sodium methoxide does not occur in dioxane.[1] Moreover, alkaline treatment of alkyl and aryl ethers of 4-nitrobenzaldoxime in water–dioxane solution leads to 4-nitrobenzonitrile, without a trace of nitro substitution.[7]

The alkylation of the oxime and the elimination–substitution reactions can be carried out in a single operation, synthetically useful for the preparation of 4-alkoxybenzonitriles from 4-nitrobenzaldehyde. Thus, treatment of 4-nitrobenzaldoxime with benzyl bromide (1 equiv) and NaH (3 equiv) in DMF at room temperature afforded the nitrile **2c** in good yields. However, the method has some limitations; thus, reaction of 4-nitrobenzaldoxime with the tertiary alkyl halide ethyl 2-bromo-2-methylpropionate did not afford the expected ethyl 2-(4-cyanophenyl)-2-methylpropionate but instead formed 4-ethoxybenzonitrile (**2e**, 68% yield). This compound can arise from nitro substitution by sodium ethoxide, probably formed in the autocondensation of the initial intermediate, sodium 2-(ethoxycarbonyl)-2-methylethoxide.

Experimental Section

NMR spectra were determined on a Perkin-Elmer R-24B (60 MHz) instrument by using internal Me_4Si as a reference. IR spectra were recorded on a Perkin-Elmer 577 spectrophotometer. Melting points were determined in a Büchi apparatus and are uncorrected. The mass spectrum was determined on a Hewlett-Packard 5930A mass spectrometer. Microanalyses were performed by Instituto de Quimica Bio-Orgânica, Barcelona.

Alkylation of 4-Nitrobenzaldoxime. To a suspension of 0.24 g (10 mmol) of sodium hydride (dispersion in oil, washed with hexane) in 25 mL of anhydrous DMF was added 1.66 g (10 mmol) of 4-nitrobenzaldoxime portionwise. The dark red solution was stirred at room temperature for 10 min, and a solution of 10 mmol of the alkylating agent (methyl iodide, epichlorohydrin, benzyl bromide or 2-butyl bromide, respectively, for **1a–d**) in 5 mL of anhydrous DMF was added dropwise. The mixture was stirred for 30 min, poured into 150 mL of water, and extracted with ether. The organic extracts were washed with water, dried, and evaporated to give the ethers **1a–d**, which were purified by vacuum distillation. ***O*-Methyl-4-nitrobenzaldoxime (1a)**: yield 89%; NMR ($CDCl_3$–CCl_4) δ 3.93 (s, 3 H, OCH_3), 7.57 (d, J = 8 Hz, 2 H, $H^{2,6}$), 7.91 (s, 1 H, CH=N), 8.07 (d, J = 8 Hz, 2 H, $H^{3,5}$). Anal. Calcd for $C_8H_8N_2O_3$: C, 53.33; H, 4.48; N, 15.55. Found: C, 53.57; H, 4.31; N, 15.72. ***O*-(2,3-Epoxypropyl)-4-nitrobenzaldoxime (1b)**: yield 90%; NMR ($CDCl_3$) δ 2.6–3.0 (AB part of an ABX, 2 H, CH_2 oxirane), 3.1–3.4 (m, 1 H, CH oxirane), 3.9–4.6 (AB part of an ABX, 2 H, OCH_2), 7.65 (d, J = 7.5 Hz, 2 H, $H^{2,6}$), 8.08 (s, 1 H, CH=N), 8.14 (d, J = 7.5 Hz, 2 H, $H^{3,5}$). Anal. Calcd for $C_{10}H_{10}N_2O_4$: C, 54.05; H, 4.54; N, 12.61. Found: C, 53.90; H, 4.59; N, 12.87. ***O*-Benzyl-4-nitrobenzaldoxime (1c)**: yield 86%; NMR ($CDCl_3$) δ 5.13 (s, 2 H, CH_2), 7.25 (s, 5 H, C_6H_5), 7.56 (d, J = 8 Hz, 2 H, $H^{2,6}$), 8.00 (s, 1 H, CH=N), 8.07 (d, J = 8 Hz, 2 H, $H^{3,5}$). Anal. Calcd for $C_{14}H_{12}N_2O_3$: C, 65.62; H, 4.72; N, 10.93. Found: C, 65.74; H, 4.59; N, 11.01. ***O*-(2-Butyl)-4-nitrobenzaldoxime (1d)**: yield 91%; NMR (CCl_4) δ 0.94 (t, 3 H, CH_2CH_3), 1.25 (d, 3 H, $CHCH_3$), 1.3–1.8 (m, 2 H, CH_2), 4.15 (m, 1 H, OCH), 7.56 (d, J = 8 Hz, 2 H, $H^{2,6}$), 7.99 (s, 1 H, CH=N), 8.05 (d, J = 8 Hz, 2 H, $H^{3,5}$). Anal. Calcd for $C_{11}H_{14}N_2O_3$: C, 59.45; H, 6.35; N, 12.61. Found: C, 59.65; H, 6.47; N, 12.64.

4-Alkoxybenzonitriles 2a–d. A solution of 5 mmol of the appropriate oxime ether **1** in 10 mL of anhydrous DMF was added to a suspension of 8 mmol of NaH in 20 mL of DMF. The mixture was stirred at room temperature for 1 h (4 h in the case of **1d**). The workup was carried out as above. **4-Methoxybenzonitrile (2a)**: yield 92%; mp 57–59 °C (lit.[8] mp 58–59 °C); IR ($CHCl_3$) 2235 cm^{-1} (CN); NMR (CCl_4) δ 3.77 (s, 3 H, OCH_3), 6.80 (d, J = 9 Hz, 2 H, $H^{3,5}$), 7.39 (d, J = 9 Hz, 2 H, $H^{2,6}$). **4-(2,3-Epoxypropoxy)benzonitrile (2b)**: yield 82%; mp 64–66 °C (lit.[9] mp 67 °C); IR ($CHCl_3$) 2235 cm^{-1} (CN); NMR (CCl_4) δ 2.5–2.9 (AB part of an ABX, 2 H, CH_2 oxirane), 3.0–3.3 (m, 1 H, CH oxirane), 3.7–4.4 (AB part of an ABX, 2 H, OCH_2), 6.86 (d, J = 7.5 Hz, 2 H, $H^{3,5}$), 7.46 (d, J = 7.5 Hz, 2 H, $H^{2,6}$); mass spectrum, m/e (relative intensity) 175 (74, M^+), 119 (91, McLafferty rearrangement), 57 (100, oxiranylmethyl cation). **4-(Benzyloxy)benzonitrile (2c)**: yield 87%; mp 91–93 °C (lit.[8] mp 94 °C); IR ($CHCl_3$) 2235 cm^{-1} (CN); NMR ($CDCl_3$) δ 4.99 (s, 2 H, CH_2), 6.85 (d, J = 8 Hz, 2 H, $H^{3,5}$), 7.25 (s, 5 H, C_6H_5), 7.40 (d, J = 8 Hz, 2 H, $H^{2,6}$). **4-(2-Butoxy)benzonitrile (2d)**: yield 89%; bp 120 °C (1 mmHg) [lit.[10] bp 109–111 °C (1.3 mmHg)]; IR (NaCl) 2235 cm^{-1} (CN); NMR (CCl_4) δ 0.95 (t, 3 H, CH_2CH_3), 1.26 (d, 3 H, $CHCH_3$), 1.4–1.9 (m, 2 H, CH_2), 4.22 (m, 1 H, OCH), 6.73 (d, J = 8 Hz, 2 H, $H^{3,5}$), 7.46 (d, J = 8 Hz, 2 H, $H^{2,6}$).

Direct Synthesis of 2c from 4-Nitrobenzaldoxime. Over a suspension of 30 mmol of NaH in 25 mL of anhydrous DMF was added 10 mmol of the oxime portionwise. The mixture was stirred at room temperature for 10 min, and then 10 mmol of benzyl bromide in 5 mL of DMF was added dropwise. After 30 min of stirring and the usual workup, nitrile **2c** was isolated in 85% yield.

Registry No. 1 (R = H), 1129-37-9; **1a**, 33499-32-0; **1b**, 86120-18-5; **1c**, 86120-19-6; **1d**, 86120-20-9; **2a**, 874-90-8; **2b**, 38791-92-3; **2c**, 52805-36-4; **2d**, 86120-21-0; **2e**, 25117-74-2; ethyl 2-bromo-2-methylpropionate, 600-00-0; methyl iodide, 74-88-4; epichlorohydrin, 106-89-8; benzyl bromide, 100-39-0; 2-butyl bromide, 78-76-2.

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Use of Phosphorus Pentoxide: Esterification of Organic Acids†

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With a view to developing a method of esterification at room temperature on a vertical column, we chose phosphorus pentoxide as the packing reagent, which was diluted with anhydrous copper sulfate and sodium sulfate to avoid the blocking of the column. Anhydrous copper sulfate served as a water scavenger and also as an indicator for the progress of the reaction and the duration of the reactivity of the column through its color change, while anhydrous sodium sulfate retained the desired porosity and was useful for the sustained activity of the column with its water-absorbing property.

Phosphorus pentoxide has been frequently used in diverse types of organic reactions, but surprisingly only one example of its use in esterification reaction has been reported.[1] Coupled with this fact, this solid acidic oxide, possessing an extraordinary dehydrating capacity, made itself a unique material of choice for the present investigation. Thus, several primary aliphatic carboxylic acids were converted into the corresponding ethyl esters in varying yields (see the Experimental Section). A striking feature of this method was that aromatic acids could be recovered unchanged. But the process was slow; moreover, there was sufficient indication through arresting the acid-catalyzed reaction that it occurred partly (20–25%) on the column and partly (40–50%) during the removal of the excess alcohol from the steam bath. Therefore, the reaction was studied at room temperature for varying time

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periods which revealed that the reaction proceeded slowly. The yields of the esters were uncertain when the excess alcohol was not removed from the steam bath before the workup; again, the aromatic acids remained unaffected (see the Experimental Section). Finally it was observed that under reflux conditions for 30 min, this packing reagent furnished the esters of primary aliphatic carboxylic acids in 50–60% yields, which became slightly better on increasing the refluxing time to 2 h; still, the aromatic acids were resistant to esterification. Thus, the separation of aromatic acids from a mixture containing primary aliphatic carboxylic acids became very easy by this method. Under this experimental condition, anhydrous sodium sulfate was totally ineffective, but copper sulfate and phosphorus pentoxide furnished ethyl esters to the extent of 0–10% and 60–80% yields, respectively, when each one of these reagents was used separately. But the handling of the packing reagent was more convenient than the use of an equivalent amount of pure phosphorus pentoxide. It was further observed that generally the yields of the ethyl esters of primary aliphatic carboxylic acids could be raised to nearly 80% (acid 0.05 mol, ethanol 50 mL, and reagent 4.0 g) through increasing the refluxing period up to 16 h, but there was a tendency of a few aromatic acids to undergo esterification (10–15%) under this condition. Hence, 2 h of heating under reflux followed by the usual workup appeared to be the ideal conditions when the separation of the two types of acids was desired.

Benzoic acid did not furnish ester on boiling for 2 h with a catalytic amount of phosphorus pentoxide. Under identical conditions sulfuric acid produced ethyl benzoate in 74% yield; phosphoric acid and ethanol gave the esters of benzoic and phenylacetic acids to the extent of 2–3% and 25–30% yields, respectively. However, with a large excess of phosphorus pentoxide (0.7 mol) and a longer period of heating (16–20 h) benzoic acid gave ethyl benzoate in 20% yield.

Thus a good method of esterification has been developed which is perfectly safe, quick, easy to work up, and capable of distinguishing between primary aliphatic carboxylic and aromatic acids. This mode of esterification has been extended successfully with methanol, 1-propanol, 1-butanol, and benzyl alcohol to primary mono- and dicarboxylic acids, but with secondary and tertiary alcohols this method is unsuitable just like with secondary and tertiary aliphatic carboxylic acids. The steric, electronic, and other factors influencing this esterification are under investigation.

Experimental Section

Rectified spirits were dried (7 days) over quicklime and distilled to furnish once-distilled ethanol. Other pure alcohols were distilled, stored over anhydrous copper sulfate for 3 days at room temperature, and decanted just before use. Derived esters were identified through satisfactory analytical data (±0.4% for C and H), comparison of the observed boiling point (uncorrected) with the reported values, IR data (1710–1750 cm^{-1}; Perkin-Elmer Infracord spectrophotometer, Model 297), and NMR data (mostly at 60 MHz, in CCl_4 with Me_4Si). Recovered acids were characterized through melting point (uncorrected) and mixture melting poing determinations.

Column Method. An intimate mixture of anhydrous copper sulfate (100 g), anhydrous sodium sulfate (100 g), and phosphorus pentoxide (20 g) was prepared, and a portion of this packing reagent was poured into a dry chromatographic column (circumference 5.8 cm) to make the packing 48 cm high. When once-distilled ethanol was poured in, the column became hot, the ethanol slowly passed down, and within 4 h dropwise elution of ethanol began while the column cooled to room temperature. Various organic acids (0.1 mol) dissolved in ethanol (50 mL) were poured successively over the column, thus prepared and protected from moisture, and were eluted by ethanol (200 mL) in course of 8 h in separate experiments. The major portion of the solvent was removed by use of a steam bath (15–20 min) in each case, and the residue was poured onto crushed ice. The reaction mixture, on the usual workup with ether and a sodium bicarbonate wash, afforded ethyl esters from the neutral fraction while the bicarbonate extract yielded the unreacted acids on acidification with mineral acid. The column was found to remain effective for at least six such esterifications, and then the efficacy began to diminish gradually while the entire column turned deep blue. The results are reported in the following order: name of the acid used (percent yield of the ethyl ester; boiling point, °C). Adipic (68; 241), succinic (61; 210), phenylacetic acid (86; 221), cinnamic (17;[2] 258). Oxalic, benzoic,[3] and salicyclic[3] acids were recovered unchanged.

A similar column was prepared, and a solution of phenylacetic acid (13.6 g) in ethanol (50 mL) was eluted through the column with more ethanol (200 mL) over the course of 8 h into the receiver containing sodium bicarbonate (2 g) and was protected from moisture. The excess of ethanol was removed (150 mL) from the steam bath, and the residue was poured onto crushed ice. On the usual workup it furnished ethyl phenylacetate (20; 220). When sodium bicarbonate was replaced either by calcium carbonate (3 g) or dry pyridine (2 g), the yields of the esters were 25% and 22%, respectively. In another experiment, the eluted material was just neutralised with sodium hydroxide before removal of the excess of ethanol. On being worked up, it gave ester in 18% yield.

At Room Temperature. Blends of various organic acids (0.05 mol), freshly prepared packing reagent (2.5 g), and ethanol (50 mL) were taken in Erlenmeyer flasks and left at room temperature for 20 h with occasional shaking. Removal of the solvent (ca. 30 mL) on a steam bath (15–20 min) left a residue which on the usual workup furnished the ethyl esters of the following acids (percent yield; boiling point, °C); formic (70; 55), tartaric (5; 155/9–10 mm), oxalic (22; 175–180), phenylacetic (80; 221), succinic (45; 208–210), adipic (54; 238), suberic (47; 270), palmitic (58; 195–200), β-phenylpropionic (67; 238), (2,4-dichlorophenoxy)acetic (43; 178/4 mm), chloroacetic (45; 143), malonic (25; 189), benzoic (5; 206). Citric, pyruvic, 2,3-dibromo-3-phenylpropionic, phthalic, salicylic,[3] *p*-toluic,[3] *p*-anisic,[3] and *m*-nitrobenzoic[3] acids were recovered unchanged.

By Heating under Reflux. A mixture of organic acid (0.05 mol), ethanol (50 mL), and the packing reagent (4.0 g) was heated under reflux for 2 h on a steam bath. Removal of ethanol (ca. 30 mL) and a workup of the residue in the usual way with ether furnished the desired ester. The results are presented in the previous form: phenylacetic (74; 221), succinic (61; 212), glutaric (61; 225), adipic (67; 112/3 mm), pimelic (61; 265), suberic (68; 270), azelaic (70; 285), sebacic (72; 298), maleic (26;[4] 215), tartaric (30;[5] 150/9 mm), diphenyl acetic (7; mp 51 °C, 33% yield after 16 h of heating), monochloroacetic (45; 143), dichloroacetic (40; 157), trichloroacetic (41; 166), pivalic acid (6; 116; 15% yield after 16 h of refluxing). Benzilic acid, benzoic acid, and its derivatives having hydroxy, methoxy, nitro, methyl, chloro, and bromo substituents at ortho, meta, and para positions remained unesterified[3] by this method.

With Alcohols Other Than Ethanol. In separate experiments, the mixture of alcohol (50 mL), organic acid (0.05 mol), and freshly prepared packing reagent (4 g) was heated under reflux for 2 h, and the excess alcohol (ca. 30 mL) was removed by distillation. The cold residue was poured into ice, and the reaction mixture on the usual workup, furnished the desired esters. Thus, phenyl acetic acid gave methyl (76; 210–213), *n*-propyl (73; 235), *n*-butyl (80;[6] 249–251), benzyl (61;[7] 170/6 mm), isopropyl (31;[8]

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(2) Recovered acid 70%.

(3) Recovered almost quantitatively.

(4) ^1H NMR δ 1.3 (6 H, t, J = 7 Hz), 4.2 (4 H, q, J = 7 Hz), 6.2 (2 H, s).

(5) ^1H NMR δ 1.35 (6 H, t, J = 7 Hz), 3.85 (2 H, s), 4.16 (4 H, q, J = 7 Hz), 4.42 (2 H, s).

(6) ^1H NMR δ 1.0 (3 H, t, J = 6 Hz), 1.5–1.6 (4 H, complex m), 3.43 (2 H, s), 3.93 (2 H, t), 7.23 (5 H, s).

(7) ^1H NMR δ 3.46 (1 H, d, J = 13 Hz), 4.4 (2 H, s), 4.93 (1 H, d, J = 13 Hz), 7.16 (5 H, s), 7.2 (5 H, s).

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%.

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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.

(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.

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

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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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