Base-Catalyzed Deuterium Exchange in Cycloheptatriene. Evidence for the Cycloheptatrienide Anion

Sir:

In response to the continuing, theoretically based assertion that the cycloheptatrienide anion should exist under experimentally accessible conditions and having failed in the approach with which Dauben and Rifi achieved such a brilliant success,[1] we looked to base-catalyzed exchange of deuterium in cycloheptatriene[2] to provide indirect support for the existence of the anion.

Deuterium exchange, determined from the mass spectral cracking pattern in the region m/e 91 and above,[3] occurred extensively when cycloheptatriene (1 ml., 91.4%, kindness of Shell Chemical Co.) was heated for 12 hr. at 115° in 100 ml. of deuterated (> 96% by infrared) triethylcarbinol (prepared by shaking 50-ml. portions of triethylcarbinol 1 hr. each with six successive 5-ml. portions of 99.5% deuterium oxide containing a little potassium carbonate and dried by treating with excess sodium and decanting) containing 5 g. of reacted potassium metal (no exchange occurred on heating pure cycloheptatriene in 10% methanolic sodium methoxide for 24 hr. at 110°). The resulting sample A contained 90.8% deuterium distributed between octadeuterio- (55.9), heptadeuterio- (25.0), hexadeuterio- (13.2), and penta- and tetradeuterio- (5.9%) cycloheptatrienes (maleic anhydride adduct, m.p. 104.5–105.0°).[4]

Disclosure of both the stepwise and the random nature of the exchange appears when perdeuterated cycloheptatriene (sample B: 86.0% deuterium as D_8: 31.9%, D_7: 39.0%, D_6: 20.4%, and D_5 and less: 8.7%), which shows only broad singlets in the n.m.r. at τ = 3.54, 3.93, 4.77, and 7.82 p.p.m. (positions 3 and 4, 2 and 5, 1 and 6, and 7.7, respectively) is exchanged for 30, 60, and 180 min. in triethylcarbinol (2 ml.) containing reacted potassium (144 mg.) at 99.5°. While the three samples revealed a regular increase in protonated species, the relative areas of the four types of hydrogen remained equal throughout within the limits of experimental error. Exchange had occurred at the same rate at all four positions. A blank experiment in which cycloheptatriene-7,7-d^2 (*vide infra*) was heated 15 min. at 97° was negative.[5]

Elegantly suited to the further study of the exchange, 7,7-dideuteriocycloheptatriene cannot be obtained in structurally homogeneous form from the photolytic reaction of benzene and deuteriodiazomethane,[6,7] which actually leads to a product having significant, but variable amounts of deuterium in the vinyl positions. This photorearrangement *per se* was brought into focus by irradiating (λ > 300 mμ) 30 μl. of 7-deuteriocycloheptatriene (from tropylium bromide and lithium aluminum deuteride in ether) and

10 μl. of benzene in an n.m.r. tube in carbon tetrachloride solution and measuring relative areas of the four types of hydrogen periodically. After irradiation for 300 min., partial redistribution of the 7-deuteron had occurred, mainly to the adjacent position: (7,7) 0.51, (1,6) 0.35, (2,5) 0.05, (3,4) 0.09.[8]

Although the extent of the photorearrangement can be decreased by irradiating with filtered light of λ > 380 mμ (Corning filter No. 3360), structurally homogeneous 7,7-dideuteriocycloheptatriene is better prepared by the decomposition of diazomethane in benzene catalyzed by copper sulfate.[9]

The random distribution of deuterium in cycloheptatriene exchanged in triethylcarbinol is occasioned by a rapid intramolecular base-catalyzed rearrangement which, being roughly 12 times faster than the exchange, prevents observations on the exchange step.

In dimethyl sulfoxide the relative rates are reversed, exchange becoming much faster than intramolecular rearrangement. A sample of 7,7-dideuteriocycloheptatriene (50 μl.) in anhydrous dimethyl sulfoxide (10 ml.) and triethylcarbinol (1 ml.) containing potassium (79 mg.) was converted in 30 min. at 25° to a sample from which 0.312 deuteron had exchanged (mass spectroscopy) and in which 0.29 deuteron had disappeared from the 7,7-position (by n.m.r.). Similarly, perdeuterated cycloheptatriene (sample A) containing 0.17 proton each in the (3,4), (2,5), (1,6), and (7,7) positions had 0.02, 0.01, 0.04, and 0.41 in these positions after 30-min. exchange.[10]

The rate of exchange being essentially equal to the rate of appearance of the solvent hydrogen at the 7-position (predicted 6/7), the intermediacy of the seven-fold symmetrical cycloheptatrienide anion is a consistent hypothesis.

(8) This photorearrangement is structurally similar to that reported by O. L. Chapman and S. L. Smith, *J. Org. Chem.*, **27**, 2291 (1962).

(9) E. Müller, H. Fricke, and W. Rundel, *Z. Naturforsch.*, **15b**, 753 (1960); G. Wittig and K. Schwarzenbach, *Ann.*, **650**, 1 (1961).

(10) *Cf.* D. J. Cram, C. C. Kingsbury, and B. Rickborn, *J. Am. Chem. Soc.*, **81**, 5835 (1959).

(11) Our gratitude to the Esso Research and Engineering Company for its partial support of this work.

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Electrogenerative Hydrogenation

Sir:

Conventional chemical hydrogenation of unsaturated compounds is effected by contact of hydrogen and substrate with a suitable catalyst. For electrochemical hydrogenation,[1] external power is utilized to generate hydrogen which adds to the unsaturated molecule. We report here a new hydrogenation technique which may be described as *electrogenerative hydrogenation*. Hydrogen is placed on one side of an electrolyte barrier while an unsaturated compound is placed on the other side. The electrolyte phase is bounded by porous, electrolyte-impermeable, catalytic electrodes. Under operating conditions, hydrogen ions are formed at one electrode and conducted through the electrolyte while electrons are conducted through an external circuit containing a variable resistor and ammeter. Hydrogenation takes place at the counter catalytic electrode where unsaturate, hydrogen ions, and electrons are combined. Hydrogenation rate or potential may be

(1) H. J. Dauben, Jr., and M. R. Rifi, *J. Am. Chem. Soc.*, **85**, 3041 (1963); *q.v.* for the bulk of references relevant to this problem.

(2) R. E. Davis and A. Tulinsky, *Tetrahedron Letters*, No. **19**, 839 (1962).

(3) That hydrogen is lost randomly in the process generating parent minus one was confirmed in the mass spectrum of cycloheptatriene-7,7-d^2. On this basis of calculation, excellent agreement with an analysis by low-voltage mass spectroscopy was obtained (kindness of Dr. J. L. Franklin, Humble Oil and Refining Co.).

(4) E. P. Kohler, M. Tishler, H. Potter, and H. T. Thompson, *J. Am. Chem. Soc.*, **61**, 1060 (1939).

(5) Apparently, the 1,5-transannular shift of A. P. ter Borg, H. Kloosterziel, and N. Van Meurs, *Proc. Chem. Soc.*, 359 (1962), does not intervene.

(6) W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **72**, 2305 (1950).

(7) Deuterated diazomethane was obtained by shaking decalin solutions of diazomethane with 20% potassium deuteroxide in deuterium oxide at 0° for 6–12 hr. and was analyzed directly by mass spectrography. Losses are substantial (15–30%). Exchange, being negligible at pH 7 or 11.6, is base-catalyzed.

(1) (a) For a recent review see: D. Popp and H. P. Schultz, *Chem. Rev.*, **62**, 19 (1962); (b) see also P. S. Farrington and D. T. Sawyer, *J. Am. Chem. Soc.*, **78**, 5536 (1956).

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

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

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

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

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

(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 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.

(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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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,

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

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

(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.