The Reaction of Divinyl Sulfone with *alpha*-Eleostearic Acid

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THE EFFICACY of such hetero atoms as oxygen and nitrogen in the functional groups of various dienophiles has been studied in this laboratory in connection with the Diels-Alder reaction of the eleostearic (9,11,13-octadecatrienoic) acids (1,2,3,4). It appeared of interest to consider the utility of a dienophile containing a sulfur atom in its activating group. Accordingly the capacity of divinyl sulfone to participate in the Diels-Alder reaction with *alpha*-eleostearic acid has been investigated. Previous work (5,6) has shown that aryl and alkyl vinyl sulfones react normally in the diene synthesis producing the expected adduct. However divinyl sulfone has received little attention as a dienophile; there appears to be only a single reference in the literature to its use as such for the conjugated fatty acids (6). In this instance it was reported that no product of definite constitution could be isolated. It is the purpose of this paper to present data regarding the formation and certain properties of the divinyl sulfone-eleostearic acid addition product and to adduce evidence which shows that the adduct is a transannular sulfone.

Experimental

Starting Materials

alpha-Eleostearic Acid. Pure *alpha*-eleostearic acid was prepared by the low-temperature fractional crystallization of the mixed fatty acids obtained from tung oil (7). The acid, m.p. 49.0–49.5°C., had an absorptivity, (a) = 176.7 at 271.5 millimicrons in cyclohexane.

Divinyl Sulfone. A commercial divinyl sulfone was used without further purification. It had a b.p. 102°C./10 mm., and $n^{20/D}$, 1.4788.

Preparation of Divinyl Sulfone-Eleostearic Acid Adduct. In a three-necked flask equipped with a reflux condenser, a thermometer, and a gas inlet tube were placed 56.0 g. of *alpha*-eleostearic acid (0.20 mole), 28.3 g. of divinyl sulfone (0.23 mole), and 0.5 g. of hydroquinone. The mixture was stirred magnetically and was maintained at 192°C. under an atmosphere of nitrogen for a period of 4 hrs. The excess divinyl sulfone was removed by vacuum-stripping on a steam bath, employing a stream of nitrogen as a sweep gas. There were obtained 77.3 g. of a viscous, crude product which could not be further purified by high-vacuum distillation.

Chromatographic Purification of the Adduct. A chromatographic procedure similar to that described by Ramsey and Patterson (8) was followed. However for elution purposes iso-octane and benzene saturated with water were employed instead of iso-octane saturated with methanol. A 400-g. portion of silicic acid was thoroughly mixed in a mortar with 90 ml. of water and 40 ml. of aqueous bromocresol green. Enough concentrated ammonium hydroxide solution (33 drops) was incorporated into the mixture to produce the green color of the indicator. The mixture was slurried with 700 ml. of iso-octane and poured into a chromatographic tube (45 mm. O.D. × 900 mm. long). A 10.6-g. sample of the adduct dissolved in 10 ml. of benzene was added to the packed column and washed down with a 5-ml. portion of benzene. A 1,000-ml. quantity of iso-octane was passed through the column first, and the fast moving band, unreacted eleostearic acid, was eluted at a peak effluent volume of 900 ml. Benzene was then added to the column, and the band containing the adduct was eluted after 1,800 ml. of benzene were passed through at a peak effluent volume of 2,800 ml. The benzene percolate was dried over anhydrous sodium sulfate, and the solvent was removed by vacuum-stripping on a steam bath with nitrogen as a sweep gas. There were obtained 7.7 g. of pure divinyl sulfone-eleostearic acid adduct.

Anal. Calcd. for $C_{22}H_{36}O_4S$: C, 66.7; H, 9.2; neut. equiv., 396.6. Found: C, 66.7; H, 9.3; neut. equiv., 396.7.

Hydrogenation of the Adduct. The amount of unsaturation present in the adduct was determined by quantitative hydrogenation, utilizing the apparatus described by Pack *et al.* (9). A 0.2832-g. sample of the adduct was hydrogenated in 25 ml. of glacial acetic acid with 0.1426 g. of 10% palladium-carbon as catalyst. Hydrogen uptake (S.T.P.): Calcd. for three double bonds, 48.0 ml.; for two double bonds, 33.0 ml. Found: 32.2 ml.

Hydrogenation of Divinyl Sulfone. A 0.1159-g. sample of divinyl sulfone was hydrogenated as described above. Hydrogen uptake (S.T.P.): Calcd. for two double bonds, 43.9 ml. Found: 44.0 ml.

Bromination of the Adduct. Bromination of the adduct was carried out according to the bromometric procedure of Kaufmann (10) for the determination of the iodine value. A 0.1098-g. sample of the adduct was treated with 25 ml. of a 0.1 N methanolic bromine solution and allowed to stand for a period of 24 hrs. Iodine Value: Calcd. for three double bonds, 182.0; for two double bonds, 123.1. Found: 122.9.

Bromination of Divinyl Sulfone. A 0.0717-g. sample of divinyl sulfone was brominated as described above. Iodine Value: Calcd. for two double bonds, 429.4. Found: 428.7.

Methyl Ester of the Adduct. A sample of the pure divinyl sulfone-eleostearic acid adduct was treated with an excess of a 0.2 M solution of diazomethane in ether. The ethereal solution was washed first with a 2% sodium carbonate solution, then with water, and finally was dried over anhydrous sodium sulfate. The solvent was first removed by distillation at atmospheric pressure, then under high vacuum.

Anal. Calcd. for $C_{23}H_{38}O_4S$: C, 67.3; H, 9.3; S, 7.8; OCH_3, 7.5; I.V., 128.0. Found: C, 67.3; H, 9.4; S, 7.5; OCH_3, 7.4; I.V. (hydrogenation), 127.9.

Molecular Weight of the Methyl Ester. The molecular weight of the methyl ester was determined cryoscopically in benzene according to the multiple-weight method prescribed by Findlay (11). Molecular weight: Calcd. 410.6. Found: 410.1, 410.5, 410.0.

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Epoxidation of the Methyl Ester. The methyl ester of the adduct was epoxidized with a perbenzoic acid-chloroform solution (12). An 8.405-g. sample of the methyl ester (20.4 millimoles) was allowed to stand with 120.0 ml. of 0.53 molar perbenzoic acid solution (63.6 millimoles) at room temperature for a period of 48 hrs. The unreacted perbenzoic acid was determined iodimetrically. Perbenzoic acid reacted (millimoles): Calcd. for three double bonds, 61.2; for two double bonds, 40.8. Found: 39.6.

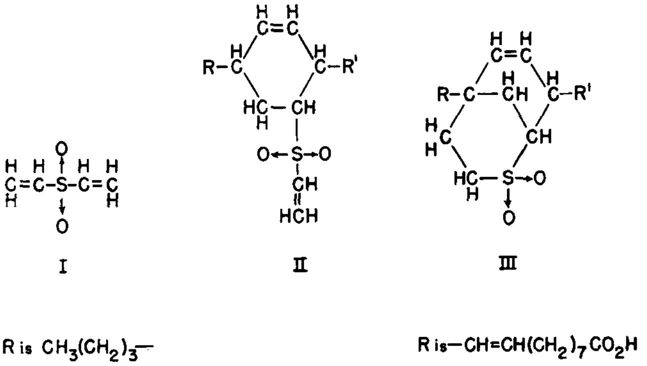
Attempted Epoxidation of Divinyl Sulfone. A 0.493-g. sample of divinyl sulfone (4.24 millimoles) was treated with 20 ml. of perbenzoic acid solution (10.6 millimoles) as outlined above. Iodimetric titration indicated that the uptake of active oxygen was nil.

Infrared Data. Infrared spectra of divinyl sulfone and of the adduct were investigated in the 2.5 to 12.5 micron region by means of the Perkin-Elmer Model 137 Spectrophotometer. The instrument had a resolution of 0.05 micron with the slit over-ride set at 25 microns. All measurements were made with an absorption cell 1.0 mm. in path length. Carbon tetrachloride solutions of divinyl sulfone and the adduct were employed at concentrations of 1.0 g./l. and 7.5 g./l., respectively. Pure carbon tetrachloride was placed in the reference beam to eliminate the absorption of carbon tetrachloride from the resulting spectra. Both spectrograms were examined for the presence of absorption bands in the 6.1 and 10.2 micron regions characteristic of the unsymmetrical vinyl groups, and in the 7.4–7.8 and 8.6–9.0 micron region where the sulfone group is known to absorb. The divinyl sulfone showed strong absorption bands at 6.1, 10.2, 7.6, and 8.8 microns while the adduct showed strong absorptions at 7.7 and 8.9 microns and a weak absorption band at 10.3 microns assigned to the internal *trans* ethylenic bond. There were no absorption bands indicating the presence of a vinyl group in the adduct.

Discussion

It has been shown that *alpha,beta*-unsaturated sulfones behave similarly to *alpha,beta*-unsaturated ketones in their reaction with substances containing an activated hydrogen (13,14). Since the addition of these prototropic reagents occurs by 1,4-addition to the conjugated system of *alpha,beta*-unsaturated ketones, it would seem that the sulfone linkage would enhance the same type of activation of the adjacent olefin bond. The activating effect of the sulfone group may be explained by the theoretical considerations of its electron configuration. Values of the parachor (15) and dipole moment (16) for various sulfones indicate an approximately tetrahedral arrangement of the valence bonds, implying that the sulfur is tetracovalent and the sulfur-oxygen bonds semipolar. This arrangement would result in the oxygen atoms having fractionally negative charges and the sulfur having a corresponding positive charge. Consequently the sulfur exerts a considerable electron attraction and facilitates a removal of an electron pair from the adjacent olefinic structure, expanding its valence shell to 10 electrons. This resonance form fulfills the requirements for a dienophile in the Diels-Alder reaction.

It might be expected that in the case of divinyl sulfone (I) each of the olefinic linkages could become activated (but not simultaneously), and capable of accepting two moles of a diene. However our preliminary work, making use of a large excess of *alpha*-eleostearic acid, showed that only one mole of the diene reacted with each mole of divinyl sulfone. This monomeric composition was ascertained by molecular weight determinations carried out on the methyl ester. Thus it appeared that structure (II) with three ethylenic bonds, one cyclic, one exocyclic, and a third belonging to the vinyl group, should predominate in the addition product. However quantitative hydrogenation and bromination experiments indicated the presence of only two double bonds in the adduct while hydrogen and bromine both reacted normally with the two vinyl groups of pure divinyl sulfone. In addition, the epoxidation of two double bonds in the adduct with the theoretical amount of perbenzoic acid and the failure of pure divinyl sulfone to react under the same conditions[2] further supports the infrared spectra, showing the absence of vinyl groups in the product. It was concluded that although a Diels-Alder type adduct was formed, the postulated structure (II) is not consonant with the analytical data.



R is $CH_3(CH_2)_3$—

R is—$CH{=}CH(CH_2)_7CO_2H$

FIG. 1.

Reference to scale models shows that while it would be sterically difficult for the remaining vinyl group of the adduct to react with another molecule of eleostearic acid, it is nevertheless free enough to form a six-membered ring by the addition of a tertiary hydrogen from the cyclohexene nucleus. It has been mentioned previously that vinyl sulfones are capable of adding prototropic substances. Therefore it is proposed that the reaction of divinyl sulfone with *alpha*-eleostearic acid proceeds in two steps. The first step consists of a normal Diels-Alder addition of one vinyl group of the divinyl sulfone across the *trans, trans*-ethylenic bonds of the *alpha*-eleostearic acid, resulting in two positional isomers which differ only in the position of the vinyl sulfone group, either on carbon atom 4 or 5 of the cyclohexene ring. In view of the fact that carbon atoms 3 and 6 of the cyclohexene nucleus of the adduct possess active hydrogen atoms, it appears probable that these can act as points of attachment with the attendant formation of a carbon-to-carbon bond involving the *beta*-carbon atom of the vinyl group and the addition of the hydrogen to the *alpha*-carbon atom. Thus the second step of reaction involves the addition of the hydrogen belonging to carbon 6 of the cyclohexene ring to the vinyl sulfone moiety situated on carbon 4, and similarly the positional isomer with the vinyl sulfone group on carbon 5 combines with the active hydrogen on carbon 3.

On the basis of the foregoing considerations it may

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[2] It is known that perbenzoic acid does not normally epoxidze vinyl compounds (17) of this type.

be concluded that the Diels-Alder adduct of divinyl sulfone and eleostearic acid exists as a transannular sulfone (III).

Summary

The reaction of divinyl sulfone with *alpha*-eleostearic acid has been studied. The reaction product was found to be monomeric, consisting of only one divinyl sulfone and one eleostearic moiety. Contrary to expectations, the adduct contained only two ethylenic linkages rather than three and the addition product is considered to be a transannular sulfone.

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Morro Seed Oil[1]

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THE MORRO TREE, *Crescentia alata* HBK, which belongs to the family *Bignoniaceae,* grows to a height of 4 meters and produces globose fruits that are borne directly on trunk and branches. These fruits, 15 cm. in diameter, are brownish yellow when ripe, contain a pulp with a characteristic agreeable odor, and have a sweetish taste that is very palatable to livestock. The seeds, which are contained in the pulp, are dark brown and flat, have a heart shape, and are 8 mm. long, 6 mm. thick; the hull is thin and the kernel yellowish white.

The average weight per indivudual seed is 40 mg., 73% of which represents the kernel and 27% the hull. With an average of 8% moisture the seeds contain 31% oil. They are utilized in El Salvador in the preparation of refreshments (called "horchata"), to which they impart their particular agreeable aroma. The seeds are sold in the markets for these purposes.

The Morro tree grows wild and is usually found growing in heavy clay soils (grumosols usually 1 or 2 meters deep over hardpan), which in spite of their level topography are not adapted to most other agricultural uses. These soils, which constitute about 3% of the agricultural land of El Salvador and which occupy large areas in other Central American countries, are generally used only for unimproved pastures consisting of native grasses. During the rainy season such soils become water-logged and, during the dry season, so dry that large cracks appear. Morro trees seem to be the climax vegetation on such soils.

The northernmost point of distribution of the Morro is Mexico while the southernmost is Colombia and Venezuela (4,5,6). The only known uses so far are that the pulp is eaten by livestock, the seeds are used for refreshments, and to a limited extent the hard epicarp is used as containers or cups by rural people.

As the fruits are attached to the trunk and branches, harvesting is done by hand. Some of the ripe fruits fall, and even though cattle can break the hard shell, the fruits are usually cut in halves and the pulp is left for the cattle to feed on.

The analysis of the whole pulp is shown in Table I.

TABLE I

Analysis of the Whole Pulp, Including Seeds, of Ripe Morro Fruits [a]

	%
Moisture	73.43
Proteins [b]	14.60
Fat [b]	13.00
Crude fiber [b]	6.75
Carbohydrates (by difference) [b]	56.35

[a] Determined by Official Methods of the A.O.A.C. (2).
[b] On dry-matter basis.

Laboratory Procedure. Hulls of the Morro seed can be separated from the kernel relatively easily by aspiration because they do not adhere to the kernel when dry.

Laboratory samples of Morro seed oil were prepared by pressing the ground kernels in a Carver hydraulic press at a temperature of 100°C. and at a pressure of 5,000 p.s.i. The moisture content of the seed when pressed was approximately 8%. Expression of the oil was easier when the moisture was increased to 10%.

Oil extracted with petroleum ether had about the same characteristics including color and flavor as the pressed oil.

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