# Sulfinic Acid Catalyzed Isomerization of Olefins

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Arenesulfinic acids catalyze the cis–trans equilibration of disubstituted olefins in high yield and without double bond migration, as evidenced by studies of the reaction of various sulfinic acids with methyl 9-octadecenoate and 4-octene. Equilibrium is attained within 15 min in refluxing dioxane at the lowest catalyst level investigated. None of the known decomposition products of sulfinic acids, including sulfinyl sulfones, appears to be responsible for the isomerization. Sulfinyl sulfones, which are formed from sulfinic acids in the initial step of the decomposition process, also catalyze the isomerization, but at a slower rate than the sulfinic acids.

Chemists have long sought mild, efficient methods for the conversion of naturally occurring cis unsaturated fatty acids to the trans isomers, and for the equilibration of isolated double bonds in general.[1] Most catalysts suffer from some disadvantage, such as toxicity, a high temperature requirement, or double bond migration. Probably the mildest and most convenient catalyst developed is nitrous acid.[1] More recently, isomerization by photochemically generated thiyl radicals[2–4] and by mercaptans in aqueous solution have been developed.[5] While in search of a new and more convenient method, we encountered two references to the use of *p*-toluenesulfinic acid for this purpose. During a study of reduction of olefins by diimide, generated by thermal decomposition of *p*-toluenesulfonylhydrazine, Garbisch et al. noted that the *p*-toluenesulfinic acid by-product of the decomposition caused the isomerization of the double bond, without specifying the nature of the isomerization.[6] It was found that the isomerization could be prevented by the addition of triethylamine to the reaction, presumably by neutralization of the sulfinic acid. Nozaki et al. found that when methyl oleate was treated with an excess of *p*-toluenesulfinic acid for 7 h in dioxane at 90 °C, an "equilibrium" mixture, containing 55% of methyl elaidate, the trans isomer, was obtained in 60% yield.[7] We chose to examine this process in more detail, to answer such questions as: Is the process catalytic, and if so, what is the nature of the catalytic species? Is thermodynamic equilibrium actually attained, since under Nozaki's conditions methyl elaidate should comprise about 75% of the oleate–elaidate mixture at equilibrium? Does double bond migration occur? And are there more favorable conditions under which the isomerization can be effected? This paper presents an initial examination which answers some of the above questions and serves to eliminate some of the more obvious candidates for the species responsible for the isomerization.

## Results and Discussion

Treatment of a solution of either methyl oleate or methyl elaidate in dioxane at reflux for 2 h with 10 mol % of *p*-toluenesulfinic acid gave an equilibrium mixture comprised of 76% of the trans isomer. The catalytic nature of the process is shown in Table I, which shows that equilibration is possible with varying catalyst–olefin ratios. Gas chromatographic analysis showed that in each instance equilibrium was obtained in less than 15 min. The incomplete equilibration observed at the lowest ratio examined suggests that the catalytic species is itself consumed by some competing process.

**Table I. Isomerization of Methyl Oleate with p-Toluenesulfinic Acid[a]**

| Catalyst ratio[b] | % trans |
|---|---|
| 1.48 | 78.7 |
| 0.148 | 81.0 |
| 0.0148 | 78.1 |
| 0.0080 | 69.1 |

[a] 1 h at reflux, in dioxane, 0.085 M. [b] Molar equivalents of sulfinic acid per mole of methyl oleate.

**Table II. Effect of Sulfinic Acid Structure on Isomerization of Methyl Oleate[a]**

| Registry no. | Sulfinic acid | % yield[b] | % trans |
|---|---|---|---|
| 618-41-7 | Benzene- | 91 | 80.8 |
| 536-57-2 | *p*-Toluene- | 88 | 80.0 |
| 100-03-8 | *p*-Chlorobenzene- | 95 | 81.0 |
| 1195-33-1 | *p*-Bromobenzene- | 91 | 79.3 |
| 1709-60-0 | *p*-Methoxybenzene- | 91 | 79.6 |
| 1199-67-3 | *o*-Nitrobenzene- | 93 | 26.6 |

[a] 10 mol % catalyst, refluxing dioxane, 3 h, 0.43 *M*. [b] Distilled product.

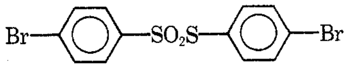
The influence of sulfinic acid catalyst structure on the isomerization is shown in Table II. It is apparent that catalytic activity is relatively independent of the structure of the sulfinic acid. The low degree of isomerization with *o*-nitrobenzenesulfinic acid is reproducible, but as yet unexplained.

The absence of double bond migration in the substrate was demonstrated by oxidation of the product from the *p*-bromobenzenesulfinic acid catalyzed reaction with the permanganate–periodate reagent.[8] Esterification of the resulting carboxylic acids with diazomethane followed by gas chromatographic analysis showed that less than 0.5% migration to the $C_8$ or $C_{10}$ positions had occurred.

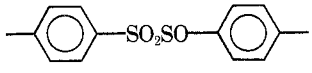
With the preliminary questions concerning the reaction thus answered, we began attempts to determine the nature of the catalytic species responsible for the isomerization. Both methyl *p*-toluenesulfinate and the sodium salt proved to be ineffective as catalysts under the conditions used in Table II and the oleate proved to be stable in refluxing dioxane in the absence of added materials. This suggests that the free sulfinic acid is required, but does not identify the catalytic species. Aromatic sulfinic acids are known to decompose thermally by disproportionation to sulfonic acid and thiolsulfonate:[9]

$$3ArSO_2H \rightarrow ArSO_3H + ArSO_2SAr + H_2O$$

Nozaki had noted that neither *p*-toluenesulfonic acid nor the neutral products of the decomposition of *p*-toluenesulfinic acid caused the isomerization of methyl oleate.[7] We confirmed this observation with regard to *p*-toluenesulfonic acid. However, 4,4′-dibromodiphenyl thiolsulfonate (1) did cause isomerization of methyl oleate in refluxing dioxane, but at a much slower rate than that shown by the sulfinic acid. Thus, equilibration of methyl oleate requires 5 h in the presence of 0.1 equiv of **1**, compared with less than 15 min with the sulfinic acids.

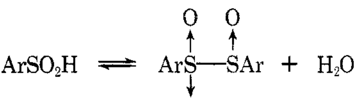


**1**



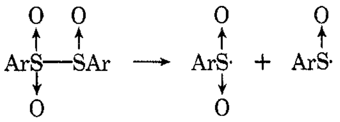
**3**

Another attractive hypothesis is that the radical intermediates in the disproportionation of the sulfinic acid are responsible for the olefin isomerization. Kice has shown, in a detailed study of this disproportionation,[10] that arenesulfinic acids form sulfinyl sulfones, **2**, which cleave thermally to sulfinyl and sulfonyl radicals:



$$2\mathrm{ArSO_2H} \rightleftharpoons \mathrm{Ar}\underset{\underset{\mathrm{O}}{\downarrow}}{\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{S}}}-\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{S}}\mathrm{Ar} + \mathrm{H_2O}$$

**2**



$$\mathrm{Ar}\underset{\underset{\mathrm{O}}{\downarrow}}{\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{S}}}-\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{S}}\mathrm{Ar} \longrightarrow \mathrm{Ar}\underset{\underset{\mathrm{O}}{\downarrow}}{\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{S}}}\cdot + \mathrm{Ar}\overset{\overset{\mathrm{O}}{\uparrow}}{\mathrm{S}}\cdot$$

Recombination and further reactions can also generate the arylthiyl radical, ArS·, as well. All of these radicals are candidates for the species responsible for the isomerization.

In an attempt to gain some information concerning this point, we obtained data for the initial rates of isomerization of *cis*-4-octene in the presence of *p*-toluenesulfinic acid and the sulfinyl sulfone **3**. Both reactions proved to be too fast at the reflux temperature of dioxane to conveniently obtain more than two data points before equilibrium was reached. That equilibrium was in fact obtained was determined by carrying out the isomerization of both *cis*- and *trans*-4-octene with both catalysts, giving in each case 76% trans isomer. The reaction with *cis*-4-octene was more conveniently studied at 70 °C, at which temperature the isomerization was found to follow good first-order kinetics for isomerization to about 20% trans isomer. The first-order rate constants for the disappearance of *cis*-4-octene in the presence of 0.1 molar equiv of either **3** or *p*-toluenesulfinic acid are shown in Table III.

**Table III**[a]

| Catalyst | $k_1 \times 10^4$, s$^{-1}$ |
|---|---|
| *p*-Toluenesulfinic acid | 9.3 ± 0.5 |
| *p*-Toluenesulfinyl-*p*-toluene sulfone (**3**) | 0.58 ± 0.01 |

[a] 70 ± 1 °C, 0.107 M in *cis*-4-octene, 0.0107 M in catalyst. Average of three runs in anhydrous dioxane.

Kice has shown that an equilibrium concentration of a few percent of the sulfinyl sulfone exists in solutions of the sulfinic acid, but that the rate of attainment of this equilibrium is very slow in the absence of strong acids. In addition, the rate of thermal cleavage of the sulfinyl sulfone is independent of the presence of sulfinic acid, and represents the rate-determining step in the sulfinic acid disproportionation reaction. Therefore, while the sulfinyl sulfone does promote isomerization of olefins at a moderate rate, presumably via the radical cleavage products, these radicals do not represent major catalytic species when sulfinic acid is used. The rapid and clean isomerization observed with the sulfinic acid must be due to the action of the acid itself or to some as yet unobserved species which is formed in competition with or prior to sulfinyl sulfone.

The nature of the catalytic species must await more thorough kinetic studies and complete product analysis to determine the fate of the sulfinic acid. An initial investigation of the latter point showed the presence of a multitude of sulfur-containing products, none of which has been identified. Whatever their nature, the reaction represents a convenient method for the equilibration of olefins in high yield and excellent purity, and should find application as a synthetic method in a variety of substrates.

## Experimental Section

**Materials.** Methyl oleate was obtained by esterification of oleic acid which had been purified by urea adduction to remove saturated acids. Gas chromatographic analysis indicated 95–98% purity. Methyl elaidate was obtained from Applied Science Laboratories. Benzenesulfinic acid and *p*-toluenesulfinic acid were obtained by acidification of aqueous solutions of the commercially available sodium salts with HCl. The other sulfinic acids were obtained by reduction of the sulfonyl chlorides with $Na_2SO_3$.[9] Recrystallization gave in each case material whose melting point was in good agreement with that cited in ref 9. *trans*-4-Octene was purchased from Aldrich and used as is. *cis*-4-Octene was prepared by reduction of 4-octyne with Pd/$BaSO_4$ catalyst poisoned with quinoline. GLC analysis showed the presence of 3.5% *trans*-4-octene.

**Analytical Procedures.** Melting points were determined on a micro hot stage and are corrected. Boiling points are uncorrected. Infrared spectra were determined on a Perkin-Elmer 257 instrument as mulls in mineral oil or in $CH_2Cl_2$ solution. High-resolution mass spectra were determined with an Atlas SM-1 spectrometer. GLC analyses for methyl oleate–methyl elaidate reactions were performed at 180 °C on a 150 ft × 0.01 in. stainless steel column coated with polyphenyl ether. The instrument used was a Perkin-Elmer 126 with flame ionization detectors. GLC analyses for the 4-octene isomers were carried out at 50 °C on a 20 ft × 0.25 in. stainless steel column packed with 20% $\beta,\beta'$-oxydipropionitrile on Gas Chrom P. The instrument used was a Varian Aerograph Model 202B with thermal conductivity detectors.

**Isomerization of Methyl Oleate with Varying Amounts of *p*-Toluenesulfinic Acid.** To a solution of 1.0 g of methyl oleate in 40 ml of dry dioxane was added 0.78 g of *p*-toluenesulfinic acid. The system was flushed with argon and heated to reflux for 1 h. After cooling, the solution was diluted with pentane and extracted with 1 N NaOH solution, then washed twice with saturated sodium chloride solution. The pentane solution was dried over $MgSO_4$, filtered, and concentrated on a rotary evaporator. GLC analysis of a pentane solution of the residue on the PPE column showed only methyl oleate and methyl elaidate in a ratio of 21.3:78.7. Reaction of the same amount of methyl oleate with *p*-toluenesulfinic acid at lower levels gave the results shown in Table I.

**Equilibration Studies.** Methyl oleate and methyl elaidate (0.20 ml) were treated separately with 2.87 ml of 0.0216 M *p*-toluenesulfinic acid in dioxane at reflux for 2 h. Duplicate runs with each ester gave averages of 75.2 and 76.0% elaidate, respectively, by quantitative infrared analysis.

**Preparative Scale Isomerization of Methyl Oleate.** A solution of 0.068 mol (20 g) of methyl oleate and 0.0068 mol of a sulfinic acid in 135 ml of dry dioxane was heated to reflux under argon for 3 h. After work-up similar to that already described, vacuum distillation gave high yields of methyl oleate–elaidate mixtures with compositions given in Table II as determined by GLC analysis. TLC of samples of distilled products at high load levels revealed the presence of trace impurities, estimated to be on the order of ≤0.1%.

**Preparation of 4-Bromobenzenethiol 4′-Bromobenzenesulfonate (1).** A solution of 0.76 g of *p*-bromobenzenesulfinic acid in 400 ml of toluene was refluxed for 1 h. The cooled solution was washed with 1 N NaOH and saturated sodium chloride solution and dried over $MgSO_4$. Chromatography of the residue after removal of solvent was carried out on 20 g of silica gel. Elution with ether gave 52.6 mg of crystals, mp 134–137 °C. Recrystallization from ether–pentane raised the melting point to 175–178 °C. TLC of this material on silica gel showed a single spot with ir (mull) $\lambda_{max}$ 6.40, 7.52, 8.77, 9.40, and 9.94 $\mu$, NMR signals at $\tau$ 2.7–3.0 ($CDCl_3$), and molecular ions at *m/e* 406, 408, and 410 in accord with the molecular formula $C_{12}H_8S_2O_2Br_2$. In addition, the mass spectrum showed major fragment ions in accord with cleavages of the C–S and S–S bonds in structure 1.

**Isomerization of Methyl Oleate with Thiolsulfonate (1).** A solution of 1.0 g (0.0034 mol) of methyl oleate and 0.139 g (0.00034 mol) of 1 in 40 ml of dioxane was heated to reflux for a total of 5 h. Periodic withdrawal of 5-ml aliquots, normal work-up, and GLC analysis gave the following results, with time in minutes and percent trans isomer: 61 (51), 126 (60), 178 (73), 249 (77), and 306 (77.5).

**Isomerization of *cis*- and *trans*-4-Octene with 3 and *p*-Toluenesulfinic Acid.** The sulfinyl sulfone 3 was prepared as previously described and gave an infrared spectrum identical with that published.[11]

For the kinetic runs, 5.0 ml of a 0.0214 M solution of 3 or the sulfinic acid in dry dioxane was added to 5.0 ml of 0.214 M *cis*-4-octene in dioxane in a round-bottom three-neck flask which had been oven dried and flushed with dry nitrogen. The octene solution was also 0.10 M in decane for use as an internal standard. The flask was immersed in an oil bath held at 70 ± 1 °C with a relay, and aliquots were withdrawn periodically via syringe through a rubber cap. After dilution with pentane and washing once with 1 N NaOH and twice with water, gas chromatographic analysis gave the amount of isomerization with an accuracy of ±0.5%. The averages of the least-squares first-order plots of three runs, taken up to 20–30% isomerization, were determined to give the initial rate constants shown in Table III. Gas chromatographically determined yields were 93% for the sulfinic acid process at equilibrium but were lower when the sulfinyl sulfone was used. A blank reaction carried out in the absence of either isomerization reagent showed no trans isomer formation after 20 h.

**Registry No.**—1, 3347-03-3; 3, 788-86-3; methyl oleate, 112-62-9; methyl elaidate, 1937-62-8; toluene, 108-88-3; *cis*-4-octene, 7642-15-1; *trans*-4-octene, 14850-23-8.

## References and Notes

(1) C. Litchfield, R. D. Harlow, A. F. Isbell, and R. Reiser, *J. Am. Oil Chem. Soc.*, **42**, 73 (1965). This reference contains a reasonably thorough bibliography of previous work.
(2) C. Moussebois and J. Dale, *J. Chem. Soc. C*, 262 (1966).
(3) D. S. Sgoutas and F. A. Kummerow, *Lipids*, **4**, 283 (1969).
(4) F. D. Gunstone and I. A. Ismael, *Chem. Phys. Lipids*, **1**, 264 (1967).
(5) W. G. Niehaus, Jr., *Bioorg. Chem.*, **3**, 302 (1974).
(6) E. W. Garbisch, Jr., S. M. Schildkraut, D. B. Patterson, and C. M. Sprecher, *J. Am. Chem. Soc.*, **87**, 2932 (1965).
(7) H. Nozaki, Y. Nisikawa, M. Kawanisi, and R. Noyori, *Tetrahedron*, **23**, 2173 (1967).
(8) D. F. Kuemmel, *Anal. Chem.*, **36**, 426 (1964).
(9) F. Muth in Houben-Weyl, "Methoden der Organischem Chemie", Vol. 9, 4th ed, Georg Thieme Verlag, Stuttgart, 1955, p 299.
(10) J. L. Kice, G. Guaraldi, and C. G. Venier, *J. Org. Chem.*, **31**, 3561 (1966), and previous references in this series.
(11) H. Bredereck, A. Wagner, H. Beck, and R-J. Klein, *Chem. Ber.*, **93**, 2736 (1960).

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# Linear Carboxylic Acid Esters from α Olefins. I. Catalysis by Homogeneous Platinum Complexes

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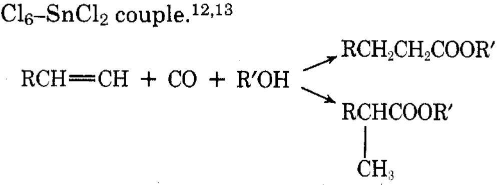
Ligand-stabilized platinum(II)–Group 4B metal halide complexes have been found to catalyze the homogeneous carbonylation of α olefins to carboxylic acids and esters, with up to 98 mol % selectivity to the linear ester. Preferred catalysts include $[(C_6H_5)_3As]_2PtCl_2–SnCl_2$, $[(C_6H_5)_2ClAs]_2PtCl_2–SnCl_2$, and $[(C_6H_5O)_3P]_2PtCl_2–SnCl_2$. The activity of each of these regioselective catalysts is highly sensitive to changes in coordinated ligand structure. The effects of catalyst and olefin composition, the nature of the nucleophilic coreactant, and other experimental variables upon both the activity and selectivity of the platinum have been examined, and are discussed in relation to the mode of this catalysis.

Carbonylation, the addition of CO to unsaturated compounds to yield carboxylic acid derivatives, may be catalyzed by a variety of soluble metal carbonyl species, including those of nickel, cobalt, iron, rhodium, ruthenium, palladium, and platinum.[1-8] α-Olefin carbonylation, as catalyzed by Reppe-type nickel and cobalt catalysts, is characterized by (a) the production of large quantities of branched, as well as linear, acid derivatives (eq 1),[3,5-7] (b) the importance of competing olefin polymerization, isomerization, and reduction reactions, and (c) severe operating conditions.[2] More recently, improved palladium catalysts have been found active under milder conditions where competing side reactions are of lesser importance,[4,9] and normal esters predominate.[10,11] Linear carboxylic acid esters have also been prepared in 67–85% selectivity with the $H_2PtCl_6–SnCl_2$ couple.[12,13]



$$\mathrm{RCH{=}CH + CO + R'OH}\ \begin{array}{l} \nearrow \mathrm{RCH_2CH_2COOR'} \qquad (1a) \\ \searrow \mathrm{RCHCOOR'} \qquad (1b) \\ \qquad\ | \\ \qquad\ \mathrm{CH_3} \end{array}$$

As part of a program to develop new routes to linear carboxylic acid derivatives, we report here the use of certain ligand-stabilized platinum(II)–Group 4B metal halide complexes as catalysts for the highly selective carbonylation of α olefins to linear carboxylic acid esters.[14]

## Results

**Effect of Platinum Catalyst Structure.** In multistep reaction sequences such as carbonylation, modification of the catalyst metal center by changes in coordinated ligand structure may dramatically affect the activity and stability of the catalyst, the selectivity to straight-chain products, and competing side reactions.[2,4,8,9,15,16] In this work, a broad range of ligand-stabilized platinum(II) complexes in combination with Group 4B metal halide cocatalysts have been screened for carbonylation activity, and methyl octanoate synthesis from 1-heptene has been selected as the model reaction (see Tables I and II).

The first distinguishing feature of this class of catalysts is their ability to produce linear acid esters, such as methyl octanoate, in at least 90 mol % selectivity. This selectivity is consistently higher than has been reported previously,[1-10,12,13] even for related palladium bimetallic catalysts.[17] The highest selectivity to methyl octanoate achieved here (98 mol %) is with dichlorobis(triphenyl phosphite)platinum(II)-tin(II) chloride (expt 5). The highest yield of meth-