Sir: It has been reported[1] that polyphosphoric acid at 200 °C promotes condensation of methanol to C_4^+ hydrocarbons. The hydrocarbon product was not unusual, being about what one would expect from condensation in highly acid medium with carbonium ion intermediates. Subsequently, aromatic-rich gasoline production from methanol was reported using a zeolite catalyst.[2] We have carried out preliminary experiments with bulk zinc iodide at 200 °C as catalyst and found that it promotes conversion of methanol directly to gasoline-range hydrocarbons. The product is quite different from that reported for polyphosphoric acid or zeolite catalysis in that it is unusually rich in highly branched compounds, particularly 2,2,3-trimethylbutane (triptane). Thus, when 39.4 g of methanol and 200 g of zinc iodide were heated together for 2 h at 200 °C under 200 psi of N_2, 7.2 g of gasoline-range hydrocarbon could readily be distilled from the reaction vessel. Careful analysis of the gasoline-range product showed it to be 49.7% triptane. The formation of this high a yield of triptane in a thermal reaction is unique to our knowledge. Only traces of hydrocarbons lighter than butane were found. The triptane was unequivocally identified by a combination of capillary gas chromatography, infrared, GC/mass spectrographic, and NMR analyses. Table I shows the composition of this gasoline as identified by capillary GC analysis. Conversion of methanol was >99%. Only traces of C_1 to C_3 hydrocarbons were found. Isobutane was the only C_4 hydrocarbon produced in <2% yield. Most of the heavier hydrocarbons were in the useful gas–oil boiling point range (230–370 °C ~56% basis carbon fed; higher boiling ~2–3% basis carbon). There was little solid residue. Carbon material balance was 98%.

Triptane is one of the most desirable known gasoline component hydrocarbons, based on its unusually high motor and research octane numbers, and its desirable boiling point. The formation, in high selectivity, of such an unusual hydrocarbon as triptane, together with the unusual nature (high branching–high octane) of the rest of the mixture produced, indicates that the reaction of methanol in the presence of zinc iodide is proceeding via unusual intermediates and/or reactions. It is highly unlikely that the products obtained could have been formed by typical carbonium ion or even free-radical reaction pathways, since the product pattern is different from acid-catalyzed isomerization and alkylation. Most likely, a novel intermediate is formed by dehydration of methanol, which condenses to form the observed products. As a working hypothesis, we postulate that the intermediate may be a carbene (CH_2) complexed with the salt, similar to the Simmons–Smith reagent.[3] Such a complexed methylene would be expected to be much more selective in its reactions than free methylene, and plausible reaction pathways have been postulated that explain the high selectivity to triptane observed in the methanol–zinc iodide reaction.

Table I. Gasoline-Range Products from Methanol

hydrocarbon product	% wt
2-methylbutane	1.8
other C_5	0.1
2,3-dimethylbutane	3.8
2-methylpentane	1.7
3-methylpentane	1.3
n-hexane	0.0
other C_6	0.1
2,2,3-trimethylbutane	49.7
2,2-dimethylpentane	0.1
2,3-dimethylpentane	2.4
2-methylhexane	0.8
3-methylhexane	0.6
n-heptane	0.1
other C_7	2.1
2,2,4-trimethylpentane	1.0
2,3,4-trimethylpentane	1.8
2,3,3-trimethylpentane	1.7
other C_8	5.0
2,2,5-trimethylhexane	1.2
2,3,5-trimethylhexane	0.9
other C_9	5.6
C_{10}–C_{13}	18.2
Total C_5–C_{13}	100.0

We shall publish supporting evidence for carbenoid and organozinc intermediates and a detailed mechanism consistent with the high triptane yield and lack of C_1, C_2, and C_3 products. The reaction has been established as catalytic in zinc iodide by recovering zinc salt and reuse. Zinc bromide also catalyzes methanol to triptane conversion at 220–245 °C, but at the high temperatures required for zinc chloride catalysis most of the unusual selectivity to triptane is lost. Subsequent publications shall give additional details of this intriguing chemistry.

References and Notes

(1) D. E. Pearson, *J. Chem. Soc., Chem. Commun.*, 397 (1974).
(2) See news release as stated by *Chem. Eng. News*, **56** (5), 26 (1978).
(3) H. W. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **80**, 5323 (1958).

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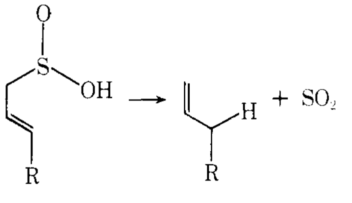
Stereochemical Course of the Fragmentation of Allylsulfinic Acids

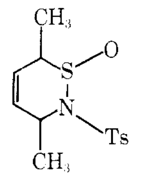
Summary: Diastereomers of 5-(*p*-tolylsulfonamido)-(*Z*)-3-hexene-2-sulfinic acid fragment in D_2O to different diastereomers of 4-deuterio-5-(*p*-tolylsulfonamido)-(*E*)-2-hexene.

Sir: The fragmentation of homoconjugated sulfinic acids is known to proceed with apparently exclusive allylic rearrangement (eq 1).[1] Recently attention has been drawn to the synthetic potential of the retro reaction as a means of isomerizing and functionalizing alkenes.[2] We report evidence of a stereochemical nature which tends to support a cyclic mechanism for this transformation.



(1)

The sulfinamides **1** and **2** have been prepared by cycloaddition of *N*-sulfinyl-*p*-toluenesulfonamide to (*E,E*)- and (*E,Z*)-2,4-hexadiene, respectively.[3] Upon treatment with aqueous sodium hydroxide (scission of S–N bond), followed by acidification of the sulfinate salt with hydrochloric acid,[1] both **1** and **2** yielded 5-(*p*-tolylsulfonamido)-(*E*)-2-hexene (**3a**) as the only isolable product (eq 2).[4]



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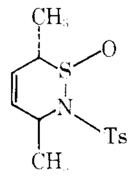

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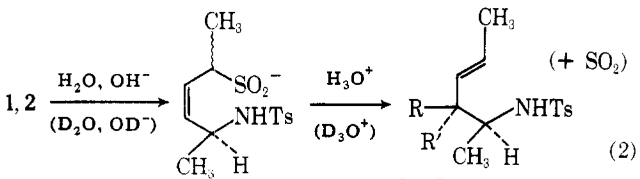
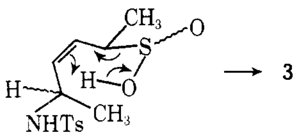


(2)

3a, R = R′ = H
b, R = D; R′ = H
c, R = H; R′ = D

When the hydrolysis sequence with **1** and **2** was repeated in deuterated medium, the isolated sulfonamides (**3**) contained approximately one atom of carbon-bound deuterium in the 4 position of the hydrocarbon chain, as estimated by NMR absorption intensity. Close inspection of the IR spectra of the hydrolysis products reveals subtle differences in **3** obtained from **1** and **2** in H_2O and D_2O. The product **3a**, whether obtained from **1** or **2**, has an absorption at 9.6 μm. This adsorption is greatly diminished in the deuterium-containing products, **3b** and **3c**. However, the product from **1** has a new adsorption a 10.6 μm, and that from **2** has a correspondingly unique (although not so well resolved) absorption at 11.25 μm.[5] It is suggested that the diastereomers **3b** and **3c** are formed stereospecifically from **1** and **2**, respectively. Although the IR analysis is semiquantitative, **3c** (as obtained from **2**) seems to be free of **3b** (<10%), and **3b** (as obtained from **1**) has at most 15% cross-contamination with **3c**. The conclusion of a stereoisomeric relationship is reaffirmed by easily recognized differences in the splittings of the pertinent NMR absorption multiplets ($\delta \sim 3.4$).[6] The assignments of **3b** and **3c** follow from mechanistic considerations, although the possibility of the reverse relative configuration may not be excluded on the evidence presented.

Formation of diastereomeric products (**3b,c**) implies diastereomeric transition states. Configurational control is succinctly rationalized by a cyclic retro-ene mechanism (eq 3).



(3)

Strong preference for a chair conformation transition state explains both predominant (*E*)-alkene formation in **3** as well as diastereomeric induction at the 4 position. As a minimum conclusion, it appears that asymmetry at the 2 position ($-CHMeSO_2H$) is transmitted to the 4 position more efficiently than is asymmetry at the adjacent 5 position (–CHMeNHTs). A contrary result (including some (*Z*)-alkene from at least one isomer) might have been expected were deuterium delivered from solvent in an extended conformation of the fragmenting sulfinic acid, although a nonconcerted mechanism involving irreversible C-protonation followed by fragmentation would be consistent with a small amount of product crossover, which the experimental evidence does not exclude.

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(3) W. L. Mock and R. M. Nugent, *J. Am. Chem. Soc.*, **97**, 6521 (1975).

(4) Isolated as a chromatographically purified oil in 81% yield, with superimposable spectra for **3a** from **1** and **2**. (*E*)-Alkene is indicated by IR absorption at 10.3 μm. The sharp and well-resolved methyl doublets in the NMR spectrum show no indication of a minor isomer [(*Z*)-alkene, <5%]. Material recovered from deuteriolysis was subjected to ND → NH exchange before spectral analysis.

(5) Such differences in vibrational frequencies have been used previously for distinguishing diastereomers: C. R. Childs and K. Bloch, *J. Org. Chem.*, **26**, 1630 (1961).

(6) For copies of NMR spectra see Ph. D. Thesis of R. M. Nugent, *Diss. Abstr. Int. B*, **33**, 4735 (1973).

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