2,3-Epoxysuccinic anhydride[1]

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During a general study of reactive diluents for epoxy resins, the highly strained 2,3-epoxysuccinic anhydride was prepared by dehydrating *cis*-2,3-epoxysuccinic acid (1–3). A successful dehydration method employed ethereal dicyclohexyldicarbodiimide to form a crystalline anhydride that was further purified by sublimation. The sublimate gave a strong anhydride absorption band in the infrared; the nuclear magnetic resonance absorption spectrum was of the simplest type, with one single absorption band at τ 5.67. The mass spectrum of the anhydride gave the molecular ion at m/e 114, with other major ions at m/e 29 (CHO^+), 42 ($C_2H_2O^+$) (ketene molecular ion), and 69 ($C_3H_2O_2{}^+$). These observations are in complete accord with the monomeric anhydride possessing the symmetry characteristics of the title compound.

Several methods did not produce a crystalline anhydride: (*i*) pyrolysis of 2,3-epoxysuccinic acid, (*ii*) reaction with acetic anhydride, and (*iii*) reaction with phenylisocyanate.[2] In methods *i* and *ii*, a mixture of 2,3-epoxysuccinic acid and 2,3-epoxysuccinic anhydride was formed; method *iii* produced a highly crystalline, nitrogen-containing product that gave an infrared spectrum very similar to that of authentic 2,3-epoxysuccinanilic acid. Elemental analysis and an acid equivalent determination demonstrated that the product from method *iii* was a mixture of the mono- and di-anilides of 2,3-epoxysuccinic acid in a 17:3 ratio.

Ring opening of the anhydride functional group with aromatic amines and aromatic hydrazines has been carried out to provide several examples of half amides and half hydrazides of 2,3-epoxysuccinic acid under reaction conditions similar to those of the ring opening of succinic anhydride.[3]

EXPERIMENTAL

All glassware was oven dried at 150 °C and stored in a vacuum oven. Traces of water were removed from all organic solvents; ether was stored over sodium wire. Nuclear magnetic resonance spectra were determined on a Varian A-60 spectrometer with deuteriochloroform as the solvent and tetramethylsilane as the internal standard. Mass spectra were determined on a double-focusing instrument (A.E.I. model MS9). Samples were introduced by a direct probe with a source temperature of 80 °C and an ionizing voltage of 70. Melting points were determined with a Reichert microscope equipped with a hot stage.

2,3-Epoxysuccinic Acid

This compound was prepared by the method of Payne and Williams in an overall yield of 58% from maleic acid (1). An alternative method that considerably shortened the preparation time utilized ion-exchange resins to form the free acid from its sodium salt.

Crude sodium epoxysuccinate (5.0 g) in ice-cold water (525 ml) was passed down a column of ice-cold Rexyn 101 (H^+ form) ion-exchange resin (wet volume, 70 ml). The column was washed with ice-cold water (150 ml). The cold eluate was diluted with chilled tetrahydrofuran (150 ml) and the product extracted with 1:1 tetrahydrofuran–ether (3 × 70 ml). The combined extracts were dried with anhydrous magnesium sulfate and concentrated under a reduced pressure to a crystalline solid (1.032 g, 28%), m.p. 146–148 °C.

2,3-Epoxysuccinic Anhydride

Dicyclohexyldicarbodiimide (0.415 g, 0.002 mole) in ether (10 ml) was added rapidly to an ethereal solution of 2,3-epoxysuccinic acid (0.264 g, 0.002 mole). *N,N'*-Dicyclohexylurea precipitated immediately and was collected by filtration after 1 h (yield 0.424 g, 95%). Concentration of the filtrates, at a reduced pressure, gave a crude solid that was recrystallized from a small volume of ether at dry ice temperature. The crude solid product exhibited a trace of hydroxyl absorption and strong carbonyl absorptions at ν_{max} 1 875 (weak), 1 810 (weak), and 1 745 (strong) cm^{-1}, respectively, in the solid phase (KBr). The nuclear magnetic resonance spectrum gave mainly a very strong absorption at τ 5.63, with two minor absorptions at τ 6.23 and τ 0.45. Authentic 2,3-epoxysuccinic acid possessed absorption bands at τ 6.23 and τ 0.45.

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[2] M. P. Lee and S. M. Creighton, unpublished experiments.

[3] D. L. Mitchell, unpublished experiments.

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TABLE I

Derivatives of 2,3-epoxysuccinic acid

				Calculated				Found			
Series	Reactants	Melting point (°C)	Molecular formula	C (%)	H (%)	N (%)	Acid equiv-alent	C (%)	H (%)	N (%)	Acid equiv-alent
Monoarylamides	Aniline–ESA*	179–180	$C_{10}H_9NO_4$	58.0	4.4	6.8	207	57.9	4.6	6.9	207
	2,5-Dichloroaniline–ESA	183–184	$C_{10}H_7Cl_2NO_4$	43.5	2.6	5.1	276	43.5	2.7	5.1	280
	4-Nitroaniline–ESA	178–179	$C_{10}H_8N_2O_6$	47.6	3.2	11.1	252	47.5	3.2	11.1	256
	1-Naphthylamine–ESA	176–178	$C_{14}H_{11}NO_4$	65.4	4.3	5.5	257	65.0	4.5	5.5	257
Monoarylhydrazides	2,5-Dichlorophenylhydrazine–ESA	198–200	$C_{10}H_8Cl_2N_2O_4$	41.3	2.8	9.6	291	41.4	3.0	9.5	291
	4-Toluenesulfonylhydrazine–ESA	200–201	$C_{11}H_{12}N_2O_6S$	44.0	4.0	9.3	300	43.8	4.0	9.5	—
	N,*N*′-Diphenylhydrazine–ESA	174–175	$C_{16}H_{14}N_2O_4$	62.9	4.9	9.8	298	63.9	5.4	8.7	300

*ESA = 2,3-epoxysuccinic anhydride.

The crude product was sublimed under a vacuum (0.1 mm) onto a cold finger that was chilled with a dry ice – acetone slurry. Sublimation took place at room temperature; a warm water bath (50–55 °C) was employed in some experiments. The first sublimation yielded 70–75% of the fluffy crystalline anhydride, whereas resublimation transferred 92–95% of the product to the cold finger. The residue in each sublimation was identified as 2,3-epoxysuccinic acid. The twice-purified sublimate melted sharply at 63–64 °C, but the melt crystallized as thin needles around 110–125 °C, with the second product melting at 146–147 °C. The melting behavior was repeated on a rock-salt wafer, and the infrared spectrum of the second crystallization product was identical with that of 2,3-epoxysuccinic acid (m.p. 148–149 °C).

The mass spectrum of the sublimate (m.p. 63–64 °C) gave the following major *m/e* peaks, with the most intense peak assigned a value of 100 (in parentheses) (all other peak heights were normalized to this peak height): 17 (6), 18 (25), 25 (4), 26 (9), 28 (9), 29 (33), 41 (6), 42 (100) (ketene ion), 44 (6), 69 (48), 114 (molecular ion).

Anal. Calcd. for $C_4H_2O_4$: C, 42.1; H, 1.8. Found: C, 42.0; H, 1.8.

2,3-Epoxysuccinanilic Acid

A solution of ethereal aniline (0.093 g, 0.001 mole) was refluxed with purified 2,3-epoxysuccinic anhydride (0.112 g, 0.001 mole). The solution was concentrated to a crystalline mass that was recrystallized several times from acetone – light petroleum, m.p. 179–180 °C.

Anal. Calcd. for $C_{10}H_9NO_4$: C, 58.0; H, 4.4; N, 6.8; acid equivalent 207. Found: C, 57.9; H, 4.6; N, 6.9; acid equivalent 207.

Derivatives of 2,3-Epoxysuccinic Acid

Ethereal solutions of purified 2,3-epoxysuccinic anhydride (0.001 mole) were heated under reflux with 0.001 mole of the aromatic amines and aromatic hydrazines described in Table I. All derivatives were recrystallized several times from acetone – light petroleum.

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Reaction of phenols with acetic anhydride – dimethyl sulfoxide[1]

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Various reactions of dimethyl sulfoxide resulting in mild oxidation of alcohols have been recognized for over seven years.[2] Recently, the valuable Moffatt technique (2), employing dimethyl sulfoxide – dicyclohexylcarbodiimide with, for example, pyridinium trifluoroacetate, has also been found (1, 4) to cause alkylation of certain phenols. By this means naphthols I*a* and IV*a* have been converted into ketones III and V, and the product of monoalkylation has been isolated by using certain phenols with free ortho or para positions (1, 4).

Recently, we became concerned with the use of a mild technique for the oxidation of an alcohol in the presence of a phenol substituent. Consequently, an attempt was made to utilize the acetic anhydride – dimethyl sulfoxide method (3). Shortly afterwards, it became evident that phenols will also react with this reagent. Support for this view was provided by allowing β-naphthol to react in an acetic anhydride – dimethyl sulfoxide solution for 20 h at room temperature. A thin-layer chromatogram of the crude product indicated the presence

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[2] A succinct review of such reactions, apparently proceeding through oxysulfonium intermediates, has been prepared (1); see also refs. 2 and 3.

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