Figure 1. Stern–Volmer plots of the fluorescence quenching of racemic (- - -) and (R)-$(-)$-1,1'-binaphthyl (—) by (S)-$(-)$-($\bullet$) and (R)-$(+)$-N,N-dimethyl-α-phenethylamines (O) in n-hexane at 22 °C. Concentration of 1,1'-binaphthyl is 1.1×10^{-5} mol/L.

Table I. Solvent Dependence of the Quenching Rate

Solvent	ϵ^a	$k_q(R\text{-}S)/$ $k_q(R\text{-}R)^b$
n-Hexane	1.89	1.90
Benzene	2.28	1.82
1,2-Dichloroethane	10.4	1.51
Acetonitrile	37.5	1.00

^{a} Dielectric constant at 20 °C. ^{b} The ratio of the fluorescence quenching rate of (R)-$(-)$-1,1'-binaphthyl ($[\alpha]_D$ $-190°$) by (S)-$(-)$- and (R)-$(+)$-N,N-dimethyl-α-phenethylamines.

ascribable mainly to an increase in the fluorescence quenching rate, since solvent scarcely alters the fluorescence lifetime of 1,1'-binaphthyl.[10]

The above steric and polarity effects upon the quenching rate can be interpreted by the following general scheme:

$$A^* + Q \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (A^* \cdots Q) \overset{k_2}{\longrightarrow} (A^- Q^+)^*$$
$$\downarrow k_3$$
$$(A^- \cdots Q^+)$$
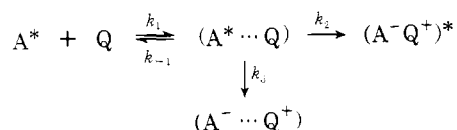
A^* is 1,1'-binaphthyl in the excited state, Q is N,N-dimethyl-α-phenethylamine, $A^* \cdots Q$ is an encounter complex, $(A^- Q^+)^*$ is an exciplex, and $A^- \cdots Q^+$ is an ion pair. The rate constant for fluorescence quenching, k_q, is therefore a function of k_1, k_{-1}, k_2, and k_3.

$$k_q = k_1 \left(\frac{k_2 + k_3}{k_{-1} + k_2 + k_3} \right)$$

We can expect that k_3 is small in less polar solvents but relatively large in polar solvents.[3] Therefore in less polar solvents k_2 determines the quenching rate. This process involves geometric and solvent relaxation of the encounter complex to an equilibrium exciplex. The steric effect on the quenching rate in n-hexane indicates that specific geometry is required between A^* and Q molecules in the equilibrium exciplex state and the relaxation rate, or the rate of the formation of the exciplex, k_2, depends on the structure of the two molecules.

On the other hand, in polar solvents quenching is governed by the electron-transfer reaction, the rate constant of which is k_3. The reaction occurs in the encounter complex in a loose structure. Therefore, the quenching rate is fast and no steric effect was discerned.[11] In solvents of medium polarity, the relaxation process is considered to compete with the electron-transfer reaction. The steric effect observed in 1,2-di-

chloroethane is due to the contribution of the exciplex quenching process, not the electron-transfer quenching process.

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Trisection of Reaction Pathways in Automerization of 6-Methylenebicyclo[3.2.1]oct-2-ene

Sir:

A previous study[1] showed that C_3 and C_9 deuterium labels redistributed themselves to C_1 and C_7, with rate constants k_3 and k_9, respectively, during pyrolysis of 6-methylenebicyclo[3.2.1]oct-2-ene-*3,9,9-d$_3$* (A, $\blacksquare$ = CD_2, Scheme 1). The observation that within experimental error $k_3 = k_9$ permitted only three formal mechanisms: (1) A $\rightleftharpoons$ B only (pure Cope rearrangement); (2) A $\rightleftharpoons$ equal amounts of C and D only; (3) any mixture of these two mechanisms, including as a special case mechanism (3a), a mixture of one-third 1 and two-thirds 2, which is indistinguishable from a randomized
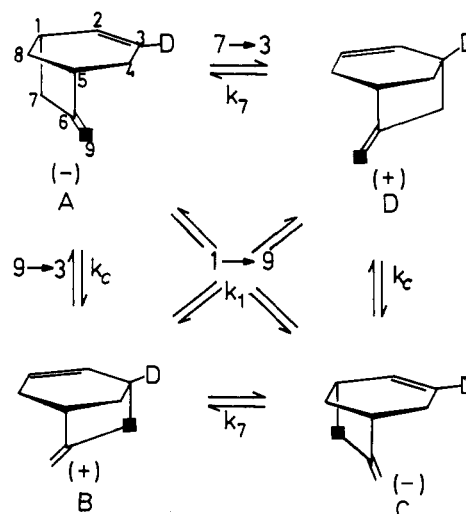
Scheme I

Table I. Percent Composition of the Products from Pyrolysis of (−)-6-Methylenebicyclo[3.2.1]oct-2-ene-*3-d-9-*^{13}C (A)

| Time, s | Temp, °C | | Products, %[a] | | | |
			A	B	C	D
7800	343.7	Obsd	51.1	29.1	8.8	11.0
7800	343.7	Calcd[b]	51.0	29.4	9.2	10.4
10980	344.3	Obsd	47.2	34.7	7.8	10.3

[a] Statistical evaluation of the experimental error gives ±1.5 units absolute for the *A* and *C* values, ±1.9 for *B* and *D*. [b] From the initial concentrations and rate constants given in the text.

biradical intermediate formed by C_1–C_7 cleavage and rapid rotation. (A → B, C, and D, in equal amounts.) The present communication eliminates mechanisms 1, 2, and 3a, leaving a nonrandom mixed mechanism (3) as the only acceptable description.

Optically active diene, $[\alpha]_D$ −113°, of 90.5% enantiomeric purity (ep), doubly labeled with deuterium at C_3 (0.9D/molecule) and ^{13}C at C_9 (0.4 ^{13}C/molecule; A, ■ = $^{13}CH_2$, Scheme I) is obtained from $^{13}CH_2PPh_3$ and optically active bicyclo[3.2.1]oct-2-en-6-one-*3-d*, $[\alpha]_D$ −150°.[2] Pyrolysis of this sample in the gas phase causes no chemical change other than automerization, which is manifested by scrambling of both the ^{13}C and deuterium labels as well as by partial racemization.

A determination[3] of the percentages of the components B, C, and D (Scheme I) in the pyrolyzed sample depends upon the fact that A and C have one enantiomeric configuration, whereas B and D comprise the antipode. If the pyrolyzed mixture is optically resolved (not necessarily to completion), and if the reasonable assumption is made that fractionation of isotope-position isomers within either enantiomer during resolution does not occur, that is that the fractions $A/(A + C)$ ($\equiv A'$) and $D/(D + B)$ ($\equiv D'$) (where italic capitals represent fractional concentrations) are constant during the processing of any given pyrolysis sample, it can be shown that λ_n, the fraction of the ^{13}C label remaining at C_9 at some particular level of ep, is given by

$$\lambda_n = A'\left(\frac{1 + P_n}{2}\right) + D'\left(1 - \frac{1 + P_n}{2}\right) \qquad (1)$$

The ep, P_n, is known from the specific rotation and is confirmed by NMR analysis of the derived bicyclo[3.2.1]oct-2-ene-6-*endo*-carboxylic acid methyl ester, using a chiral shift reagent.[4a] From the relationships $A_n + C_n = (1 + P_n)/2$ and $D_n + B_n = 1 − (1 + P_n)/2$, and from the values of A' and D' obtained by simultaneous solution of two sets of eq 1 (e.g., for the cases $n = 0$, $n = 1$, representing, respectively, the pyrolysis sample and a re-resolved sample), A' and D' and hence the fractional concentrations of the pyrolysis sample can be derived.

In practice, direct re-resolution of 6-methylenebicyclo[3.2.1]oct-2-ene, at least in our hands, is difficult. Therefore, the pyrolyzed sample is converted to bicyclo[3.2.1]oct-2-ene-6-*endo*-carboxylic acid by a regiospecific hydroboration–oxidation to the carbinol and dichromate oxidation to the acid, which is readily resolved with cinchonidine to high ep in both enantiomers. Measurements on the (+) and (−) acids provide an internal check on the final fractional composition values. Additional confirmation comes from quantitative ^{13}C NMR spectroscopy.[4b]

Table I shows the results of two separate pyrolyses. It is immediately clear that the major but not exclusive reaction is a Cope rearrangement (A ⇌ B). This rules out all of the limiting mechanisms, 1, 2, and 3a.[5]

The detailed interpretation of the minor component of the reaction depends upon the relative values of the two [1,3] sigmatropic rate constants, k_1 and k_7. If the previous apparent

equivalence of k_3 and k_9 (defined above) is taken at face value, it follows that $k_1 = k_7$, since, neglecting isotope effects, $k_1 = k_9 − k_c$, and $k_7 = k_3 − k_c$. On this basis, symmetry requires that the concentrations of C and D *formed from A* must be equal at all times. Table I shows an apparent slight excess of D, but this is a remainder from the 4.75% (+) enantiomer[6] originally present in the 90.5% ep reactant, (−)-A.

In fact one can quantitatively fit the observed composition data of Table I (343.7 °C) by insertion of the set of rate constants $k_1 = k_7 = 1.26 \times 10^{-5}$ s^{-1}, and $k_c = 8.26 \times 10^{-5}$ s^{-1}, into a computer program[7,8] that numerically integrates the differential equations of Scheme I by Runge–Kutta successive approximations and calculates the composition-time behavior of each component from the initial composition $A = 95.25\%$, $D = 4.75\%$. Table I shows these calculated values, which do not vary significantly over a plausible range of secondary hydrogen or ^{13}C isotope effects.

On the other hand, the limits of analytical accuracy and the small contributions of the [1,3] sigmatropic paths allow fits to the composition data of Table I and to the apparent equivalence of k_3 and k_9 with sets of rate constants in which k_1 and k_7 are unequal. For example, the values ($\times 10^5$ s) $k_c = 8.13$, $k_7 = 1.62$, $k_1 = 0.97$ reproduce the 7800-s data point of Table I[9] and predict the value $k_3/k_9 = 1.07$, which is hardly distinguishable from the near equivalence (1.03 ± 0.08) previously observed.[3]

Unequal values of k_1 and k_7 would signify two different [1,3] sigmatropic rearrangements competing with the Cope process. Equal values of k_1 and k_7, unless fortuitous, are difficult to rationalize without a *true metastable intermediate*. One possible mechanism involves a single common twofold symmetric intermediate for all three rearrangements, A → D and A → C ([1,3] sigmatropic) and A → B ([3,3] sigmatropic or Cope). However, of the imaginable such species, only those in which the original C_7 and C_9 of A flank the symmetry plane (**1** or its variant **1a**) have properties that lead automatically to $k_1 = k_7$. In particular, the "bisected" symmetric species **2** does not.
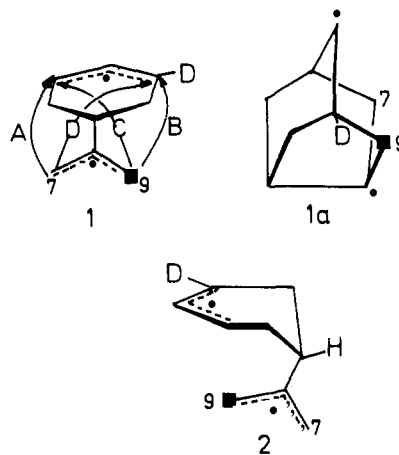
Alternatively, the mechanism may be described as a competition between a concerted Cope rearrangement with (rate constant k_R) and a biradical pathway. Among the permissible intermediates for the biradical branch of the mechanism is a fully randomized species, formed with rate constant k_4, which can cyclize at equal rates (rate constant k_5) to all four components. In this formulation, the data require that at 344 °C, $k_R/k_4 < 3.3$, and $\Delta G^{\ddagger}$ (biradical) − $\Delta G^{\ddagger}$ (Cope) < 1.5 kcal/mol.[10,11] This would imply that nearly all of the 23-kcal/mol benefit of concert in the four-center Cope rearrangement of acylic dienes[12] has been obliterated.

Society, for partial support of this work. We are also grateful to the National Science Foundation (GP-33909X) for partial support. We wish to acknowledge the support of the Southern New England High Field NMR Facility made possible by a grant from the Biotechnology Resources Program of the National Institutes of Health (RR-798).

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(5) A hypothetical mechanism for racemization would involve reversible [1,3] sigmatropy of C_8 from C_1 to C_3 through an achiral 5-methylenebicyclo[4.1.1]oct-2-ene intermediate. However, this process would leave the C_3 deuterium unscrambled and therefore would predict $k_3/k_\alpha = 0$. We find instead that $k_3 = k_\alpha$ within experimental error of ~5%, so that this mechanism cannot be important.
(6) This (+) contaminant is not identical with D, since it has a C_3 deuterium rather than a C_1 deuterium. However, the polarimetric and ^{13}C analyses do not distinguish it from D itself.
(7) Kindly provided by Professor Martin Saunders and slightly modified by Dr. B. K. Carpenter for use on the PDP-1145 system.
(8) The labor of guessing trial rate constants is substantially reduced in the present case by assuming perfect kinetic symmetry for Scheme I (that is, no secondary isotope effect) and solving directly for the rate constants using an explicit solution for the general symmetrical four-component system kindly provided to us by Dr. Barry K. Carpenter, Cornell University.
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Received August 29, 1977

Heterogeneous Photocatalytic Synthesis of Methane from Acetic Acid—New Kolbe Reaction Pathway

Sir:

Recent investigations have described the application of the principles of semiconductor electrodes (currently being studied in photoelectrochemical cells for the utilization of solar energy[1]) to the design of systems for heterogeneous photocatalysis.[2,3] In these systems the absorption of light on a semiconductor powder suspended in a liquid promotes electron-transfer reactions of substances in solution.[4] Synthetic applications of these techniques have not yet been demonstrated. We report here the heterogeneous photocatalytic decomposition of acetic acid on n-type TiO_2 to yield (almost exclusively) methane and carbon dioxide:

$$CH_3CO_2H \rightarrow CH_4 + CO_2 \qquad (1)$$
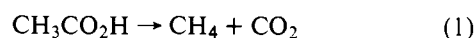
This unprecedented facile and efficient decarboxylation of an unactivated (saturated aliphatic) carboxylic acid at ambient temperature to give the corresponding alkane contributes to
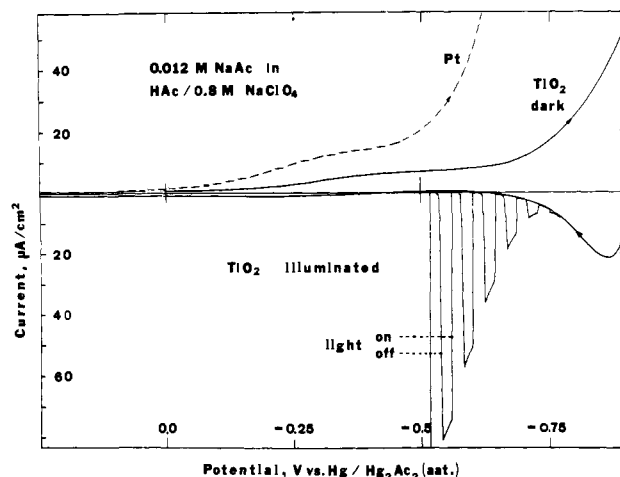

Figure 1. Current-potential curves for Pt and n-type TiO_2 (rutile, single crystal) in the dark and under chopped illumination with 450-W xenon lamp.

our understanding of photocatalysis at semiconductors[5] and provides a new technique in synthetic organic methodology. Moreover it represents a third, and so far unknown, reaction pathway in the sequence of a Kolbe reaction.[6]

When a stirred, deaerated suspension of 100 mg of platinized n-type TiO_2 powder[7] in a mixture of 4.5 mL of glacial acetic acid and 45 mL of distilled water at 55 °C contained in a Pyrex cell was illuminated with white light from a 2500-W xenon lamp (operated at 1600 W), a continuous stream of gas bubbles was observed to rise out of the depth of the solution near the illuminated area. These gaseous products, which accumulated at a rate of 8.1 mL/h were collected in a gas volumetric system and analyzed by mass spectroscopy and gas chromatography. The mass spectrum (m/e (rel intensity)) consisted of signals of carbon dioxide, 44 (100); ethane,[8] 30 (2), 29 (1.5), 28 (~7), 27 (2), 26 (1.5); methane,[8] 16 (91), 15 (79), 14 (5); and hydrogen, 2 (4), with small background signals due to air (oxygen, 32 (2); nitrogen, 28 (~8)); and water, 18 (13). The ratio of methane to ethane of the gaseous products was estimated by gas chromatography to be 11:1. Moreover the yield of CO_2 was determined quantitatively[9] in a subsequent run under identical conditions to account for 160 μmol/h (corresponding to 3.7 mL of gas at 1 atm) and therefore for about half the volume of the gaseous reaction products, in full accord with eq 1. The dominant reaction products of the decomposition of acetic acid were carbon dioxide and methane (ratio ~1:1); only small amounts of ethane and hydrogen were formed (total ~10 vol %, in roughly a ratio of 1:1). Qualitatively and quantitatively similar results were obtained with pure acetic acid as solvent and reactant or with acetic acid containing 0.8 M sodium acetate. Side reactions attributable to photocatalytic decomposition of water seem to be unimportant. Blank experiments without TiO_2 photocatalyst (under 1 atm of O_2) and similarly with untreated TiO_2 powder (TiO_2 reagent, MCB, anatase, under N_2 atmosphere) under similar conditions as described above resulted in only minute amounts of CO_2 (trapped as $BaCO_3$) corresponding to ~2 μmol/h (±1-μmol/h error limit).

The production of methane is surprising, in view of the usual products of a Kolbe reaction with acetic acid/acetate

$$2CH_3CO_2^- \rightarrow CH_3CH_3 + 2CO_2 \qquad (2)$$
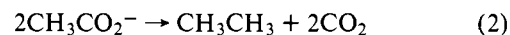
and our recent results[3] on the facile photoassisted decarboxylation of acetate of an illuminated n-type TiO_2 electrode in acetonitrile solution, giving almost exclusively carbon dioxide and ethane.

The photocatalytic activity of suspended TiO_2 powder can be correlated with the behavior of n-type TiO_2 electrodes in