The reaction may be represented as

Anode:
$$H_2 \longrightarrow 2H^+ + 2e$$
 (1)

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

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 Niedrach² and Elmore and Tanner³ 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 $T\,=\,25^\circ,\,1~N$ fluoroboric acid electrolyte

Calculated

Hydro- carbon	Catalyst, mg./ Anode Cat	′cm.² Open circui hode voltage	open t eircuit voltage ^a		oltage at 80 ma.	
Ethylene	—Pt, 9-	- 0.48-0.49	0.51	0.17	0.10	
Ethylene	Pt, 9 Pd	l,7 .45– .48	.51	.22	.14	
Propylene	—Pt, 9-	4852	.44	.17	.10	
Propylene	Pt, 9 Pd	,7.4748	.44	.19	.10	
Isobutylene	—Pt, 9-	7782	.40	.19	.09	
" Calculated from standard free energies of formation						

^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 Gerischer⁵ 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 Joncich⁶ have studied hydrogenation of

(2) L. W. Niedrach, J. Electrochem. Soc., 109, 1092 (1962).

(3) G. V. Elmore and H. A. Tanner, *ibid.*, **108**, 669 (1961).
(4) W. T. Grubb, "Proceedings of the 16th Annual Power Sources Conference," PSC Publications Committee, Red Bank, N. J., pp. 31-34.

(5) F. Beck and H. Gerischer, Z. Elektrochem., 65, 504 (1961).

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 surface8 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.

(6) M. Kowaka and M. J. Joncich, Mem. Inst. Sci. Ind. Res., Osaka Univ., 16, 107 (1959); Chem. Abstr., 54, 5226 (1960).

(7) G. C. Bond, "Catalysis by Metals," Academic Press, New York, N. Y., 1962, p. 272.

(8) (a) S. J. Stephens, J. Phys. Chem., 62, 714 (1958); (b) D. W. McKee, J. Am. Chem. Soc., 84, 1109 (1962); (c) O. Beeck, Discussions Faraday Soc., 8, 118 (1950); (d) see also F. G. Gault, J. J. Rooney, and C. Kimball, J. Catalysis, 1, 255 (1962); reference 6, Chapter 11 and cited references.

(9) R. P. Eischens and W. A. Pliskin, Advan. Catalysis, 10, 1 (1958); N. Sheppard, Rev. Pure Appl. Chem., 13, 80 (1963); G. V. Smith and R. L. Burwell, J. Am. Chem. Soc., 84, 925 (1962).

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RECEIVED JULY 29, 1963

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,

$$\begin{array}{c} \text{RCH} = \text{CHCH}_2\text{X} \rightleftharpoons \text{RCH}_2\text{CH} = \text{CHX} \\ \text{I} & \text{II} \end{array} \tag{1}$$

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 esters1 and salts2 of unsaturated acids and of nitriles³ (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 Price⁵ 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 tbutyl alcohol for 4 hr. at 60° (eq. 2) gave a 40% yield⁹ of

(1) G. A. R. Kon, R. P. Linstead, and G. W. G. MacLennan, J. Chem. Soc., 2454 (1932).

(2) R. P. Linstead and E. G. Noble, ibid., 614 (1934).

(3) A. Kandiah and R. P. Linstead, ibid., 2139 (1929).

(4) D. S. Tarbell and W. E. Lovett, J. Am. Chem. Soc., 78, 2259 (1956).

(5) C. C. Price and W. H. Snyder, J. Org. Chem., 27, 4639 (1962).

(6) T. J. Prosser, J. Am. Chem. Soc., 83, 1701 (1961). (7) C. C. Price and W. H. Snyder, Tetrahedron Letters, No. 2, 69 (1962).

(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. Caled. for C₁₂H₂₄OS: 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).

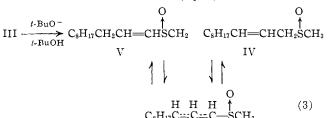
$$\begin{array}{c} OH & O \\ \downarrow & \uparrow \\ C_{9}H_{19}CHCH_{2}SCH_{3} \xrightarrow{t-BuO^{-}} C_{8}H_{17}CH = CHCH_{2}SCH_{3} \quad (2) \end{array}$$

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 6.65τ 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 6.6τ region, while its olefinic proton absorption was centered at 3.7 τ (compared with 4.4τ for IV) with none above 3.9τ . 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,

(10) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, New York, N. Y., 1959, pp. 59–60.



ported¹¹ 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.

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 $-SOCH_3$.

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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(11) G. A. Russell, E. G. Janzen, H. Becker, and F. J. Smentowski, J. Am. Chem. Soc., 84, 2652 (1962).

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Popcorn Polymer as a Support in Multistep Syntheses¹ Sir:

The recent publication by Merrifield² 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

(1) This research was supported by the National Science Foundation, grant G25069, and by the Division of General Medical Sciences of the National Institutes of Health, grant GM 10265-01.

(2) R. B. Merrifield, J. Am. Chem. Soc., 85, 2149 (1963).