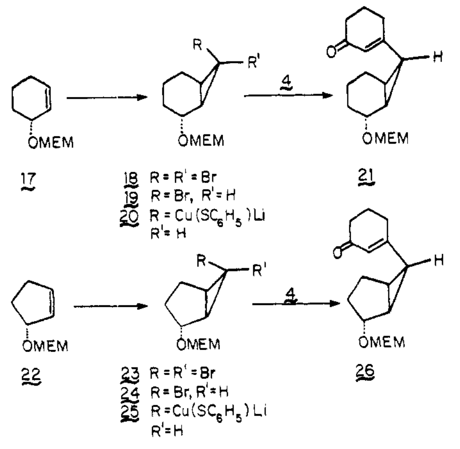
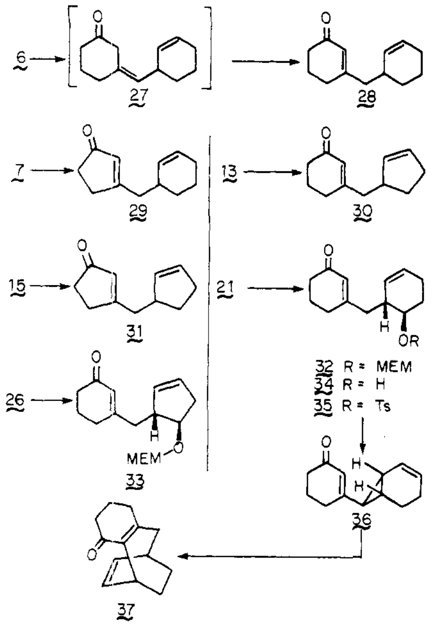
Scheme II



Scheme III



mocyclopropanes 18 and 23 was accomplished (83, 84%, respectively) by standard methodology ($CHBr_3$, NaOH–H_2O–EtOH, $C_6H_5CH_2N^+Et_3Cl^-$; Scheme II).[14,15] Reduction (18: Zn, HOAc; 23: n-Bu_3SnH) of these dibromo compounds, followed by chromatographic purification of the crude products, afforded the pure *endo*-bromides 19 and 24. The latter substances were transformed into the corresponding cuprate reagents 20 and 25 which, upon reaction with the iodo enone 4, gave the unsymmetrical tricyclic derivatives 21 and 26 (97 and 62%, respectively).

Although the *endo*-enones 6, 7, 13, 15, 21, and 26 were sufficiently stable to withstand purification by distillation under reduced pressure (e.g. 21 was distilled at 150–160 °C, 0.1 mm), each of these compounds rearranged smoothly and cleanly when heated (neat) at temperatures >200 °C (Scheme III). For example, when 6 was heated at 210–215 °C for 10 min, the substituted cyclohexenone 28 was obtained in 95% yield. Clearly, under these conditions, the product 27 initially formed by homo-[1,5]-sigmatropic hydrogen migration[16] isomerized to the more stable conjugated isomer 28. In similar fashion, enones 7, 13, and 15 could be smoothly transformed into the corresponding rearrangement products 29 (98%), 30 (87%), and 31 (90%), respectively.

Thermolysis of the unsymmetrical *endo*-enones 21 and 26 represent especially interesting examples of the present methodology. In each case, the rearrangement process was very clean (32, 89%; 33, 78%), and a careful analysis of each of the crude reaction products (after brief treatment with NaOMe–MeOH[17]) failed to produce evidence for the formation of any other product. At present, the reasons underlying the highly site-selective nature of these homo-[1,5]-sigmatropic hydrogen shifts remains obscure. However, it is clear that these high selectivities could be very useful from a synthetic point of view.

Removal of the MEM group ($ZnBr_2$, CH_2Cl_2)[13] from 32, followed by tosylation of the resultant alcohol 34, gave the tosylate 35. Brief treatment of the latter with 1.2 equiv of *t*-BuOK in *t*-BuOH (15 min, room temperature) gave (68% from 34) the *exo*-enone 36.[18,19] When a solution of 36 in *o*-dichlorobenzene (bp 179 °C) was refluxed for 40 h, the tricyclic enone 37 (resulting from Cope rearrangement[20]) was formed in 94% yield.

Work in this area is continuing.

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References and Notes

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(2) (a) E. Piers, C. K. Lau, and I. Nagakura, *Tetrahedron Lett.*, 3233 (1976); (b) E. Piers and I. Nagakura, *ibid.*, 3237 (1976).
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(5) Cf. C. L. Osborn, T. C. Shields, B. A. Shoulders, J. F. Krause, H. V. Cortez, and P. D. Gardner, *J. Am. Chem. Soc.*, **87**, 3158 (1965).
(6) All compounds reported herein exhibited spectral data in full accord with assigned structures. New compounds gave satisfactory elemental analysis and/or high-resolution mass spectrometric measurements.
(7) The various *endo*-monobromocyclopropane derivatives reported herein could readily be distinguished from their exo epimers by ^1H NMR spectroscopy. Details will be reported in a full paper.
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(11) Cf. D. Seyferth, R. L. Lambert, Jr., and M. Massol, *J. Organomet. Chem.* **88**, 255 (1975).
(12) Attempted reduction of **8** with Zn–HOAc gave very poor yields of **9** and **10**.
(13) E. J. Corey, J-L. Gras, and P. Ulrich, *Tetrahedron Lett.*, 809 (1976).
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(15) For steric reasons, dibromocyclopropanation of **17** and **22** would be expected to occur from the side of the molecule opposite the O–MEM group. Independent evidence for the stereochemistry of **18** was obtained as follows. Removal of the MEM group, followed by oxidation of the resultant alcohol A, gave the corresponding ketone. Reduction of the latter afforded an alcohol which was clearly epimeric with A.
(16) For a recent review regarding this type of reaction, see S. W. Spangler, *Chem. Rev.*, **76**, 187 (1976).
(17) In these cases, the initial thermolysis products contained small amounts of the unconjugated ketones (analogous to **27**), which were isomerized to the conjugated isomers by the base treatment.
(18) Compound **36** could also be obtained by reaction of 3-iodo-2-cyclohexen-1-one with the cuprate reagent derived from *exo*-7-bromo-2-norcarene.
(19) The facility with which the transformation of **35** into **36** occurred also provided excellent evidence to support the stereochemical assignment made for compound **17** (see ref 15) and for the subsequent intermediates derived from **17**.
(20) Cf. S. J. Rhoads and N. R. Raulins, *Org. React.*, **22**, 54 (1975).
(21) On sabbatical leave from Moorhead State University, Moorhead, Minnesota.

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One-Step Catalytic Synthesis of 2,2,3-Trimethylbutane from Methanol

Summary: Catalytic reaction of methanol in the presence of zinc iodide produces butane and higher hydrocarbons with a high degree of branching and an unexpectedly high triptane (2,2,3-trimethylbutane) content.

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

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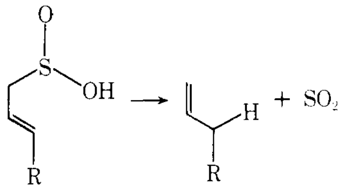
Stereochemical Course of the Fragmentation of Allylsulfinic Acids

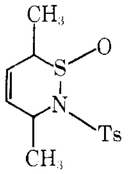
Summary: Diastereomers of 5-(*p*-tolylsulfonamido)-(*Z*)-3-hexene-2-sulfinic acid fragment in D_2O to different diastereomers of 4-deuterio-5-(*p*-tolylsulfonamido)-(*E*)-2-hexene.

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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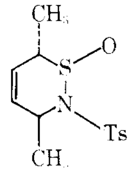

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