

**Figure 14.** Expected shapes of FMOs of (a) 1,3-cyclohexadiene in the transition structure for the disrotatory electrocyclic reaction, (b) the FMOs of cyclopropane in a monorotatory isomerization, (c) linear and nonlinear CC bond-breaking processes, and (d) linear and nonlinear hydrogen shifts.

orbital (see Figure 14). The stronger the donor, the greater the tendency for outward rotation, while acceptors should show a smaller preference. Cyclopropane isomerizations involve the breaking of  $\sigma$  bonds and mainly the rotation of only one terminus.<sup>33</sup>

As shown in Figure 14b, donors should prefer location a at the rotating terminus and c at the stationary terminus, while strong acceptors may prefer site b at the rotating terminus and d at the nonrotating. In general, for reactions which involve  $\sigma$  bond breaking in a linear fashion (Figure 14c), no stereochemical preference of the type described above is possible, but for nonlinear processes, donors will prefer the site which minimizes overlap with the breaking bond, while acceptors will seek to maximize such overlap. Similarly, in sigmatropic shifts, stereoselectivity may be influenced by overlap of substituents with the bonds to the migrating atom. As demonstrated in Figure 14d, no effect is possible for a linear hydrogen transfer, but for nonlinear transfer the effects are qualitatively similar to those described for electrocyclicization. Donor substituents will prefer to be located on the positions marked "out", while very strong acceptors may prefer to move "in".

The ramifications of these effects are being investigated in these laboratories.

**Acknowledgment.** We are grateful to the National Science Foundation for financial support of this research, to Professors Wolfgang Kirmse and William R. Dolbier, whose experimental results and suggestions prompted this study, and to the Alexander von Humboldt Foundation for a U.S. Senior Scientist Award to K.N.H., which made the collaboration with Professor Kirmse possible.

**Registry No.** Cyclobutene, 822-35-5; *trans*-3,4-dimethylcyclobutene, 1517-13-1; *trans*-3,4-dihydroxycyclobutene, 95070-00-1.

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## Mechanisms for Interconversions among $C_3H_4$ Hydrocarbons: Deuterium Isotope Effects and Independent Generation of Vinylmethylene Intermediates in Photoisomerizations of Allenes and Cyclopropenes

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**Abstract:** Direct photolysis of 4,4-dimethyl-1,1-diphenyl-1,2-pentadiene (**1**) in *tert*-butyl alcohol yields 1-*tert*-butyl-3,3-diphenylcyclopropene (**2**),  $\Phi = 0.0087 \pm 0.0017$ , 4,4-dimethyl-1,1-diphenyl-2-pentyne (**3**),  $\Phi = 0.0046 \pm 0.0006$ , and 1-*tert*-butyl-3-phenylindene (**4**),  $\Phi = 0.0112 \pm 0.0014$ . Involvement of vinylmethylenes as potential intermediates in **1** photoisomerizations was assessed by independent generation with cyclopropene **2**, the tosylhydrazone **11** of 2,2-dimethyl-5,5-diphenyl-4-pentene-3-one, and 3-*tert*-butyl-5,5-diphenyl-3*H*-pyrazole (**13**). Quantum yields for direct photolysis of **2** were as follows: **1**,  $\Phi = 0.050 \pm 0.001$ , **4**,  $\Phi = 0.096 \pm 0.003$ , and 2-*tert*-butyl-3-phenylindene (**5**),  $\Phi = 0.023 \pm 0.002$ . **1** (3.8%), **2** (19%), and **4** (40%) were products of nitrogen photoextrusion from **13**, and similar results were obtained from the sodium salt **12** of tosylhydrazone **11**. Flash vacuum pyrolysis (FVP) of **2** at 400 °C produced **4** (76%) and 3-*tert*-butyl-1-phenylindene (**15**) (24%). FVP of **4** also gave **15** (26%) and recovered **4** (74%). Allene **1** was recovered in 98% yield after FVP (400 °C). Deuterium labeling of photoproducts was determined for 4,4-dimethyl-1,1-diphenyl-1,2-pentadiene-3-*d*<sub>1</sub> (**1-d**<sub>1</sub>); a  $\Phi_H/\Phi_D(3) = 3.07$  suggests that the second 1,2-H shift is rate determining as opposed to the small  $\Phi_H/\Phi_D$  of 1.36 for total products, **2** + **3** + **4**, implicating only a low excited-state barrier in the first step. KIEs are derived. Funneling from the singlet excited state to the ground state is suggested for formation of **1** in photolyses of **2**. Discrete ground-state vinylmethylenes adequately account for thermolysis products. Alternative mechanisms are discussed.

The photoisomerization of allene to cyclopropene and methyllacetylene was first reported for direct photolyses conducted at 8 K with matrix isolation techniques.<sup>1</sup> We subsequently reported<sup>2</sup> that conventional solution-phase conditions can be used to effect

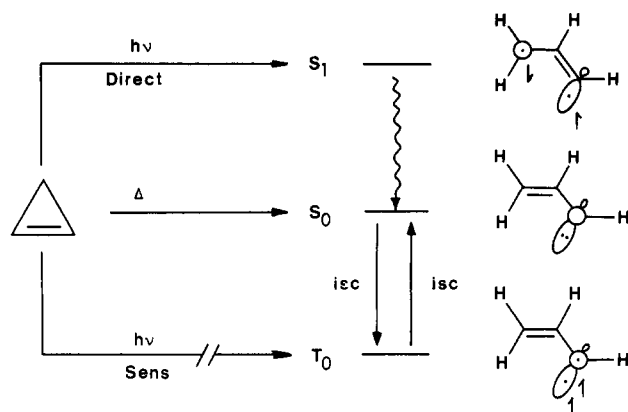
comparable photorearrangements of 1,1-diphenylallenes in good yield provided a bulky substituent, i.e., a *tert*-butyl group, is present at C<sub>3</sub>. Otherwise, lower temperatures (−10 °C) have proven effective in suppressing competing dimerization in the case of triphenyl- and tetraphenylallene.<sup>3</sup> The generality of allene  $C_3H_4$

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Scheme I. Specific Generation of Vinylmethylene Electronic States from Cyclopropenes



photochemistry has now been established by recent extensions encompassing the far-UV (185 nm) photochemistry of vinylidenecycloalkanes<sup>4,5</sup> as well as cyclic allenes, e.g., 1,2-cyclononadiene ( $\lambda > 220$  nm).<sup>6</sup>

A stepwise mechanism whereby hydrogen migrates to the central allenic carbon followed by either cyclization or a second consecutive 1,2-H shift from a vinylmethylene intermediate accounts for the gross features of allene isomerizations. However, inconsistencies are encountered when comparisons are made to more established methods for vinylmethylene generation. The isomeric alkyne products of phenylallenes are generally absent in photorearrangements of phenylcyclopropenes<sup>2-4,7,8</sup> or nitrogen photoextrusion processes of structurally related tosylhydrazone sodium salts<sup>2-4</sup> or 3*H*-pyrazoles.<sup>2,4,9</sup> The difference is not attributable to an inherent inability of vinylmethylenes deriving from cyclopropenes to undergo 1,2-H shifts since methylacetylenes are in fact major products of thermolyses and photolyses of a number of simple alkyl-substituted cyclopropenes.<sup>10-12</sup>

Vinylmethylene intermediates differing in electronic structure and geometry can be invoked to reconcile differences between allene and cyclopropene photochemistry.<sup>2,4</sup> At least three species, denoted  $T_0$ ,  $S_0$ , and  $S_1$  in Scheme I, merit consideration, although some simplification is achieved if the triplet species,  $T_0$ , is assumed to require intersystem crossing<sup>13</sup> to the lowest singlet state, the closed-shell carbene denoted  $S_0$ , as a prerequisite to intramolecular rearrangement.<sup>14</sup> Scheme I which summarizes the theoretical

relationships of vinylmethylenes to cyclopropene<sup>15</sup> is based on calculations of potential surfaces for ring opening.<sup>16,17</sup> Vinylmethylene  $S_1$ - $S_0$  radiationless decay has experimental significance in regioselective photoisomerization of phenyl-substituted spirocyclopropenes,<sup>7b</sup> and an  $S_1$  species has recently been proposed to account for the apparent state selective photochemistry of spiro[2.4]hept-1-ene.<sup>12</sup> Additional evidence can be cited for participation of higher carbene excited states in direct photolyses of alkyl-substituted diazoalkenes<sup>18</sup> and diazoalkanes.<sup>19</sup> The carbene mechanism for  $C_3H_4$  interconversions assumes greater complexity if not only anti (as depicted in Scheme I) but also syn forms<sup>17</sup> (stereochemistry with respect to inversion at the divalent carbon) of vinylmethylene are included as possible intermediates.

We now report in full on the photoisomerization exhibited by 4,4-dimethyl-1,1-diphenyl-1,2-pentadiene (**1**) and the  $C_3$  deuterated derivative **1-*d*<sub>1</sub>**. Deuterium labeling results and primary isotope effects were found to be consistent with intramolecular rearrangement by a carbene mechanism. Mechanistic alternatives are discussed. Evidence for state selective reactivity of  $S_0$  and  $S_1$  vinylmethylenes was obtained by comparing photolyses and flash vacuum pyrolyses of 1-*tert*-butyl-3,3-diphenylcyclopropene (**2**), and additional comparisons were made to independent generation of vinylmethylenes through nitrogen photoextrusion from 3-*tert*-butyl-5,5-diphenyl-3*H*-pyrazole (**13**) and the tosylhydrazone sodium salt **12** of 2,2-dimethyl-5,5-diphenyl-4-penten-3-one. Differences in product distributions of **1**, **2**, and **13** are discussed in the context of correlation diagrams.

## Results

**Synthesis of 4,4-Dimethyl-1,1-diphenyl-1,2-pentadiene (1) and  $C_3$ -Deuterated Derivative 1-*d*<sub>1</sub>.** Deprotonation of 4,4-dimethyl-1,1-diphenyl-2-pentyne (**3**) using 1 equiv of *n*-butyllithium in THF at  $-5^\circ\text{C}$  produced a red-colored solution from which **1** was isolated after acidification with glacial acetic acid at  $-78^\circ\text{C}$ . Use of either conventional silica gel column chromatography or medium pressure liquid chromatography (MPLC) effected separation of the small amount (3.3%) of unreacted alkyne **3** to give allene **1** in 68% yield. The regioselectivity observed in the protonation step was typical of the reported behavior exhibited by hard electrophiles toward other mesomeric 1,1-diphenyl-2-butynyl anions.<sup>20</sup> Substitution of acetic acid-*d*<sub>1</sub> (98 atom % D) in the above acidification step gave  $C_3$ -labeled allene **1-*d*<sub>1</sub>** with deuterium incorporation in excess of 95% according to  $^1\text{H}$  NMR and MS analysis.

**Preparative Scale Photolyses of Allenes 1 and 1-*d*<sub>1</sub>.** Direct photolyses of  $10^{-2}$  M solutions of **1** in deoxygenated *tert*-butyl alcohol using a Vycor-filtered 450-W medium pressure mercury lamp gave 1-*tert*-butyl-3,3-diphenylcyclopropene (**2**), alkyne **3**, 1-*tert*-butyl-3-phenylindene (**4**), and 2-*tert*-butyl-3-phenylindene (**5**) at 75% conversion (eq 1). Cyclopropene **2** and alkyne **3** were isolated in pure form by column chromatography and identified by comparing spectral data and reverse-phase HPLC retention times to authentic samples. Since indenenes **4** and **5** could not be freed of **1** by preparative silica gel chromatography, a mixture of the three was characterized by comparing  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectral data in addition to GC and reverse-phase HPLC retention

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(15) The correlations of states depicted follow the discussion of ref 7a and 16a.

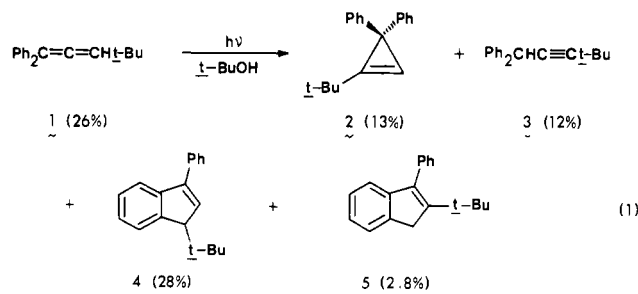
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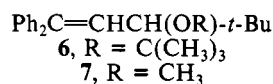
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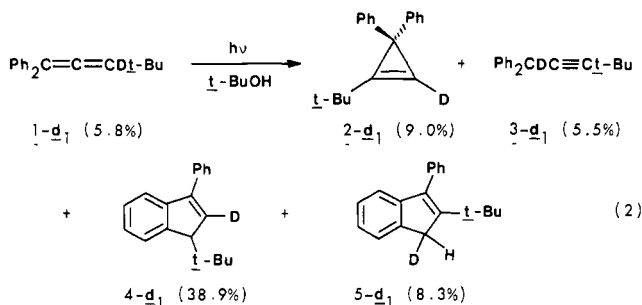
(20) Grovenstein, E.; Chui, K.-W.; Bhalchandra, B. P. *J. Am. Chem. Soc.* **1980**, *102*, 5848.



times to authentic samples. The <sup>1</sup>H NMR spectrum showed **1** + **4** + **5** present in a 9.3:10.0:1.0 ratio in agreement with a parallel GC assay. Polar material, stripped from the chromatographic column with diethyl ether, accounted for the remaining weight percent mass balance. There was no evidence in <sup>1</sup>H NMR spectra of the crude photolysate or chromatographic fractions of formation of allylic ether **6** from trapping of a potential zwitterionic allene excited state<sup>21</sup> or a vinylmethylene species.<sup>8</sup> Photolyses of **1** were also conducted in methanol. Once again there was no indication that an ether, in this case **7**, was formed, and product yields were similar to runs conducted in *tert*-butyl alcohol as the solvent (Experimental Section).

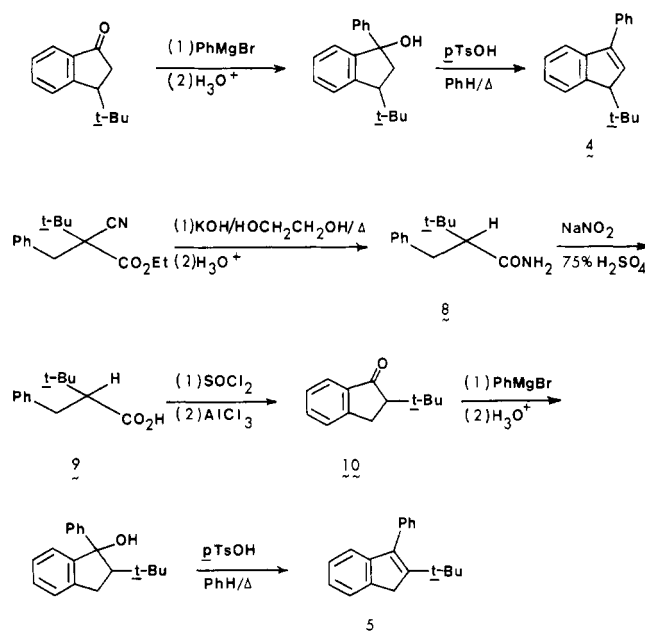


The deuterium labeling results and product yields for direct photolyses of **1-d<sub>1</sub>** are summarized in eq 2 and described in detail in the Experimental Section. The complete absence of detectable



peaks in <sup>1</sup>H NMR spectra corresponding to the C<sub>2</sub> olefinic proton of **2** (δ 6.74), and in the case of **3** the C<sub>1</sub> methine proton (δ 4.83), was the basis for the labeling assignments. <sup>1</sup>H NMR analysis of the mixture of **1-d<sub>1</sub>** + **4-d<sub>1</sub>** + **5-d<sub>1</sub>** obtained after direct phase medium pressure liquid chromatographic separation of **2** and **3** clearly indicated exclusive (>95%) labeling of the olefinic position of **1** (δ 5.58) and **4** (δ 6.45). Additional evidence for C<sub>2</sub> deuteration of **4-d<sub>1</sub>** was the disappearance at δ 3.27 (C<sub>1</sub> methine) of the usual 2-Hz allylic coupling observed with unlabeled **4**. The methylene position of **5-d<sub>1</sub>** was labeled by one deuterium as shown by <sup>1</sup>H NMR integration relative to the well-resolved signal of the *tert*-butyl group. In addition to <sup>1</sup>H NMR analysis, GC-MS analysis of each of the above chromatographic fractions confirmed that no exchange of deuterium had occurred in unreacted **1** or in products **2**-**5**.

The multiplicity of the excited state involved in the photoisomerization of **1** was established as the singlet. Sensitized photolysis using *m*-methoxyacetophenone (*E*<sub>T</sub> = 72.5 kcal mol<sup>-1</sup>)<sup>22</sup> failed to give products **2**-**5**, and 98% of the allene **1** reactant was recovered by column chromatography. In contrast, benzophenone or *m*-methoxyacetophenone sensitization of a less hindered allene, 1,1-diphenyl-1,2-hexadiene,<sup>2</sup> led to formation of polar products and low recoveries of the allene possibly as a result of oligomerization.<sup>23</sup> Such a process might be less important if a bulky

Scheme II. Independent Synthesis of Indenes **4** and **5**

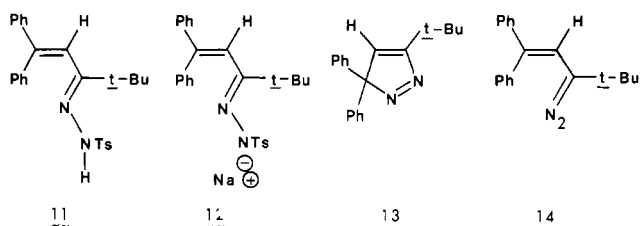
**Table I.** Product Yields from Direct Irradiations of Tosylhydrazone Sodium Salt **12**, 3*H*-Pyrazole **13**, and Cyclopropene **2**

| reactant                           | yield, % |                 |   |    |     | conversion, % |
|------------------------------------|----------|-----------------|---|----|-----|---------------|
|                                    | 1        | 2               | 3 | 4  | 5   |               |
| <b>12</b>                          | 3.6      | 19              | 0 | 32 | 0   | 100           |
| 3 <i>H</i> -pyrazole <b>13</b>     | 3.8      | 19              | 0 | 40 | 0   | 100           |
| cyclopropene <b>2</b> <sup>a</sup> | 6.5      | 39 <sup>b</sup> | 0 | 21 | 3.9 | 61            |

<sup>a</sup>Vycor sample tube and Rayonet photolysis apparatus (254 nm) used. <sup>b</sup>Recovered reactant.

terminal substituent is present as with **1**.

**Product Structure Proofs.** Independent syntheses of indenenes **4** and **5** are outlined in Scheme II. Alkyne **3** was prepared in 58% yield from reaction of the magnesium acetylide of *tert*-butylacetylene with bromodiphenylmethane in THF (Experimental Section). Photoextrusion of nitrogen from either the sodium salt **12** of tosylhydrazone **11** or 3-*tert*-butyl-5,5-diphenyl-3*H*-pyrazole (**13**) followed by chromatographic separation of allene **1** and indene **4**, which also were products, gave preparatively practical yields of cyclopropene **2** (Table I). The photoextrusion reactions were studied further to assess the potential role of vinylmethylene intermediates in allene **1** photoisomerizations and cyclopropene **2** rearrangements.



**Independent Generation of Potential Intermediates in Allene **1** Photoisomerizations.** Tosylhydrazone sodium salt **12**, prepared by stirring **11** and sodium methoxide in THF under nitrogen overnight<sup>24</sup> in an immersion-well photolysis apparatus, was irradiated through a uranium glass filter sleeve (λ > 330 nm) to prevent secondary photolysis of the products. The methodology used to separate and characterize the products is described above for allene **1** photolyses, and the yields are summarized in Table I. Most striking was the absence of alkyne **3** and the unexpected formation of allene **1**. The possibility that alkoxide base had catalyzed the isomerization of **3** as it formed to give allene **1** as

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**Table II.** Quantum Yields for Direct Photolyses of Allenes **1** and **1-d<sub>1</sub>** and Cyclopropene **2**

| reactant                             | $\Phi$ , products |                     |                     |                     |                   | conversion, % |
|--------------------------------------|-------------------|---------------------|---------------------|---------------------|-------------------|---------------|
|                                      | 1                 | 2                   | 3                   | 4                   | 5                 |               |
| <b>1<sup>a</sup></b>                 |                   | 0.0087 $\pm$ 0.0017 | 0.0046 $\pm$ 0.0006 | 0.0112 $\pm$ 0.0014 | 0                 | 1.6–4.0       |
| <b>1-d<sub>1</sub><sup>a,b</sup></b> |                   | 0.0072 $\pm$ 0.0015 | 0.0015 $\pm$ 0.0007 | 0.0093 $\pm$ 0.0019 | 0                 | 0.91–3.0      |
| <b>2<sup>c</sup></b>                 | 0.050 $\pm$ 0.001 |                     | 0                   | 0.096 $\pm$ 0.003   | 0.023 $\pm$ 0.002 | 2.5–3.6       |

<sup>a</sup> Error limits are standard deviations for seven independent runs for each reactant and represent error in HPLC assay. <sup>b</sup> Products are mono-deuterated (eq 2). <sup>c</sup> Two independent runs.

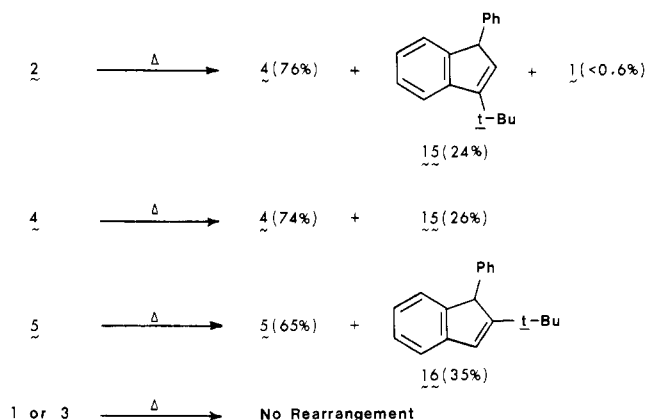
the observed product<sup>25</sup> was considered but ruled out when reinvestigation<sup>9</sup> of the base-free method of photoextrusion, direct photolysis of 3*H*-pyrazole **13** in cyclohexane ( $\lambda > 330$  nm), was found to give comparable yields of the same products as **12** (Table I).

The results for direct photolysis of 10<sup>-3</sup> M solutions of cyclopropene **2** in pentane qualitatively resembled photolyses of **12** and **13** (Table I). Significantly, alkyne **3** was not formed unless conversions exceeded 80% in which case secondary photolysis of allene **1** probably occurred.

Of fundamental importance was whether reactivity of ground state  $S_0$  and excited state  $S_1$  vinylmethylenes (Scheme I) differed. The stepwise<sup>26</sup> two-photon nitrogen photoextrusion from **13** (Table I) was considered a potential example of the latter. Our attempts to generate  $S_0$  carbenes from photochemical ring opening of 3*H*-pyrazole **13** followed by thermolysis<sup>26</sup> rather than photolysis to extrude nitrogen from **14** were foiled by secondary photolysis of the diazoalkene despite the use of filtered light. By following the progress of the photolysis of **13** by UV, a weak diazoalkene band at 510 nm and a short-wavelength absorption which partially obscured the 366 nm  $n \rightarrow \pi^*$  band of **13** were observed at an early stage. These new absorptions were stable at -71 °C in the dark but decreased in intensity on continued photolysis. Product ratios of -71 °C photolyses of **13** did not differ significantly from those reported in Table I (Experimental Section). A second approach for generating the ground state carbene of interest, pyrolysis of the tosylhydrazone sodium salt **12**, gave instead 3*H*-pyrazole **13** in >80% yield.

Quantum yields of disappearance of 3*H*-pyrazole **13** were modest ( $\Phi = 0.32$ ) even though thermal reversion of **14** to **13** potentially<sup>26a</sup> competes with photochemical nitrogen loss in the second step. Quantum yields for product formation were as follows: cyclopropene **2**,  $\Phi = 0.12$ ; indene **4**,  $\Phi = 0.17$ ; allene **1**,  $\Phi = 0.020$ . The triplet sensitized photolysis of **13** was also studied. Benzophenone was unsuitable as a sensitizer due to competitive absorption of light by **13**, so *m*-methoxyacetophenone was used instead. The inefficient sensitized reaction<sup>27</sup> that was observed ( $\Phi = 0.017$ ) might have resulted from residual absorption of light by **13** or singlet energy transfer.

The difficulties encountered above were circumvented by turning to thermal ring opening of cyclopropenes as a route to  $S_0$  vinylmethylenes (Scheme III). Flash vacuum pyrolysis (FVP) of cyclopropene **2** produced indene **4** and an additional product, 3-*tert*-butyl-1-phenylindene (**15**), the structure of which was assigned by comparing <sup>1</sup>H NMR and GC retention times to an authentic sample. Neither alkyne **3** nor indene **5** were detected in the product mixture by GC analysis, and the yield of allene **1**, as an upper limit, was found to be at least tenfold less than the 6.5% formed on photolysis of **2** (Table I). A control run established that the lack of significant amounts of **1** in thermolyses was not due to decomposition or isomerization to **4** and/or **15**; allene **1** was recovered completely unchanged in essentially quantitative yield (98%). A control run with alkyne **3** resulted in 81.7% recovered **3**. An additional 9.5% of the material was accounted for by a yellow residue which formed during volatilization of the sample. Indene **15** was thought to be a product of further re-

**Scheme III.** Flash Vacuum Pyrolysis of Cyclopropene **2**, Indenes **4** and **5**, Allene **1**, and Alkyne **3** at 400 °C (1 mm Nitrogen Flow)

arrangement of indene **4** since product distributions from FVP of both **2** and **4** were practically identical. Pyrolysis of indene **5** led to still another indene, **16**, which was also found in 15% yield with **5** (85%) when the latter indene was heated with triethylamine in pyridine. The indene thermal isomerizations have a close analogy in the work of Almy and Cram<sup>28a</sup> and most likely involve C<sub>1</sub>-C<sub>2</sub> and C<sub>2</sub>-C<sub>3</sub> 1,5-H migrations through an isoidene intermediate. A number of examples can be cited.<sup>28b-d</sup>

**Quantum Yields.** Quantum yields were determined by using a semi-micro optical bench apparatus as described previously.<sup>29a</sup> The bench was calibrated by ferrioxalate actinometry<sup>29b</sup> for the light output of the lamp (270 nm for runs in Table II) before, during, and after each run with the splitting ratio technique (Experimental Section).<sup>29a</sup> The results for allenes **1** and **1-d<sub>1</sub>** as well as cyclopropene **2** are reported in Table II. In the case of allenes **1** and **1-d<sub>1</sub>** care was taken to ensure that the quantum yields were representative of primary photochemistry, particularly in view of the high efficiencies for photorearrangement of **2**. Thus, conversions were kept low and in the range of 1–4% since above 5–7% conversions minor indene **5** began to appear as a product, most likely from the secondary photolysis of cyclopropene **2**.

Isotope effects on product quantum yields,  $\Phi_H/\Phi_D$ , of allenes **1** and **1-d<sub>1</sub>** are as follows: cyclopropene **2**, 1.21  $\pm$  0.29; alkyne **3**, 3.07  $\pm$  0.48; indene **4**, 1.20  $\pm$  0.24.

## Discussion

**Mechanisms for Allene Photorearrangements.** In our preliminary communication a stepwise mechanism involving vinylmethylene intermediates was proposed to account for the gross features of allene photoisomerizations. This mechanism, which we denote Mech A, is summarized in Scheme IV (vide infra). Alternative mechanisms not excluded by our results are, for example, Mech B as a route to cyclopropenes<sup>30</sup> or Mech C (Hückel, four-electron, photochemically allowed<sup>31</sup>) for interconverting allene

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(26) (a) Pincock, J. A.; Mathur, N. C. *J. Org. Chem.* **1982**, *47*, 3699. (b) Arnold, D. R.; Humphreys, R. W.; Leigh, W. J.; Palmer, G. E. *J. Am. Chem. Soc.* **1976**, *98*, 6225.

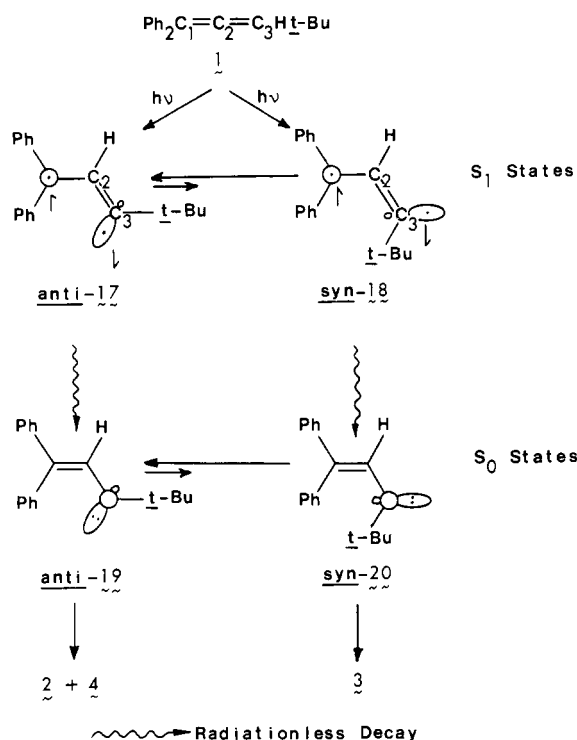
(27) Inefficient triplet-sensitized nitrogen expulsion from 3*H*-pyrazoles has precedent: Zimmerman, H. E.; Hovey, M. C. *J. Org. Chem.* **1979**, *44*, 2231.

(28) (a) Almy, J.; Cram, D. J. *J. Am. Chem. Soc.* **1970**, *92*, 4316. (b) Miller, L. L.; Boyer, R. F. *Ibid.* **1971**, *93*, 650. (c) Miller, L. L.; Greisinger, R.; Boyer, R. F. *Ibid.* **1969**, *91*, 1578. (d) Manning, C.; McClory, M. R.; McCullough, J. J. *J. Org. Chem.* **1981**, *46*, 919 and references cited therein.

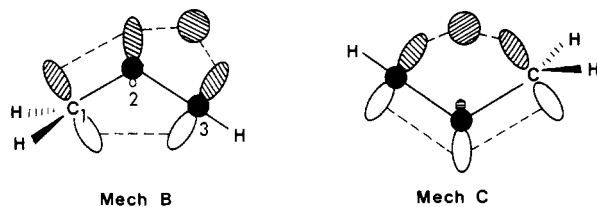
(29) (a) Zimmerman, H. E. *Mol. Photochem.* **1971**, *3*, 281. (b) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London* **1956**, *235*, 518.

(30) A bicyclic cyclopropene is the sole primary product of 1,2-cyclo-nonadiene<sup>6</sup> photochemistry whereas cyclopropenes, methylacetylenes, as well as other primary products are formed from vinylidenecycloalkanes.<sup>4,5</sup>

Scheme IV. The Vinylmethylene Mechanism (Mech A) for Allene 1 Photorearrangements



and methylacetylene. The latter [1,3] sigmatropic shift mechanism is not significantly operative in the ground state, however, as a recent deuterium labeling study has shown,<sup>32</sup> and arguments based on kinetics and thermochemical calculations as well as ab initio potential surfaces<sup>17c</sup> have been advanced supporting the intermediacy of vinylmethylenes.<sup>4,10,32,34</sup> Mech B has been suggested to account for the exclusive formation of a bicyclic cyclopropane on direct photolysis of 1,2-cyclononadiene<sup>30</sup> and may be a potential pathway to allenes from photoexcited cyclopropanes.



The key distinction between allene 1 photochemistry and independent generation is that alkyne 3 is not observed for three methods typically used for exemplifying vinylmethylene reactivity: direct photolysis of cyclopropane 2 or photoextrusion of nitrogen from structurally related 3*H*-pyrazole 13 or tosylhydrazone sodium salt 12 (Table I). Scheme IV is useful for discussing this difference in terms of a stepwise carbene mechanism.<sup>17d</sup> Here a dual stereochemical outcome for allene 1 photochemical 1,2-hydrogen migration leading to *anti*-vinylmethylenes 17 and 19 as well as *syn* isomers 18 and 20 is shown, as opposed to the initial anti selectivity for cyclopropane ring opening expected on the basis of theoretical calculations.<sup>16,17a</sup> In the second step of allene photorearrangement a *syn* precursor to 3 seems most reasonable since within the *anti* manifold hydrogen migration forming alkyne would have to compete with cyclization to 2 and 4.

The importance of cyclization processes in reactivity involving ring opening of cyclopropanes is especially apparent in the case of thermolyses (Scheme III) and photolyses (Table I) of 2. To

account for the absence of 3 within the context of Scheme IV, a necessary condition is that the relative rate of *anti*-19 to *syn*-vinylmethylene 20 must be slower than the rates of cyclization of 19 to 2 and 4. By assuming a difference in rates of >100-fold, we estimate a relative  $E_{\text{act}}$  for the two processes of >2 kcal mol<sup>-1</sup>.  $S_0$  *anti*-vinylmethylene 19 is a reasonable precursor to indene 4 in thermolyses. It is also plausible that  $S_1$ -17 is formed initially from photoexcited 2, although a radiationless decay pathway, i.e., an avoided crossing,<sup>16a</sup> is available for the "incipient"<sup>7a</sup> ring-opened 1,3-diradicaloid species to revert to 2 or form  $S_0$ -19. Nonetheless, there is evidence that  $S_1$  vinylmethylenes are initially formed photochemically and undergo reclosure to cyclopropanes at a faster rate than internal conversion to the  $S_0$  carbene.<sup>7b</sup> Analogous pathways from  $S_1$ -17 would lead to 2 and possibly 4. It thus seems unlikely that any of vinylmethylenes within the *anti* manifold are penultimate precursors to alkyne 3 in allene 1 photochemistry. To our knowledge there is no report of an alkyne being observed as a product of ground or excited state rearrangement of a  $C_3$ -substituted phenyl-, vinyl-, or acyl-substituted cyclopropane; in each case the typical outcome is respectively cyclization to indenenes, cyclopentadienes, or furans along with minor amounts of allenes<sup>3-5,7,8</sup> in the photochemical rearrangements.

Ab initio calculations using the GVB/CI method<sup>17a</sup> indicate the following barriers for in-plane  $C_2$ - $C_3$ -H bending converting *anti*- to *syn*-vinylmethylenes:  $S_0$  state, 18 kcal mol<sup>-1</sup>;  $S_1$  state, 1.6 kcal mol<sup>-1</sup>;  $T_0$  state, 8.8 kcal mol<sup>-1</sup>. The calculations suggest that barriers to *syn*-*anti* interconversion in  $T_0$ ,<sup>35</sup>  $S_0$ , and  $S_1$  are at least plausible, but only a limited range of geometries have been considered, and a complete description of  $S_0$ ,  $S_1$ , and  $S_2$  surfaces at critical intermediate geometries between bent and linear forms of vinylmethylene is unavailable by ab initio or semiempirical methods. This is especially important since the crossing of  $S_0$  and  $S_2$  should be avoided in this region.<sup>36</sup> At present, our results are qualitatively accommodated by the schematic diagram of phenylmethylene states proposed some time ago by Hoffmann, Zeiss, and Van Dine;<sup>36</sup> the parallel between vinylmethylene and phenylmethylene potential surfaces was noted at that time. There is the additional question as to whether the actual reaction coordinate should be a composite of in- and out-of-plane bending as shown by an EH contour diagram<sup>36</sup> of the  $S_0$  surface in which case the  $S_0$  barrier to *syn*-*anti* interconversion could be as little as 1.8 kcal mol<sup>-1</sup>. Extensive mixing of  $S_1$  and  $S_0$  configurations has been noted<sup>37</sup> for out-of-plane motion, so it is premature to draw a quantitative conclusion as to the barrier height. Although it may become necessary to postulate precursors to 3 other than  $S_0$ -20, kinetic isotope effects (vide infra), which suggest that the second step of the allene photorearrangement to 3 is rate determining, are best accommodated by discrete intermediates such as 20. Equilibration of 20 to  $S_1$ -19 followed by 1,2-H shift to 3 would also be possible, depending on the magnitude of the  $S_0$ - $S_1$  gap, and would provide an electronic reason for hydrogen to migrate. The STO-3G/CI<sup>16a</sup> and MINDO/3<sup>16b</sup> calculated gap for unsubstituted vinylmethylene is 23 and 13 kcal mol<sup>-1</sup>, respectively, but only 2-3 kcal mol<sup>-1</sup> according to ab initio GVB/CI and STO-3G/CI calculations at MCSCF optimized geometries. However, we note that the use of unsubstituted vinylmethylenes is questionable here since the magnitude of the gap may vary with substitution.

**Mechanisms for Cyclopropane Rearrangements.** In Scheme V we propose mechanistic relationships to account for differences between cyclopropane 2 ground and excited state chemistry as well as to accommodate similarities in photochemical product distributions (Table I) of 2, 11, and 13. Since thermolyses of 2 do not yield significant amounts of 1, the allene is suggested as deriving from a singlet excited state precursor (vide infra). We

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(32) Hopf, H.; Priebe, H.; Walsh, R. J. *Am. Chem. Soc.* **1980**, *102*, 1210.

(33) York, E. J.; Dittmar, W.; Stevenson, J. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1973**, *95*, 5680; **1972**, *94*, 2882.

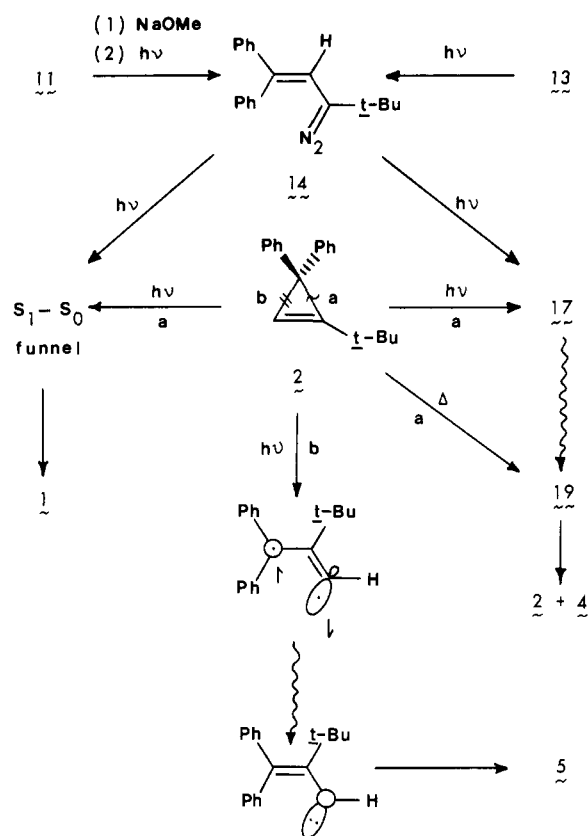
(34) Gajewski, J. J. *Org. Chem.* **1981**, *44*, 21.

(35) (a) There is ESR evidence for discrete *syn*- and *anti*-vinylmethylenes in the triplet state.<sup>35b</sup> (b) Hutton, R. S.; Manion, M. L.; Roth, H. D.; Wasserman, E. *J. Am. Chem. Soc.* **1974**, *96*, 4680.

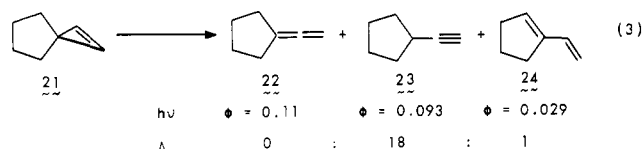
(36) Hoffmann, R.; Zeiss, G. D.; Van Dine, G. W. *J. Am. Chem. Soc.* **1968**, *90*, 1485.

(37) Mixing of  $S_0$  and  $S_1$  states has been noted for out-of-plane hydrogen motion in ref 17b, footnote 20.

Scheme V. Independent Generation of Vinylmethylenes



note that the apparent state selective reactivity of **2** is analogous to the differing ground and excited state reactivity observed with spirocyclopropane **21** (eq 3).<sup>12</sup> Here allene **22** was the major



product on direct photolysis at 185 nm whereas thermolysis led primarily to alkyne **23** as well as **24**, a minor product. The formation of **23** in the thermolyses is not unusual in this case, since the formation of alkynes is well preceded in ground state rearrangements of simple alkyl-substituted cyclopropanes. The simplest interpretation of this result is that  $S_0$  vinylmethylenes can undergo 1,2-H migration when competing cyclization pathways other than reclosure are unavailable. To account for the photochemical preference for allene **22**, we suggested that the initially formed ring-opened vinylmethylene species has access via radiationless decay to a maximum on the ground state surface corresponding to the transition state for the least favorable thermal rearrangement pathway, that which offers the closest approach to  $S_1$ . Such a rationale when applied to cyclopropane **2** would imply that  $S_1$  vinylmethylene **17** would be the penultimate precursor to allene **1**, but this would seem to require a large  $S_1$ - $S_0$ -**19** energy gap.

Perhaps more likely is a mechanism for cyclopropane excited state rearrangement to **1** which would entail funneling to the ground state at a critical geometry. This critical geometry is more likely to approximate that of a transition state for vinylmethylene rearrangement to **1** than that of valence structure **17**. Thus, structure **17** might more appropriately be considered a minimum on the excited state surface from which internal conversion to **19** can occur. Although the apparent state selective behavior of **2** or **21** is most simply interpreted in terms of the relatively large STO-3G/CI or MINDO/3 calculated energy difference between the  $S_1$  and  $S_0$  electronic states of vinylmethylene, the smaller  $S_1$ - $S_0$

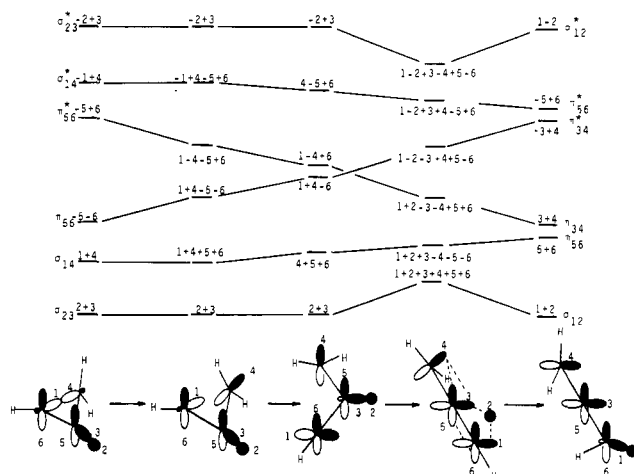


Figure 1. MO correlation diagram transforming cyclopropane to allene.

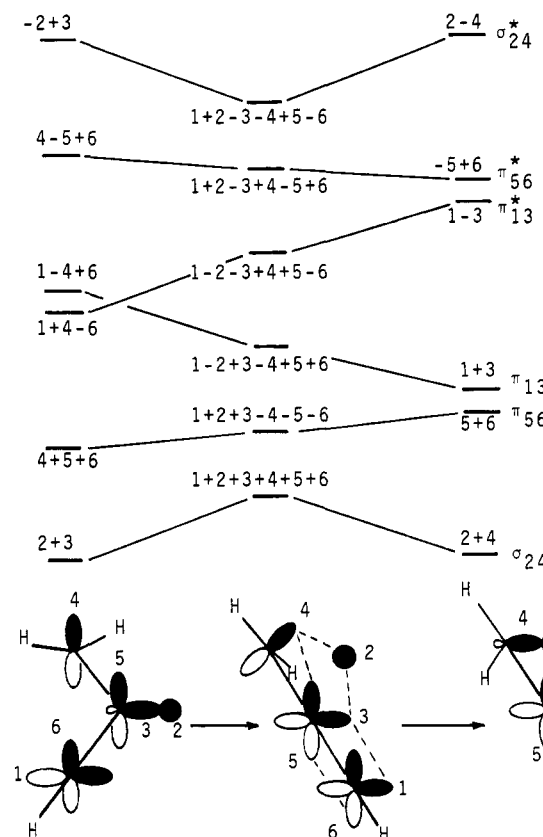
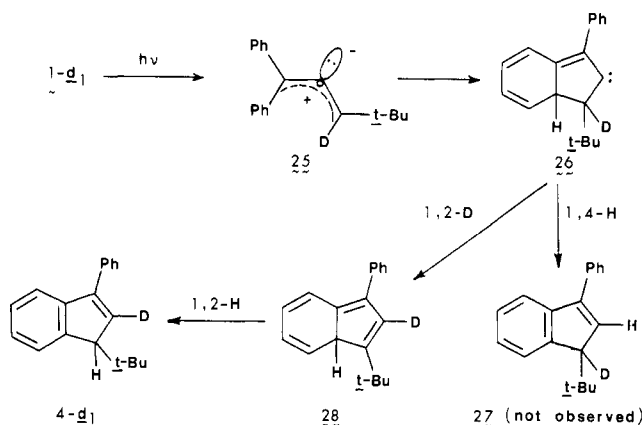


Figure 2. MO correlation diagram for the second half-reaction of the cyclopropane to 1-propyne transformation.

gap of GVB and STO-3G MCSCF geometry optimized calculations with CI<sup>17</sup> can also be accommodated if the funnel leading to **1** is not accessible from **17**.

A funneling mechanism for photorearrangement of **2** to **1** would be consistent with the orbital array depicted as Mech B (vide supra). A related application of Mech B to a cyclopropane photorearrangement would involve  $C_2$ - $C_1$  1,2-H shift to 1-propyne instead of  $C_2$ - $C_3$  1,2-H shift giving allene. If 1,2-H migration is delayed and  $C_1$  rotation is permitted, then correlation diagrams (Figures 1 and 2) can be constructed by using Zimmerman's MO following method.<sup>38</sup> An element of concertedness is implied for the overall photorearrangement which means that the ring-opened  $S_1$  species at half-reaction would be converted as it is formed to a point on the ground state surface leading to the allene. Since there is no obvious difference between Figures 1 and 2 that would

(38) Zimmerman, H. E. *Acc. Chem. Res.* **1972**, 5, 393.

Scheme VI. Hypothetical Zwitterionic Mechanism for Photoisomerization of Allene 1-d<sub>1</sub> to Indene 4-d<sub>1</sub>

favor allene **1** over alkyne **3** as potential photoproducts of **2**, the controlling factor might be the relative proximity to S<sub>1</sub> of maxima corresponding to transition states for ground state rearrangements of **19** to the alkyne and the allene. If the latter S<sub>0</sub> pathway is more energy demanding as with **21**,<sup>12</sup> then the S<sub>1</sub>-S<sub>0</sub> surface jump to the allene potential surface would be favored.

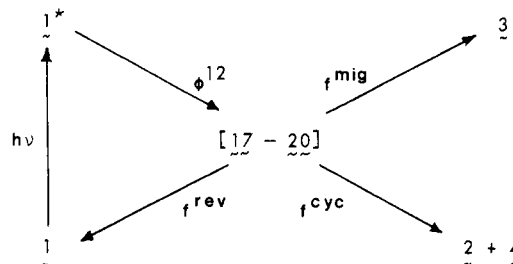
A second controversial point concerns the aspect of a common mechanism for the nitrogen photoextrusion and cyclopropene photochemistry (Scheme V). Electronically excited carbenes have previously been invoked to account for state selective reactivity observed when direct photolyses are compared to thermolyses of simple alkyl-substituted diazoalkanes and diazoalkenes.<sup>18,19</sup> Of relevance to the former is an ab initio calculation which shows initial generation of S<sub>1</sub> methylene for singlet excited state loss of nitrogen from diazomethane.<sup>39</sup> However, product distributions of nitrogen photoextrusion and cyclopropene photochemistry have been known to differ.<sup>40</sup> An element of concertedness in the cyclopropene **2** to allene **1** photorearrangement (Figure 1) would seem to account for the smaller 3:1 (Table I) or 2:1 (Table II) ratio of indene **4**:allene **1** than the 8–10:1 ratio observed in the case of **12** or **13** (Table I) photochemistry.

**Deuterium Labeling.** The exclusive (>95%) labeling of 2-d<sub>1</sub>-4-d<sub>1</sub> photoproducts of allene 1-d<sub>1</sub> at the positions indicated (eq 2) in addition to the complete retention of deuterium in recovered allene 1-d<sub>1</sub> mitigates against significant involvement of bimolecular pathways that might exchange hydrogen for deuterium, e.g., adventitious base catalyzed isomerization of **1** to alkyne **3**. We also considered the possibility that indene **4** derived from cyclization (Scheme VI) of a bent, planar, zwitterionic allene excited state, i.e., **25**,<sup>42,41,42</sup> However, the mechanism in Scheme VI does not account for the observed deuterium labeling at C<sub>2</sub> of 4-d<sub>1</sub> if 1,4-H migration restoring aromaticity is strongly preferred to 1,2-D shift which results in isoindene **28**.

The position labeled with deuterium in each of 2-d<sub>1</sub> and 4-d<sub>1</sub> requires a 1,2-D shift at some stage in the photorearrangement

of 1-d<sub>1</sub> with the source of the proton at C<sub>1</sub> of 4-d<sub>1</sub> being a phenyl group of the allene. Scheme IV adequately accounts for the labeling of cyclic products. Either Mech C (vide supra) or two consecutive 1,2-D shifts (Mech A) account for the C<sub>1</sub> deuterium labeling of alkyne 3-d<sub>1</sub>.

**Deuterium Isotope Effects.** Given the Scheme IV mechanism for allene **1** photoisomerizations, each of products 2–4 would have, in principle, a common photochemical 1,2-hydrogen migration pathway which leads to vinylmethylenes as intermediates as shown below. Deuterium isotope effects on product quantum yields can then be dissected into kinetic isotope effects (KIE) for partitioning of the intermediates among final products. This is primarily of



interest in the case of **3** where a large isotope effect on the quantum yield was observed; the  $k_H/k_D$  corresponding to the 1,2-H(D) shift in the second step can be obtained from the product quantum yields by using eq 4 if the secondary isotope effect on the rate of cyclization of a vinylmethylene to cyclopropene **2** and indene **4** is small. The data of Table II yield  $k_H(3)/k_D(3-d_1) = 2.6$ . Essentially the same value within experimental error is obtained if cyclization efficiencies for **2** or **4** instead of the sum is used in the ratio expression.

$$\frac{\Phi_H(3)/[\Phi_H(2) + \Phi_H(4)]}{\Phi_D(3-d_1)/[\Phi_D(2-d_1) + \Phi_D(4-d_1)]} = \frac{k_H(3)/[k_H(2) + k_H(4)]}{k_D(3-d_1)/[k_D(2-d_1) + k_D(4-d_1)]} \quad (4)$$

The KIE for **3** is consistent with involvement of a discrete intermediate such as *syn*-**20** (Scheme IV) undergoing 1,2-hydrogen migration via an unsymmetrical, highly bent transition state.<sup>43</sup> Choosing a precise model for comparison to the present example is difficult. Our KIE is significantly higher than the  $k_H/k_D$  of 1.2–1.5 for carbene 1,2-H shifts forming 2-methylstyrenes, a value consistent with a low or zero barrier to migration,<sup>44a</sup> yet lower than the KIE for 1,5-H migration of cyclopentadiene (5.75 at 27 °C),<sup>44b</sup> via a symmetrical transition state. The KIE is comparable to that (2.7–2.9) determined for isoindene to indene isomerizations.<sup>28a</sup>

$$\frac{\Phi_H^{cyc}}{\Phi_D^{cyc}} = \frac{\Phi_H^{12} f_H^{cyc}}{\Phi_D^{12} f_D^{cyc}} \quad (5)$$

An inverse isotope effect on the efficiency for total cyclization,  $\Phi_H^{cyc}/\Phi_D^{cyc}$ , would be expected since the KIE for **3** implies a re-partitioning of vinylmethylene intermediates to increase the fraction,  $f^{cyc}$ , of cyclization products of **2** + **4**. It is not surprising that the magnitude of the effect lies within the bounds of our experimental error as  $f_H^{cyc}/f_D^{cyc} < 1$  would likely be counterbalanced by the isotope effect on the efficiency,  $\Phi^{12}$ , for 1,2-H(D) shift from singlet excited **1** (eq 5). Interestingly, if the extent of reversion of the intermediates to allene is simply neglected, then the isotope effect on the ratio of quantum efficiencies for formation of all products yields  $\Phi_H^{tot}/\Phi_D^{tot} = \Phi_H^{12}/\Phi_D^{12} = 1.36$ . Obtaining the corresponding excited state KIE in this case requires determining the isotope effect on total rate of radiationless decay of the allene

(39) (a) A correlation diagram depicting the behavior of the singly excited <sup>1</sup>B<sub>1</sub> state of diazomethane is given for the linear pathway for nitrogen extrusion in ref 39b. For the thermally allowed<sup>39c</sup> nonlinear mode details are not provided for the singly excited state, and only the doubly excited singlet and the ground state potential surfaces are shown.<sup>39d</sup> (b) Lievin, J.; Verhaegen, G. *Theor. Chim. Acta* **1976**, *42*, 47. (c) Woodward, R. B.; Hoffman, R. "The Conservation of Orbital Symmetry"; Verlag Chemie, Academic Press, Inc.: Weinheim, Germany, 1970; p 152. (d) Lievin, J.; Verhaegen, G. *Theor. Chim. Acta* **1977**, *45*, 269. (e) For further discussion, see 25a.

(40) (a) For example, direct photolysis of 1,2-diphenyl-3,3-dimethylcyclopropene affords isomeric 1,3-dienes<sup>40b</sup> whereas photolysis or thermolysis of the related diazoalkene gives the aforementioned cyclopropene to the exclusion of 1,3-dienes.<sup>40b-d</sup> A plausible rationale to account for the difference is given in ref 4, p 93. (b) Pincock, J. A.; Morchat, R. M.; Arnold, D. R. *J. Am. Chem. Soc.* **1973**, *95*, 7536. (c) Arnold, D. R.; Morchat, R. M. *Can. J. Chem.* **1977**, *55*, 393.

(41) (a) Seeger, R.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1977**, *99*, 7103.

(42) Lam, B.; Johnson, R. P. *J. Am. Chem. Soc.* **1983**, *105*, 7479.

(43) (a) Melander, L.; Saunders, W. H. "Reaction Rates of Isotope Molecules"; Wiley: New York, 1980. (b) Westheimer, F. H. *Chem. Rev.* **1961**, *61*, 265. (c) More O'Ferrall, R. A. *J. Chem. Soc.* **1970**, 785.

(44) (a) Su, D. T. T.; Thornton, E. R. *J. Am. Chem. Soc.* **1978**, *100*, 1872. (b) McLean, S.; Webster, C. J.; Rutherford, R. J. D. *Can. J. Chem.* **1969**, *47*, 1555.



singlet excited state, although it would be surprising if this were large.<sup>45</sup> Assuming then that  $\Phi_{\text{H}}^{12}/\Phi_{\text{D}}^{12}$  parallels the excited state KIE for 1,2-H shift, the value would appear to be comparable to the KIE of  $1.3 \pm 0.1$  for photochemical 1,2-H(D) shift in 1,2-cyclononadiene which was determined by an internal competition experiment in conjunction with <sup>2</sup>H NMR.<sup>46</sup> The precise magnitude of  $\Phi_{\text{H}}^{12}/\Phi_{\text{D}}^{12}$  in the present case is questionable in light of the experimental error in determining quantum yields (Table II).

The relative isotope effects on efficiencies for **3** vs. **2** or **4** are also consistent with the known angular dependence of the KIE for hydrogen transfer via a four-center vs. a three-center transition state.<sup>43</sup> Thus, alkyne **3** might be formed directly from photoexcited **1** by a 1,3-hydrogen migration pathway (Mech C) that is independent of 1,2-H shift pathways eventually leading to **2** and **4**. Significant deuterium isotope effects for singlet excited state 1,3-hydrogen migration have been noted for isopropylidene-cyclopentane.<sup>47a</sup> An analogous comparison of 1,2-H vs. 1,3-H shifts in photoisomerizations of 3,4-benzotropyliene to 2,3-benzonorcaradiene vs. 1,2-benzotropyliene is possible providing an alternative mechanism for the latter product can be ruled out.<sup>47b</sup>

## Experimental Section

Melting points were determined on a Fisher-Johns hotstage apparatus and are uncalibrated. Spectra were recorded with the following spectrometers: Varian A60 or EM360L (<sup>1</sup>H NMR), JOEL FX60Q (<sup>13</sup>C NMR), Perkin-Elmer 700 (IR), Perkin-Elmer 320 (UV).

Preparative liquid chromatographic separations were effected with 60–200 mesh silica gel (Davison, grade 62) for gravity columns. Otherwise 40–60  $\mu\text{m}$  silica gel (EM, grade 60, 230–400 mesh) was used for flash chromatography<sup>48</sup> or medium pressure liquid chromatography (MPLC) with hexane as the eluant unless noted otherwise. MPLC column A, 25 mm  $\times$  600 mm, was connected via a septum injector to a Gilson 302 pump equipped with a 100 mL/min capacity head. The preparative head was exchanged for a 5-mL/min analytical head connected to a pulse dampener and a Rheodyne 7125 injector for analytical HPLC separations. Reverse-phase column B, 4.6 mm  $\times$  25 cm, was 5  $\mu\text{m}$  Spherisorb ODS-II (Custom LC) with 75% methanol water eluant (v/v) at 0.75-mL/min flowrate unless specified otherwise. The UV detector (ISCO UA-5) was calibrated for the response of each component with a standard mixture.

Gas chromatography was performed on HP 5710A or Varian 1400 gas chromatographs equipped with flame ionization detectors and HP 3380A or HP 3390A electronic integrating recorders. Detector response was calibrated against standard mixtures. Column C was 10% QF-1 on 100/120 Supelcoport (10 ft  $\times$  1/8 in.) at 170 °C with a nitrogen carrier gas flow rate of 30 mL/min. GC-MS analyses used glass column D, 3% OV-101 on 100/120 Chrom W (6 ft  $\times$  1/8 in.), He as carrier gas (20 mL/min), and temperature programming: 115 °C (15 min), then 5 °C/min to 140 °C.

**4,4-Dimethyl-1,1-diphenyl-2-pentyne (3).** Ethyl magnesium bromide was prepared from 7.6 g (70 mmol) of bromoethane and 1.7 g (0.070 g-atom) of magnesium turnings in 50 mL of dry THF (distilled from sodium benzophenone ketyl) and then added to a solution of 3,3-dimethyl-1-butyne<sup>49</sup> (5.0 g, 61 mmol) in 50 mL of dry THF with stirring under nitrogen. After 1 h at room temperature, a gray precipitate formed on cooling in an ice bath. The mixture was brought to room temperature and two-thirds of a solution of 15 g (61 mmol) bromodiphenylmethane in 30 mL of THF was slowly added; the addition was completed while the mixture was heated to reflux. After being refluxed for 16 h, the mixture was concentrated in vacuo, and to the resultant gray solid was added 250 mL of hexane followed by suction filtration of the suspension. The filtrate was washed with water and saturated sodium chloride, dried over anhydrous magnesium sulfate, and concentrated in vacuo to obtain 8.8 g of a yellow oil which was purified by MPLC (column A). The

alkyne, obtained as a colorless oil (5.5 g, 36%), was >99% pure by GC (column C) and gave a satisfactory elemental analysis. The spectral data follow: <sup>1</sup>H NMR (CCl<sub>4</sub>)  $\delta$  7.03–7.27 (m, 10 H, arom), 4.83 (s, 1 H, methine), 1.25 (s, 9 H, *tert*-butyl); <sup>13</sup>C NMR (CDCl<sub>3</sub>) ppm 142.2, 127.9, 127.3, 126.1, 93.3, 42.9, 31.1, 27.5; IR (CHCl<sub>3</sub>) 3.24, 3.36, 3.46, 4.42, 6.04, 6.29, 6.71, 6.80, 6.90, 7.35, 7.58, 7.87, 8.51, 8.70, 9.26, 9.76, 10.0, 10.64, 10.93, 11.70, 14.49  $\mu\text{m}$ ; UV (95% ethanol)  $\lambda_{\text{max}}$  251 nm ( $\epsilon$  3630). Anal. Calcd for C<sub>19</sub>H<sub>20</sub>: C, 91.88; H, 8.12. Found: C, 91.66; H, 8.03.

**4,4-Dimethyl-1,1-diphenyl-1,2-pentadiene (1) and 4,4-Dimethyl-1,1-diphenyl-1,2-pentadiene-3-*d*<sub>1</sub> (1-*d*<sub>1</sub>).** To a solution of 8.80 g (35.5 mmol) of 4,4-dimethyl-1,1-diphenyl-2-pentyne (**3**) in 250 mL of dry THF under nitrogen was added, via syringe, 23.8 mL (36.9 mmol) of 1.55 M *n*-butyllithium in diethyl ether while maintaining the temperature at ca. –5 °C with periodic cooling with a dry ice/acetone bath. The resultant red-orange solution was then cooled to –78 °C followed by addition of 10 mL of glacial acetic acid after which the mixture was allowed to warm to room temperature. After removal of the THF in vacuo and addition of hexane, the mixture was washed with water, 10% sodium carbonate, and saturated sodium chloride, and dried over anhydrous magnesium sulfate. Distillation of the hexane in vacuo gave 6.2 g of a dark oil which was purified by MPLC (column A) to obtain 6.0 g (68%) of the allene and 0.29 g (3.3%) of recovered alkyne in a later fraction. GC assay (column C) indicated >99% pure allene. The spectral data follow: <sup>1</sup>H NMR (CCl<sub>4</sub>)  $\delta$  7.03–7.42 (m, 10 H, arom), 5.58 (s, 1 H, vinyl), 1.13 (s, 9 H, *tert*-butyl); <sup>13</sup>C NMR (CDCl<sub>3</sub>) ppm 201.9, 136.9, 127.8, 126.5, 110.7, 105.7, 33.1, 30.2; IR (CHCl<sub>3</sub>) 3.24, 3.36, 4.26, 5.15, 6.27, 6.71, 6.90, 7.37, 7.94, 8.47, 11.11, 12.20  $\mu\text{m}$ ; UV (95% ethanol)  $\lambda_{\text{max}}$  260 ( $\epsilon$  12300), 290 nm (1680). Anal. Calcd for C<sub>19</sub>H<sub>20</sub>: C, 91.88; H, 8.12. Found: C, 91.90; H, 8.04.

Deuterated allene 1-*d*<sub>1</sub> was prepared by an identical procedure, except that acetic acid-*d*<sub>1</sub> (98 atom % D) was substituted for glacial acetic acid in the acidification step. The deuterium label was incorporated at C<sub>3</sub> as shown by the absence of the olefinic proton at  $\delta$  5.58. MS indicated >95% monodeuteration.

**1-*tert*-Butyl-3-phenylindene (4).** Phenylmagnesium bromide was first prepared from 0.254 g (0.0104 g-atom) of magnesium turnings and 1.66 g (10.6 mmol) of bromobenzene in 50 mL of dry diethyl ether. This solution was then added dropwise to a solution of 2.00 g (10.6 mmol) of 3-*tert*-butyl-1-indanone<sup>50</sup> in 50 mL of ether under nitrogen with stirring. After 1 h of reflux, the mixture was poured onto iced aqueous ammonium chloride and ether extracted. The combined extracts were washed with water and saturated sodium chloride, dried over anhydrous magnesium sulfate, and concentrated in vacuo to give 2.60 g of an oil. Partial dehydration of the alcohol occurred during workup, so the residue was not purified further. A 1.0-g (3.8 mmol) portion of the crude alcohol was dissolved in 50 mL of benzene along with 0.5 g of *p*-toluenesulfonic acid and refluxed 1 h with a Dean Stark trap to remove water. The mixture was then washed with 10% sodium carbonate and saturated sodium chloride, dried over anhydrous magnesium sulfate, and concentrated in vacuo to obtain 800 mg of a yellow oil which was purified by MPLC (column A) to afford 700 mg (74.3%) of analytically pure indene. The spectral data follow: <sup>1</sup>H NMR (CCl<sub>4</sub>)  $\delta$  7.00–7.63 (m, 9 H, arom), 6.45 (d, 1 H, *J* = 2 Hz, vinyl), 3.27 (d, 1 H, *J* = 2 Hz, methine), 1.03 (s, 9 H, *tert*-butyl); <sup>13</sup>C NMR (CDCl<sub>3</sub>) ppm 146.7, 144.6, 144.4, 131.1, 134.9, 128.4, 127.7, 127.4, 126.2, 125.1, 124.4, 120.1, 59.9, 34.6, 28.6; IR (CHCl<sub>3</sub>) 3.23, 3.36, 3.45, 5.81, 6.21, 6.67, 6.85, 7.22, 7.30, 9.26, 9.62, 9.90, 10.36, 10.81, 11.30, 11.63, 11.98, 14.29  $\mu\text{m}$ ; UV (95% ethanol)  $\lambda_{\text{max}}$  258 ( $\epsilon$  6900), 283 (2360), 295 nm (1040). Anal. Calcd for C<sub>19</sub>H<sub>20</sub>: C, 91.88; H, 8.12. Found: C, 91.77; H, 8.17.

**2-*tert*-Butyl-3-phenylindene (5).** Minor indene **5** was prepared from 2.00 g (10.6 mmol) of 2-*tert*-butyl-1-indanone<sup>51</sup> by using exactly the same procedure described for 1-*tert*-butyl-3-phenylindene (**4**). A 1.0-g portion of the 2.7 g of crude alcohol was dehydrated to obtain 800 mg (85%) of analytically pure indene **5** after purification by MPLC (column A). The spectral data follow: <sup>1</sup>H NMR (CCl<sub>4</sub>)  $\delta$  7.43–6.50 (m, 9 H, arom), 3.47 (s, 2 H, methylene), 1.10 (s, 9 H, *tert*-butyl); <sup>13</sup>C NMR (CDCl<sub>3</sub>) 152.1, 148.9, 141.0, 138.3, 137.7, 129.7, 127.9, 126.1, 123.9, 122.9, 119.6, 39.7, 34.7, 31.6 ppm; IR (CHCl<sub>3</sub>) 3.23, 3.28, 3.33, 3.39, 3.42, 6.21, 6.25, 6.69, 6.76, 6.86, 6.90, 7.14, 7.30, 7.94, 8.33, 9.26, 9.71, 10.53, 11.05, 14.18  $\mu\text{m}$ ; UV (95% ethanol)  $\lambda_{\text{max}}$  258 ( $\epsilon$  11500), 266 (9600), 282 (1230), 292 nm (478). Anal. Calcd for C<sub>19</sub>H<sub>20</sub>: C, 91.88; H, 8.12. Found: C, 91.90; H, 8.04.

**2-*tert*-Butylindanone.** The indanone was prepared from 2-benzyl-3,3-dimethylbutanoic acid by the literature method.<sup>51</sup> The preparation<sup>51</sup>

(45) (a) Since quantum yields for **1** rearrangements are low, 1,2-H(D) shift pathways are expected to make only a minor contribution to the total rate of singlet excited-state decay,  $k_{\text{d}}$ . Rotation and decay at planar allene geometries<sup>41,42</sup> is likely to dominate  $k_{\text{d}}$ , but isotope effects on this process should be small. For example, deuterium substitution does not affect the twisting process in S<sub>1</sub> of stilbene.<sup>45b</sup> (b) Saltiel, J.; D'Agostino, J. T.; Herkstroeter, W. G.; Saint-Ruf, G.; Buu-Hoi, N. P. *J. Am. Chem. Soc.* **1973**, *95*, 2543.

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of the carboxylic acid, however, was modified as described below.

**2-Benzyl-3,3-dimethylbutanoic Acid.** The procedure reported in the literature<sup>51</sup> was modified to facilitate the conversion of 2-benzyl-3,3-dimethylbutamide to the carboxylic acid with a method adapted from Tsai, Miwa, and Newman.<sup>52</sup> A solution of 10.0 g (38.6 mmol) of ethyl 2-benzyl-2-cyano-3,3-dimethylbutanoate,<sup>51</sup> 24.0 g (43.2 mmol) of potassium hydroxide, and 6 mL of distilled water in 106 mL of ethylene glycol was refluxed under nitrogen for 3 days. The solution was cooled and extracted with diethyl ether. The aqueous phase was acidified with concentrated HCl (Congo Red indicator) and then ether extracted. The combined extracts were washed with 10% sodium carbonate, water, and saturated sodium chloride, dried over anhydrous magnesium sulfate, and concentrated in vacuo to obtain brown needles. Crystallization from hexane gave 6.25 g (78%) of 2-benzyl-3,3-dimethylbutanoic acid as colorless needles, mp 87–89 °C (lit.<sup>51</sup> mp 88.5–90.0 °C). The spectral data follow: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.0–7.3 (m, 5 H, arom), 5.42 (br s, 2 H, NH<sub>2</sub>), 2.4–3.1 (AB of ABX pattern, J<sub>AB</sub> = 13 Hz, 2 H, methylene), 2.05 (X of ABX, 1 H, methine), 1.06 (s, 9 H, *tert*-butyl); IR (CHCl<sub>3</sub>) 2.84, 2.92, 3.34, 5.95, 6.23, 6.29, 6.69, 6.80, 6.87, 7.14, 7.30, 7.72, 8.20, 9.26, 9.62, 14.3 μm.

A solution of 4.29 g (20.9 mmol) of amide in 75% aqueous sulfuric acid was heated to 80 °C in an oil bath, and 11.0 g (159 mmol) of solid sodium nitrite was added in small portions during which gas evolution and a color change to red-brown occurred. The mixture was then cooled and diluted with water followed by ether extraction. The combined extracts were dried over anhydrous magnesium sulfate and concentrated in vacuo to obtain an oil which crystallized on standing. Crystallization from pentane gave 3.7 g (84%) of the carboxylic acid as colorless needles, mp 69–70 °C (lit.<sup>51</sup> mp 70 °C). The spectral data follow: <sup>1</sup>H NMR (CCl<sub>4</sub>) δ 7.0–7.2 (m, 5 H, arom), 2.13–2.93 (complex multiplet of ABC, 3 H, methylene and methine), 1.03 (s, 9 H, *tert*-butyl); IR (CHCl<sub>3</sub>) 3.23, 3.34, 5.88, 6.21, 6.67, 6.76, 6.85, 7.04, 7.09, 7.17, 7.81, 8.44, 8.81, 9.22, 9.61, 10.6, 11.8, 13.7, 14.3 μm.

**Tosylhydrazone of 2,2-Dimethyl-5,5-diphenyl-4-penten-3-one.** The ketone was prepared by the Meyer-Schuster<sup>53</sup> reaction of 4,4-dimethyl-1,1-diphenyl-2-pentyn-1-ol in acetic acid as described previously.<sup>54</sup> The tosylhydrazone was obtained by refluxing 6.05 g (23.3 mmol) of 2,2-dimethyl-5,5-diphenyl-4-penten-3-one and 4.34 g (23.3 mmol) of *p*-toluenesulfonylhydrazide in 100 mL of 25% benzene in ethanol (v/v) for 2 days. The mixture was then concentrated to half its volume and cooled to –15 °C to crystallize the tosylhydrazone. The 5 g (50%) of colorless needles obtained were then recrystallized from ethanol to give analytically pure material, mp 168–169 °C. The spectral data follow: <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>) δ 9.00 (s, 1 H, NH), 7.0–7.8 (m, 14 H, arom), 6.18 (s, 1 H, vinyl), 2.47 (s, 3 H, methyl), 0.90 (s, 9 H, *tert*-butyl); IR (KBr) 3.13, 3.40, 6.25, 6.69, 6.77, 6.84, 6.92, 7.25, 7.60, 8.03, 8.62, 8.93, 9.13, 9.62, 10.15, 10.70, 10.87, 11.43, 12.27, 12.74, 12.90, 13.51, 14.39 μm.

Anal. Calcd for C<sub>26</sub>H<sub>28</sub>N<sub>2</sub>O<sub>2</sub>S: C, 72.19; H, 6.25; N, 6.48. Found: C, 72.01; H, 6.63; N, 6.32.

**3-*tert*-Butyl-5,5-diphenyl-3H-pyrazole (13).** The colorless crystalline 3H-pyrazole was isolated in 37% yield, mp 144–146 °C (lit.<sup>9</sup> mp 140–143 °C) from 2.07 g (10.7 mmol) of diphenyldiazomethane and 7.01 g (85.5 mmol) of 3,3-dimethyl-2-butyne after 2 weeks reaction in the dark as per the literature<sup>9</sup> procedure. Recrystallization from 95% ethanol gave material, mp 159–160 °C, having <sup>1</sup>H NMR spectral data identical with those previously reported.<sup>9</sup> The UV spectrum follows: λ<sub>max</sub> (95% EtOH) 252 (ε 2820), 364 nm (133).

Alternatively, a mixture of 2.00 g (4.60 mmol) of the tosylhydrazone of 2,2-dimethyl-5,5-diphenyl-4-penten-3-one and 0.202 g (8.42 mmol) of sodium hydride in 40 mL of anhydrous THF was stirred for 15 min and then refluxed for 5 h under nitrogen. After removal of the solvent in vacuo the residue dissolved in dichloromethane was washed with water, the wash was extracted with dichloromethane, and the combined organics when dried and concentrated gave 1.30 g of a colorless solid. Crystallization from 95% ethanol gave 0.90 g (70%) of the 3H-pyrazole (mp 155–156 °C) and an additional crop of 0.15 g (12%), mp 148–155 °C. <sup>1</sup>H NMR analysis of a second run taken to 50% conversion of the tosylhydrazone showed 50% 3H-pyrazole and no additional products.

**Preparative Direct Photolysis of 4,4-Dimethyl-1,1-diphenyl-1,2-pentadiene (1).** A solution of 4,4-dimethyl-1,1-diphenyl-1,2-pentadiene (770 mg, 3.10 mmol) in 250 mL of *tert*-butyl alcohol was purged with nitrogen for 1.5 h and then irradiated for 1 h with a 450-W Hanovia medium pressure mercury lamp fitted with a Vycor filter. After the solvent was removed in vacuo, the residue was chromatographed on a 125 × 2.5 cm

silica gel column eluting with hexane taking 40-mL fractions. Fraction 42–51, 432 mg, was a mixture of 1-*tert*-butyl-3-phenylindene (4), 2-*tert*-butyl-3-phenylindene (5), and 4,4-dimethyl-1,1-diphenyl-1,2-pentadiene (1) in a ratio of 10.0:1.0:9.3, respectively, by NMR. This ratio corresponds to absolute yields of 212 mg (28%) for 1-*tert*-butyl-3-phenylindene (4), 21 mg (2.8%) for 2-*tert*-butyl-3-phenylindene (5), and 198 mg (26%) of recovered 4,4-dimethyl-1,1-diphenyl-1,2-pentadiene (1). Fraction 54–68, 99.3 mg (12.9%), was essentially pure 1-*tert*-butyl-3,3-diphenylcyclopropene (2) by NMR.<sup>9</sup> Fraction 69–100, 91.5 mg (11.9%) of a colorless oil, was essentially pure 4,4-dimethyl-1,1-diphenyl-2-pentyne (3) by NMR. The mass balance was 620 mg (81%) at 74% conversion. The products were identified by comparison of <sup>13</sup>C and <sup>1</sup>H NMR spectra as well as HPLC retention times (column B) to authentic samples. The <sup>13</sup>C spectrum of fraction 54–68, the mixture of allene 1 + indene 4 + indene 5, was an exact juxtaposition of spectra of the individual components, and no peak was unaccounted for; the composition of the mixture by NMR was found to be in agreement with GC (column C) analysis.

The photolysis of 278 mg (1.12 mmol) of allene 1 was repeated with methanol as the solvent. <sup>1</sup>H NMR analysis of the crude photolysate showed that indenenes 4 and 5, cyclopropene 2, and alkyne 3 were present; no additional absorptions attributable to a product of methanol addition or any other product were detected in the range δ 1.4–6.7. Column chromatography as above gave 107 mg (38.4%) of recovered allene 1, 77.1 mg (27.7%) of the major indene 4, 8.6 mg (3.1%) of the minor indene 5, 21.5 mg (7.7%) of alkyne 3, and 29.0 mg (10.4%) of cyclopropene 2 (87.3% mass balance). The remainder of the mass balance eluting with ether was yellow material which exhibited complex, non-descript absorptions in the <sup>1</sup>H NMR spectrum at δ 0.6–1.3 and 6.7–7.4.

**Preparative Direct Photolysis of 4,4-Dimethyl-1,1-diphenyl-1,2-pentadiene-3-*d*<sub>1</sub> (1-*d*<sub>1</sub>).** A solution of 253 mg (1.02 mmol) of 4,4-dimethyl-1,1-diphenyl-1,2-pentadiene-3-*d*<sub>1</sub> in 250 mL of *tert*-butyl alcohol was purged with nitrogen for 1.5 h and irradiated for 2 h with a 450-W Hanovia medium pressure mercury lamp fitted with a Vycor filter. The solvent was removed in vacuo and the residue chromatographed by MPLC (column A) eluting with hexane at 18 mL/min flow rate taking appropriate cuts. Fraction 1, retention time 30 min, 134 mg, was a mixture of 1-*tert*-butyl-3-phenylindene-2-*d*<sub>1</sub>, 2-*tert*-butyl-3-phenylindene-1-*d*<sub>1</sub>, and 4,4-dimethyl-1,1-diphenyl-1,2-pentadiene-3-*d*<sub>1</sub> in a ratio of 6.73:1.43:1.00 by NMR; the ratio corresponds to absolute yields of 98.5 mg (38.9%) of 1-*tert*-butyl-3-phenylindene-2-*d*<sub>1</sub> (4-*d*<sub>1</sub>), 20.9 mg (8.26%) of 2-*tert*-butyl-3-phenylindene-1-*d*<sub>1</sub> (5-*d*<sub>1</sub>), and 14.6 mg (5.8%) of 4,4-dimethyl-1,1-diphenyl-1,2-pentadiene-3-*d*<sub>1</sub> (1-*d*<sub>1</sub>). Fraction 2, retention time 45 min, was 22.9 mg (9.03%) of 1-*tert*-butyl-3,3-diphenylcyclopropene-2-*d*<sub>1</sub> (2-*d*<sub>1</sub>). Fraction 3, retention time 68 min, 13.9 mg (5.48%), was 4,4-dimethyl-1,1-diphenyl-2-pentyne-1-*d*<sub>1</sub> (3-*d*<sub>1</sub>). The mass balance was 171 mg (67.5%) at 94.2% conversion. The NMR analysis of each fraction is described in the Results section. GC–MS analysis of fractions 1, 2, and 3 indicated >95% retention of one deuterium in each product and recovered allene. One GC peak was observed for cyclopropene 2 in GC–MS analyses.

**Sensitized Photolysis of 4,4-Dimethyl-1,1-diphenyl-1,2-pentadiene (1).** A solution of 256 mg (1.03 mmol) of allene and 450 mg (3.00 mmol) of *m*-methoxyacetophenone in 250 mL of *tert*-butyl alcohol was purged with nitrogen for 1.5 h and then irradiated for 2 h with a 450-W Hanovia medium pressure mercury lamp with a Pyrex filter sleeve. A <sup>1</sup>H NMR of the photolysate showed no products had formed. The photolysate was concentrated in vacuo and chromatographed by flash chromatography (vide supra) to recover 252 mg (98.5%) of allene. GC assay (column C) confirmed that the allene was unchanged and the only component.

**Preparative Direct Photolysis of the Tosylhydrazone Sodium Salt 12 of 2,2-Dimethyl-5,5-diphenyl-4-penten-3-one.** A mixture of 815 mg (1.89 mmol) of tosylhydrazone 11 and 0.28 g (5.2 mmol) of sodium methoxide in 500 mL of dry THF (distilled from sodium benzophenone ketyl) was stirred 16 h in the dark under nitrogen and then irradiated 1.5 h with a Hanovia 450-W medium pressure mercury lamp equipped with a uranium filter sleeve which transmits light of λ > 330 nm. The photolysate was concentrated in vacuo to obtain a white oily solid to which pentane was added followed by a wash with water. The aqueous phase was extracted with pentane, and the combined extracts were dried over anhydrous sodium sulfate. The pentane was removed in vacuo and the residue analyzed by NMR. No 4,4-dimethyl-1,1-diphenyl-2-pentyne (3) was detected among the products. The residue was chromatographed by MPLC (column A). Fraction 1, 165 mg, was a mixture of 1-*tert*-butyl-3-phenylindene and 4,4-dimethyl-1,1-diphenyl-1,2-pentadiene in a ratio of 8.7:1.0 by NMR. This ratio corresponds to absolute yields of 148 mg (32%) of 1-*tert*-butyl-3-phenylindene (4) and 17.0 mg (3.6%) of 4,4-dimethyl-1,1-diphenyl-1,2-pentadiene (1). Fraction 2, 88.4 mg (18.9%), was 1-*tert*-butyl-3,3-diphenylcyclopropene (2).<sup>9</sup> The mass balance was 253 mg (54%) at 100% conversion. Later fractions were

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monitored by UV, NMR, and GC (column C) to confirm the absence of alkyne as a product.

**Preparative Direct Photolysis of 3-*tert*-Butyl-5,5-diphenyl-3*H*-pyrazole (13).** A solution of 640 mg (2.32 mmol) of 3*H*-pyrazole in 250 mL of cyclohexane was purged with nitrogen for 1 h and then irradiated 8 h with a Hanovia 450-W medium pressure mercury lamp equipped with a uranium filter sleeve ( $\lambda > 330$  nm). After the photolysate was concentrated in vacuo, the resultant brown oil was analyzed by NMR. 4,4-Dimethyl-1,1-diphenyl-2-pentyne (3) was not detected among the products. The mixture was chromatographed by MPLC (column A), eluting with hexane taking appropriate cuts. Fraction 1, 250 mg, was a mixture of 1-*tert*-butyl-3-phenylindene and 4,4-dimethyl-1,1-diphenyl-1,2-pentadiene in a ratio of 10.3:1.0 by NMR. This ratio gave absolute yields of 228 mg (40%) of 1-*tert*-butyl-3-phenylindene (4) and 22 mg (3.8%) of 4,4-dimethyl-1,1-diphenyl-1,2-pentadiene (1). Fraction 2, 170 mg (30%), was 1-*tert*-butyl-3,3-diphenylcyclopropene (2).<sup>9</sup> The mass balance was 420 mg (74%) at 100% conversion. The alkyne was not detected by UV or NMR in later fractions.

**Photochemical Generation of Diazoalkene from 3*H*-Pyrazole 13.** A  $1.02 \times 10^{-2}$  M solution of 3*H*-pyrazole in nitrogen-purged anhydrous THF was irradiated in a low-temperature apparatus (a Dewar mounting a transverse 1 cm  $\times$  2.2 cm diameter cell) at  $-71^\circ\text{C}$  (dry ice/ethanol) at 366 nm with light passed through a monochromator (20-nm bandpass) from a focused 200-W high pressure mercury lamp. The photolysis was monitored by UV spectroscopy; an intense band appeared at 350 nm accompanied by a weak absorption at 510 nm which was attributable to formation of a diazoalkene. No change in absorbance was noted at 510 nm during a 1-h period at  $-71^\circ\text{C}$  with the lamp off, so the diazoalkene appeared to be kinetically stable under these conditions. In a repeat run at  $21^\circ\text{C}$  maximum absorbance values of  $A_{350} > 2$  and  $A_{510} = 0.017$  were achieved after 6 min of photolysis, and then the rate of disappearance of the diazoalkene band in the dark was determined to be, roughly,  $7 \pm 2 \times 10^{-4} \text{ s}^{-1}$ , using the  $\ln(A - A_\infty)$  method at 510 nm. The rate was not retarded on addition of 5% (v/v) pyridine.

The product distribution for the low-temperature photolysis of the 3*H*-pyrazole was determined next. A solution of 41.1 mg (0.149 mmol) of 3*H*-pyrazole in 46 mL of anhydrous THF (0.00324 M) in a jacketed quartz cylindrical cell of 8 cm path length was purged with nitrogen for 30 min and then taken down to  $-69$  to  $-71^\circ\text{C}$  by circulating methanol which was precooled via a copper heat exchanger immersed in dry ice/ethanol. The cell was mounted flush to the nitrogen-purged monochromator and photolyzed as above for 1.5 h.  $^1\text{H}$  NMR of the photolysate showed 85% conversion of the 3*H*-pyrazole to allene 1:cyclopropene 2:indene 4, 1.0:3.4:11. Repeat runs at  $21^\circ\text{C}$  gave ratios of 1:2.4 of 1.0:4.0:10 (68% conversion) and 1.0:4.3:10 (92% conversion).

**Preparative Direct Photolysis of 1-*tert*-Butyl-3,3-diphenylcyclopropene (2).** A solution of 80.0 mg (0.323 mmol) of cyclopropene in 134 mL of pentane in a Vycor tube was purged with nitrogen for 1 h and then irradiated in a Rayonet photolysis apparatus fitted with sixteen 254-nm lamps for 15 min. After the pentane was removed in vacuo, NMR analysis revealed that 4,4-dimethyl-1,1-diphenyl-2-pentyne (3) was not among the products. The residue was chromatographed by MPLC (column A). Fraction 1, 27.5 mg, was a mixture of 1-*tert*-butyl-3-phenylindene, 2-*tert*-butyl-3-phenylindene, and 4,4-dimethyl-1,1-diphenyl-1,2-pentadiene in a ratio of 5.3:1.0:1.7 by NMR. This ratio corresponds to absolute yields of 18 mg (21%) of 1-*tert*-butyl-3-phenylindene (4), 3.4 mg (3.9%) of 2-*tert*-butyl-3-phenylindene (5), and 5.8 mg (6.5%) of 4,4-dimethyl-1,1-diphenyl-1,2-pentadiene (1). Fraction 2, 31.1 mg (38.9%), was 1-*tert*-butyl-3,3-diphenylcyclopropene (2) by NMR. The alkyne was not detected by UV or NMR in later fractions. The mass balance was 59 mg (73%) at 61% conversion.

**Procedure for Quantum Yield Determinations.** A semi-micro optical bench for quantum yield determinations was constructed along the lines specified by Zimmerman.<sup>29a</sup> Light from a 200-W high pressure mercury lamp was passed through an Oriel monochromator set at 270 nm with entrance and exit slits set at 3.0 mm to give a 20-nm bandpass at half-peak height. Light was collimated through a lens and passed through a beam splitter which diverted 18% of the light to a cell perpendicular to the light path containing actinometer. A jacketed, quartz cylindrical cell, 2.5 cm  $\times$  8 cm of 38 mL volume, which contained the photolysate, was mounted in line with optics, monochromator, and lamp. Light output was monitored by ferrioxalate actinometry,<sup>29b</sup> using the splitting ratio technique.<sup>29a</sup> The temperature was regulated by circulating water from a constant temperature bath maintained at  $26^\circ\text{C}$  through the jacketed photolysis cell.

Photolyses employed *tert*-butyl alcohol (distilled from calcium hydride) as solvent unless noted otherwise. All solutions were purged with nitrogen for 1 h before and during the irradiations.

**Summary of Quantum Yields for Direct Photolyses of 4,4-Dimethyl-1,1-diphenyl-1,2-pentadiene (1) and 4,4-Dimethyl-1,1-diphenyl-1,2-pen-**

**tadiene-3-*d*<sub>1</sub> (1-*d*<sub>1</sub>).** The procedure using the semi-micro optical bench apparatus is described above. After each photolysis triphenylmethane internal standard was added, the photolysate was concentrated in vacuo, and product analyses were performed by HPLC (column B, vide supra). The retention times were as follows: triphenylmethane, 18 min; 4,4-dimethyl-1,1-diphenyl-2-pentyne (3), 22 min; 1-*tert*-butyl-3,3-diphenylcyclopropene (2), 27 min; 4,4-dimethyl-1,1-diphenyl-1,2-pentadiene (1), 40 min; 1-*tert*-butyl-3-phenylindene (4), 49 min. The data are summarized for quantum yields for direct photolyses of 4,4-dimethyl-1,1-diphenyl-1,2-pentadiene and 4,4-dimethyl-1,1-diphenyl-1,2-pentadiene-3-*d*<sub>1</sub> in Table II. A potential product, 2-*tert*-butyl-3-phenylindene (5), was not observed at low conversions of allenes 1 or 1-*d*<sub>1</sub> at a retention time (column 6) of 43 min.

**Summary of Quantum Yields for the Direct Photolysis of 1-*tert*-Butyl-3,3-diphenylcyclopropene (2).** The procedure using the semi-micro optical bench apparatus is described above. Pentane (Aldrich, Gold Label) was used as solvent. After the photolysis and removal of the solvent in vacuo, flash chromatography (vide supra) was used to carefully separate the unreacted cyclopropene from the photoproducts. Triphenylethylene internal standard was added and the product mixture analyzed by GC (column C). The retention times were as follows: 4,4-dimethyl-1,1-diphenyl-1,2-pentadiene (1), 8.6 min; 2-*tert*-butyl-3-phenylindene (5), 13.4 min; 1-*tert*-butyl-3-phenylindene (4), 16.9 min; triphenylethylene, 24.2 min. The potential product 4,4-dimethyl-1,1-diphenyl-2-pentyne (3) was not observed at a retention time of 6.5 min. The results are summarized below.

**Run 1:** 1-*tert*-butyl-3,3-diphenylcyclopropene (2) reactant, 0.0431 mmol; 0.0093 mEinstein absorbed; 4,4-dimethyl-1,1-diphenyl-1,2-pentadiene (1), 0.00045 mmol,  $\Phi = 0.049$ ; 2-*tert*-butyl-3-phenylindene (5), 0.00024 mmol,  $\Phi = 0.025$ ; 1-*tert*-butyl-3-phenylindene (4), 0.00087 mmol,  $\Phi = 0.093$ ; 3.3% conversion.

**Run 2:** 1-*tert*-butyl-3,3-diphenylcyclopropene (2) reactant, 0.055 mmol; 0.0079 mEinstein absorbed; 4,4-dimethyl-1,1-diphenyl-1,2-pentadiene (1), 0.00041 mmol,  $\Phi = 0.051$ ; 2-*tert*-butyl-3-phenylindene (5), 0.000168 mmol,  $\Phi = 0.021$ ; 1-*tert*-butyl-3-phenylindene (4), 0.00081 mmol,  $\Phi = 0.10$ ; 2.6% conversion.

**Comparison between Triplet Sensitized and Direct Photolyses of 3-*tert*-Butyl-5,5-diphenyl-3*H*-pyrazole (13).** A semiquantitative comparison was made by using the semi-micro optical bench apparatus. In order to maximize light received by the samples, photolysates or actinometer solutions were mounted directly behind the monochromator. Ferrioxalate actinometry was done after each run at each wavelength.

**Direct Run.** A solution of 52.7 mg (0.190 mmol) of 3*H*-pyrazole in 38 mL of cyclohexane was purged with nitrogen for 1 h and then irradiated for 2 h at 366 nm (20 nm bandpass) in an 8 cm path length cylindrical cell. The light absorbed was 0.47 mEinstein.  $^1\text{H}$  NMR analysis showed 0.042 mmol of unreacted 3*H*-pyrazole, 78% conversion,  $\Phi_{\text{dis}} = 0.32$ ; 2-*tert*-butyl-3,3-diphenylcyclopropene (2), 0.059 mmol,  $\Phi = 0.12$ ; 1-*tert*-butyl-3-phenylindene (4), 0.082 mmol,  $\Phi = 0.17$ ; 4,4-dimethyl-1,1-diphenylallene (1), 0.010 mmol,  $\Phi = 0.020$ .

**Sensitized Run.** To minimize direct light absorption by 3*H*-pyrazole, *m*-methoxyacetophenone was chosen as sensitizer at 315 nm (20-nm bandpass). A solution of 101 mg (0.37 mmol) of 3*H*-pyrazole 13 and 97 mg (0.65 mmol) of *m*-methoxyacetophenone in 38 mL of cyclohexane was purged with nitrogen for 1 h and irradiated for 50.4 h under nitrogen. The light absorbed was 4.07 mEinstein.  $^1\text{H}$  NMR analysis of the photolysate showed 0.30 mmol of unreacted 3*H*-pyrazole, 20% conversion,  $\Phi_{\text{dis}} = 0.017$ ; 1-*tert*-butyl-3,3-diphenylcyclopropene (2), 0.026 mmol,  $\Phi = 0.0063$ ; 1-*tert*-butyl-3-phenylindene (4), 0.044 mmol,  $\Phi = 0.0109$ ; 4,4-dimethyl-1,1-diphenyl-1,2-pentadiene (1), 0.003 mmol,  $\Phi = 0.0008$ .

**Flash Vacuum Pyrolyses.** The apparatus consisted of an unpacked Pyrex tube (25 mm  $\times$  335 mm) mounted in a Lindberg tube furnace.<sup>55</sup> All runs were conducted at  $400^\circ\text{C}$  with nitrogen as a carrier gas, maintaining the pressure at 1 mm. Weighed samples were evaporated over a period of 3–5 h into the hot zone of the tube by heating the sample chamber to  $37$ – $45^\circ\text{C}$ . Product mass balance was determined gravimetrically.  $^1\text{H}$  NMR and GC analysis (column C) were used to establish the identity and composition of product mixtures. Individual runs are given below.

**Run 1.** Pyrolysis of 42.1 mg (0.170 mmol) of 1-*tert*-butyl-3,3-diphenylcyclopropene (2) gave 42.1 mg (100% mass balance) of 1-*tert*-butyl-3-phenylindene (4) and 3-*tert*-butyl-1-phenylindene (15) in a ratio of 3.2:1.0, respectively, by  $^1\text{H}$  NMR analysis. This ratio corresponds to 76% 4 and 24% 15. GC analysis revealed trace amounts of four additional components, one of which (0.56%) matched 4,4-dimethyl-1,1-diphenyl-1,2-pentadiene (1) in retention time. Alkyne 3 and indene 5 were not detected. The indenenes were identified by comparison to authentic

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samples. The independent synthesis of indene **15** is given below.

**Run 2.** Pyrolysis of 57.4 mg (0.232 mmol) of 1-*tert*-butyl-3-phenylindene (**4**) gave 57.3 mg (100% mass balance) of indene **4** (74%) and indene **15** (26%) in a ratio of 2.8:1.0, respectively, by  $^1\text{H}$  NMR. GC retention times were matched against authentic samples.

**Run 3 (Control).** Pyrolysis of 50.0 mg (0.202 mmol) of 4,4-dimethyl-1,1-diphenyl-1,2-pentadiene (**1**) gave 49.2 mg (98.4%) of recovered allene **1**;  $^1\text{H}$  NMR showed the allene as completely unchanged; no detectable conversion to products had occurred.

**Run 4 (Control).** Pyrolysis of 65.2 mg (0.263 mmol) of 4,4-dimethyl-1,1-diphenyl-2-pentyne (**3**) gave 53.3 mg (81.7%) of recovered alkyne **3**; 6.2 mg (9.5%) of a yellow residue remained behind in the glass boat inside the sample chamber. NMR showed only recovered alkyne and no additional products.

**Run 5.** Pyrolysis of 59.8 mg (0.241 mmol) of 2-*tert*-butyl-3-phenylindene (**5**) gave 59.8 mg (100% mass balance) of indene **5** (64%) and a product identified as 2-*tert*-butyl-1-phenylidene (**16**, 36%) in a ratio of 1.8:1.0, respectively, by  $^1\text{H}$  NMR. The spectral data of indene **16** follow:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  6.4–7.5 (m, 9 H, arom), 6.30 (d, 1 H,  $J = 2$  Hz, olefinic), 4.50 (d, 1 H,  $J = 2$  Hz, methine), 1.05 (s, 9 H, *tert*-butyl). Indene **16** was also a product of triethylamine catalyzed isomerization<sup>28d</sup> of indene **5**. Thus, a solution of 307 mg (1.24 mmol) of indene **5** and 2.9 mL of triethylamine in 30 mL of dry pyridine was heated to 45 °C for 20 h.  $^1\text{H}$  NMR indicated 5% conversion to **16**. After a total of 51 h NMR analysis showed 84.8% indene **5** and 15.2% indene **16**. The GC retention times of the indenenes in the mixture matched indenenes **5** and **16** in the pyrolysis reaction mixture.

**Independent Synthesis of 3-*tert*-Butyl-1-phenylindene (**15**).** Indene **15** was prepared from 9.5 mmol of *tert*-butyl magnesium chloride in 50 mL of dry THF by addition of 2.0 g (9.5 mmol) of 3-phenylindanone<sup>56</sup> in 50 mL of THF following the procedure given for 3-*tert*-butyl-1-methylindene.<sup>57</sup> The crude product, obtained by using the literature workup, was chromatographed on a 20 mm  $\times$  330 mm silica gel column eluting with hexane. The first 200-mL fraction gave 28.1 mg of indene **15**. A 1.5 g (75%) recovery of 3-phenylindanone was obtained by stripping the column with diethyl ether eluant. The spectral data for indene **15** follow:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.0–7.7 (m, 9 H, arom), 6.20 (d, 1 H,  $J = 2$  Hz,

olefinic), 4.43 (d, 1 H,  $J = 2$  Hz, methine), 1.40 (s, 9 H, *tert*-butyl); IR ( $\text{CCl}_4$ ) 3.21, 3.25, 3.32, 3.42, 6.21, 6.67, 6.83, 7.14, 7.30, 8.03, 8.26, 8.55, 9.22, 9.62, 9.90, 11.30, 11.70, 14.18  $\mu\text{m}$ .

**Acid-Catalyzed Rearrangements of 1-*tert*-Butyl-3,3-diphenylcyclopropene (**2**) and Resemblance to Wall Effects in Pyrolyses.** A pyrolysis of 48.8 mg (0.197 mmol) of cyclopropene **2** was run at a much lower temperature, 250 °C (1 mm), than the runs described above. Condensation onto the hot walls of the tube resulting in catalyzed isomerization of cyclopropene **2** seemed likely since the products were those obtained from rearrangement catalyzed by protic acid. After the pyrolysis, 48.8 mg (100% mass balance) of an oil was obtained;  $^1\text{H}$  NMR analysis showed 60% unreacted cyclopropene **2**, 28% 2-*tert*-butyl-3-phenylindene (**5**), and 12% 1-*tert*-butyl-3-phenylidene (**4**). For comparison a solution of 45.0 mg (0.182 mmol) of cyclopropene **2** and 5.8 mg (0.031 mmol) of *p*-toluenesulfonic acid in 0.5 mL of benzene- $d_6$  was heated at 68 °C for 2 days (10% conversion to products) and then at 75 °C for 20 h.  $^1\text{H}$  NMR analysis showed 25% conversion of cyclopropene **2** to indenenes **5** and **4** in the ratio 1.5:1.0, respectively.

**Acknowledgment.** We thank Peter E. Reed for performing exploratory low-temperature photolyses. Support of this research by a Cottrell Grant from Research Corporation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Office of Research Support, Marquette University Graduate School, for a summer fellowship and a regular research grant, is gratefully acknowledged. We also acknowledge departmental Grants NSF TFI-8020268 (NMR spectrometer) and NSF PRM-8201885 (UV spectrometer).

**Registry No.** **1**, 81740-70-7; **1-d<sub>1</sub>**, 95191-86-9; **2**, 42842-57-9; **2-d<sub>1</sub>**, 95191-92-7; **3**, 95191-85-8; **3-d<sub>1</sub>**, 95191-96-1; **4**, 32338-54-8; **4-d<sub>1</sub>**, 95191-90-5; **5**, 95191-88-1; **5-d<sub>1</sub>**, 95191-91-6; **8**, 57985-60-1; **9**, 53483-12-8; **10**, 38206-36-9; **11**, 95191-89-2; **11-Na**, 81740-71-8; **13**, 42842-76-2; **14**, 95191-93-8; **15**, 95191-94-9; **16**, 95191-95-0;  $\text{D}_2$ , 7782-39-0; bromoethane, 74-96-4; 3,3-dimethyl-1-butyne, 917-92-0; bromodiphenylmethane, 776-74-9; bromobenzene, 108-86-1; 3-*tert*-butyl-1-indanone, 50438-04-5; 3-*tert*-butyl-1-phenylindan-1-ol, 95191-87-0; ethyl 2-benzyl-2-cyano-3,3-dimethylbutanoate, 57985-59-8; 2,2-dimethyl-5,5-diphenyl-4-penten-3-one, 844-39-3; 4,4-dimethyl-1,1-diphenyl-2-pentyn-1-ol, 1522-15-2; diphenyldiazomethane, 883-40-9; *tert*-butylmagnesium chloride, 677-22-5; 3-phenylindanone, 16618-72-7.

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## Mechanism of Solvolysis of 2,2-Dimethylcyclopentyl *p*-Bromobenzenesulfonate

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**Abstract:** Solvolysis of the title compound in ethanol–water, trifluoroethanol–water, and hexafluoroisopropyl alcohol–water mixtures yields >90% products of methyl migration. The rate of solvolysis relative to the cyclopentyl analogue is 0.19 in 80% ethanol–water, 4.0 in 97% trifluoroethanol–water, and 10.0 in 90% hexafluoroisopropyl alcohol–water. The  $\alpha$ - $d$  and  $\beta$ - $d_2$  rate effects in solvolysis range respectively from 1.19–1.20 to 1.26–1.30. The results are interpreted in terms of a mechanism which involves reversible formation of the tight ion pair followed by rate-determining methyl migration.

An important question in the study of carbonium ion reactions concerns the timing of the bonding changes which are involved in Wagner–Meerwein rearrangements; does the neighboring group migration occur simultaneously with or subsequent to carbonium ion formation? For example, neopentyl sulfonate esters solvolyze

with participation by a neighboring methyl group during irreversible ionization,<sup>1,2</sup> whereas pinacolyl (3,3-dimethyl-2-butyl)-sulfonate esters solvolyze with methyl migration after irreversible ionization.<sup>1,3</sup> We now wish to report for the first time an example

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