controlled by the resistance of the external circuit. In electrogenerative hydrogenation, favorable thermodynamic factors are used to bring about reaction at the electrolyte–catalyst interface. The "hydrogenation cell" also gives an open circuit voltage.

The reaction may be represented as

$$\text{Anode: } H_2 \longrightarrow 2H^+ + 2e \quad (1)$$

$$H^+ \text{ transported through electrolyte} \quad (2)$$

$$\text{Cathode: } 2H^+ + 2e + RCH{=}CHR' \longrightarrow RCH_2{-}CH_2R' \quad (3)$$

In contrast to conventional electrochemical hydrogenation, which consumes power, the system described above generates power. The course of hydrogenation may be followed by monitoring the current generated by the system or the hydrogen consumed from the anode compartment.

The electrolyte phase may be an ion-exchange membrane, free electrolyte, or membrane saturated with electrolyte. It may be acidic or basic. Electrode reactions are changed for the latter, but the net process is hydrogenation.

For the work with hydrocarbon gases reported here, we used five sheets of filter paper saturated with aqueous electrolyte as the liquid phase. Some aqueous electrolytes were 1 *N* fluoroboric, 6 *N* phosphoric, and 1 *N* *p*-toluenesulfonic acids. Schematically, cell construction was similar to that described by Niedrach[2] and Elmore and Tanner[3] for a fuel cell. The electrode exposed area was 4.9 cm.^{2}. Electrodes were molded platinum or palladium black–polytetrafluoroethylene supported on a 50-mesh tantalum screen.[3,4] The face plates were fitted with additional outlets to hydrogen and hydrocarbon reservoirs so that changes in gas volume could be observed and compared with generated current when desired. Current generated by the "hydrogenation cell" was equivalent to hydrogen consumed. Some operating results for several hydrocarbon gases flowing through the cell are shown in Table I.

TABLE I

ELECTROGENERATIVE HYDROGENATION

T = 25°, 1 *N* fluoroboric acid electrolyte

Hydrocarbon	Catalyst, mg./cm.^{2} Anode	Cathode	Open circuit voltage	Calculated open circuit voltage[a]	Cell voltage at 10 ma.	80 ma.
Ethylene	—Pt, 9—		0.48–0.49	0.51	0.17	0.10
Ethylene	Pt, 9	Pd, 7	.45– .48	.51	.22	.14
Propylene	—Pt, 9—		.48– .52	.44	.17	.10
Propylene	Pt, 9	Pd, 7	.47– .48	.44	.19	.10
Isobutylene	—Pt, 9—		.77– .82	.40	.19	.09

[a] Calculated from standard free energies of formation.

Other work has shown that the hydrogen electrode polarizes little (<0.01 v.) at the current densities used here and the cell voltages measured relate the voltage of the catalytic hydrogenating electrode to a reversible hydrogen electrode. The observed currents are a measure of the rate of hydrogenation [50 ma.-min. ~0.4 ml. of H_2] and the rate of hydrogenation can be controlled with the variable resistor of the external circuit. Recently, Beck and Gerischer[5] have reviewed and studied changes in potential at an operating hydrogenating electrode. However, in their system, as in previous systems, hydrogen and substrate are not separated by an electrolyte barrier as is done here. Kowaka and Joncich[6] have studied hydrogenation of ethylene using a palladium thimble as a barrier and an electrolytic process to drive hydrogen through the palladium. In addition to other differences from "electrogenerative hydrogenation," such studies are limited to palladium because of its unique permeability to hydrogen.

Electrogenerative hydrogenation would have particular advantage where difficulty arises from excessive adsorption of hydrogen at the catalytic surface.[7]

The failure to develop theoretical open circuit voltages may arise from decomposition on the catalyst surface[8] or surface bonding.[8d,9] Nevertheless, with suitable catalyst and cell it may be possible to measure reliable standard open circuit potentials for hydrogenation. Electrogenerative hydrogenation offers a novel approach to studies of catalytic reactions as well as to coulometric analysis of mixtures containing olefins, where separation of the olefins is not desired.

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Influence of the Sulfinyl Group on the Equilibrium in Base-Catalyzed Isomerization of Olefins

Sir:

The effect of a substituent X upon the equilibrium position in the olefinic system shown in eq. 1 in all cases reported heretofore has been one of stabilization of the double bond in the α,β-position. For example,

$$\underset{\text{I}}{RCH{=}CHCH_2X} \rightleftharpoons \underset{\text{II}}{RCH_2CH{=}CHX} \quad (1)$$

Linstead and co-workers found that II was favored at equilibrium over I in ratios ranging from 2:1 to 20:1 in studies of the esters[1] and salts[2] of unsaturated acids and of nitriles[3] (X in eq. 1 = $-CO_2R'$, $-CO_2^-$, and $-CN$, respectively). Similarly, base-catalyzed isomerization of allyl sulfides (I, X = SR′, R = H) has given propenyl sulfides (II, X = SR′, R = H) in yields of 60–70%,[4] while Price[5] has recently demonstrated propenyl–allyl ratios of at least 99:1 in this isomerization. Allyl ethers give up to 97% propenyl ethers upon treatment with a basic catalyst,[6] while propenylamines are highly favored over allylamines in base-catalyzed equilibria.[7]

We wish to report the first example of a system of this type in which the β,γ-unsaturated isomer is favored over the α,β-unsaturated isomer.[8] Treatment of 0.15 mole of 1-methylsulfinyl-2-hydroxyundecane (III) with 0.18 mole of potassium *t*-butoxide in 250 ml. of *t*-butyl alcohol for 4 hr. at 60° (eq. 2) gave a 40% yield[9] of

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(8) E. A. Fehnel (*J. Am. Chem. Soc.*, **74**, 1569 (1952)) has reported a similar example in a cyclic system. Δ^3-Dihydrothiopyran 1,1-dioxide is greatly favored over the Δ^2-isomer at equilibrium.

(9) A 30% yield of 3-hydroxy-1-undecene, b.p. 56° (0.2 mm.), was also isolated. Methods of identification and its mode of formation will be discussed later.

1-methylsulfinyl-2-undecene (IV), b.p. 131° (0.2 mm.). *Anal.* Calcd. for $C_{12}H_{24}OS$: C, 66.5; H, 11.2; S, 14.8. Found: C, 66.2; H, 11.3; S, 14.4. Neither 1-methylsulfinyl-1-undecene (V) nor 1-methylsulfinyl-2-*t*-butoxyundecane was isolated, although a minor amount of V was present in IV (*vide infra*).

$$\underset{\text{III}}{C_9H_{19}CHCH_2\overset{\uparrow}{S}CH_3} \xrightarrow[t\text{-BuOH}]{t\text{-BuO}^-} \underset{\text{IV}}{C_8H_{17}CH{=}CHCH_2\overset{\uparrow}{S}CH_3} \quad (2)$$

The position of the double bond in IV was assigned on the basis of its n.m.r. spectrum (10% solution in carbon tetrachloride on a Varian A-60 spectrometer) which showed the presence of methylene protons between the double bond and the sulfinyl group (multiplet centered at 6.65 τ, relative area 1.9), as well as methylsulfinyl protons (sharp band at 7.58 τ, area 3.0), and allylic protons (multiplet centered at 7.9 τ, area 2.0). Other features of the spectrum resulted from the vinyl protons (complex multiplet centered at 4.4 τ, area 1.9) and protons of the alkyl chain (multiplet at 8.7 τ, area 12.0, and multiplet centered at 9.0–9.1 τ, area 3.0). The band at 6.65 τ is at lower field than that observed for protons adjacent to either a sulfinyl group or a double bond. Shifts due to adjacent groups are known to be approximately additive,[10] and this peak is shifted from the absorption region for unactivated methylene protons by an amount about equal to the sum of the shifts produced by the carbon–carbon double bond and the sulfinyl group.

To compare the n.m.r. spectrum of IV with that of an α,β-unsaturated sulfoxide a sample of 1-methylsulfinyl-1-dodecene (VI) (mixture of *cis* and *trans* isomers), b.p. 132° (0.15 mm.) (*Anal.* Calcd. for $C_{13}H_{26}OS$: C, 67.7; H, 11.37; S, 13.9. Found: C, 67.6; H, 11.6; S, 13.6) was prepared by the free radical addition of methyl mercaptan to 1-dodecyne and subsequent oxidation of the sulfide. The n.m.r. spectrum of VI differed from that of IV in two important respects. VI did not absorb in the 6.6 τ region, while its olefinic proton absorption was centered at 3.7 τ (compared with 4.4 τ for IV) with none above 3.9 τ. Thus, by comparison of the peak area at 3.5–3.9 with that at 3.9–4.8 τ, we estimate that the maximum percentage of V present in the equilibrium mixture of IV and V is 4%. Treatment of 0.043 mole of VI with 0.012 mole of potassium *t*-butoxide in 200 ml. of *t*-butyl alcohol for 5 hr. at room temperature converted it to 1-methylsulfinyl-2-dodecene containing 4% of VI, demonstrating that equilibrium had been attained during the elimination reaction.

That the β,γ-isomer is favored under equilibrium conditions was shown independently by deuterium exchange experiments. When 1.0 g. of IV was stirred for 24 hr. at room temperature with 1.0 g. of potassium *t*-butoxide in 10 ml. of *t*-butyl alcohol-O-*d*, exchange occurred at both the α- and γ-positions to yield $C_8H_{17}CD{=}CHCD_2SOCD_3$ (n.m.r. spectrum indicated relative area of 1.0 at 4.4 τ and virtual elimination of 6.65 and 7.58 τ bands). A sample of IV treated with potassium *t*-butoxide in *t*-butyl alcohol under identical conditions was unchanged as shown by its n.m.r. spectrum. These results demonstrate that equilibrium between IV and V is readily established, since deuterium in the γ-position must arise from formation of the α,β-unsaturated isomer followed by conversion to the β,γ-unsaturated isomer. It follows that IV is the predominating product in the elimination reaction because it is thermodynamically more stable than V, not because it is the kinetically favored product. It seems quite probable that elimination first yields V, which then isomerizes to IV (eq. 3). Russell has reported[11] the similar formation of an α,β-unsaturated compound from 1-methylsulfinyl-2-phenyl-2-hydroxyethane, but in that system a β,γ-unsaturated isomer does not exist.

$$\text{III} \xrightarrow[t\text{-BuOH}]{t\text{-BuO}^-} \underset{\text{V}}{C_8H_{17}CH_2CH{=}CH\overset{\uparrow}{S}CH_2} \rightleftharpoons \underset{\text{IV}}{C_8H_{17}CH{=}CHCH_2\overset{\uparrow}{S}CH_3} \rightleftharpoons C_8H_{17}C{\equiv}C{-}\overset{\uparrow}{S}CH_3 \quad (3)$$

In equilibria between allyl (I, R = H) and propenyl (II, R = H) compounds, determination of the effect of a substituent is complicated by the simultaneous change of two substituents on the double bond, *i.e.*, the double bond of I holds three hydrogens and a $-CH_2X$ group, whereas that of II holds two hydrogens, a methyl group, and an X group. However, in the equilibrium between IV and V, if we make the reasonable assumption that the effects of the C_8H_{17} and C_9H_{19} groups are essentially identical, then the difference in thermodynamic stability between IV and V is due solely to the difference between the stabilizing effects of the $-CH_2SOCH_3$ group and the $-SOCH_3$ group. Thus, the $-SOCH_3$ group has a destabilizing effect compared to that of $-CH_2SOCH_3$.

This result strongly suggests that ground-state resonance between the sulfur atom and the adjacent unsaturated system is unimportant, since conjugation would favor the α,β-unsaturated isomer.[1,3] Further discussion will await completion of the studies now in progress.

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Popcorn Polymer as a Support in Multistep Syntheses[1]

Sir:

The recent publication by Merrifield[2] describing the synthesis of a tetrapeptide on polymer beads prompts us to report at this time experiments carried out independently which demonstrate the feasibility of using a modified "popcorn" polymer as a supporting matrix in repetitive-step syntheses.

In principle it appears that the manipulations involved in the stepwise synthesis of polypeptides and polynucleotides may be materially reduced, thereby rendering possible the construction of more complex substances, if the polymer is held to a solid support throughout the synthetic sequence. To function properly the support should (a) be insoluble in the solvents and inert to the reagents employed, (b) contain a functional group to which the initial monomer unit

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