ture of 1,2- and 2,3-dimethylcyclopentene. This equilibrium, consisting of seven times as much 1,2-dimethylcyclopentene as 2,3-dimethylcyclopentene, was observed with or without a potential applied to the working electrode, and was obtained with either cycloolefin as reactant. On raising the adsorption potential to 0.50 V, however, gas chromatographic analysis of the desorbed products revealed compounds with retention times corresponding to those of cyclohexane and methylcyclohexane along with the expected *cis*- and *trans*-1,2-dimethylcyclopentanes.

The correspondence of retention times of the pulse products with cyclohexane and methylcyclohexane knowns on two dissimilar column materials (Table I) indicates that the pulse products and the knowns are identical. A typical run produces approximately 2.8 × 10^{-3} mmol of total pulse products, of which between 18 and 24% are six-membered-ring compounds. Cyclohexane accounts for about 60% of the cyclohexyl products. Demethylation of adsorbed cyclic olefins has been observed to occur under similar conditions[5] and probably accounts for the observation of cyclohexane. The inability to detect cyclohexane or methylcyclohexane in the products from the 0.30-V adsorption potential or on passing the olefin over the electrode at 0.05 V indicates that the rearrangement takes place as a result of the more anodic adsorption potential and is not a consequence of the cathodic pulse, since the pulse is independent of adsorption potential. If the rearrangement were a result of the pulse, cyclohexyl products should be seen after all adsorption potentials. Likewise, the rearrangement cannot be simply a consequence of the temperature and electrolyte acidity, or again cyclohexyl products should be seen from all potentials or even without an imposed potential.

Table I. Comparison of Retention Times of Cyclohexane and Methylcyclohexane with Pulse Products of 1,2-Dimethylcyclopentene Adsorption

	Squalane, 91°	Squalane, 62°	Carbowax, 81°
Cyclohexane	4 min, 05 sec	6 min, 57 sec	4 min, 21 sec[a]
Pulse product	4 min, 05 sec	6 min, 57 sec	4 min, 21 sec[a]
Methylcyclohexane	6 min, 42 sec	12 min, 03 sec	b
Pulse product	6 min, 42 sec	12 min, 03 sec	b

[a] Occurs as a shoulder on the *trans*-dimethylcyclopentane peak.
[b] Occurs under the *cis*-dimethylcyclopentane peak.

There are numerous examples of cyclopentyl ring expansions in strong Lewis acids[10] and under catalytic dehydrogenation[11] and hydrogenolysis.[12] However, to our knowledge, this is the first example of a hydrocarbon ring expansion which occurs on a platinum black electrode. The previously observed electrochemical similarities of cyclohexyl systems[5,13] to aromatics suggest that attainment of an aromatic π-adsorbed intermediate may provide the driving force for this rearrangement.

Further work is in progress on the mechanism of this ring expansion.

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An Activation Energy in the Quenching of a Triplet State

Sir:

Electronically excited states can be deactivated not only by unimolecular paths but also by quenching collisions with other compounds. The quenching process can involve energy transfer or a chemical interaction (with or without formation of a stable product), and both processes have been invoked in the photochemistry of ketones.[1-7]

Usually studies of photochemical quenching have been restricted to systems at a fixed temperature, and generally the kinetics have been interpreted on the basis of rate constants at room temperature. However, we have recently reported[8] lifetimes for the triplet state of 2,3-pentanedione in the gas phase at temperatures between 25 and 90° which allow a study of the temperature dependence of the quenching ability of added compounds. In this preliminary communication, we report preexponential factors and activation energies for the quenching of the triplet state of 2,3-pentanedione by acrolein, crotonaldehyde, and methyl vinyl ketone.

2,3-Pentanedione in the gas phase (concentrations in the range 5–20 × 10^{-4} *M*) was excited by a xenon flash lamp (lifetime 3.8 × 10^{-6} sec), and the incident light was passed through a Corning CS 5-60 glass filter. The phosphorescence of 2,3-pentanedione passed through a Corning CS 3-71 filter and was detected by a RCA 1P28 photomultiplier. The output of the photomultiplier was displayed on an oscilloscope and photographed. The quenching abilities of acrolein, crotonaldehyde, and methyl vinyl ketone were determined at the different temperatures by measuring the changes in the pentanedione triplet lifetime when various concentrations of the quenching compounds were present.

The behavior of the triplet state of 2,3-pentanedione in the photolysis of pure pentanedione is described[8] by

$$\mathrm{P} + h\nu \longrightarrow {}^1\mathrm{P_v} \longrightarrow {}^3\mathrm{P_0}$$

$${}^3\mathrm{P_0} \longrightarrow \mathrm{P} + h\nu_\mathrm{p} \qquad k_2 = 47\ \mathrm{sec}^{-1}$$

$${}^3\mathrm{P_0} \longrightarrow {}^3\mathrm{P_n} \qquad k_3 = 1.3 \times 10^3\ \mathrm{sec}^{-1}$$

$${}^3\mathrm{P_0} \longrightarrow \text{product?} \qquad k_4 = 10^{11}e^{-11.0/RT}\ M^{-1}\ \mathrm{sec}^{-1}$$

$${}^3\mathrm{P_0} + \mathrm{P} \longrightarrow \text{removal} \qquad k_5 = 9 \times 10^{10}e^{-7.5/RT}\ M^{-1}\ \mathrm{sec}^{-1}$$

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If the step

$$^3P_0 + Q \longrightarrow \text{removal} \qquad k_6$$

is added to the mechanism to explain the quenching by added molecules Q, then a steady-state treatment predicts that $\tau_0/\tau = 1 + k_6\tau_0[Q]$, where τ_0 and τ are the lifetimes in the absence and presence of the quencher. This relation is in agreement with the experimental results, and so the proposed mechanism is sufficient to explain the experimental behavior. The rate constants (M^{-1} sec^{-1}) for the quenching of triplet pentanedione by acrolein, crotonaldehyde, and methyl vinyl ketone at various temperatures (°C) are shown in Table I.

Table I. Rate Constants for Quenching of Triplet 2,3-Pentanedione

Acrolein	Crotonaldehyde	Methyl vinyl ketone
3.8×10^4 at 42.2°	4.6×10^5 at 60.2°	6.8×10^4 at 62.5°
1.1×10^5 at 50.8°	1.0×10^6 at 71.5°	1.1×10^5 at 70.8°
1.5×10^5 at 68.3°	1.6×10^6 at 84.4°	1.5×10^5 at 80.5°
5.5×10^5 at 88.3°		

For each of the compounds the quenching efficiency increases with temperature and is of the Arrhenius form. The data for crotonaldehyde yield $k_6 = 10^{13.8\pm1.5}e^{-(12.4\pm2.4)/RT}$ and for methyl vinyl ketone $k_6 = 10^{11.7\pm1.0}e^{-(10.4\pm1.5)/RT}$. A weighted least-squares treatment of the acrolein data gives $k_6 = 10^{14.0\pm1.5}e^{-(13.7\pm2.1)/RT}$. The errors in the preexponential factors and activation energies are large because only a short temperature range is accessible experimentally. At low temperature the quenching molecules have low vapor pressures and there is only a small effect on the triplet lifetime. At high temperature the triplet diketone has a very short lifetime and again only a small effect of quencher can be observed. Although the quenching rate constant is not large, it is unlikely that impurity in the quencher could explain the observations; that would entail an unrealistically high value for the preexponential factor.

The quenching behavior is followed by its effect on the phosphorescence lifetime so that only the interaction of the triplet state of pentanedione and the quencher need be considered. The quenching process could involve either a chemical interaction or an endothermic energy transfer to form the triplet state of the quencher.

The energy of the triplet state of 2,3-pentanedione is about 55 kcal,[8] but the energies of the unsaturated carbonyl compounds are less certain. It has been suggested[9,10] that the energy of the π^*,n triplet state of acrolein is about 69 kcal, and there is a report that the triplet energy of crotonaldehyde is similar.[11] The triplet energy of methyl vinyl ketone is not available. It has been suggested,[12] however, that the energy of the triplet state of acetone is lower than that of acetaldehyde. The triplet energy of methyl vinyl ketone could be lower than that of acrolein; this would be necessary if the quenching process involves energy transfer. If triplet states of the quenching are formed in the system then reverse energy transfer from the triplet state of the quencher to the ground state of the diketone could complicate the kinetics. Separate experiments, however, showed that reverse transfer is improbable.

An alternative explanation of the data is that the chemical interaction of the triplet state of the diketone and the ground state of the quencher involves an activation energy. There are no experiments reported of the photolysis of simple α-diketones in the presence of enones, but products have been isolated from the photolysis in solution of a complex α-diketone in the presence of dienes.[13] The preexponential factors for the quenching process are larger than might be expected, but a large value was also noted[8] in the self-quenching process Thus a chemical interaction between the triplet state of the diketone and the ground state of the enone is also possible.

In conclusion, the above data show that the processes removing the triplet state of 2,3-pentanedione change with temperature and that certain quenching processes can have significant activation energies. Further research is planned to decide between quenching by energy transfer and chemical reaction.

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The Facile Redistribution of Trialkylboranes with Aryl Borates. A General Synthesis of Dialkylborinic Acids and Esters

Sir:

Trialkylboranes undergo a facile redistribution with aryl borates, under the catalytic influence of borane in THF, forming the corresponding dialkylborinic esters in nearly quantitative yield (eq 1). Since the equilibrium goes essentially to completion, the crude reaction product can often be utilized directly. Alternatively, the crude reaction products are readily converted to relatively stable, easily handled 8-hydroxyquinolinates. These are easily purified and converted to the corresponding free acids or methyl esters. Consequently, it now becomes possible to synthesize a wide range of dialkylborinic acids and esters not previously available because of their instability toward the distillation conditions required to isolate them from the redistribution reaction mixtures.

$$2R_3B + B(OAr)_3 \xrightarrow[100^\circ]{\text{cat. } H_3B\text{-THF}} 3R_2BOAr \qquad (1)$$

Dialkylborinic acids and esters are now finding important applications in the new chemistry of organoboranes. Thus, the reduction of methyl dialkylborinates with lithium aluminum hydride in the presence of olefins provides a convenient synthesis of mixed organo-