Table II

Melting Points and Analyses of Hydroxystyryl Compounds

Compound[a]	M.p., °C.	Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
1.	176–178	61.12	5.13	3.75	60.73	4.99	3.70
2.	213–215 (dec.)	59.55	5.25	..	59.39	5.12	..
3.	204 (dec.)	65.25	5.00	3.31	64.90	4.85	3.86
4.	188–190	61.12	5.13	3.75	60.65	5.11	3.76
5.	227 (dec.)	59.55	5.25	3.47	59.13	5.02	3.05
6.	188–190	65.25	5.00	3.31	65.65	4.69	3.02
7.	160–161	52.33	4.94	3.81	52.39	5.35	3.96
8.	159–160	51.39	5.07	3.53	51.79	5.60	3.58
9.	227–229	57.56	4.83	3.36	57.32	4.80	3.66

[a] Numbers refer to Table I.

the precipitated methosulfates were filtered, washed with ether, and recrystallized three times from methanol.

Compounds 1–9 were also prepared by refluxing equimolar amounts of N-methylquinaldinium or N-methyllepidinium methosulfates or 5-ethyl-2-methylpyridinium iodide and the appropriate aldehyde in isopropyl alcohol for 1 hr. The precipitated products were washed with ether and recrystallized from methanol.

All ultraviolet and visible spectra were recorded with a Beckman DK-2 spectrophotometer. The water–dioxane mixtures were prepared by volume, and 0.2 ml. of a saturated solution of each compound in aqueous potassium hydroxide was added to 25 ml. of solvent. Infrared spectra of all compounds were obtained in potassium bromide pellets using a Baird AB-2 spectrophotometer.

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The Epoxidation of Allyl-Substituted Phenols and Ethers[1,2]

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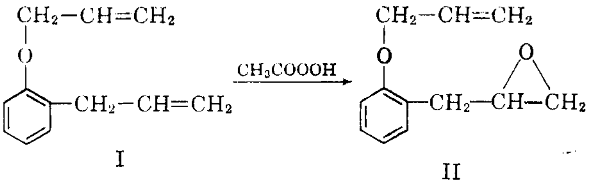
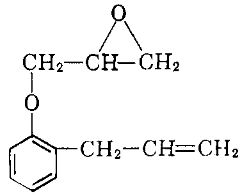
During the preparation of various polyepoxy compounds for testing as thermoset resins, the epoxidation of *o*-allylphenyl allyl ether (I) was carried out. It was found that although it was relatively easy to introduce one epoxy group, it was quite difficult to introduce two. Evidence indicated that the monoepoxy compound was *o*-glycidylphenyl allyl ether (II) rather than *o*-allylphenyl glycidyl ether (III). To check this the latter compound was prepared by treating *o*-allylphenol with epichlorohydrin. The physical properties—e.g., boiling point and refractive index of the product obtained by the epoxidation of I—were nearly identical to those of III and a mixture of them was not separated into two components in one trial by gas liquid chromatography.



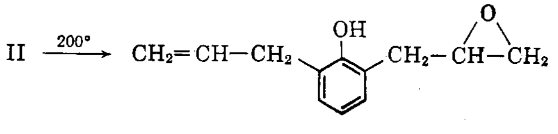
I II



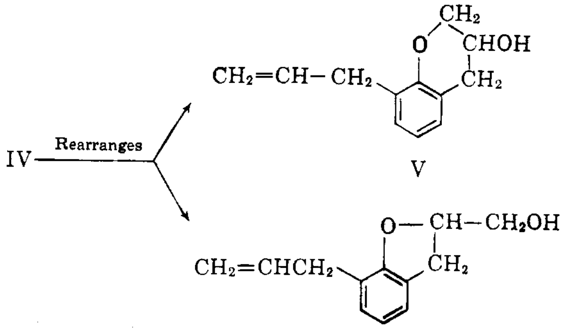
III

It was decided to heat the compounds to 200° and note if any change occurred. The ether (II) should undergo the Claisen rearrangement whereas III should remain substantially unchanged. When this was done, it was found that the glycidyl ether (III) did not change appreciably; however, the compound obtained by epoxidizing I underwent a profound change.

The product was not the expected 2-glycidyl-6-allylphenol (IV), since it had no oxirane oxygen in it. It was reasoned that IV cyclized at the rearrangement temperature to give V or VI or a mixture of the two. Further work with the product indicated that it was largely one material.



IV



V

VI

Since V is a secondary alcohol and VI is a primary alcohol, a test frequently used in carbohydrate work for differentiating between primary and secondary alcohols was applied.[3] This test consists of warming an acetone solution of the tosyl ester of the alcohol with sodium iodide. The tosylates of primary alcohols forms the iodides and

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(1) Paper No. 240 Journal Series, Research Laboratories, General Mills, Inc.

(2) Part of a paper presented at the 136th Meeting of the American Chemical Society in Atlantic City, New Jersey.

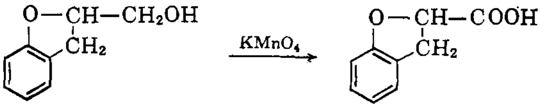
(3) J. W. H. Oldham and J. K. Rutherford, *J. Am. Chem. Soc.*, **54**, 366 (1932).

precipitate sodium *p*-toluenesulfonate, whereas the tosylates of the secondary alcohols are unchanged. The tosylate of the rearrangement product of III gave a quantitative precipitate of sodium *p*-toluene sulfonate indicating that it was the primary alcohol (VI) (2-hydroxymethyl-7-allylcoumaran).

Since *o*-glycidylphenol should close the ring on heating in the same manner as the rearranged allyl ether (IV), it was decided to investigate this material with the simpler structure. It was found that it had been prepared by Pannsevich-Kolyada and Idelchik[4] by epoxidizing *o*-allyl phenol. When the latter work was repeated it was found that the product had no oxirane content. This has also been observed and reported by Tinsley.[5]

Our results are in complete agreement with those of Tinsley. The structure of the cyclic product (VII) was proved by oxidation and by the fact that this alcohol also gave the qualitative test for a primary alcohol.

The oxidation with alkaline permanganate gave a mixture of two acids. One was salicylic acid and the other corresponded to VIII. There was no evidence of any ketone which would have resulted from the six membered ring alcohol.



VII VIII
+
Salicylic acid

It is concluded, therefore, that when *o*-allylphenyl allyl ether (I) is epoxidized, the chief product is *o*-glycidylphenyl allyl ether (II), which cyclizes *via* IV on rearrangement at high temperature to give largely 7-allyl-2-hydroxymethyl coumaran (VI).

Experimental

Preparation of *o*-Glycidylphenyl Allyl Ether (II).—*o*-Allylphenyl allyl ether[6] (I), n^{30}_D 1.5263 (348 g.), was added rapidly to a solution of 32 g. of anhydrous sodium acetate in 804 ml. of 40% peracetic acid at 17–18°. The solution was stirred for 7 hr. at 20–25° and poured into 4 l. of saturated brine. The brine was extracted with three 1-l. portions of methyl isobutyl ketone. The extracts were combined and washed with saturated brine containing sodium carbonate, then with brine containing a small amount of sodium sulfite. The washed extract was dried over anhydrous sodium sulfate, filtered, and the methyl isobutyl ketone removed, crude yield 382 g. The product was fractionated under vacuum using a one foot Vigreux column. A center cut (55%), b.p. 100–102°, at 0.6 mm. was taken (n^{30}_D 1.5289. Per cent oxirane oxygen calcd.: 8.42; found: 7.95). After refractionation through an 8-mm. Podbielniak Whirling Heliband column, a fraction (b.p. 96° at 0.74 mm., n^{30}_D 1.5282) was taken. Per cent oxirane oxygen found, 8.35%.

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.79; H, 7.37. Found: C, 76.24; H, 7.38.

Rearrangement of *o*-Glycidylphenyl Allyl Ether (II) to 2-hydroxymethyl-7-allylcoumaran (VI).—The *o*-glycidylphenyl allyl ether (67 g.) was heated to 200° for 3 hr. The refractive index increased to n^{30}_D = 1.5490. The mixture was fractionated through a 12-inch Vigreux column. The main fraction (48.5 g.) had an oxirane oxygen content of 0.8% and an index of refraction of n^{30}_D 1.5472. This fraction was heated for another hour at 200° and refractionated. The main fraction (36 g.) distilled at 104° at 0.8 mm. and had an oxirane oxygen content of 0.2%; n^{30}_D 1.5522.

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.79; H, 7.37; OH No. 295.3. Found: C, 75.76; H, 7.42; OH No. 294.5.

Tosylate.—The tosyl ester was made in the conventional manner by treating the alcohol (5 g.) with *p*-toluenesulfonyl chloride (10 g.) in pyridine (yield, 7 g.). Six grams of the liquid tosylate was dissolved in 18 g. of acetone. To this 5 g. of sodium iodide was added and the solution left to stand at room temperature for 3 days. A precipitate of 1.7 g. of sodium *p*-toluenesulfonate was filtered off. The filtrate was refluxed for 36 hr. during which time an additional 3.4 g. of salt came out. This amounted to better than 80% of the theoretical amount of sodium *p*-toluenesulfonate. An analysis on the salt confirmed that it was sodium *p*-toluenesulfonate. This was good evidence that the alcohol was primary rather than secondary.[3]

Epoxidation of *o*-Allylphenol.—Fifty grams of *o*-allylphenol was added over a period of 40 min. to 88.5 g. of 40% peracetic acid containing 3.6 g. of sodium acetate. The temperature was maintained at 25° ± 1° during the addition and for 5.5 hr. thereafter. The solution was then poured over iced brine. A small part of the product was separated, washed with cold brine, and sodium bicarbonate solution. After quickly drying, the resulting oil its oxirane oxygen content was determined and found to be 5.4% (theory, 10.7%). After standing at room temperature for 16 hr., the oxirane oxygen content had dropped to 0.6%. The remainder of the product was extracted with methyl isobutyl ketone and the extract washed with cold brine and sodium bicarbonate solution. After drying over anhydrous sodium sulfate, the solvent was stripped leaving 45.4 g. of oil which was fractionated through a 10-in. Vigreux column. A fraction (23 g.) b.p. 124–125° at 5 mm. (VII) was obtained, n^{20}_D 1.5583.

Anal. Calcd. for $C_9H_{10}O_2$: C, 72.0; H, 6.67, oxirane oxygen, 0; Found: C, 71.95; H, 6.70; oxirane oxygen, 0.2%.

Tosylate of VII.—The tosylate was prepared in the conventional manner from 5 g. of the alcohol (VII) and 10 g. of *p*-toluenesulfonyl chloride in pyridine. The solid product which resulted was purified by recrystallization from hexane. The tosylate (9.5 g.) came out as white needles, m.p. 70.8 to 71°.

Anal. Calcd. for $C_{16}H_{16}SO_4$: C, 63.16; H, 5.26; S, 10.52. Found: C, 62.9; H, 5.47; S, 10.49.

The tosylate gave the test for primary alcohol ester[3] as had the tosylate of the rearranged product (VI) from *o*-glycidyl phenyl allyl ether (II).

Oxidation of 2-Hydroxymethylcoumaran (VII).—Four grams of VII was dissolved in 20 cc. of acetone and added rapidly at room temperature to a solution of 6 g. of potassium permanganate in 100 cc. of acetone. The permanganate color disappeared almost immediately. The mixture was then poured into 800 cc. of water and the manganese dioxide filtered off. The filtrate was acidified with dilute sulfuric acid and concentrated to about 50 cc. under water pump vacuum. A brownish oil separated during the concentration. This was extracted with ether. The ether extract was washed with water, then twice with 10% sodium bicarbonate solution, and finally with water. The ether was dried over sodium sulfate and evaporated leaving 1.9 g. of oil which proved to be starting material. Infrared analyses showed no evidence of carbonyl band which would have re-

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(4) V. I. Pannsevich-Kolyada and Z. B. Idelchik, *Zh. Obshch. Khim.* **24**, 807 (1954).

(5) S. W. Tinsley, *J. Org. Chem.*, **24**, 1197 (1959). This paper issued about the same time that the present paper was presented before the 136th National Meeting of the American Chemical Society.

(6) L. Claisen, *Ann.*, **418**, 90 (1919).

sulted from the oxidation of a secondary alcohol. The bicarbonate washings were acidified with dilute sulfuric acid and extracted with ether. The ether extracts were washed with water, dried, and evaporated leaving a residue of 0.4 g. of solid. Recrystallization from hexane gave a mixture which melted from 116 to 137°. The mixture was separated into two components by adsorption on a column of aluminum oxide "nach Brockmann." A hexane solution of the mixture was put through the column. Examination with ultraviolet light showed two bands near top of the column. These were developed by successively putting the following solutions through the column: 50:50 hexane–ethyl ether and 50:50 hexane–acetone. The chromatogram developed into two areas which were cut apart and each extracted with 10% sodium carbonate solution. The extracts were acidified, taken up in ether, washed, etc. After recrystallizing from hexane, the acid extracted from the upper layer had a m.p. of 117.2–118°. Its analysis corresponded to 2-carboxycoumaran (VIII).

Anal. Calcd. for $C_9H_8O_3$: C, 65.85; H, 4.88; neut. equiv. wt., 164.15. Found: C, 66.05; H, 5.07; neut. equiv. wt., 172.

The recrystallized acid from the lower band, m.p. 157–159° proved to be salicylic acid.

Acknowledgment.—The authors wish to thank Professor Fred Smith of the University of Minnesota for helpful suggestions regarding this work.

Organic Disulfides and Related Substances. VII. Reaction of Lead Tetraacetate with Alkyl Disulfides[1,2]

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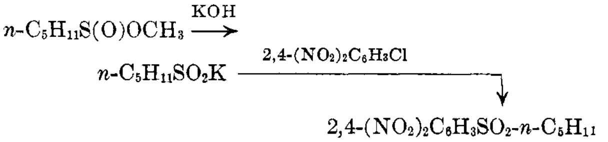
Received January 2, 1962

A preliminary report showed that reaction of various disulfides and thiols with lead tetraacetate in a mixture of chloroform and an alcohol afforded a promising synthesis of sulfinic esters, probably according to the equation[4]

$$\mathrm{RSSR + 3Pb(OAc)_4 + 4R'OH \longrightarrow 2RS(O)OR' + 3Pb(OAc)_2 + 4AcOH + 2AcOR'}$$

Preparation of methyl 1-pentanesulfinate was reported, with the reservation that the utility of the reaction for preparing alkanesulfinates from alkyl disulfides would be clear only after further work.[4] A subsequent report elaborated on the reaction for certain systems other than aliphatic ones.[2] This paper describes results with some alkyl disulfides.

Reaction of *n*-pentyl disulfide with lead tetraacetate in chloroform–methanol gave methyl 1-pentanesulfinate (I) in 35% yield. Evidence for the structure of I is afforded by: (1) elemental analysis; (2) molar refraction; (3) infrared absorption in the regions characteristic of sulfinates[2]; (3) saponification, followed by preparation of a known sulfone, according to the equation



$$n\text{-}\mathrm{C_5H_{11}S(O)OCH_3} \xrightarrow{\mathrm{KOH}} n\text{-}\mathrm{C_5H_{11}SO_2K} \xrightarrow{\mathrm{2,4\text{-}(NO_2)_2C_6H_3Cl}} \mathrm{2,4\text{-}(NO_2)_2C_6H_3SO_2}\text{-}n\text{-}\mathrm{C_5H_{11}}$$

and (4) consumption of potassium permanganate in accord with expectation and isolation of methyl 1-pentanesulfonate (53%).

Modification of the usual addition time (two hours) of lead tetraacetate from one to eleven hours gave virtually the same yield. In instances in which these latter products were analyzed however, results were unsatisfactory, thus strongly indicating that the reaction is not a smooth reliable means of preparing alkanesulfinates. Evidently, rapid concurrent reactions lead to by-products which cannot be separated practicably, even with an efficient fractionating column. Even so, close similarity of the infrared spectra and the refractive index showed that the principal component of the product was always I. The nature of some of the contaminants is suggested by early work in which but little methanol was used; acetoxylated species appeared to be present. When methanol was omitted altogether, reaction of some kind ensued but no pure product could be obtained; here again, a proper study of products was prevented by an inability to effect purification. Similar results were encountered with ethyl disulfide when it was used in the hope of obviating decomposition during distillation, which seemed a possible cause of the difficulty in obtaining a rigorously pure sulfinic ester. Methyl ethanesulfinate (II) was isolated in 31% yield. Analysis indicated presence of a small amount of impurity, but the identity of the bulk of the product was demonstrated by items (1)–(3) which were mentioned for I.

Methyl sulfite was obtained in 9% yield, along with the sulfinate II. Like II, the methyl sulfite could not be purified completely, but comparison of its infrared spectrum with that of authentic material (and saponification equivalent) left no doubt of its identity. That both methyl groups originated from methanol is suggested by isolation of *n*-butyl sulfite (in low yield) when *n*-butyl alcohol was substituted for methanol.

Efforts were made to improve the yield and purity of II. Since both the sulfinate and sulfite are

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(1) Research supported by the U. S. Army Research Office, Durham, North Carolina. Abstracted from portions of Ph.D. dissertations, Vanderbilt University, of J.M.L. (January, 1962), C.B.H. (January, 1960), and J.E.L. (August, 1957). Presented in part at Southeastern Regional Meetings of the American Chemical Society at Durham, North Carolina (November 14–16, 1957), and Birmingham, Alabama (November 3–5, 1960).

(2) Paper VI, L. Field, C. B. Hoelzel, and J. M. Locke, *J. Am. Chem. Soc.*, **84**, 847 (1962).

(3) DuPont Postgraduate Teaching Fellow, 1955–1957.

(4) L. Field, C. B. Hoelzel, J. M. Locke, and J. E. Lawson, *J. Am. Chem. Soc.*, **83**, 1256 (1961).