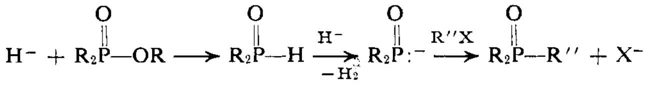
alkoxide with hydride, a second hydride, acting as a base, presumably pulls off the new, relatively acidic proton on phosphorus, forming the sodium dialkylphosphine oxide.[6,7] This would then react with



$$H^- + R_2\overset{\overset{O}{\|}}{P}{-}OR \longrightarrow R_2\overset{\overset{O}{\|}}{P}{-}H \xrightarrow[-H_2]{H^-} R_2\overset{\overset{O}{\|}}{P}{:}^- \xrightarrow{R''X} R_2\overset{\overset{O}{\|}}{P}{-}R'' + X^-$$

the alkyl halide in a nucleophilic substitution to give phosphine oxide and sodium halide.[5] The last two entries in Table I support this mechanism.

Some attempts have been made at improving the yields of certain of the reactions reported; further work in this area is now in progress. We are also attempting to extend the reaction to other phosphorus systems[8] and are investigating the reaction mechanism in greater detail.

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(6) It has been shown that the reaction of R(R′O)P(O)H with R′′X and sodium hydride in dimethylformamide gives R(R′O)P(O)R′′ [W. B. Farnham, R. K. Murray, Jr., and K. Mislow, *J. Amer. Chem. Soc.*, **92**, 5809 (1970)].

(7) It appears that the situation may be somewhat more complex in the reactions of phosphonates and phosphates.

(8) For example, it may be possible, by starting with the appropriate dialkyl dibromoalkylphosphonates, to prepare the elusive bicyclics, 1-phosphabicyclo[2.2.1]heptane and 1-phosphabicyclo[2.2.2]octane.

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The Thermal Gas-Phase Partitioning of 1-Methyl- and 2-Methylbicyclo[2.1.0]pent-2-ene

Sir:

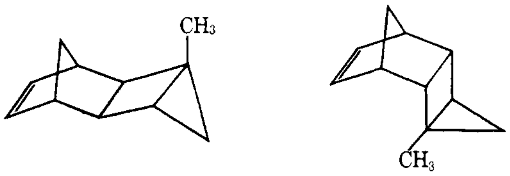
The facile thermal isomerization of bicyclo[2.1.0]-pent-2-ene to cyclopentadiene[1-5] was originally thought to occur through a disrotatory and orbital symmetry disallowed diradical mediated process.

Consideration of alternative mechanisms led us to deuterium labeling experiments, demonstrating that the C-5 methylene group remained intact during the isomerization,[6] and to the discovery that 2-methylbicyclo[2.1.0]pent-2-ene rearranges directly to 1-methylcyclopentadiene.[7] This result, wholly inexplicable by diradical mechanisms, was interpreted through a $[_\sigma 2_s + _\sigma 2_a]$ symmetry-allowed mechanistic formulation.

The latter finding has been challenged by McLean and Findlay,[8] and the rearrangement course has thus been left open to question.[9]

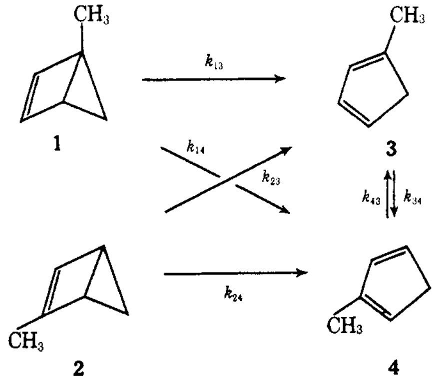
We now report the first isolation of 1-methylbicyclo[2.1.0]pent-2-ene and gas-phase kinetic work on both 1- and 2-methylbicyclopentene. The results provide grounds for delimiting the mechanistic controversy.

Photolysis of the isomeric methylcyclopentadienes and isolation of the bicyclic products[10] gave a mixture of 2-methylbicyclo[2.1.0]pent-2-ene and the previously undetected 1-methyl isomer, having nmr absorptions in $CDCl_3$ at δ 6.2 (2 H, J_{AB} = 2 Hz), 2.2 (1 H, m), 1.8 (1 H, m), 1.5–1.4 (1 H, m), and 1.47 (3 H, s). The 1-methyl isomer was thermally convertible to methylcyclopentadienes, and reacted with cyclopentadiene to give both exo,anti and endo,anti isomers of 3-methyltetracyclo[5.2.1.0^{2,6}.0^{3,5}]dec-8-ene.[11]



The 1-methyl isomer is much more prone to isomerization during glpc collection than 2-methylbicyclopentene but, with adequate care, it may be obtained uncontaminated by isomeric materials.

Kinetic data for the gas-phase thermal equilibration of bicyclics **1** and **2**, and of dienes **3** and **4**, were obtained at 50°, using glpc on a 0.3 × 600 cm aluminum column packed with β,β'-oxydipropionitrile on non-acid-washed Chromosorb P as the analytical method. Three or more runs with each of the four starting materials and with various reaction flasks gave results sufficiently reproducible to discount vagrant catalytic effects. Three runs with bicyclo[2.1.0]pent-2-ene gave $k = (1.39 \pm 0.02) \times 10^{-4}\ \text{sec}^{-1}$, which may be compared with $1.1 \times 10^{-4}\ \text{sec}^{-1}$ interpolated from data obtained by others[3,4] using an ultraviolet method. All kinetic data could be fit to a scheme involving partitioning of both methyl-labeled bicyclics to both methylcyclopentadienes; the numerical values for the rate constants are given in Table I.



The interconversion of 1-methyl- and 2-methylcyclopentadiene is so slow relative to the isomerizations of **1** and **2** that accurate measurements of the kinetically controlled product distribution may be readily obtained. The partitioning ratios $k_{13}/k_{14} = 1.6$ and $k_{24}/k_{23} = 1.3$ are remarkably similar. The total spread in rate constants for isomerizations from the bicyclics is only a factor of 5.4; unlabeled bicyclopentene falls within

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(1) J. I. Brauman, L. E. Ellis, and E. E. van Tamelen, *J. Amer. Chem. Soc.*, **88**, 846 (1966).

(2) E. E. van Tamelen, L. E. Ellis, and J. I. Brauman, *ibid.*, **89**, 5073 (1967).

(3) J. I. Brauman and D. M. Golden, *ibid.*, **90**, 1920 (1968).

(4) D. M. Golden and J. I. Brauman, *Trans. Faraday Soc.*, **65**, 464 (1969).

(5) E. E. van Tamelen, J. I. Brauman, and L. E. Ellis, *J. Amer. Chem. Soc.*, **93**, 6145 (1971).

(6) J. E. Baldwin, R. K. Pinschmidt, Jr., and A. H. Andrist, *ibid.*, **92**, 5249 (1970).

(7) J. E. Baldwin and A. H. Andrist, *Chem. Commun.*, 1561 (1970).

(8) Private communication.

(9) Reference 5, footnote 15.

(10) A. H. Andrist, J. E. Baldwin, and R. K. Pinschmidt, Jr., *Org. Syn.*, in press.

(11) *Cf.* J. E. Baldwin and R. K. Pinschmidt, Jr., *J. Amer. Chem. Soc.*, **92**, 5247 (1970).

Table I. First-Order Rate Constants at 50° for the Gas-Phase Isomerizations of Methylbicyclopentenes and Methylcyclopentadienes

Starting isomer	Product	k, sec^{-1}
1	**3**	1.94×10^{-4}
1	**4**	1.2×10^{-4}
2	**3**	3.6×10^{-5}
2	**4**	4.64×10^{-5}
3	**4**	8.2×10^{-6}
4	**3**	5.8×10^{-6}

the spread. No thermal interconversion of **1** and **2** was detected; kinetic schemes postulating $k_{14} = k_{23} = 0$, but k_{12}, $k_{21} \neq 0$, cannot be made to accommodate the results.

The [$_{\sigma}2_s + {}_{\sigma}2_a$] intramolecular cycloaddition formulation advanced previously[7] satisfies the gas-phase results, both with respect to partitioning to two methylcyclopentadienes (since each of the two may react using bonds 12,54 or 43,51) and the relatively tight spread of rate constants; mechanisms based on diradical intermediates can do neither.

While the quantitative discrepancies between the solution-phase isomerization results obtained in our earlier work[7] and by McLean and Findlay[8] must still be resolved, the direct isomerization of **2** to **3** is fully authenticated and the sa symmetry-allowed isomerization rationale remains the only suggested mechanism consistent with uncontested experimental findings.

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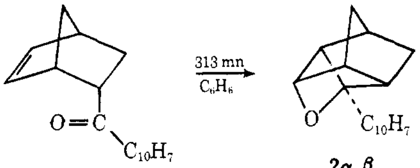
Intramolecular Photocycloadditions of Naphthyl Ketones[1]

Sir:

Despite the intense effort being devoted to the study of cycloaddition reactions between carbonyl derivatives and olefins, very little information is available on the photoreactivity of naphthyl systems. In an important study, Yang and coworkers[2] have shown that oxetanes may be formed from certain naphthyl ketones and 2-methyl-2-butene, but that the quantum yields are relatively low (<0.005). These workers concluded that factors other than the nature of the low-lying triplet states may contribute to the photochemical behavior of these compounds. Wagner and Hammond[3] have made the intriguing suggestion that the reactive state in these cycloadditions may be the singlet state, the π,π^* triplets being unreactive. In view of the widespread interest in the mechanism of photocycloaddition,[4] we initiated kinetic studies on the photocyclizations of naphthoylnorbornenes **1α** and **1β**.[5]



1α, β

2α, β

Quantum yields were routinely determined by monitoring the rate of disappearance of the carbonyl chromophore by ultraviolet absorption spectroscopy. It was shown independently for **1α** that this rate corresponded with the rate of appearance of oxetane **2α**, and that no other products were formed. In addition, high yields of oxetanes were produced in both cases. Quantum yield and quenching data are shown in Table I from which it can be seen that both reactions proceed *via* two excited states one of which is quenchable and the other not. These conclusions were reached by studying the dependency of Φ_{-K} on the concentration of 1,3-cyclohexadiene concentration. Plots of Φ_0^{-K}/Φ^{-K} *vs.* [Q] gave lines which rose steeply between quencher concentrations of 2.10^{-5}–10^{-4} *M* and then became level from *ca.* 10^{-3} to 1 *M* quencher concentrations. The $k_q\tau$ values given in Table I were calculated from the lower ranges of quencher concentrations and it is believed that loss of quencher due to dimerization is minimal since the concentrations were low and Φ_{ISC} is small. It is likely that those portions of these reactions which are quenchable involve the π,π^* states owing to the estimated lifetimes: **1α**, 2.5×10^{-6}; **1β**, 4.8×10^{-6} sec.[6] Furthermore, it was possible to effect cyclization of **1α** by the use of Michler's ketone (E_T = 61 kcal/mol) as a photosensitizer. A limiting value of 0.39 was found for ketone disappearance by extrapolation of the quantum yield data to zero concentration of sensitizer.[7] This value

Table I. Quantum Yield and Quenching Data

Ketone	E_T[a]	ϕ(total)	ϕ_T[b]	$k_q\tau$,[c] M^{-1}	ϕ_{ISC}[f]
1α	57.5[d]	0.135	0.065	5000	0.16
1β	59[e]	0.175	0.065	4300	0.13

[a] Triplet excitation energy in kcal/mol. [b] Quantum yield of ketone disappearance which can be quenched by 1 *M* 1,3-cylohexadiene. [c] Initial slopes. [d] Measured by A. A. Lamola; τ_p = 0.52 sec. [e] Assigned by analogy to 2-acetonaphthone; see J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 298. [f] Determined by the method of A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

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(1) Presented at the XXIIIrd IUPAC Meeting, Boston, Mass., July 1971, Abstracts, p 96.

(2) N. C. Yang, M. Nussim, M. J. Jorgenson, and S. Murov, *Tetrahedron Lett.*, 3657 (1964).

(3) P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, **5**, 99 (1968).

(4) (a) N. J. Turro and P. A. Wriede, *J. Amer. Chem. Soc.*, **92**, 320 (1970); (b) N. C. Yang and W. Eisenhardt, *ibid.*, **93**, 1277 (1971); (c) K. Shima, Y. Sakai, and H. Sakurai, *Bull. Chem. Soc. Jap.*, **44**, 215 (1971); (d) R. A. Caldwell and S. P. James, *J. Amer. Chem. Soc.*, **91**, 5184 (1969); (e) H. Morrison and S. R. Kurowsky, Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, ORGN 142.

(5) See R. R. Sauers, W. Schinski, and M. M. Mason, *Tetrahedron Lett.*, 79 (1969), for a discussion of the chemical aspects of these studies. Pure endo isomers were used in the present studies and the oxetanes formed were isolated in good yields. The long-wavelength ultraviolet absorption maxima are given for benzene solutions: **1α**, 296 nm (ϵ 6380); **1β**, 284 (ϵ 8700), 327 (ϵ 1550), and 342 nm (ϵ 1500).

(6) These values were obtained by assuming a quenching rate of 5×10^9 l./(mol sec). For comparison, the lifetime $(k_d)^{-1}$ of 2-acetonaphthone has been shown to be 3×10^{-6} sec by G. S. Hammond and P. A. Leermakers [*J. Amer. Chem. Soc.*, **84**, 207 (1962)].