224), and *tert*-butyl (5; 230–235) esters. Succinic acid gave methyl (68; 195) *n*-propyl (77; 235), *n*-butyl (80; 267), and isopropyl (10; 210) esters, and *tert*-butyl alcohol failed to react.

Separation of Aromatic Acids from Primary Acids. A mixture of primary aliphatic carboxylic acid (0.05 mol), aromatic acid (0.05 mol), ethanol (100 mL), and the packing reagent (8 g) was heated under reflux for 2 h on a steam bath. The workup of the reaction mixture in the aforementioned method afforded a neutral product which was identified as the ethyl ester of the primary acid used. The sodium bicarbonate extract, obtained during the workup, furnished, on acidification, the aromatic acid. Thus, the following mixtures were separated: (i) benzoic and phenylactic acids (recovered benzoic acid, 96%, mp 121 °C; ethyl phenylacetate, 70%, bp 220 °C); (ii) benzoic acid and succinic acids (recovered benzoic acid 98%, mp 118 °C; diethyl succinate, 65%,[9] bp 205–210 °C); (iii) salicylic acid and phenylacetic acids (recovered salicylic acid, 94%, mp 155 °C; ethyl phenylacetate, 85%, bp 220 °C); (iv) *m*-nitrobenzoic and adipic acids (recovered *m*-nitrobenzoic acid, 95%: mp 137 °C; diethyl adipate, 87%,[9] bp 242 °C); (v) diphenylacetic and phenylacetic acids (recovered diphenylacetic acid, 90%, mp 144 °C; ethyl phenylacetate, 87%, bp 220 °C); (vi) diphenylacetic and adipic acids (recovered diphenylacetic and adipic acids (recovered diphenylacetic acid, 82%, mp 146 °C; diethyl adipate, 76%, 240 °C; (vii) benzilic and phenylacetic acids (recovered benzilic acid, 88%, mp 148 °C; ethyl phenylacetate, 85%, bp 219 °C); (viii) benzilic and adipic acids (recovered benzilic 90%, mp 148 °C; diethyl adipate, 78%, bp 241 °C); (ix) pivalic and phenylacetic acids (pivalic acid was not recovered; ethyl phenylacetate, 87%, 220 °C); (x) pivalic and adipic acids (ethyl pivalate, bp 116–118 °C, not obtained; diethyl adipate, 72%, bp 242 °C).

With Phosphorus Pentoxide. A mixture of organic acid (0.05 mol), ethanol (50 mL), and phosphorus pentoxide (0.5 g) was heated on the steam bath for 2 h. The reaction mixture on the usual workup gave phenylacetic (80; 215), succinic (65; 210), adipic (68; 270), and chloroacetic (48; 140) esters. Under similar conditions, salicylic, *m*-nitrobenzoic, *p*-toluic, and *p*-anisic acids remained unaffected. However, these aromatic acids (0.05 mol) in ethanol (50 mL) with a larger quantity of phosphorus pentoxide (5 g) after 2 h of heating furnished esters and recovered acids in nearly 10% and 90% yields, respectively. With benzoic acid (0.05 mol) and ethanol (50 mL) the following observations were recorded: (i) phosphorus pentoxide (0.5 g), 2 h of heating, ester nil and acid 95%; (ii) phosphorus pentoxide (5 g), 2 h of heating, ester 10% and acid 88%; (iii) phosphorus pentoxide (5 g), 16 h of heating, ester 20% and acid 72%; (iv) 89% phosphoric acid (2.5 mL), 2 h of heating, ester 2–3% and acid 96% (cf. phenylacetic acid furnished 30% ester and 60% recovered acid); (v) 98% sulfuric acid (2.5 mL), 2 h of heating, ester 74%, acid 15%.

Registry No. Phosphorus pentoxide, 1314-56-3; adipic acid, 124-04-9; succinic acid, 110-15-6; phenylacetic acid, 103-82-2; diethyl adipate, 141-28-6; diethyl succinate, 123-25-1; ethyl phenylacetate, 101-97-3; cinnamic acid, 621-82-9; ethyl cinnamate, 103-36-6; ethyl formate, 109-94-4; diethyl tartrate, 87-91-2; diethyl oxalate, 95-92-1; diethyl suberate, 2050-23-9; ethyl palmitate, 628-97-7; ethyl β-phenylpropionate, 2021-28-5; ethyl (2,4-dichlorophenoxy)acetate, 533-23-3; ethyl chloroacetate, 105-39-5; diethyl malonate, 105-53-3; ethyl benzoate, 93-89-0; tartaric acid, 87-69-4; oxalic acid, 144-62-7; suberic acid, 505-48-6; palmitic acid, 57-10-3; β-phenylpropionic acid, 501-52-0; (2,4-dichlorophenoxy)acetic acid, 94-75-7; chloroacetic acid, 79-11-8; malonic acid, 141-82-2; glutaric acid, 110-94-1; diethyl glutarate, 818-38-2; pimelic acid, 111-16-0; diethyl pimelate, 2050-20-6; azelaic acid, 123-99-9; diethyl nonanedioate, 624-17-9; sebacic acid, 111-20-6; diethyl

decanedioate, 110-40-7; maleic acid, 110-16-7; diethyl maleate, 141-05-9; diphenylacetic acid, 117-34-0; ethyl diphenylacetate, 3468-99-3; dichloroacetic acid, 79-43-6; ethyl dichloroacetate, 535-15-9; trichloroacetic acid, 76-03-9; ethyl trichoroacetate, 515-84-4; pivalic acid, 75-98-9; ethyl pivalate, 3938-95-2; methyl phenylacetate, 101-41-7; propyl phenylacetate, 4606-15-9; butyl phenylacetate, 122-43-0; benzyl phenylacetate, 102-16-9; isopropyl phenylacetate, 4861-85-2; *tert*-butyl phenylacetate, 16537-09-0; dimethyl succinate, 106-65-0; dipropyl succinate, 925-15-5; dibutyl succinate, 141-03-7; diisopropyl succinate, 924-88-9.

Studies of Sulfinyl Radicals. 2. Reversibility of Addition to Styrene[1]

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Received January 25, 1983

The reactions that sulfinyl radicals are known to undergo so far are only coupling reactions[2] and thiosulfonates (RSS(O$_2$)R) from self-coupling reactions are considered to be formed through disulfoxides (RS(O)S(O)R)[3] and/or sulfenyl sulfinates (RS(O)OSR). Unlike thiyl and sulfonyl radicals, attempts to obtain addition products of sulfinyl radicals from diphenylethylene,[4] styrene,[5] cyclohexene,[6] and 2-butene[7] are all unsuccessful. It may be ascribed to a greater stability[1,2a] of sulfinyl radicals than thiyl and sulfonyl radicals.

We report here the observation suggesting the reversibility of the addition reaction of sulfinyl radicals. Benzhydryl *p*-tolyl sulfoxide (BTSO) and benzhydryl methyl sulfoxide (BMSO) are thermally decomposed at 120 °C in the presence of *cis*-β-deuteriostyrene. Thermal decompositions of these sulfoxides, which give sulfinyl and benzhydryl radicals by carbon–sulfur bond fission, were investigated in the previous paper,[1] and first-order rate constants are 4.8 × 10^{-4} and 5.0 × 10^{-4} s^{-1} at 120 °C for BTSO and BMSO, respectively. We have measured the NMR spectra of reaction mixtures of thermal decomposition of BMSO in benzene-d_6 in the presence of *cis*-styrene. As the decomposition of BMSO proceeds, with a half-life period of 23 min (120 °C), the signals due to β-protons of *trans*-styrene, namely, the doublet ($J = 16$ Hz) at δ 5.60, appeared and its intensity gradually increased with decreasing signal intensity of δ 5.08 (doublet, $J = 11$ Hz) due to *cis*-styrene. Polymerization or any other reaction of styrene was not observed under these experimental conditions.

We already reported that similar isomerizations of *cis*-styrene to *trans*-styrene were observed in radical copolymerization of styrene with sulfur dioxide at 50 °C[8] and

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(8) ^{1}H NMR δ 1.2 (6 H, dd, *J* = 6 Hz), 3.5 (2 H, s), 4.9 (1 H, heptate, *J* = 6 Hz), 7.2 (5 H, s).
(9) IR spectrum indicated the absence of aromatic ester.

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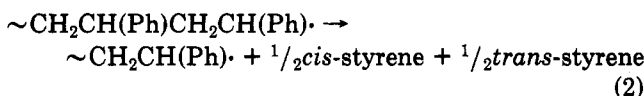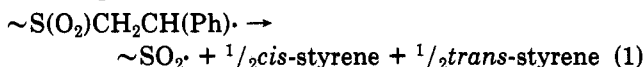
Table I. Thermal Decompositions of the Sulfoxides and (Phenylazo)diphenylmethane in the
Presence of *cis*-β-Deuteriostyrene at 120 °C

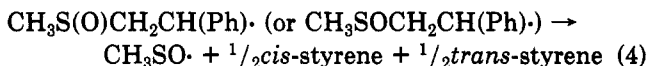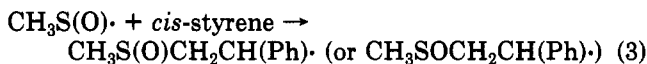| radical source (concn, 10^4 M)	*cis*-styrene, 10^4 M	C_6D_6, mL	pyridine-d_5, mL	trans/cis ratio at $\cong 50\%$ convn (convn, %; reactn time, min)
p-Tol-S(O)CHPh$_2$ (3.3)	4.3	0.40	0.01[a]	0.67 (58,[b] 30)
CH$_3$S(O)CHPh$_2$ (4.3)	4.3	0.40	0.01[a]	0.26 (55,[c] 30)
CH$_3$S(O)CHPh$_2$ (4.3)	4.3	0.40	0.40	0.44 (55,[c] 45)
PhN=NCHPh$_2$ (3.7)	4.3	0.40		0.00 (51,[c] 240)

[a] A small amount of pyridine was added to inhibit the ionic reaction.[1] [b] Calculated from the rate constant in ref 1.
[c] Measured from NMR by using the area ratios of total phenyl protons vs. methyl or methine protons of the radical sources.

in its homopolymerization at 250 °C.[9] Reactions 1 and 2 are responsible for these isomerizations. It is clear that

$$\sim S(O_2)CH_2CH(Ph)\cdot \rightarrow$$
$$\sim SO_2\cdot + {}^1/_2 cis\text{-styrene} + {}^1/_2 trans\text{-styrene} \quad (1)$$

$$\sim CH_2CH(Ph)CH_2CH(Ph)\cdot \rightarrow$$
$$\sim CH_2CH(Ph)\cdot + {}^1/_2 cis\text{-styrene} + {}^1/_2 trans\text{-styrene} \quad (2)$$

the low bond dissociation energy of the carbon–sulfur bond makes reaction 1 rapid even at low temperature (50 °C). The isomerization observed in the present study can be explained similarly, namely, by addition–elimination reactions of sulfinyl radicals (eq 3 and 4[10]). Table I shows

$$CH_3S(O)\cdot + cis\text{-styrene} \rightarrow$$
$$CH_3S(O)CH_2CH(Ph)\cdot \text{ (or } CH_3SOCH_2CH(Ph)\cdot) \quad (3)$$

$$CH_3S(O)CH_2CH(Ph)\cdot \text{ (or } CH_3SOCH_2CH(Ph)\cdot) \rightarrow$$
$$CH_3SO\cdot + {}^1/_2 cis\text{-styrene} + {}^1/_2 trans\text{-styrene} \quad (4)$$

the molar ratio of *trans*- to *cis*-styrene at nearly 50% conversion. From the table it can be seen that BTSO in benzene-d_6 and BMSO in pyridine-d_5 also isomerize *cis*-styrene considerably.

Other isomerization mechanisms without involving sulfinyl radicals may be excluded from the results in Table I. (Phenylazo)diphenylmethane was used to check that isomerization was not induced by benzhydryl radical, which is another radical formed in decompositions of the sulfoxides. Table I shows that thermal decomposition of (phenylazo)diphenylmethane in the presence of *cis*-styrene in benzene-d_6 at 120 °C, half-life period of which is about 240 min from NMR, gave no *trans*-styrene after the half-life period. In this reaction polystyrene was formed and styrene concentration gradually decreased.

Boothe, Greene, Shevlin, Willcott, Inners, and Cornelis[7] have found that the β-phenylsulfinyl *sec*-butyl radical eliminates the phenylsulfinyl radical and the elimination is so rapid that the formations of 2-butenes are stereoselective when diastereomeric precursors are used. Our conclusion that sulfinyl radicals may add styrene but that its reverse reaction is much faster is in accord with their findings and it can explain an inertness of sulfinyl radicals toward olefinic compounds described before.

Experimental Section

General Remarks. NMR spectra were obtained by using a JEOL JNM-PS-100 (100 MHz) spectrometer.

Materials. *cis*-β-Deuteriostyrene (KOR ISOTOPES) was uses without further purification. The content of *cis*-styrene was over 99% from NMR analysis. Benzhydryl *p*-tolyl sulfoxide (BTSO)

and benzhydryl methyl sulfoxide (BMSO) were prepared by the method described in the previous paper.[1] (Phenylazo)diphenylmethane was prepared by the method of Cohen and Wang[11] and checked for purity by NMR analysis of the methine proton (δ 6.14 in benzene-d_6, singlet).

Thermal Decompositions of BTSO, BMSO, and (Phenylazo)diphenylmethane in the Presence of *cis*-β-Deuteriostyrene. Degassed and sealed NMR tubes containing radical precursor (BTSO, BMSO, or (phenylazo)diphenylmethane) and *cis*-styrene in benzene-d_6 (see Table I) were immersed in a water bath regulated at 120 °C, and NMR measurements were taken at room temperature after the tubes were cooled to stop the reaction at regular time intervals. The main products in BTSO or BMSO decompositions are the coupling products, namely, the corresponding thiosulfonates (RSS(O$_2$)R) and tetraphenylethane, like the case without styrene in the previous paper,[1] and for (phenylazo)diphenylmethane, polystyrene and tetraphenylethane were identified from the NMR spectrum of the reaction mixture.

As shown in Table I a small amount of pyridine-d_5 was added in the decompositions of BTSO (or BMSO) in benzene-d_6, since the absence of pyridine gave products such as benzhydryl *p*-tolyl sulfone, bis(diphenylmethyl) ether, *p*-tolyl disulfide, and benzhydryl *p*-tolyl sulfide other than the coupling products (the thiosulfonate and tetraphenylethane), which may be formed by ionic reactions.[1]

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Photoinitiation of the S$_{RN}$1 Reaction by Excitation of Charge-Transfer Complexes

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Extensive studies during the last decade of S$_{RN}$1 aromatic substitutions have demonstrated the importance of this reaction class, both from a mechanistic and synthetic viewpoint.[1,2] Substitutions proceeding by this mechanism can be effected under mild conditions and without the use of highly activating substituents. Because of the myriad of synthetically useful transformations brought about in this fashion, definitive work is now available which characterizes both the propagation[3] cycle, summarized in Scheme I and the termination[4] steps of this reaction.

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