ability of approximately 0.25 Hz for the excess broadening of the outer lines of the H-2 multiplet by dephasing of H-2 spins in **4** *via* the known hyperfine interaction[9] ($a = 4.06$ G) with the unpaired electron in the allyl radical. Such broadening effects are well known in nmr spectra of molecules undergoing rapid exchange with small amounts of paramagnetic species[10] and give rise to a contribution to the nmr line width, $T_{2,\mathrm{ex}}^{-1}$, given by eq 5 (assuming the lifetime, τ_R, of the radical is less than the relaxation time of the unpaired electron).[10b] Thus, $\tau_\mathrm{R} \leqslant 1 \times 10^{-8}$ sec or $k_\mathrm{e} \geqslant 1 \times 10^7$

$$T_{2,\mathrm{ex}}^{-1} = \frac{2}{\tau}\frac{(a\tau_\mathrm{R})^2/4}{[1 + (a\tau_\mathrm{R})^2/4]} \tag{5}$$

M^{-1} sec^{-1} which is in excellent agreement with the previous estimate and is *independent* of the estimate of allyl radical concentration.

The estimate of the rate constant for thermoneutral iodine atom transfer thus shows that this process, at least for the allyl system, proceeds at a rate several orders of magnitude faster than radical recombination. If such rates also are characteristic of nonconjugated alkyl radicals,[11] they can easily explain the transfer of nonequilibrium nuclear spin populations to alkyl iodide reagents undergoing free-radical reactions.

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(9) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

(10) (a) E. deBoer and H. van Willigen, *Progr. Nucl. Magn. Spectrosc.* 111 (1967); (b) C. S. Johnson, Jr., *J. Chem. Phys.*, **39**, 2111 (1963).

(11) The rate constant for abstraction of iodine from 1-iodopropane by methyl radical in the gas phase may be estimated indirectly to be 4×10^5 M^{-1} sec^{-1} at 100° [D. M. Tomkinson and H. O. Pritchard, *J. Phys. Chem.*, 70, 1579 (1966)]. The 100-fold acceleration reported here for allyl is in accord with the lower carbon-iodine bond energy in allyl iodide [F. P. Lossing, K. U. Ingold, and J. H. S. Henderson, *J. Chem. Phys.*, 22, 1489 (1954)].

Rearrangements of Dihydrodicyclopentadiene Derivatives in Phosphoric Acid. 1,4-Hydride Shifts

Sir:

In 1948 the dehydration of 9-*exo*-hydroxytetrahydro-*exo*-dicyclopentadiene (I) with orthophosphoric acid was reported to give 1,2-dihydro-*exo*-dicyclopentadiene (II).[1] Later the product was found to be 9,10-dihydro-*exo*-dicyclopentadiene (III).[2] The behavior of several compounds related to I in phosphoric acid under a set of standardized conditions has now been studied, and we wish to report that alcohols I and IV and alkenes II and V afford III and 9,10-dihydro-*endo*-dicyclopentadiene (VI) in very nearly a constant ratio.

Products were identified by retention times using gas–liquid partition chromatography on a 5 ft × 1/8 in., 10% diisodecyl phthalate on 60–80 Chromosorb W column at 50° and 25 ml/min helium flow rate and by their nmr traces.[3] Peak areas were determined by weighing the excised graph paper and product mixture compositions were calculated assuming equivalent thermal conductivities for the isomers.

The reaction of alcohol I with phosphoric acid (1:1 by weight) at 150° for 30 min gave a mixture of alkenes containing 65% III and 25% VI, and alcohol IV gave 67% III and 25% VI. Alkene II under the same conditions gave 63% III and 23% VI while alkene V yielded 67% III and 20% VI. In each reaction, small amounts (9–14%) of the alkanes, *endo*- and *exo*-tetrahydrodicyclopentadienes, were observed. On dilution of alcohol IV with H_3PO_4 and $CHBr_3$, as an immiscible cosolvent, to concentrations of 6×10^{-4} M, a constant amount of olefin (98%) was obtained in a ratio of 9:1 (*cf.* Table I). The product alkenes III and VI were found to be completely stable under the conditions employed. At 180° and 60 min, however, VI did rearrange to give 14% III, the most stable of the four dihydrodicyclopentadienes.

Table I

Concn of IV, mol l.$^{-1}$	% III	% VI	% saturated
9.4 (1:1 by wt)[a]	67	25	8
1.2[a]	73	17	10
1.2 in H_3PO_4 + 1 ml of $CHBr_3$[b]	67	20	13
0.12	68	16	16
0.012[a]	51	6	43
0.012 in H_3PO_4 + 5 ml of $CHBr_3$[b]	85	10	5
0.012 in H_3PO_4 + 10 ml of $CHBr_3$[a,b]	84	10	6
0.012 in H_3PO_4 + 20 ml of $CHBr_3$[a,b]	82	11	7
0.0012[a]	56	6	38
0.0012 in H_3PO_4 + 5 ml of $CHBr_3$[a,b]	89	9	~2
0.0006 in H_3PO_4 + 5 ml of $CHBr_3$[a,b]	89	9	~2

[a] Average value of duplicate runs; deviation from mean ±1%.
[b] The addition of $CHBr_3$ as an immiscible cosolvent greatly increases the effective dilution factor. The slow diffusion of organic alcohol into H_3PO_4 from $CHBr_3$ greatly enhances the dilution effect over the apparent dilution factor.

These results may be rationalized by a reaction scheme (Scheme I) involving equilibrated tautomeric ions (VII and VIII) or by a common intermediate IX. The endo ring fused reactants IV and V give cation VII or IX in which a 1,2 alkyl shift is competitive with an intermolecular or an intramolecular hydride shift. The exo ring fused reactants I and II give cation VIII or IX in which a 1,3 hydride shift is competitive with a 1,2 alkyl shift. Dilutions to concentrations of 10^{-3}–10^{-4} M have been used to minimize intermolecular hydride shifts.[4] Our dilution studies show a limiting amount of olefin VI which at these concentrations would be expected to arise only from an intramolecular hydride shift.

We have also dehydrated 9-*exo*-hydroxy-2,2-dimethyl-9,10-dihydro-*endo*-dicyclopentadiene (X)[5,6] at 150° for

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(1) H. A. Bruson and T. W. Riener, *J. Amer. Chem. Soc.*, 70, 2809 (1948).

(2) P. von R. Schleyer and M. M. Donaldson, *ibid.*, **78**, 5702 (1956); P. Wilder, Jr., and G. T. Youngblood, *ibid.*, **78**, 5706 (1956).

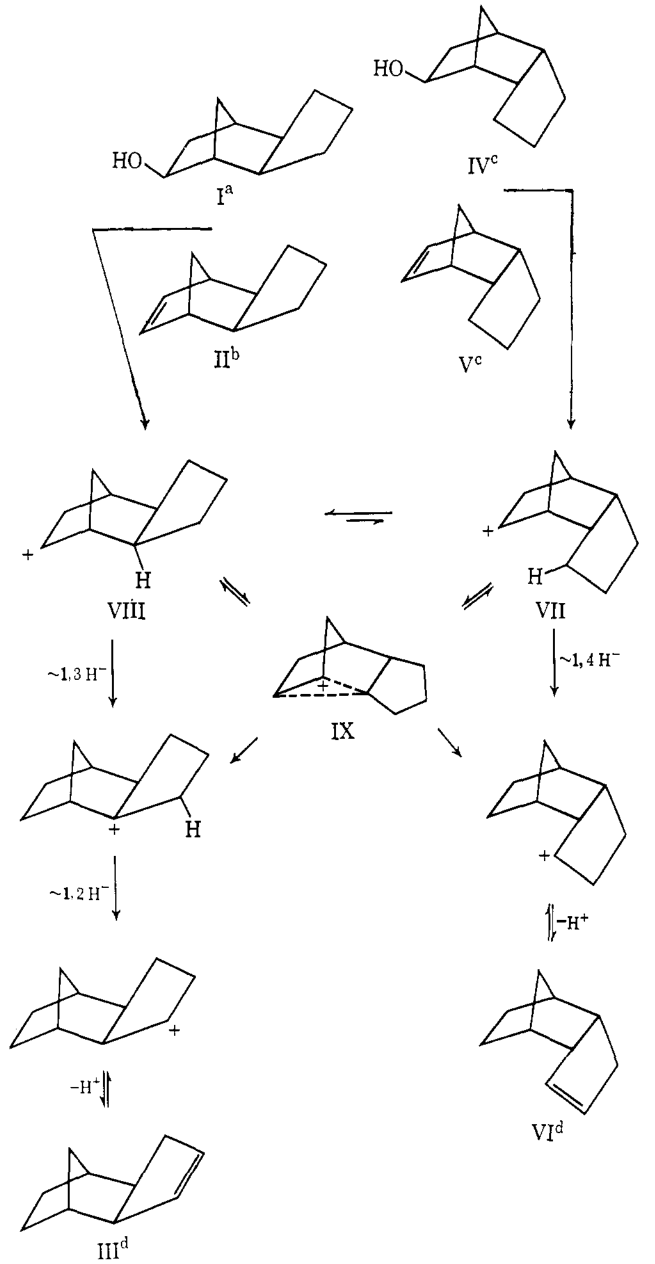
(3) S. Cesca, M. L. Santostasi, W. Marconi, and N. Palladino, *Ann. Chim.* (*Rome*), **55** (7), 704 (1965).

(4) P. von R. Schleyer, *Angew. Chem.*, **81**, 539 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 529 (1969).

(5) H. C. Brown and P. Geoghegan, *J. Amer. Chem. Soc.*, **89**, 1522 (1967).

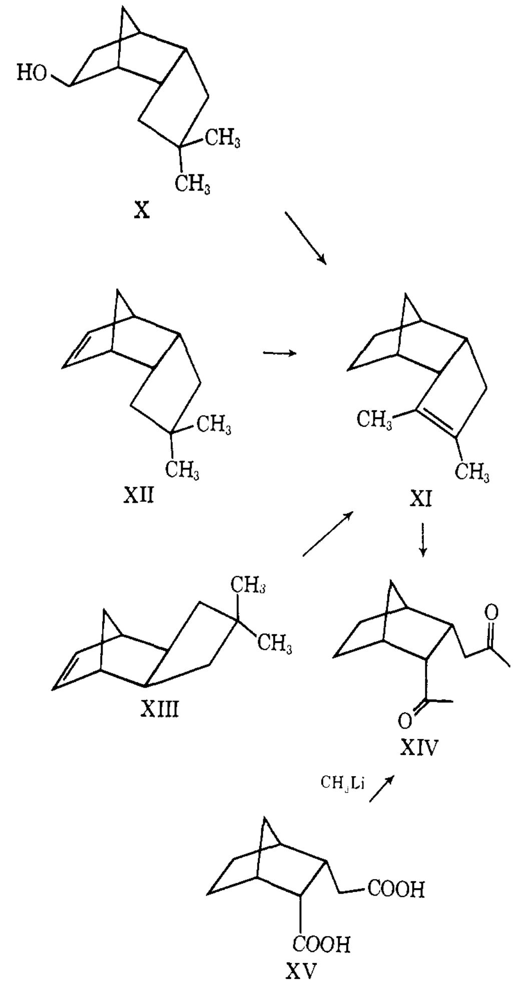
(6) C. F. Culberson and P. Wilder, Jr., *J. Org. Chem.*, **26**, 4289 (1961).

Scheme I



[a] H. A. Bruson and T. W. Riener, *J. Amer Chem. Soc.*, **67**, 723 (1945). [b] H. A. Bruson and T. W. Riener, *ibid.*, **67**, 1178 (1945). [c] Alcohol IV was prepared by reaction of *endo*-dicyclopentadiene with mercury(II) acetate[5] followed by catalytic hydrogenation of the unsaturated *endo* alcohol. Alkene V resulted from the dehydration of alcohol IV *via* the Tsugaev method. [d] P. D. Bartlett and A. Schneider, *J. Amer. Chem. Soc.*, **68**, 6 (1946); G. B. Clemans, Ph.D. Thesis, Duke University, 1964. While alkenes III and VI are stable under the conditions of the reaction, both alkenes are found to undergo exchange in the presence of D_3PO_4 under the standardized reaction conditions.

Scheme II



30 min (Scheme II). The product, isolated in 85% yield, is 1,2-dimethyl-9,10-dihydro-*endo*-dicyclopentadiene (XI). Further, both 2,2-dimethyl-1,2-dihydro-*endo*- (XII)[6] and 2,2-dimethyl-1,2-dihydro-*exo*-dicyclopentadiene (XIII)[6] afforded XI, also in 85% yield. Dilution of XII and XIII to 10^{-3} *M* in H_3PO_4 and $CHBr_3$ gave 14% XI, starting material, and traces of saturated hydrocarbon. The predominance of endo ring fused product in these cases suggests that the 1,4-hydride shift is even more facile than in the nor-dimethyl compounds.

The stable alkene XI decolorized bromine in cyclohexane, but was not hydrogenated when shaken over Adams' catalyst for 4 hr. The proton magnetic resonance spectrum showed no vinyl protons, but did show two clear vinyl methyl singlets at 1.20 and 1.35 ppm. The structure of XI was confirmed by oxidation with potassium permanganate to the diketone XIV, which was identified by comparison of glc retention times with a sample independently synthesized from the known dicarboxylic acid XV[7] with methyllithium.[8] The *cis*-*endo*-diketone XIV was characterized as its bis-2,4-dinitrophenylhydrazone, mp 210°. The *cis*-*exo*-diketone was also prepared and its bis-2,4-dinitrophenylhydrazone melted at 221°.

The isolation of XI from alcohol X and olefins XII and XIII is consistent with an intramolecular 1,4 hydride shift, followed by a Nametkin shift and loss of a proton.

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(7) K. Alder and G. Stein, *Justus Liebigs Ann. Chem.*, **485** 223 (1931).

(8) M. S. Newman and J. R. Mangham, *J. Amer. Chem. Soc.*, **71**, 3342 (1949); M. S. Newman and T. S. Bye, *ibid.*, **74**, 905 (1952).

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Use of a Porous Electrode for *in Situ* Mass Spectrometric Determination of Volatile Electrode Reaction Products

Sir:

The interpretation of the origin of products isolated after a bulk electrolysis is frequently subject to the problems caused by chemical reactions occurring between electrode intermediates and other species present in solution. In such situations, it is ordinarily considered desirable to identify an electrode intermediate as soon as possible after its production at the electrode, *i.e.*, at the electrode surface. We have developed a combined electrochemical–mass spectrometric technique that allows *in situ* qualitative and quantitative analysis of volatile intermediates and products generated during an electrochemical reaction. Our method uses a porous electrode, one side of which contacts the solution being electrolyzed, while the other side contacts the mass spectrometer's high-vacuum system.

As will be reported in the near future,[1] we have used this electrode to identify the gaseous products NO and N_2O generated at different potentials during the reduction of NO_2^- in 0.1 *M* $HClO_4$. The surface concentrations of these species have been determined quantitatively (estimated error 5–10%). We have also used the porous electrode under open-circuit conditions as a porous catalytic surface, verifying the well-known, spontaneous decomposition of hydrazine into nitrogen and hydrogen peroxide into oxygen. To our knowledge, this is the first report of the use of a controlled-porosity surface to interface a mass spectrometer directly to the site of a reaction. We believe this technique will be extremely useful for studying heterogeneous reactions involving gaseous products and/or reactants.

The electrode design we have used in the above-mentioned studies is shown in Figure 1 and allows only gas to be transported into the mass spectrometer inlet system. The electrode was fabricated by rubbing finely divided platinum into the slightly wetted fine glass frit. An aqueous TFE–Teflon dispersion was gently sucked into the frit, dried and baked to fuse the Teflon, and the teflonization procedure repeated until no more liquid would pass through the frit when a 1-atm pressure differential existed across it. Further details are given elsewhere.[2]

The purpose of this communication is to report the results we have obtained with the model system, the electrochemical generation of oxygen from 0.1 *M* $HClO_4$. Oxygen was generated from the oxygen-free perchloric acid solution at the porous electrode using selected constant anodic currents.

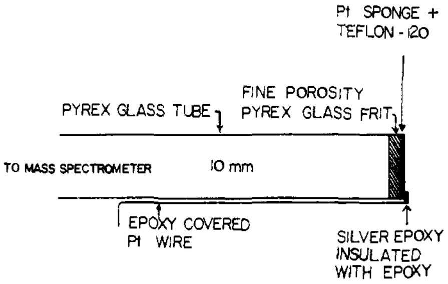

Figure 1. Schematic representation of porous electrode. Fritted end submerged in solution. Hitachi Perkin-Elmer RMU-6E instrument used.

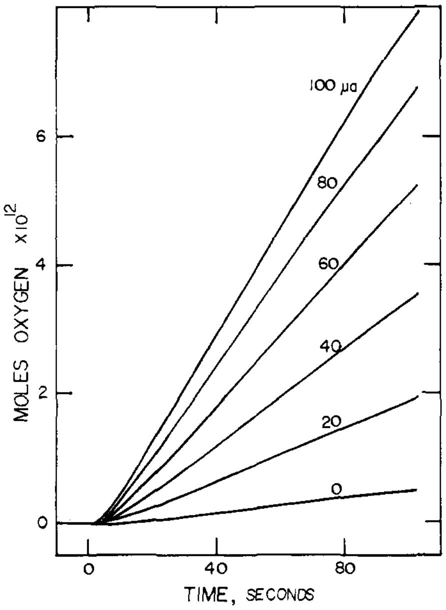

Figure 2. Mass-32 response *vs.* oxygen generation time.

The experiment shown in Figure 2 was performed by pumping out the vacuum system to 5 × 10^{-7} Torr, closing off the vacuum system from the pump, and recording the electron multiplier current at mass 32, using an *X*-time recorder, for the selected constant currents. The mass-32 response was calibrated in terms of moles of O_2 in the mass spectrometer by introducing a known quantity of oxygen.

The mass-32 response in Figure 2 rapidly becomes linear, and the slope of the linear portion is a measure of the rate of the electrochemical production of oxygen. The straight line portions do not pass through zero time, and there is evidence in Figure 2 for sorption effects within the vacuum system. These effects do not interfere in the interpretation of the linear portion of the response-time line.

Figure 3 is a plot of the limiting slope of the lines in Figure 2 *vs.* generation current. A straight line with a slope of 9.1 × 10^{-7} mol of O_2/C and a nonzero intercept corresponding to the leak rate of atmospheric oxygen into the mass spectrometer is obtained. The experimental slope indicates that 36% of the electrochemically generated oxygen enters the vacuum system of the mass spectrometer. Similar collection efficiencies have been obtained for hydrogen generated by constant-current reduction of 0.1 *M* $HClO_4$. These high collection efficiencies suggest that, in addition to gases, many or-

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(1) S. Bruckenstein and R. Rao Gadde, paper in preparation.
(2) S. Bruckenstein and R. Rao Gadde, submitted for publication, *Anal. Chem.*