much persulfate (2.7%) and bisulfite (1.33%) for the same amount of monomer. Polymer B was prepared similarly using twice as much persulfate (2.7%) and bisulfite (1.33%) for a 7.6% solution of 1.35 g. of salt in 16.5 ml. of water except that the solution was not stirred during the polymerization. The thoroughly dried polymer is quite hygroscopic and has the unusual property of decrepitating as it absorbs water.

*Anal.* Calcd. for $(C_8H_7KO_3S)_x$: C, 43.22; H, 3.18. Found: C, 39.48, 39.75; H, 3.67, 3.48.

**Viscosity Determinations.**—The viscosities were determined on successive dilutions of aqueous solutions of the polymers in modified Ostwald viscometers at 30°. The data are presented in Fig. 1. The comparative values of the specific viscosity for solutions of 1.0 g. of the polymer in 100 ml. of solution are: A, 0.731; B, 0.453; C, 0.999; and D, 2.63.

LOUISVILLE, KENTUCKY

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[CONTRIBUTION FROM HERCULES EXPERIMENT STATION]

# The Preparation and Reactions of Methyl 9-Oxo-14-hydroperoxydehydroabietate

BY PAUL F. RITCHIE, THOMAS F. SANDERSON AND LANE F. MCBURNEY

RECEIVED AUGUST 14, 1953

Methyl 9-oxodehydroabietate, prepared by chromic acid oxidation of methyl dehydroabietate, has been oxidized with molecular oxygen to mixtures containing methyl 9-oxo-14-hydroperoxydehydroabietate. The hydroperoxide has been converted to four new phenanthrene derivatives and the structures of the compounds have been proved.

The primary attack of molecular oxygen upon the dehydroabietic acid nucleus[1] occurs at the 9-position, as was shown in previous communications.[1,2] It was demonstrated[2] that reaction also occurs at the 14-position but products of this secondary reaction were not isolated. In the present research a derivative of dehydroabietic acid in which the 9-position was not readily available for further oxidation, that is, methyl 9-oxodehydroabietate (II), was oxidized in the molten state at 90° in the presence of a benzoyl peroxide initiator. Oxidation was accomplished by continuously circulating oxygen through the reaction mixtures at atmospheric pressure while following the course of the reaction by measuring the volume of oxygen absorbed. The major initial product of this oxidation proved to be methyl 9-oxo-14-hydroperoxydehydroabietate (III) which was not isolated but was converted to four new, isolable phenanthrene derivatives (IV, V, VI and VII).

The methyl 9-oxodehydroabietate used in these experiments was prepared by a procedure hitherto unreported. Methyl dehydroabietate was oxidized with acetic acid solutions of chromic acid at temperatures of 30–50° to mixtures from which, after chromatographic adsorption on alumina, was obtained crystalline methyl-9-oxodehydroabietate in yields of 30–35%. An alternative method of isolating the ketone consisted of countercurrent extraction of the oxidation mixtures with isoöctane and methanol containing 5% of water as the solvent pair and by crystallization of the fraction recovered from the aqueous methanol phase. The ketone was isolated in yields comparable to those cited above but, even after repeated recrystallization resulting in apparent high purity, contained oxida-

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(1) A. E. Drake (to Hercules Powder Co.), U. S. Patent 2,434,643 (Jan. 20, 1948).

(2) P. F. Ritchie, T. F. Sanderson and L. F. McBurney, THIS JOURNAL, 75, 2610 (1953).