Photoinduced Methyl Migrations of Methylindenes in the Gas Phase[1]

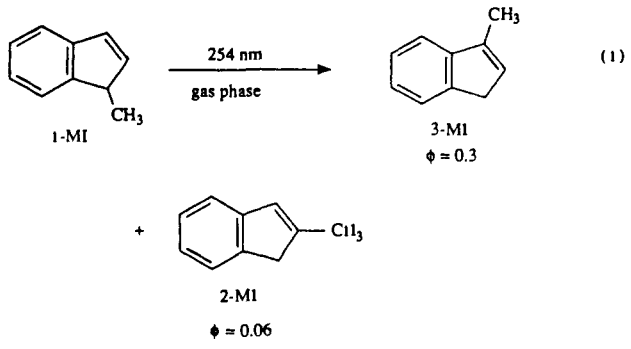
Robert J. Duguid and Harry Morrison*

Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907. *Received November 19, 1990*

Abstract: The mechanisms for photoinitiated methyl migration of methylindenes in solution and the gas phase have been studied with the ^{13}C-labeled substrates [1-^{13}C]-2-methylindene ([1-^{13}C]-2-MI) and [3-^{13}C]-3-methylindene ([3-^{13}C]-3-MI). Photolysis of [1-^{13}C]-2-MI in hexane produces 1- and 3-methylindene products labeled at C2, consistent with the previously proposed skeletal rearrangement mechanism. Photolysis of the labeled substrates in the gas phase gives products with labeling patterns consistent with the operation of two mechanisms, skeletal rearrangement and alkyl-shift chemistry (the latter accompanied by hydrogen shifts). The presence of a collisional quenching gas (butane) in the gas-phase photolysis reduces the role of the alkyl-shift mechanism and increases the contribution of skeletal rearrangement. It is proposed that, for these alkylindenes, the alkyl and hydrogen shifts derive from an upper electronically or vibrationally excited state while skeletal rearrangement is characteristic of a vibrationally relaxed S_1 state.

The relatively facile, formal 1,2-migration of alkyl groups in alkylindenes upon photolysis in dilute solution has been extensively studied and the mechanism shown to involve a C1/C2 transposition of the indenyl skeleton (henceforth referred to as the "skeletal rearrangement") rather than a true alkyl shift.[2] This is illustrated in Scheme I for the prototypical case of 2-methylindene (2-MI).

Recently, we reported that alkylindenes form analogous products upon photolysis in the gas phase, potentially, but not necessarily, derived from skeletal rearrangement.[3] These reactions are more complex than in the solution phase and afford products the formation of which are inexplicable by skeletal rearrangement.[3] This is exemplified, in part, by eq 1, wherein photolysis of 1-

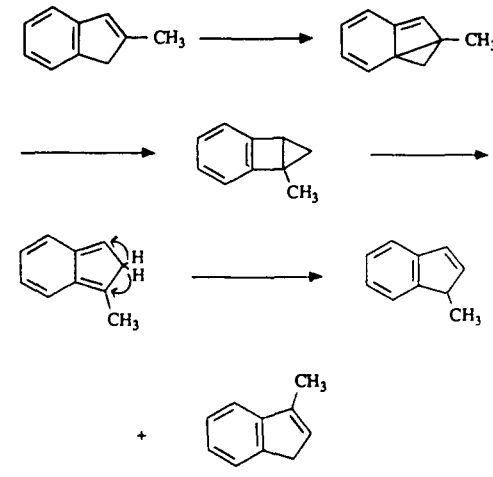


(1)

methylindene (1-MI) gives rise to the possible transposition product 2-MI as well as an apparent hydrogen-shift product, 3-methylindene (3-MI).[3] In fact, each alkylindene photolyzes to give the other possible isomers, so that photolysis of 2-MI vapor produces 1-MI and 3-MI and photolysis of 3-MI vapor gives 1-MI and 2-MI.[3]

Experiments utilizing inert quencher gases indicated that these photochemical reactions are derived from an upper singlet state (S_2) or from vibrationally excited S_1 (S_1^{vib}). When deuterium-labeled substrates were photolyzed, the products invariably were found to contain the label statistically distributed throughout the indenyl five-membered ring, and no combination of hydrogen 1,3-shifts, dual hydrogen 1,5-shifts, or skeletal rearrangements could explain this observation. We proposed, as a consequence of these results, that the excited methylindene could undergo a

Scheme I. Mechanism for Solution-Phase Skeletal Rearrangement of Alkylindenes[2]



series of sequential hydrogen and methyl 1,2-migrations that virtually equilibrate the hydrogen and methyl distributions about the indenyl five-membered ring.[3,4] A representation of such a mechanism utilizing the intermediacy of diradical species is illustrated in Scheme II for [2,3-d_2]-1-MI. In quantum mechanical terms, the mechanism may be represented as an excited methylindene exploring the excited-state surface high above the energy barriers for methyl and hydrogen migration, eventually funneling down to the product ground state by intermolecular collisions. A key feature of this mechanism is the movement of the methyl group around the indenyl five-membered ring while the indenyl skeleton remains intact. This is in contrast to the skeletal rearrangement mechanism that operates in solution. In order to establish the validity of the methyl/hydrogen migration mechanism and to determine the relative role, if any, of skeletal rearrangement in the gas phase, we have synthesized methylindenes labeled in the five-membered ring with carbon-13 and present herein the results of our photolyses of these compounds.

Results

Preparation of Starting Materials. The two methylindenes chosen for this study were [1-^{13}C]-2-methylindene ([1-^{13}C]-2-MI) and [3-^{13}C]-3-methylindene ([3-^{13}C]-3-MI). The syntheses of these molecules are outlined in Schemes III and IV. [1-^{13}C]-2-MI was prepared from [α-^{13}C]benzyl chloride in 33% overall conversion after purification by silica gel chromatography. [3-

(1) Organic Photochemistry. 91. Part 90: Mohammad, T.; Baird, W.; Morrison, H. *Bioorg. Chem.*, in press. Part 89: Wu, Z. Z.; Morrison, H. *Tetrahedron Lett.* **1990**, *31*, 5865-5868. Part 88: Duguid, R. J.; Morrison, H. *J. Am. Chem. Soc.*, in press. Abstracted, in part, from Duguid, R. Doctoral Dissertation, Purdue University, West Lafayette, IN, December, 1989. Dedicated to Professor Kurt Schaffner in honor of his 60th birthday.

(2) Morrison, H.; Giacherio, D.; Palensky, F. J. *J. Org. Chem.* **1982**, *47*, 1051-1058.

(3) Suarez, M. L.; Duguid, R. J.; Morrison, H. *J. Am. Chem. Soc.* **1989**, *111*, 6384-6391.

(4) For a recent extension of these observations to alkyldihydronaphathlenes, see: Duguid, R. J.; Morrison, H. *J. Am. Chem. Soc.*, in press.

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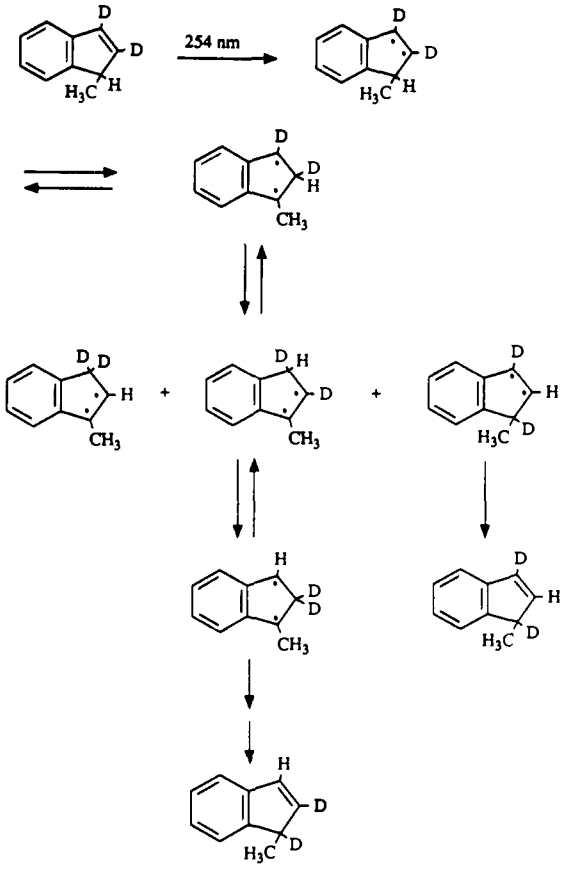
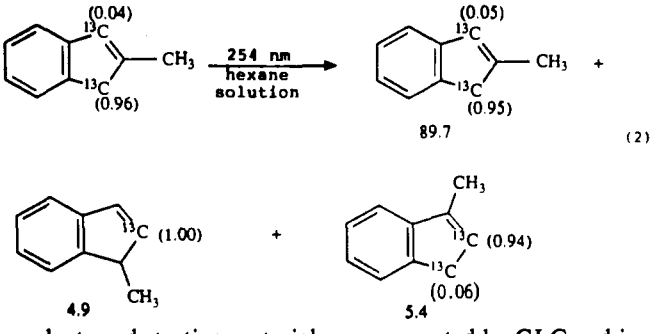
Scheme II. Diradical Mechanism for Scrambing of Deuterium in the Gas-Phase Photolysis of [2,3-d_2]-1-MI[3]



^{13}C]-3-Mi was prepared from K^{13}CN in 41% overall conversion after purification by silica gel chromatography. The products were identified by their ^{1}H and ^{13}C NMR spectra, which indicated that [1-^{13}C]-2-MI contained 96% ^{13}C at the C1 position and [3-^{13}C]-3-MI contained 100% ^{13}C at the C3 position.

Photolysis of [1-^{13}C]-2-MI in Hexane Solution. We decided to first confirm the proposed skeletal rearrangement mechanism for methylindenes in solution (Scheme I) by photolyzing 8.05 mM [1-^{13}C]-2-MI in hexane at 254 nm for 1.5 h. The products and their relative capillary GC peak areas are reported in eq 2. The



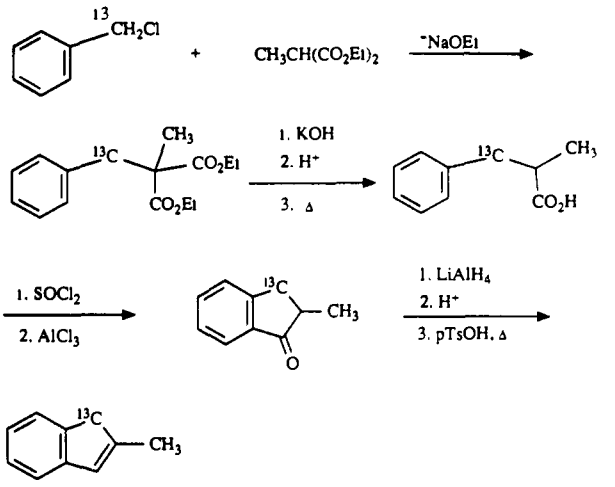
(2)

products and starting material were separated by GLC and individually analyzed by ^{1}H and ^{13}C NMR spectroscopy (the ^{13}C chemical shifts of the methylindenes have been reported in the literature[5]). The ^{13}C NMR spectra showed resonances at C1 and C3 for recovered 2-MI, a resonance at C2 for 1-MI, and resonances at C1 and C2 for 3-MI. The distributions of ^{13}C in the products and recovered starting material were determined by integration of the ^{13}C satellites in the ^{1}H NMR spectrum and are shown in eq 2.

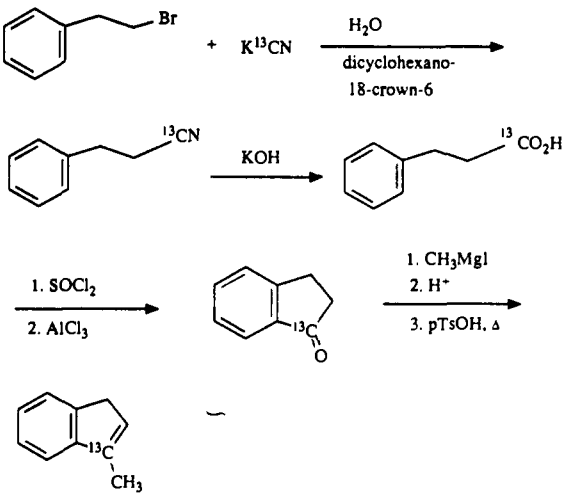
Photolysis of [1-^{13}C]-2-MI Vapor. A preparative gas-phase photolysis of [1-^{13}C]-2-MI vapor was performed with 254-nm light.

(5) Edlund, U. *Org. Magn. Reson.* **1978**, *11*, 516–519.

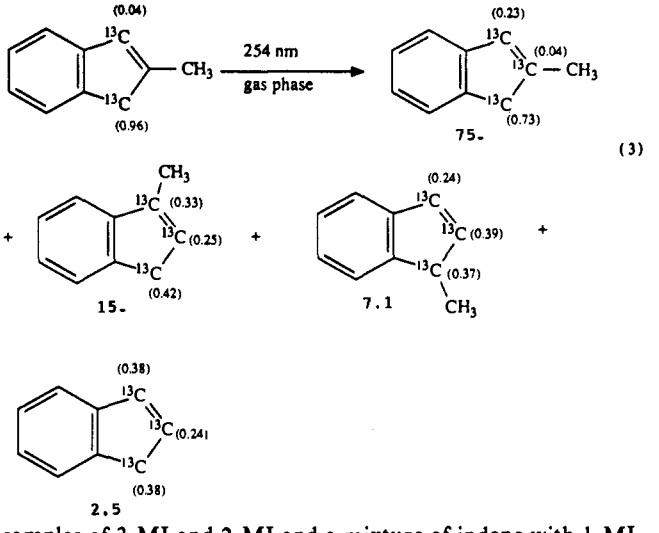
Scheme III. Synthetic Scheme for Preparation of [1-^{13}C]-2-MI



Scheme IV. Synthetic Scheme for Preparation of [3-^{13}C-3]-MI



The pot flask was cooled to reduce the flow rate ($P \simeq 60$ mTorr) so as to minimize intermolecular collisions and increase residence time in the light zone (see Experimental Section for descriptions of the several different conditions used in these gas-phase studies). Under these conditions, indene is formed in addition to the alkyl rearrangement products 3-MI and 1-MI;[3] the relative product GLC areas are shown in eq 3. Preparative GLC afforded pure

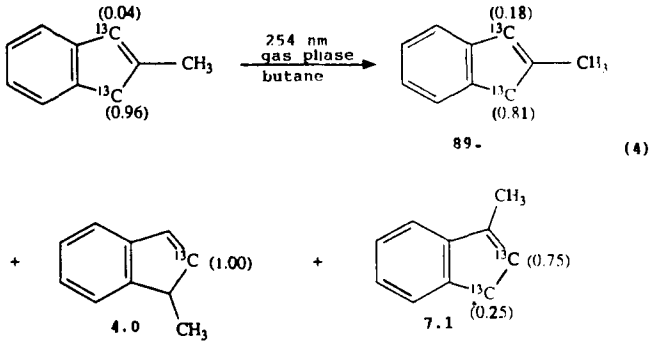


(3)

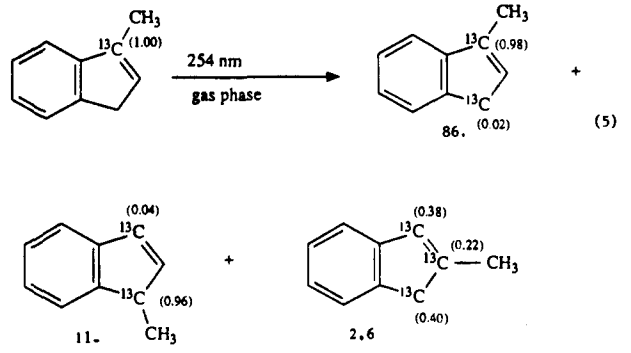
samples of 3-MI and 2-MI and a mixture of indene with 1-MI. The ^{13}C distributions were determined by quantitative ^{13}C NMR[6]

(see Experimental Section for details) and are also presented in eq 3.

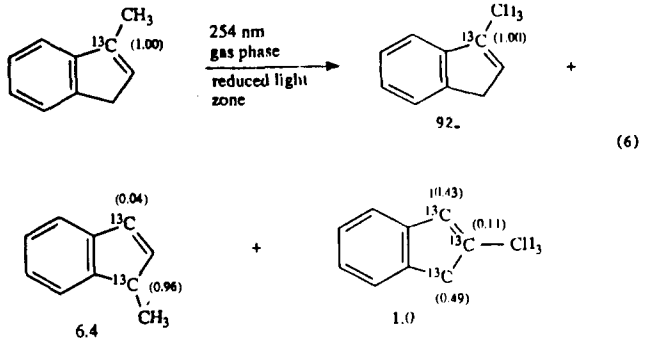
The effect of collisional quenching on the mechanism of methyl migration was determined by photolyzing [1-^{13}C]-2-MI in the presence of butane buffer gas. Several "static" (cf. Experimental Section) gas-phase photolyses were performed at 700–750 mTorr in the presence of butane, the product mixtures were combined, and the composite was analyzed by capillary GLC and by quantitative ^{13}C NMR spectroscopy. The relative product areas and the ^{13}C distributions within each product are shown in eq 4. (No indene is formed under these conditions.)



Photolysis of [3-^{13}C]-3-MI Vapor. [3-^{13}C]-3-MI was photolyzed with 254-nm light under flowing conditions ($P \simeq 250$–300 mTorr) and found to produce 1-MI, 2-MI, and 3-MI in the relative amounts shown in eq 5. Analysis of each product by quantitative ^{13}C NMR gave the ^{13}C distributions that are also reported in eq 5.

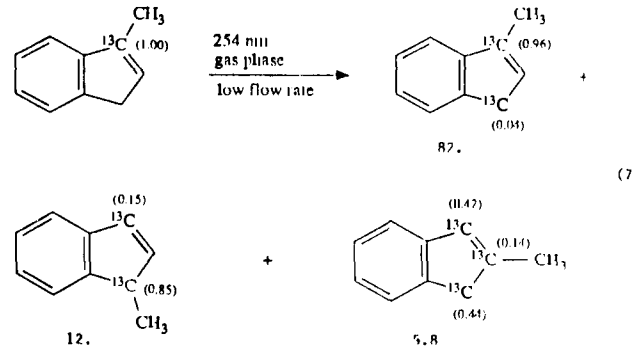


The labeled 3-MI was also photolyzed with the photolysis chamber partially masked in order to reduce the zone exposed to the incident light and thus minimize secondary photochemistry. The ^{13}C distribution within each product was determined by quantitative ^{13}C NMR, and the results are reported in eq 6.



Finally, [3-^{13}C]-3-MI was photolyzed with use of a cooled pot flask as described above for 1-MI. 1-MI and 2-MI were produced in the relative amounts shown in eq 7. Analysis of each product by quantitative ^{13}C NMR gave the ^{13}C distributions that are also reported in eq 7.

(6) Freeman, R.; Hill, H. D. W.; Kaptein, R. *J. Magn. Reson.* **1972**, *7*, 327–329.



Summary. For each of the above equations, the relative product areas can be combined with the ^{13}C distributions within the indenyl five-membered ring to give the relative amounts of each labeled product. The results are tabulated in Table I. Furthermore, each of these labeled products can be characterized as having originated from a single "net" transformation or from a combination of transformations, and this information is included under pathway in the table. The relative contributions of each pathway for each photochemical reaction are collated in Table II.

Discussion

Summary of Labeling Experiments. The results of the ^{13}C-labeling studies provide confirmatory evidence in support of the currently accepted mechanism for the solution-phase rearrangement and contribute a number of new insights into the nature of the processes operative in the gas phase.

1. The photolysis of [1-^{13}C]-2-MI in hexane (eq 2) leads virtually exclusively to products labeled at C2, as predicted by the skeletal rearrangement mechanism outlined in Scheme I.

2. This skeletal rearrangement mechanism is also operative in the gas phase, as evidenced by the formation of [2-^{13}C]-1-MI and [2-^{13}C]-3-MI from [1-^{13}C]-2-MI.

3. The labeling pattern for products formed in the gas phase require that, in addition to the skeletal rearrangement process, a mechanism is operating in which the methyl group actually detaches from the indenyl ring and reattaches to other ring positions. Of course, concomitant hydrogen migrations must be occurring. Examples where net methyl 1,2-shifts occur include the formation of [1-^{13}C]-1-MI and [1-^{13}C]- and [3-^{13}C]-3-MI from [1-^{13}C]-2-MI (eq 3) and the formation of [3-^{13}C]-2-MI and [1-^{13}C]-2-MI from [3-^{13}C]-3-Mi (eqs 4 and 5).

4. In fact, both net 1,2- and net 1,3-migrations of the methyl group are observed. An example of the latter is the formation of [3-^{13}C]-1-MI from [3-^{13}C]-3-MI (eq 5). However, when the opportunity for secondary photochemistry is minimized, as in the reduced light zone photolysis of [3-^{13}C]-3-MI (eq 6), the relative contribution of net methyl 1,3-migration to the 1-MI product is appreciably diminished, while the fraction of 2-MI resulting from net methyl 1,2-migration is minimally affected.

5. The presence of *n*-butane greatly reduces the contribution of methyl 1,2-migration while simultaneously enhancing the relative formation of skeletal rearrangement products.

Mechanisms for Methyl Group Rearrangement Reactions in the Gas Phase. As noted in 1, 2, and 3 above, though skeletal rearrangement is the primary source of alkylindene isomerization in solution, there are clearly two different mechanisms operative in the gas phase for translocation of the methyl group, i.e., the C1/C2 transposition reaction (path D) and a net methyl 1,2-shift with accompanying hydrogen shifts (path A).[7] However, the quencher-gas studies confirm that these processes do not originate from a common precursor, since photolysis of [1-^{13}C]-2-MI vapor

(7) The photochemical migration of alkyl groups in indenes in the gas phase has little precedent in the literature. Padwa has noted a photochemical 1,3-migration of the allyl group in 1-allyl-1-methyl-3-phenylindene and has proposed the dissociation and recombination of allyl and indenyl radicals to explain the rearranged product.[9] We are unaware of photochemical alkyl migrations of indenes or cyclopentadienes in solution, though 1,5-migrations of 1-substituted arylindenes to produce isoindene intermediates have been reported by several researchers.[10]

Table I. Products and Reaction Pathways for the Gas-Phase Photolyses of [1-^{13}C]-2-MI and [3-^{13}C]-3-MI

startg mater	photol cond	prdt	rel amt[a]	pathway[b]
[1-^{13}C]-2-MI	hexane	[3-^{13}C]-2-MI	0.9	C
		[2-^{13}C]-1-MI	4.9	D
		[1-^{13}C]-3-MI	0.3	E
		[2-^{13}C]-3-MI	5.1	D
[1-^{13}C]-2-MI	vapor[c]	[2-^{13}C]-2-MI	3.0	F
		[3-^{13}C]-2-MI	17.3	C
		[1-^{13}C]-1-MI	2.6	A
		[2-^{13}C]-1-MI	2.8	D
		[3-^{13}C]-1-MI	1.7	A
		[1-^{13}C]-3-MI	6.3	A
		[2-^{13}C]-3-MI	3.8	D
		[3-^{13}C]-3-MI	5.0	A
[1-^{13}C]-2-MI	vapor + butane	[3-^{13}C]-2-MI	16.0	C
		[2-^{13}C]-1-MI	4.0	D
		[1-^{13}C]-3-MI	1.8	A or E
		[2-^{13}C]-3-MI	5.3	D
[3-^{13}C]-3-MI	vapor	[1-^{13}C]-3-MI	1.7	B
		[1-^{13}C]-1-MI	10.6	C
		[3-^{13}C]-1-MI	0.4	B
		[1-^{13}C]-2-MI	1.0	A
		[2-^{13}C]-2-MI	0.6	E
		[3-^{13}C]-2-MI	1.0	A
[3-^{13}C]-3-MI	vapor[d]	[1-^{13}C]-1-MI	6.1	C
		[3-^{13}C]-1-MI	0.2	B
		[1-^{13}C]-2-MI	0.5	A
		[2-^{13}C]-2-MI	0.1	E
		[3-^{13}C]-2-MI	0.4	A
[3-^{13}C]-3-MI	vapor[c]	[1-^{13}C]-3-MI	3.3	B
		[1-^{13}C]-1-MI	10.2	C
		[3-^{13}C]-1-MI	1.8	B
		[1-^{13}C]-2-MI	2.6	A
		[2-^{13}C]-2-MI	0.8	E
		[3-^{13}C]-2-MI	2.4	A

[a] Product ratio = (GC area ratio)(% ^{13}C). [b] A = net CH_3 1,2-shift; B = net CH_3 1,3-shift; C = H 1,3-shift; D = Cl/C2 transposition; E = C + D; F = A + D. [c] Low flow rate conditions. [d] Reduced light zone.

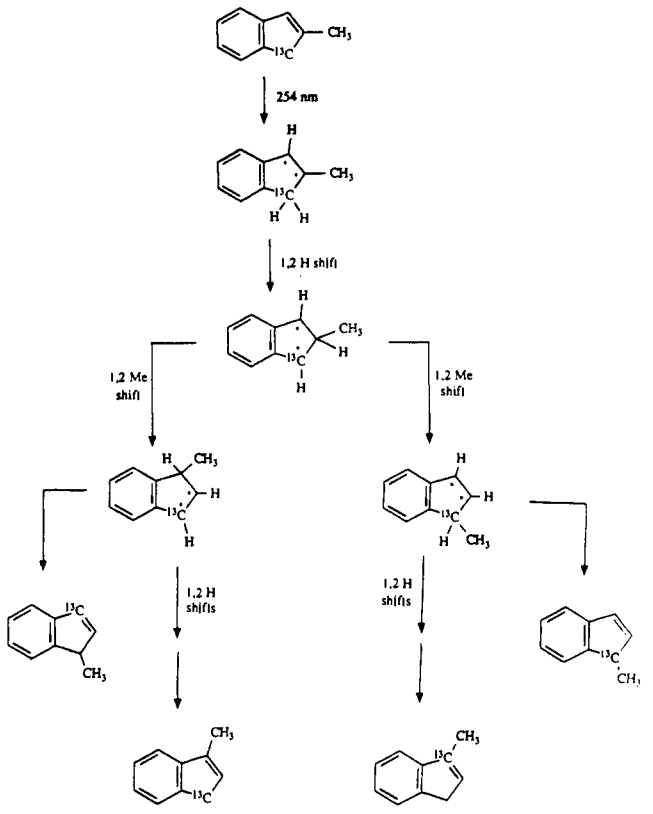
Table II. Product Distributions from the Photolyses of ^{13}C-Labeled Methylindenes

	percent of total prdt[a,b]					
photol cond	A	B	C	D	E	F
[1-^{13}C]-2-MI, hexane	0.0		8.0	89.0	2.7	0.0
[1-^{13}C]-2-MI, vapor[c]	37.0		41.0	16.0	0.0	7.0
[1-^{13}C]-2-MI, vapor + butane	(6.6)		59.0	34.0	(6.6)	0.0
[3-^{13}C]-3-MI, vapor	13.0	14.0	69.0	0.0	3.9	0.0
[3-^{13}C]-3-MI, vapor[d]	12.0	2.7	84.0	*d*	1.4	0.0
[3-^{13}C]-3-MI, vapor[c]	24.0	24.0	48.0	*d*	3.8	0.0

[a] A = net CH_3 1,2-shift; B = net CH_3 1,3-shift; C = H 1,3-shift; D = Cl/C2 transposition; E = C + D; F = A + D. [b] For example, the formation of products via path A from [1-^{13}C]-2-MI vapor is calculated as follows: {([1-^{13}C]-1-MI (2.6) + [3-^{13}C]-1-MI (1.7) + [1-^{13}C]-3-MI (6.3) + [3-^{13}C]-MI (5.0))/(Sum of all products (42.5))}(100) = 37%. [c] Low flow rate conditions. [d] Degenerate reaction, would not be observable. [e] Reduced light zone.

in the presence of butane enhances the overall product contribution of skeletal rearrangement (from 16 to 34%) while decreasing the contribution of the alternative net methyl 1,2-shift process (from 37 to ca. ≤7%).[8] Thus, the methyl 1,2-shift reaction must originate from an upper vibrational or electronic state, with collisional quenching of this state giving rise to the state(s) reactive in solution, presumably lower vibrational levels of S_1.

Scheme V. Mechanism for Formation of Methyl-Migrated Products From the Gas-Phase Photolysis of [1-^{13}C]-2-MI



As noted at the outset, the methyl-shift reaction (and perforce, accompanying hydrogen 1,2-shifts) can be viewed as proceeding through a series of diradical intermediates as illustrated in Scheme V for the formation of methyl-migrated products from [1-^{13}C]-2-MI. In fact, there is evidence from the literature to support the formation of such diradical-like species from S_2. Salisbury and co-workers have studied the photophysics of several acyclic and ring-constrained styrene derivatives (including indene) in the gas phase using fluorescence decay and gated emission spectroscopy.[11-13] These researchers observed that excitation into the S_2 manifold of these compounds produced nonexponential decay. A short-lived component (1–5 ns) was attributed to decay from the upper vibrational levels of S_1 generated by internal conversion from the S_2 state. A higher energy, long-lived component (45–70 ns) was attributed to decay from a singlet state of twisted π-bond character formed from an initially populated Franck–Condon S_2 state. It seems reasonable to ascribe the diradical chemistry we observe for the methylindenes to such a twisted π-bond species.[4] It is noteworthy that such a long-lived state was observed for a compound with a greater degree of ring strain than would be expected for the indene ring, e.g., 1-phenylcyclobutene, though no such emission was observed in the most strained example studied (1-phenylnorbornene).

Finally, it is interesting to note that the amount of net methyl 1,2-shift chemistry (path A), relative to hydrogen-shift chemistry (path B), significantly increases when 3-MI is photolyzed under the "low flow rate" conditions. (The effect is even more dramatic if one includes path B alkyl-shift chemistry as well; see below.) We have previously observed that cooling the sample flask during the photolysis not only increases conversions to products but also favors alkyl-shift products to hydrogen-shift products.[3] The lowered pressure of the reaction chamber at these temperatures

(8) Interestingly, it is now evident that the apparent insensitivity of the gas-phase photochemistry of unlabeled 2-MI vapor to the addition of collisional quencher gases[3] is actually a consequence of the inability to distinguish the two operative mechanisms with such a substrate.

(9) Padwa, A.; Goldstein, S.; Pulwer, M. *J. Org. Chem.* **1982**, *47*, 3893–3902.

(10) (a) McCullough, J. J.; McClory, M. R. *J. Am. Chem. Soc.* **1974**, *96*, 1962–1963. (b) McCullough, J. J.; Yarwood, A. J. *J. Chem. Soc., Chem. Commun.* **1975**, 485–486. (c) de Fonseka, K. K.; Manning, C.; McCullough, J. J.; Yarwood, A. J. *J. Am. Chem Soc.* **1977**, *99*, 8257–8261. (d) Padwa, A.; Goldstein, S.; Loza, R.; Pulwer, M. *J. Org. Chem.* **1981**, *46*, 1858–1868.

(11) Steer, R. P.; Swords, M. D.; Crosby, P. M.; Phillips, D.; Salisbury, K. *Chem. Phys. Lett.* **1976**, *43*, 461–464.

(12) Ghiggino, K. P.; Phillips, D.; Salisbury, K.; Swords, M. D. *J. Photochem.* **1977**, *7*, 141–146.

(13) Ghiggino, K. P.; Hara, K.; Mant, G. R.; Phillips, D.; Salisbury, K.; Steer, P.; Swords, M. D. *J. Chem. Soc., Perkin Trans. 2* **1978**, 88–91.

Table III. ^1H NMR Data for the Photolysis of [1-^{13}C]-2-MI in Hexane

compd	proton reson (δ)	assgnt	integrated amt
[1-^{13}C]-2-MI, unphotolyzed	7.08–7.37 (m)	aryl	3.8 H
	6.48 (d, J = 8.2 Hz)	C3 CH	0.6 H
	3.07, 3.50 (d, J = 127.4 Hz)	C1 $^{13}CH_2$	2.4 H
	3.30 (s)	C1 $^{12}CH_2$	0.1 H
	2.15 (d, J = 3.5 Hz)	CH_3	3.0 H
[1-^{13}C]-2-MI, recovered	7.09–7.37 (m)	aryl	4.2 H
	6.48 (d, J = 8.1 Hz)	C3 CH	0.7 H
	3.08, 3.50 (d, J = 127.4 Hz)	C1 $^{13}CH_2$	2.1 H
	3.30 (s)	C1 $^{12}CH_2$	0.1 H
	2.15 (d, J = 3.5 Hz)	CH_3	2.8 H
[^{13}C]-1-MI	7.18–7.43 (m)	aryl	3.9 H
	6.76 (m)	C3 ^{12}CH + C2 ^{13}CH	1.2 H
	6.49 (m)	C2 ^{12}CH	0.1 H
	6.20 (m)	C2 ^{13}CH	0.4 H
	3.50 (m)	C1 CH_2	1.2 H
	1.32 (m)	CH_3	3.3 H
[^{13}C]-3-MI	7.18–7.47 (m)	aryl	3.9 H
	5.92, 6.48 (dd, J_1 = 165.6, J_2 = 1.2 Hz)	C2 ^{13}CH	0.8 H
	6.20 (br s)	C2 ^{12}CH	0.05 H
	3.10, 3.50 (d, $J \simeq$ 135 Hz)	C1 $^{13}CH_2$	0.2 H
	3.32 (m)	C1 $^{12}CH_2$	2.1 H
	2.17 (m)	CH_3	3.0 H

creates a low-collision environment, which should slow down electronic and vibrational relaxation of the excited species and thus favor higher energy (e.g., alkyl-shift) pathways.

Secondary Photochemistry. There are two pathways needed to explain the label distributions summarized in Tables I and II that require two photochemical steps and must therefore involve secondary photochemistry. For example, the formation of [2-^{13}C]-2-MI from [3-^{13}C]-3-MI requires an initial hydrogen shift to [1-^{13}C]-1-MI followed by a skeletal rearrangement (path E). Likewise, the formation of [2-^{13}C]-2-MI from [1-^{13}C]-2-MI involves a C1/C2 transposition followed by a net methyl 1,2-shift (path F).

In fact, the data indicate that the net methyl 1,3-shift (path B) is also primarily a secondary photochemical reaction. This is evidenced by the change in product distribution observed when [3-^{13}C]-3-MI was photolyzed with use of a reduced light zone, conditions that should diminish the opportunity for secondary photochemistry. A dramatic drop in the fraction of chemistry proceeding via path B is observed (Table II), by contrast with the changes seen for paths A and C. (As expected (see above), there is also an almost 3-fold drop in the relative contribution of path E). Because earlier studies[3] with deuterated 3-MI are inconsistent with the net methyl 1,3-migration reaction occurring via a series of concerted hydrogen and methyl 1,3-shifts, we attribute the path B products to multiple path A processes. Further support for the coupling of these two pathways comes from the invariant (ca. 1:1) ratio of paths A and B products under normal and reduced flow conditions (Table II).

Conclusions. These studies confirm the existence of two mechanisms for the net methyl 1,2-migration reaction of alkylindenes in the gas phase. One of these is the skeletal rearrangement mechanism first observed in these laboratories for alkylindene rearrangement in solution and derives from lower vibrational levels of S_1. The second mechanism involves S_2 (or vibrationally excited S_1) and proceeds through a stepwise series of methyl and hydrogen 1,2-shifts within diradical-like intermediates.

Experimental Section

The detailed experimental procedures for this research may be found in the doctoral dissertation of R.J.D. The salient features are summarized below.

Materials. The following chemicals from Aldrich were stored at room temperature and used as received unless otherwise stated: [α-^{13}C]benzyl chloride, stored at −20 °C; 2-(bromoethyl)benzene, distilled; dicyclohexano-18-crown-6, stored at −20 °C; diethyl methylmalonate, distilled; potassium cyanide-^{13}C. Lithium aluminum hydride (Alfa), silica gel (EM Science), aluminum chloride (Mallinckrodt), and *p*-toluenesulfonic acid monohydrate (Baker) were stored at room temperature and used as received. Iodomethane (EM Science) was stored at −20 °C, and thionyl chloride (EM Science) was distilled prior to use. Hexane used in photochemical studies was from Burdick and Jackson (spectroquality). For synthetic reactions, benzene and ethanol were distilled under nitrogen from sodium and diethyl ether was distilled under nitrogen from benzophenone ketyl. Butane (99.5% pure) obtained from Matheson was used as received.

Table IV. ^{13}C NMR Data for the Photolysis of [1-^{13}C]-2-MI in Hexane

compd	carbon reson (δ)	assgnt
[1-^{13}C]-2-MI, unphotolyzed	126.2	C3
	43.3	C1
[1-^{13}C]-2-MI, recovered	127.1	C3
	42.7	C1
[^{13}C]-1-MI	141.3	C2
[^{13}C]-3-MI	128.7	C2
	37.6	C1

Gas Chromatography. Analytical GLC analyses were performed on a Hewlett-Packard Model 5710A instrument equipped with a capillary injector and on a Varian Model 3700 capillary GLC. Both chromatographs were equipped with a flame ionization detector and Hewlett-Packard Model 3390A integrators. The following analytical columns were used: A, 30 m × 0.25 mm i.d., DB-Wax, capillary (J & W Scientific), 0.50-μm film thickness; B, 30 m × 0.25 mm i.d., RSL-150 capillary (Alltech), 0.25-μm film thickness. Preparative GLC separations were performed on a Varian Model 3300 instrument modified to accommodate 0.25-in. columns and coupled to either a Hewlett-Packard 3390A or 3393A integrator. The column used was 16 ft × 0.25 in. 25% XF-1150 on 60/80 AW Chromosorb P, with 50–60 mL of He/min (column C).

Spectroscopy. Qualitative and quantitative ^1H and ^{13}C NMR spectra were obtained on a General Electric QE-300 300-MHz NMR spectrometer. The method of Freeman, Hill, and Kaptein[14] was used to obtain quantitative ^{13}C NMR spectra on the QE-300 NMR spectrometer. This method involves the suppression of NOE enhancement of the signal via proton decoupling only during data acquisition. The delay time between pulses was set to 5 times the longest relaxation time (T_1) of the sample (usually a delay of 1–2 min). Integration of the spectra was also enhanced by correcting for filter droop of the spectrum caused by the audio filters in the spectrometer. Approximations of the T_1's of ^{13}C-labeled methylindenes were obtained by the T_1 inversion-recovery method.[15] The T_1 of C2 in 2-MI was approximately 29 s, and the T_1 of C3 in 3-MI was approximately 14 s.

Mass spectra were obtained on a Finnigan 4000 mass spectrometer interfaced to a gas chromatograph containing an OV-17 or OV-101 packed column. EI mass spectra were recorded at an ionization energy of 70 eV.

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Table V. ^1H NMR Data for the Photolysis of [1-^{13}C]-2-MI Vapor

compd	proton reson (δ)	assgnt	integrated amt
[^{13}C]-2-MI	7.06–7.36 (m)	aryl	4.0 H
	6.20, 6.74 (d, J = 162 Hz)	C3 ^{13}CH	0.27 H
	6.48 (d, J = 9 Hz)	C3 ^{12}CH	0.64 H
	3.06, 3.49 (d, J = 129 Hz)	C1 $^{13}CH_2$	1.60 H
	3.27 (d, J = 3 Hz)	C1 $^{12}CH_2$	0.54 H
	2.14 (d, J = 4 Hz)	CH_3	2.9 H
[^{13}C]-1-MI + [^{13}C]indene	7.16–7.60 (m)	aryl	
	6.27, 6.55, 6.89	C2 + C3 (indene)	
	6.21, 6.46, 6.77, 7.04	C2 + C3 (1-MI)	
	3.28, 3.50, 3.70	C1 (1-MI)	
	3.18, 3.40, 3.62	C1 (indene)	
	1.32 (m)	CH_3 (1-MI)	
[^{13}C]-3-MI	7.18–7.47 (m)	aryl	3.8 H
	6.20 (m)	C2 ^{12}CH	0.63 H
	5.92, 6.47 (d, J = 165.6 Hz)	C2 ^{13}CH	0.24 H
	3.32 (m)	C1 $^{12}CH_2$	1.33 H
	3.10, 3.52 (d, $J \simeq$ 135 Hz)	C1 $^{13}CH_2$	0.94 H
	2.17 (d, J = 1.4 Hz)	CH_3	3.1 H

Photolyses. Gas-phase photolyses were performed either as a "flowing" experiment with use of a previously described apparatus[3] or as a static experiment in our modified Rayonet reactor[3] with use of a 0.5-L cylindrical quartz tube equipped with a needle valve and vacuum attachment to hold the sample.[3,4] In some flowing runs, the photolysis vessel was partially covered with aluminum foil to vary the reaction light zone. Low flow rate photolyses involved cooling of the sample flask to 0 °C during the photolysis.[3,16] All gas-phase experiments employed low-pressure mercury resonance lamps. Solution photolyses were performed in quartz photolysis tubes in a turntable reactor equipped with a Hanovia Model 688A-45 low-pressure mercury resonance lamp.

Preparation of [1-^{13}C]-2-Methylindene. [3-^{13}C]-2-Methyl-3-phenylpropionic acid was prepared via the method of Adams and Kamm[17] for condensing diethyl methylmalonate with [α-^{13}C]benzyl chloride. The method of Reid and Ruhoff[18] was adapted for the decarboxylation of the malonic acid. The [3-^{13}C]-2-methyl-3-phenylpropionic acid product was used immediately in the next step without further purification. This involved formation of the acid chloride with thionyl chloride and ring closure with aluminum chloride[19] to form [3-^{13}C]-2-methyl-1-indanone. Reduction with lithium aluminum hydride and acid-catalyzed dehydration afforded the crude product, which was purified by silica gel chromatography (hexane eluent) to produce [1-^{13}C]-2-MI in 32.8% overall conversion from [α-^{13}C]benzyl chloride. Analysis by GLC on column A at 110 °C indicated the 2-MI to be 98.2% pure (retention time of 25.0 min). The proton NMR is consistent with 2-MI ^{13}C-labeled in the C1 position: ^1H NMR ($CDCl_3$, 300 MHz) δ 7.08–7.37 (m, aromatic, 4 H), 6.48 (d, $J_{^{13}CH}$ = 8.2 Hz, C3 vinyl coupled to ^{13}C, 1 H), 3.07, 3.50 (d, $J_{^{13}CH}$ = 127.4 Hz, C1 methylene coupled to ^{13}C, 2 H), 2.15 (d, $J_{^{13}CH}$ = 3.5 Hz, methyl, 3 H); ^{13}C NMR ($CDCl_3$, 75.6 Hz) δ 126.2 (C3), 125.3, 124.4, 122.6, 122.4, 118.8 (vinyl or Ar CH), 43.3 (C1), 17.9 (CH_3).

Preparation of [3-^{13}C]-3-Methylindene. [1-^{13}C]hydrocinnamonitrile was prepared by the two-phase nucleophilic substitution of phenethyl bromide with K^{13}CN.[20] Analysis of the crude product by GLC on column D at 90 °C showed the hydrocinnamonitrile to be 99% pure. The product was used in the next step without further analysis. The nitrile was hydrolyzed to [1-^{13}C]-3-phenylpropionic acid by basic hydrolysis in aqueous methanol.[21] The crude acid was used without further purification to synthesize [1-^{13}C]-1-indanone by formation of the acid chloride and Lewis acid catalyzed condensation.[19] The indanone was used without further purification or analysis to prepare [3-^{13}C]-3-MI. This involved reaction with methylmagnesium iodide and ammonium chloride catalyzed dehydration. The crude product was purified by silica gel chromatography (hexane eluent): low-resolution MS (EI) m/e 131 (M^+), 130 (M – H), 116 (M – CH_3); low-resolution MS (CI) m/e 132 (M + H); ^1H NMR ($CDCl_3$, 300 MHz) δ 7.18–7.47 (m, aromatic, 4 H), 6.20 (br s, C2 vinyl, 1 H), 3.31 (br s, C1 methylene, 2 H), 2.15–2.18 (m, methyl, 3H); ^{13}C NMR (APT) ($CDCl_3$, 75.6 MHz) δ 139.9 (C3), 128.7 (d, C2), 126.0 (aryl CH), 124.4 (aryl CH), 123.6 (aryl CH), 118.8 (aryl CH), 37.6 (C1), 13.0 (d, methyl). The ^1H NMR spectrum was identical with that for unlabeled 3-MI except for the added ^{13}C–H long-range couplings. There are no ^{13}C satellites, an indication that all the ^{13}C label is at C3.

Table VI. Quantitative ^{13}C NMR Data for the Photolysis of [1-^{13}C]-2-MI Vapor

compd	carbon reson (δ)	assgnt	integrated amt (% ^{13}C) 1	2	3	av
[^{13}C]-2-MI[a]	146.1	C2	4.0	4.0	3.2	3.7 ± 0.5
	127.1	C3	23.0	24.0	23.2	23.4 ± 0.5
	42.7	C1	73.0	72.0	73.7	72.9 ± 0.8
[^{13}C]-1-MI[b]	141.3	C2	26.3	22.2		24.2 ± 2.9
	130.1	C3	38.6	38.9		38.8 ± 2.7
	45.1	C1	35.1	38.9		37.0 ± 2.7
[^{13}C]indene[b]	134.2	C2	23.8	25.0		24.4 ± 0.8
	132.0	C3	38.1	37.5		37.8 ± 0.4
	39.0	C1	38.1	37.5		37.8 ± 0.4
[^{13}C]-3-MI[c]	139.9	C3	34.3	35.5	30.3	33.4 ± 2.7
	128.7	C2	23.9	26.2	24.2	24.8 ± 1.2
	37.6	C1	41.8	38.3	45.5	41.9 ± 3.6

[a] Pulse delay 40 s; no. of acquisitions 64, 64, and 64. [b] Pulse delay 60 s; no. of acquisitions 497 and 566. [c] Pulse delay 72 s; no. of acquisitions 456, 433, and 97.

Table VII. Quantitative ^{13}C NMR Data for the Photolysis of [1-^{13}C]-2-MI and Butane

compd	carbon reson (δ)	assgnt	percent ^{13}C by peak height
[^{13}C]-2-MI	146.1	C2	0.0
	127.1	C3	18.2
	42.7	C1	81.8
[^{13}C]-1-MI	141.3	C2	100.0
	130.1	C3	0.0
	45.1	C1	0.0
[^{13}C]-3-MI	139.9	C3	0.0
	128.7	C2	75.0
	37.6	C1	25.0

Photolysis of [1-^{13}C]-2-MI in Hexane. Ten quartz photolysis tubes were filled with 5 mL of 8.05 mM [1-^{13}C]-2-MI in hexane and the solutions degassed by argon bubbling for 20 min. The solutions were photolyzed at 254 nm for 1.5 h while being rotated on a turntable, combined, and concentrated to a total volume of approximately 1 mL. The products and starting material were separated by GLC on column C at 150 °C (retention times: 1-MI, 27.3 min; 3-MI, 38.7 min; 2-MI, 45.9 min). The GLC peak areas of 1-MI and 3-MI were 4.9 and 5.4% of the total volatile product mixture, repsectively. The products and recovered starting material were analyzed by ^1H (Table III) and ^{13}C NMR (Table IV); for reference, the ^1H and ^{13}C NMR Data for unphotolyzed [1-^{13}C]-2-MI are also shown in the tables.

(16) A typical normal flow rate experiment has a P_1 of 250 mTorr and a P_2 of 1.0 Torr (where P_2 and P_1 are the inlet and outlet pressures of the photolysis chamber, respectively). A typical low flow rate experiment has a P_1 of 60 mTorr and a P_2 of 225 mTorr.

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Table VIII. ^{1}H NMR Data for the Photolysis of [1-^{13}C]-3-MI Vapor

compd	proton reson (δ)	assgnt	integrated amt
[3-^{13}C]-3-MI, unphotolyzed	7.18–7.46 (m)	aryl	4.0 H
	6.20 (s)	C2 ^{12}CH	0.9 H
	3.32 (br s)	C1 $^{12}CH_2$	2.1 H
	2.16–2.18 (m)	CH_3	3.0 H
[^{13}C]-3-MI, recovered	7.17–7.45 (m)	aryl	3.4 H
	6.18–6.20 (m)	C2 ^{12}CH	0.76 H
	3.29–3.31 (m)	C1 $^{12}CH_2$	2.5 H
	2.14–2.18 (m)	CH_3	3.3 H
[^{13}C]-1-MI	7.17–7.42 (m)	aryl	3.9 H
	6.77 (m)	C3 ^{12}CH	0.72 H
	6.48 (m)	C2 ^{12}CH	0.74 H
	3.27, 3.70 (dq, J_1 = 7.5 Hz, J_2 = 127 Hz)	C1 ^{13}CH	1.1 H
	1.30 (dd)	CH_3	3.6 H
[^{13}C]-2-MI	7.11–7.37 (m)	aryl	3.9 H
	6.25, 6.78 (d, J = 158 Hz)	C3 ^{13}CH	0.38 H
	6.52 (d, J = 7.6 Hz)	C3 ^{12}CH	0.43 H
	3.08, 3.50 (d, J = 127.5 Hz)	C1 $^{13}CH_2$	0.91 H
	3.28 (d, J = 4.4 Hz)	C1 $^{12}CH_2$	1.45 H
	2.15 (d, J = 5.0 Hz)	CH_3	2.9 H

Table IX. Quantitative ^{13}C NMR Data for the Photolysis of [3-^{13}C]-3-MI Vapor

compd	carbon reson (δ)	assgnt	integrated amt (% ^{13}C) 1	2	av
[^{13}C]-3-MI[a]	139.9	C3	98.0		98.0
	37.6	C1	2.0		2.0
[^{13}C]-1-MI[b]	130.1	C3	3.8	4.5	4.2 ± 0.5
	45.1	C1	96.2	95.5	95.8 ± 0.5
[^{13}C]-2-MI[c]	146.1	C2	22.4	22.2	22.3 ± 0.1
	127.1	C3	37.3	38.9	38.1 ± 1.1
	42.7	C1	40.3	38.9	39.6 ± 1.0

[a] Pulse delay 72 s; no. of acquisitions 32. [b] Pulse delay 60 s; no. of acquisitions 514 and 52. [c] Pulse delay 110 and 140 s; no. of acquisitions 300 and 204.

Gas-Phase Photolysis of [1-^{13}C-2]-MI. A preparative flowing gas-phase photolysis was performed on 48.6 mg of [1-^{13}C]-2-MI vapor with the sample vessel cooled to 0 °C (pressure ca. 60 mTorr). Analysis of the isolated product mixture by GLC on column A at 110 °C gave the following product distribution: 73.4% 2-MI, 14.7% 3-MI, 6.9% 1-MI, and 2.4% indene. The products were separated by preparative GLC on column C at 150 °C and analyzed by ^{1}H NMR (Table V) and quantitative ^{13}C NMR (Table VI). The 1-MI and indene products could not be separated, so the NMR data are reported on the mixture. The complexity of the ^{1}H NMR spectra due to ^{13}C satellites prohibited extracting quantitative information on ^{13}C scrambling in the indenyl ring. However, the quantitative ^{13}C spectra clearly established the amount of ^{13}C at each of the five-membered-ring carbons.

Gas-Phase Photolysis of [1-^{13}C]-2-MI and Butane. The static gas-phase photolysis cell was cooled to −196 °C in liquid nitrogen, and 700–750 mTorr of the 2-MI was condensed into the flask. The portion of the vacuum line above the cell was filled with 200 Torr of butane, and this was also condensed into the cell. The cell was thawed, and the gases were allowed to mix for 0.5 h. The gaseous mixture was photolyzed for 1.0 min at 254 nm (four lamps), and this procedure was repeated seven times. The combined product mixture was dissolved in $CDCl_3$ and analyzed by GLC on column A at 110 °C. The product mixture by GC integration was 87.5% 2-MI, 6.2% 3-MI, and 3.5% 1-MI. No indene was formed in the photolysis, but trace amounts of several unknown products were formed. The product mixture was also analyzed by quantitative ^{13}C NMR (Table VII).

Gas-Phase Photolysis of [3-^{13}C]-3-MI. A preparative flowing gas-phase photolysis was performed on 93.4 mg of [3-^{13}C]-3-MI at 254 nm with the sample vessel kept at room temperature (≃ 25 °C) and the flowing pressure at 250–300 mTorr. The sample was allowed to evaporate for 2 min, which transferred approximately 25 mg of the sample. The products were collected, and analysis by GLC on column A at 110 °C indicated a product distribution of 82.8% 3-MI, 10.8% 1-MI, 2.5% 2-MI, and 0.4% indene. The products were separated by GLC on column C at 150 °C and analyzed by GLC on column A at 110 °C and by ^{1}H and ^{13}C NMR spectroscopy. Purities were 1-MI (96.6%), 2-MI (89.0%), and 3-MI (99.6%). The ^{1}H NMR and quantitative ^{13}C data are shown in Tables VIII and IX, respectively.

Table X. Quantitative ^{13}C NMR Data for the Reduced Light Zone Photolysis of [3-^{13}C]-3-MI Vapor

compd	carbon reson	assgnt	integrated amt (% ^{13}C) 1	2	3	av
[^{13}C]-3-MI[a]	139.9	C2	99.1			99.1
	37.6	C1	0.9			0.9
[^{13}C]-1-MI[b]	130.1	C3	3.6			3.6
	45.1	C1	96.4			96.4
[^{13}C]-2-MI[c]	146.1	C2	9.7	14.7	8.3	10.9 ± 3.4
	127.1	C3	38.7	41.2	41.7	43.3 ± 5.9
	42.7	C1	51.6	44.1	50.0	48.6 ± 4.0

[a] Pulse delay 72 s; no. of acquisitions 32. [b] Pulse delay 60 s; no. of acquisitions 554. [c] Pulse delay 110 and 140 s; no. of acquisitions 305, 208, and 242.

Table XI. Quantitative ^{13}C NMR Data for the Low Flow Rate Photolysis of [3-^{13}C]-3-MI Vapor

compd	carbon reson	assgnt	integrated amt (% ^{13}C) 1	2	av
[^{13}C]-3-MI[a]	139.9	C3	96.1		96.1
	37.6	C1	3.9		3.9
[^{13}C]-1-MI[b]	130.1	C3	15.5	13.9	14.7 ± 1.1
	45.1	C1	84.5	86.1	85.3 ± 1.1
[^{13}C]-2-MI[c]	146.1	C2	13.8	14.9	14.4 ± 0.8
	127.1	C3	40.2	43.6	41.9 ± 2.4
	42.7	C1	46.0	41.5	43.8 ± 3.2

[a] Pulse delay 72 s; no. of acquisitions 32. [b] Pulse delay 60 s; no. of acquisitions 32 and 528. [c] Pulse delay 110 s; no. of acquisitions 32 and 288.

Reduced Light Zone Gas-Phase Photolysis of [3-^{13}C]-3-MI. The photolysis vessel was wrapped in aluminum foil so that only 10 cm in the center of the quartz vessel was exposed to the light, and 150 mg of [3-^{13}C]-3-MI vapor was photolyzed at 254 nm with the flowing pressure at 160–250 mTorr. The products were collected, and analysis by GLC on column A at 110 °C indicated 92.0% 3-MI, 6.4% 1-MI, 1.0% 2-MI, and 0.2% indene. The products were separated by GLC on column C at 150 °C and analyzed by GLC on column A at 110 °C and by quantitative ^{13}C NMR. Purities were 1-MI (96.2%), 2-MI (69.7%), and 3-MI (99.7%). The 2-MI contained 28.5% 3-MI as an impurity. The ^{13}C NMR data are shown in Table X.

Low Flow Rate Gas-Phase Photolysis of [3-^{13}C]-3-MI. The labeled 3-MI sample was purified by GLC on column C at 150 °C, and 110 mg was photolyzed at 254 nm with the sample vessel maintained at 0 °C with an ice–water bath (flowing pressure of 70 mTorr). The transfer of 35 mg took 20–30 min. Analysis of the collected products by GLC on column A at 110 °C indicated 80.2% 3-MI, 11.4% 1-MI, 5.7% 2-MI, and 1.0% indene. The products were separated by GLC on column C at 150 °C and by quantitative ^{13}C NMR (Table XI).

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