

intermediate generates the boat biradical (e.g., **13b** and **13d**) which cyclizes to the tricyclo[2.2.0.0^{2,6}]hexane ring system at a faster rate than bond fragmentation. This contention is substantiated by the fact that cyclopropenes **9** and **11** are not isomerized under conditions where substantial quantities of tricyclohexanes **10** and **12** are formed.

It is interesting to note that the thermolysis of diastereomer **5b** results in a significantly larger quantity of the tricyclohexane ring system than is obtained from the thermolysis of **5a**. This can be attributed to the fact that the initially formed biradical intermediate (**13a**, axial methyl) undergoes ring inversion to **13b** (equatorial methyl) at a rate which is competitive with bond fragmentation. Thus, **5b** reacts about equally from each of the conformers **13a** and **13b**. However, **5a** gives mainly cyclopropene **11**, a result indicating preferential reaction from conformer **13c** (equatorial methyl). It should also be pointed out that in the case of cyclopropene **5**, there is a distinct preference for that product arising from bonding between the terminal olefinic carbon and the cyclopropene carbon bearing the methyl group. This is undoubtedly related to the fact that π - π bridging will give the most stable biradical and thus lead to the preferential formation of cyclopropenes **9** and **11** rather than to cyclopropene **6**. Finally, the reluctance of cyclopropenes **9** and **11** to undergo the reverse Cope reaction can be attributed to thermodynamic differences of the allyl substituted cyclopropenes.

In conclusion, the above data are most consistent with the interpretation that the Cope rearrangements of these allyl substituted cyclopropenes are not pericyclic reactions but involve derivatives of 1,4-cyclohexylene as intermediates.

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- Compound **4**: NMR (CDCl₃, 100 MHz) τ 9.08 (d, 3 H, $J = 7.0$ Hz), 8.6 (s, 3 H), 7.40 (p, 1 H, $J = 7.0$ Hz), 4.92-5.16 (m, 2 H), 4.08 (ddd, 1 H, $J = 16.0, 9.0$, and 7.0 Hz), and 2.28-2.92 (m, 10 H). Compound **5**: NMR (CDCl₃, 100 MHz) τ 9.02 and 9.08 (d, 3 H total, $J = 7.0$ Hz), 7.72 (s, 3 H), 6.66 (p, 1 H, $J = 7.0$ Hz), 4.96-5.20 (m, 2 H), 4.02-4.42 (m, 1 H), and 2.52-3.08 (m, 10 H).
- Cyclopropene **7** was prepared from the reaction of diphenylmethylcyclopropenyl cation with lithio-*tert*-butyl acetate⁷ followed by chromatographic separation of the isomeric acetates. The 1,2-diphenyl-substituted isomer was used to prepare cyclopropenes **9** and **11**.
- W. Rathke and D. F. Sullivan, *J. Am. Chem. Soc.*, **95**, 3050 (1973).
- We have tentatively assigned the stereochemistry of **10** as *exo*-3-methyl-1,2-diphenyl-6-methyltricyclo[2.2.0.0^{2,6}]hexane on the basis of its spectral properties. Complete spectroscopic details will be provided in a later publication.
- It should be noted that the thermolysis of **11** produced a tricyclohexane whose structure has been assigned as *endo*-3-methyl-1,2-diphenyl-6-methyltricyclo[2.2.0.0^{2,6}]hexane (**12**). Also noteworthy is the fact that the tricyclohexanes obtained from **9** and **11** differ from the tricyclohexane (**8**) obtained from the thermolysis of either **4** or **6**.
- Doering has recently shown that 2,5-diphenyl-1,5-heptadiene undergoes internal 2 + 2 thermal cycloaddition thereby providing reasonable analogy for the formation of the tricyclo[2.2.0.0^{2,6}]hexane ring system: see ref 3b, footnote 43.
- The formation of tricyclohexane **10** from cyclopropene **9** occurs at a much slower rate than the formation of **10** from **5b**, thereby eliminating the sequential process **5b** \rightarrow **9** \rightarrow **10**. This observation indicates that the tricyclic products are not formed by a separate path but rather are produced in competition with the Cope products.

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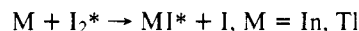
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Laser-Induced Chemiluminescence: Variation of Reaction Rates with Reagent Approach Geometry

Sir:

A basic premise in chemistry is that reactivity in bimolecular processes depends upon reagent orientation. Indirect confirmation of the stereochemical control of a reaction mechanism through the subsequent analysis of the products is common, but direct confirmation of the role of reagent orientation during a reactive encounter is exceedingly rare.¹ We describe a new technique for preparing aligned or oriented reagents using optical pumping. This technique is applied to the atom + diatom exchange reaction



carried out in a single-collision environment. For both In and Tl we find a marked preference for collinear vs. perpendicular approach to the I-I bond in those collisions yielding excited-state products.

The metal beam enters a vacuum chamber filled with I₂ at a pressure of $\sim 5 \times 10^{-5}$ Torr. The 514.5-nm output of an argon ion laser intersects the metal beam at right angles and pumps I₂ in the intersection volume to the $v' = 43, J' = 12, 16$ levels of the B³ Π (0⁺u) state.² The resulting chemiluminescence is viewed by a 1-m spectrometer through a port in the vacuum chamber. The viewing direction is perpendicular to the plane formed by the metal beam and the laser beam. A polarization scrambler (wedge) is placed in front of the entrance slit so that the spectrometer response is independent of the polarization of the emission.

The laser beam is linearly polarized; the polarization vector

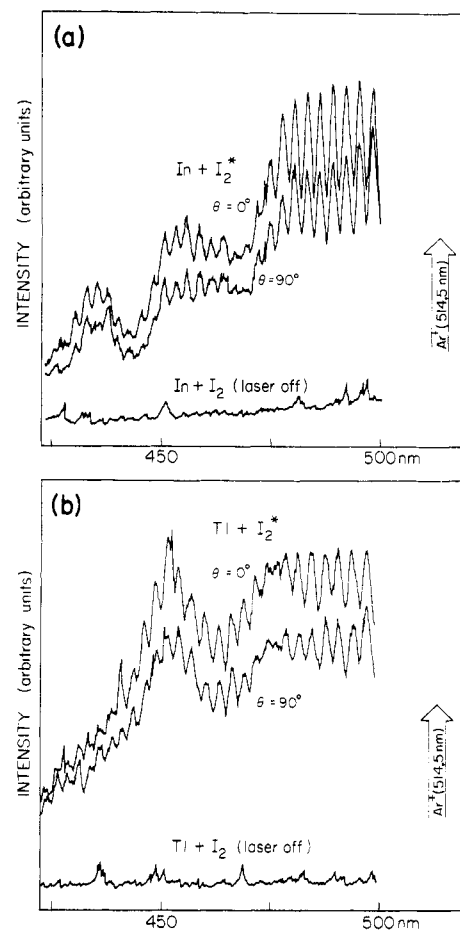


Figure 1. Laser-induced chemiluminescence spectra: (a) In + I₂*; and (b) Tl + I₂*. The angle θ is measured from the metal beam direction to the polarization vector of the plane polarized light.

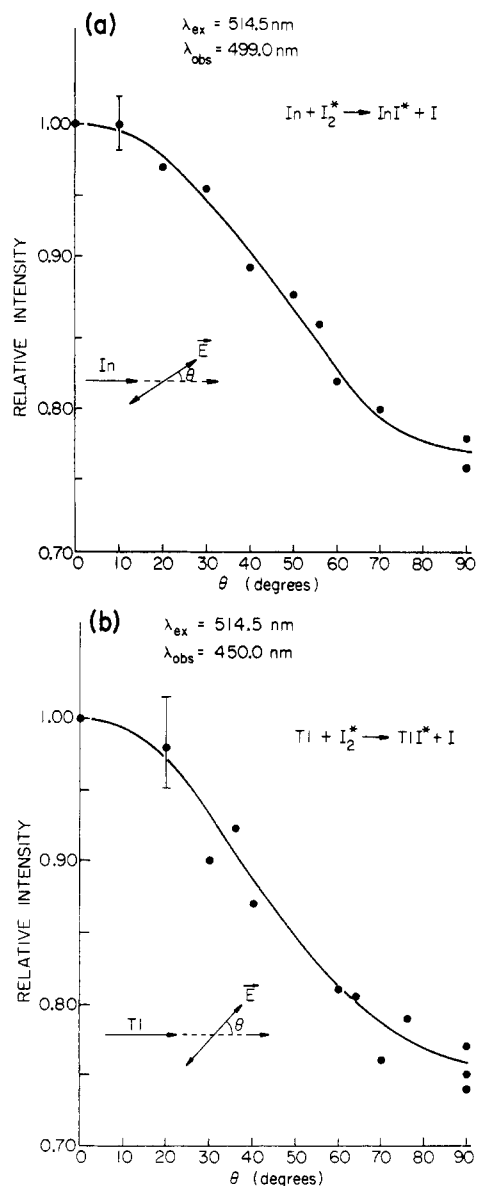


Figure 2. Variation of the chemiluminescent signal with the angle θ : (a) $\text{In} + \text{I}_2^*$; and (b) $\text{Tl} + \text{I}_2^*$. The solid curve is to aid visualization.

$\vec{\epsilon}$ is rotated by a half-wave Fresnel rhomb from $\theta = 0^\circ$ (along the metal beam) to $\theta = 90^\circ$ (perpendicular to the metal beam). The I_2 B-X transition has its electric dipole transition moment $\vec{\mu}$ along the internuclear axis of the molecule. The probability for absorbing a laser photon is proportional to $|\vec{\mu} \cdot \vec{\epsilon}|^2$. Thus, the linearly polarized laser beam selects I_2^* molecules whose internuclear axes have an initial distribution of $\cos^2 \Theta$, where Θ is the angle between $\vec{\mu}$ and $\vec{\epsilon}$. The I_2^* molecules rotate prior to collision. However, they do retain a "memory" of their initial photoselected distribution, although the final spatial distribution of the internuclear axes is altered from $\cos^2 \Theta$ to $1 + \cos^2 \Theta$.³ We vary the angle θ between the direction of the metal beam and $\vec{\epsilon}$, thus presenting to the metal atoms different I_2^* targets: for $\theta = 0^\circ$, the metal atom "sees" on the average an I_2^* molecule that is "end-on" and for $\theta = 90^\circ$, "broadside". For the maximum extent of alignment, the direction of the linearly polarized light beam must be perpendicular to the plane formed by $\vec{\epsilon}$ and by \vec{v}_{rel} , the relative initial velocity vector. We assume in this experiment that we have essentially a beam-gas arrangement for which case \vec{v}_{rel} points, on the average, along the direction of the metal beam.

Figure 1 shows chemiluminescent spectra of both reactions for the two extreme orientations of I_2^* , as well as background

spectra with the laser off. The intense I_2^* fluorescence hinders the observation of product emission to the long-wavelength side (red) of the laser pump line; however, to the short-wavelength side (blue), the characteristic MI^* B-X and A-X band systems are recognized.^{4,5} The MI bands are not assigned because the resolution is insufficient to isolate individual (v', v'') bands and spectroscopic information about the high v' levels is lacking. Figure 1 demonstrates the observation of laser-induced chemiluminescence; moreover, the spectra for $\theta = 0^\circ$ is in both cases more intense than for $\theta = 90^\circ$, indicating that the reaction rate for the production of MI^* is enhanced for collinear collisions of the reagents.

Figure 2 shows the variation of reaction rate with the "orientation angle" θ for In and Tl. In both cases, there is approximately a 25% reduction between $\theta = 0^\circ$ and $\theta = 90^\circ$.⁶ The falloff can be fit to various geometrical models and is a subject of continuing investigation.

By inserting a polarization analyzer (sheet of polaroid) before the polarization scrambler (wedge), we observe that the MI^* emission is linearly polarized⁷ at all orientation angles θ for both $\text{In} + \text{I}_2^*$ and $\text{Tl} + \text{I}_2^*$. Such measurements show that the angular momentum vector of the products has an anisotropic distribution and will permit more detailed information to be extracted about the nature of the reaction dynamics.^{8,9}

The I_2^* molecule is particularly well suited for laser-induced chemiluminescence studies. Its long radiative lifetime ($\sim 3 \mu\text{s}$)¹⁰ enhances the probability that a reactive collision will occur before decay.¹¹ Even so, only a small fraction ($\leq 1\%$) of the I_2 molecules in the thermal beam (spray) are pumped to the excited state and the observation of the MI^* product attests to the sensitivity of chemiluminescent detection.

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- (3) The initial $\cos^2 \Theta$ distribution of internuclear axes corresponds to a $\sin^2 \Theta$ distribution of angular momentum vectors. Although the molecule rotates, the direction of angular momentum is preserved in space provided there are no collisions. For a derivation of the form of the anisotropy, see R. N. Zare, Ph.D. Thesis, Harvard University, 1964. This derivation will also appear in a future publication. Note that in some cases the use of circularly polarized light may also have some advantage: it may be used to orient a symmetric top molecule so that its angular momentum vector points preferentially along or opposite to the direction of the top's translational motion.
- (4) For InI, see M. Wehrli and E. Miescher, *Helv. Phys. Acta*, **7**, 298 (1934); for TlI, see K. Butkow, *Z. Physik*, **58**, 232 (1929).
- (5) The spectra in Figure 1 do not result from fluorescence of MI (high v') pumped by the argon ion laser. Such fluorescence would be expected to be sharper in appearance.
- (6) We note here that we have tacitly assumed that the variation of chemiluminescent intensity is independent of the angular distribution of products. In the present experimental arrangement we collect $\sim 7\%$ of the total chemiluminescence.
- (7) Typically, the degree of linear polarization is about $15 \pm 5\%$.
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- (11) This suggests the possibility of related experiments in which oriented I_2^* molecules are replaced by long-lived vibrationally excited reagent molecules aligned or oriented by infrared laser pumping.

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