

alteration in relative intensities of ion peaks as depicted in Figure 2, which showed constant decrease for  $a + H^+$  and  $b + H^+$  and increase for  $d + H^+$  within the reaction time of 24 h. These semiquantitative data are consistent with the  $^{31}P$  NMR traced experiment<sup>6</sup> and are in agreement with the expected change of the concentration of the four species in the reaction mixture.

These results suggested that the principal ions obtained are the direct response of the major species existing in the liquid reaction medium and are not FAB-induced artifacts or fragments.

We fail to get similar results for  $\gamma,\delta$ -pentenoic acid, which is the typical example of iodolactonization. It is likely that the ease of the direct detection of a-d by FAB MS is due to the existence of the dialkoxyphosphinyl moiety, which has been proved to have very high sensitivity for FAB MS analysis.<sup>11</sup> Hence, the FAB mass spectra provide direct evidence for the existence of the cyclic phosphonium ion intermediate and further evidence for the iodine addition product intermediate in the iodine cyclization reaction of unsaturated organophosphorus compounds.

### Experimental Section

The preparation of compounds I-IV will be published elsewhere. The reaction was carried out in chloroform. The molar ratio of the reactant to iodine was 1:2. The reaction mixture was kept at room temperature and protected from light.

FAB mass spectral data were obtained on a KYKY ZhP-5 double focusing mass spectrometer (Scientific Instrument Factory, Beijing) equipped with a standard KYKY fast atom gun (from the same supplier). A neutral argon beam was used at the energy of 7 keV and gun monitor current of 1.2 mA. The accelerating voltage was 6 kV, and the resolution was kept at 1500. The spectra were recorded on UV-sensitive paper. The  $m/z$  values and relative intensities were manually counted and measured, respectively. The accurate mass measurement was carried out by peak-matching technique on the same instrument at the resolution of 4000.

An aliquot of 0.5  $\mu$ L of the reaction mixture was transferred into a drop of glycerol ( $\sim 1 \mu$ L) on the probe target by microsyringe. Spectra were taken 30 s after insertion of the probe to let the ion current become optimized and stabilized.

**Acknowledgment.** This project is supported by both the Science Fund of the Chinese Academy of Sciences (83)-616 and the Chinese Science Fund for the Young Scientists (85).

(11) Chai, W.-G.; Yan, L.; Wang, G.-H.; Liang, X.-Y.; Zhao, Y.-F.; Ji, G.-J., submitted for publication in *Biomed. Environ. Mass Spectrom.*

### Unsymmetrical Alkenes by Carbene Coupling from Diazirine Decomposition in the Presence of Diazo Compounds

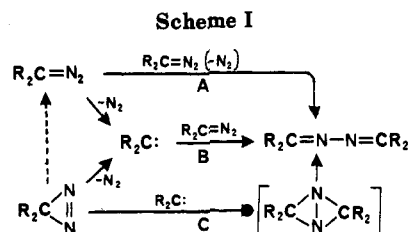
Michael P. Doyle,\* Alvaro H. Devia, Kathlene E. Bassett, Jan W. Terpstra, and Surendra N. Mahapatro

Department of Chemistry, Trinity University, San Antonio, Texas 78284

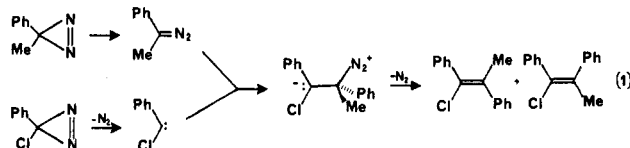
Received October 14, 1986

Thermal and photochemical decomposition of diazirines results in the formation of azines with carbene dimers formed in much lower amounts.<sup>1</sup> Azine production has

(1) (a) Liu, M. T. H. *Chem. Soc. Rev.* 1982, 11, 127. (b) Schmitz, E. *Adv. Heterocycl. Chem.* 1979, 24, 63.

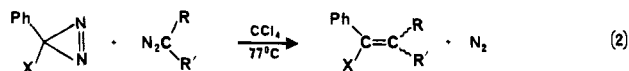


been viewed as a bimolecular reaction between two diazo compounds, formed by diazirine isomerization, followed by elimination of dinitrogen (path A, Scheme I),<sup>2,3</sup> as a coupling between a carbene and a diazo compound (path B),<sup>4</sup> and as an addition of a carbene to a diazirine followed by rearrangement (path C).<sup>5,6</sup> By inference, alkene products are formed through carbene coupling. However, these mechanisms are apparently inconsistent with experimental results obtained by Liu and Ramakrishnan<sup>7</sup> who showed that, although thermal decomposition of either 3-chloro-3-phenyldiazirine or 3-methyl-3-phenyldiazirine resulted in nearly quantitative azine formation, decomposition of an equimolar mixture of these two diazirines produced the carbene dimer from this reactant combination without azine. The mixed carbene dimer was proposed to have resulted from nucleophilic attack of 1-phenyldiazoethane, presumed to have been formed from 3-methyl-3-phenyl-diazirine, on chlorophenylcarbene (eq 1). Since alternate explanations for these observations



are possible, the present investigation was undertaken to determine the validity of this mechanistic interpretation and to evaluate the feasibility of alkene synthesis by reactions between diazo compounds and carbenes thermally generated from diazirines.

3-Halo-3-phenyldiazirines were prepared from benzamide hydrochloride by Graham's procedure.<sup>8</sup> The decomposition of these thermally unstable halophenylcarbene precursors was performed in refluxing carbon tetrachloride. Diazirine decomposition in the presence of a representative selection of diazo compounds produced the carbene coupling products (eq 2) in remarkably high yields (Table I). Since diazo compounds such as ethyl



diazoacetate are stable to decomposition at these temperatures, the coupling products must have arisen by electrophilic addition of the thermally generated halophenylcarbene to the diazo compound with subsequent loss of dinitrogen to form the observed products. No evidence for unsymmetrical azines was obtained.

The effectiveness of this transformation is demonstrated by the high yields of products obtained from nearly stoi-

- (2) Overberger, C. G.; Anselme, J.-P. *J. Org. Chem.* 1964, 29, 1188.  
 (3) Yates, P.; Farnum, D. G.; Wiley, D. H. *Tetrahedron* 1962, 18, 881.  
 (4) Bethell, D.; Newall, A. R.; Stevens, G.; Wittaker, D. *J. Chem. Soc. B* 1969, 749.  
 (5) Padwa, A.; Eastman, D. *J. Org. Chem.* 1969, 34, 2728.  
 (6) Gale, D. M.; Middleton, W. J.; Krespan, C. G. *J. Am. Chem. Soc.* 1966, 88, 3617.  
 (7) Liu, M. T. H.; Ramakrishnan, K. *Tetrahedron Lett.* 1977, 3139.  
 (8) Graham, W. H. *J. Am. Chem. Soc.* 1965, 87, 4396.

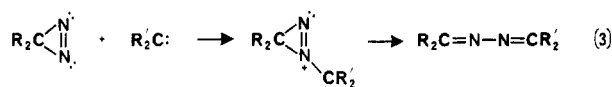
**Table I. Mixed Carbene Coupling Products from Thermal Decomposition of 3-Halo-3-phenyldiazirines in the Presence of Diazo Compounds<sup>a</sup>**

diazo compd	3-halo-3-phenyl-diazirine, X	product	yield, % <sup>b</sup>	Z/E <sup>c</sup>
PhCHN <sub>2</sub>	Cl	PhCH=CClPh	92	21
Ph <sub>2</sub> CN <sub>2</sub>	Cl	Ph <sub>2</sub> C=CClPh	86	
N <sub>2</sub> CHCOOEt	Cl	PhCCl=CHCOOEt	95	1.8
N <sub>2</sub> CHCOOEt	Br	PhCBr=CHCOOEt	91	2.2
PhCOCHN <sub>2</sub>	Cl	PhCCl=CHCOPh	87	4.3
PhCOCHN <sub>2</sub>	Br	PhCBr=CHCOPh	77	6.2
N <sub>2</sub> CHCONMe <sub>2</sub>	Cl	PhCCl=CHCONMe <sub>2</sub>	87	3.0
N <sub>2</sub> CHCON( <i>i</i> -Pr) <sub>2</sub>	Cl	PhCCl=CHCON( <i>i</i> -Pr) <sub>2</sub>	91	3.4
N <sub>2</sub> CHCOC(CH <sub>3</sub> ) <sub>3</sub>	Cl	PhCCl=CHCOC(CH <sub>3</sub> ) <sub>3</sub>	99	2.6

<sup>a</sup> Reactions performed in refluxing carbon tetrachloride with 1.1–1.2 molar equiv. of diazo compound. <sup>b</sup> Weight yield of isolated mixed carbene coupling product. <sup>c</sup> Determined by GC and/or NMR analyses.

chiometric ratios of reactants. Even phenyldiazomethane, an exceptionally acid-sensitive diazo compound, gave  $\alpha$ -chlorostilbene in 92% yield. However, reactions of dimethyl diazomalonate with 3-chloro-3-phenyldiazirine produced the unsymmetrical carbene dimer in low yield (<25%); azine and the carbene dimers from 3-chloro-3-phenyldiazirine were the major products, and unreacted dimethyl diazomalonate was recovered.

Transition-metal-catalyzed reactions of diazo compounds are well-known to undergo carbene transfer from intermediate metal carbenes to Lewis bases.<sup>9</sup> The general facility by which these reactions occur prompted us to examine the rhodium(II) acetate catalyzed decomposition of diazo compounds in the presence of 3-chloro-3-phenyldiazirine. With ethyl diazoacetate, diethyl maleate and diethyl fumarate were the major products, the mixed coupling products were formed in <10% yield, and neither the carbene dimers from 3-chloro-3-phenyldiazirine nor its azine product were observed. However, the unsymmetrical azine was detected, albeit in low yield, and its presence suggests that azine formation, resulting from the thermal decomposition of diazirines, occurs by carbene association with the diazirine followed by rearrangement (eq 3) rather



than by any of the pathways described in Scheme I. Accordingly, we suggest that alkene formation is dependent on the extent of diazirine to diazo isomerization, whereas azine formation results from carbene association with the intact diazirine.

### Experimental Section

Diazo compounds were prepared by standard procedures: phenyldiazomethane by thermal decomposition of benzaldehyde *p*-tosylhydrazone,<sup>10</sup> diphenyldiazomethane by oxidation of benzophenone hydrazone,<sup>11</sup>  $\alpha$ -diazoacetophenone and 1-diazo-3,3-dimethyl-2-butanone from diazomethane reactions with their respective acid chlorides,<sup>12</sup> and *N,N*-dimethyl- and *N,N*-diisopropyl diazoacetamides from the corresponding amine and diketene followed by diazo transfer and hydrolytic deacylation.<sup>13</sup> Instrumentation employed for structural and analytical determinations included the Hewlett-Packard Model 5995C GC/MS

system, the JEOL FX-90Q FT-NMR spectrometer, the Perkin-Elmer Model 283 IR Spectrometer, and Hewlett Packard 5890A capillary GC systems with flame ionization detectors. Elemental analyses were performed by Galbraith Laboratories, Inc., on product samples that were isolated and purified by gas chromatography.

**General Procedure.** The 3-halo-3-phenyldiazirine (2.0 mmol) and diazo compound (2.1–2.2 mmol) in 10 mL of dry carbon tetrachloride contained in a round-bottom flask fitted with a reflux condenser were heated to boiling and maintained at reflux for 3 hr. Following evaporation of the solvent, the crude mixture was weighed and analyzed directly by GC and spectral methods. The symmetrical azine formed from the diazirine was present in amounts ranging from 1% to 5% (based on reactant) in each of the reaction solutions. Benzalazine was produced from phenyldiazomethane in amounts dependent on its molar excess relative to 3-chloro-3-phenyldiazirine. Column chromatography on silica gel separated azines from olefinic products. Mixed carbene coupling products were identified by GC/MS analyses from their molecular ions and fragmentation patterns and from the characteristic <sup>1</sup>H NMR spectra of those compounds derived from ethyl diazoacetate and diazoacetamides. With the exception of the last two entries of Table I, all of the unsymmetrical alkenes have been prepared by alternative synthetic methods.<sup>14</sup> Conversion of ethyl 3-chloro-3-phenylpropenoate to its derivative *N,N*-diisopropyl amide provided characterization of the product derived from decomposition of 3-chloro-3-phenyldiazirine in the presence of *N,N*-diisopropyl diazoacetamide: <sup>1</sup>H NMR (CDCl<sub>3</sub>) [Z isomer]  $\delta$  7.7–7.2 (m, 5 H), 6.34 (s, =CH), 3.55 (heptet, 2 H), and 1.27 (d, 12 H), [E isomer]  $\delta$  7.7–7.2 (m, 5 H), 6.61 (s, =CH), 3.35 (heptet, 2 H), and 0.81 (d, 12 H); IR (CCl<sub>4</sub>) 1630 cm<sup>-1</sup> (C=O).

**1-Chloro-1-phenyl-4,4-dimethyl-1-penten-3-one:** <sup>1</sup>H NMR (CDCl<sub>3</sub>) [Z isomer]  $\delta$  7.37 (s, 5 H), 6.90 (s, 1 H), and 1.15 (s, 9 H), [E isomer]  $\delta$  7.8–7.3 (m, 5 H), 7.06 (s, 1 H), and 1.04 (s, 9 H); IR (thin film) 1690 cm<sup>-1</sup> (C=O); mass spectrum, *m/e* (relative abundance) [Z isomer] 224 (2.0, M + 2), 222 (5.8, M), 196 (2.0), 194 (6.2), 167 (33), 165 (100), 129 (55), 102 (44), 75 (19), and 57 (50), [E isomer] 224 (1.1, M + 2), 222 (3.1, M), 196 (2.3), 194 (6.9), 167 (33), 165 (100), 129 (57), 102 (25), 75 (7.2), and 57 (8.7). Anal. Calcd for C<sub>13</sub>H<sub>15</sub>ClO<sub>2</sub>: C, 70.11; H, 6.79. Found: C, 7.22; H, 6.73.

**Rhodium(II) Acetate Catalyzed Decomposition of Ethyl Diazoacetate in the Presence of 3-Chloro-3-phenyldiazirine.** To 0.246 g of diazirine (1.5 mmol) and 7.0 mg of rhodium(II) acetate (1.0 mol %) in 5.0 mL of dichloromethane was added 0.174 g of ethyl diazoacetate (1.5 mmol) in 5.0 mL of the same solvent through a syringe pump over a 5-h period. Chromatographic separation of the catalyst through neutral alumina and evaporation of the solvent provided a residue whose major constituents were diethyl maleate and fumarate (50–60%). 3-Chloro-3-phenyldiazirine was recovered in 55–65% yield. Mass spectral analysis confirmed the presence of the carbene coupling product (<10%) and suggested the unsymmetrical azine (15%): *m/e* (relative abundance) 240 (0.2, M + 2), 238 (0.6, M), 203 (6.2, M-Cl), 194

(9) Doyle, M. P. *Chem. Rev.* 1986, 86, 919.

(10) Creary, X. *Org. Synth.* 1985, 64, 207.

(11) Smith, L. I.; Howard, K. L. *Organic Synthesis*; Wiley: New York, 1955; Collect. Vol. III, p 351.

(12) Eistert, B.; Regitz, M.; Heck, G.; Schwall, H. *Methoden der Organischen Chemie (Houben-Weyl-Muller)*, 4th ed.; Georg Thieme Verlag: Stuttgart, 1968; Vol. 4, p 714.

(13) Doyle, M. P.; Dorow, R. L.; Terpstra, J. W.; Rodenhouse, R. A. *J. Org. Chem.* 1985, 50, 1663.

(14) See, for example: (a) Viehe, H. G.; Janousek, Z. *Angew. Chem. Int. Ed. Engl.* 1973, 12, 806. (b) Baum, J. S.; Viehe, H. J. *Org. Chem.* 1976, 41, 183. (c) Youssef, A.-H.; Abdel-Maksoud, H. M. *J. Chem. Soc., Chem. Commun.* 1974, 288.

(2.7, M + 2 - EtOH), 192 (7.9, M - EtOH), 167 (22, M + 2 - COOEt), 165 (68, M - COOEt), 140 (10), 138 (29), 103 (100), 77 (60), 76 (44).

**Acknowledgment.** We are grateful to the National Science Foundation and to the Robert A. Welch Foundation for their support of this research. Partial funding for the mass spectrometer system was provided by the National Science Foundation.

**The Chemistry of the  
*trans*-Trimethylenenorbornene Ring System. 4.  
A Kinetic and Molecular Mechanics Study of the  
Thermal Rearrangement of  
9-Carbomethoxy-*trans*-5,6-trimethylene-2-norbornene<sup>1</sup>**

George B. Clemans\* and Jean K. Blaho<sup>2</sup>

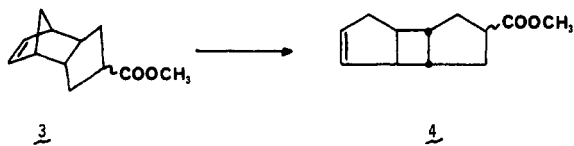
*Department of Chemistry, Bowling Green State University,  
Bowling Green, Ohio 43403*

*Received September 5, 1986*

Thermal rearrangements of bicyclo[3.2.0]heptenes to norbornenes (e.g., 1 → 2) have been known<sup>3</sup> for some time and have been used by Berson<sup>4</sup> to establish the steric course of such 1,3-sigmatropic carbon migrations generally. In most reported cases,<sup>4,5</sup> however, these reactions occur at higher temperatures (>300 °C) and yield a number of products of which some are unstable under the reaction conditions.



We have described<sup>6</sup> the facile rearrangement of the *trans*-trimethylenenorbornene 3 to the tricyclodecene 4, a process that is analogous to those above, but that occurs in the opposite direction. This rearrangement, however, is observed at temperatures well below 200 °C and yields 4 as the sole product. Since it is the first such rear-



rangement of a norbornene derivative to be reported, we have undertaken a combined kinetic and molecular mechanics investigation to elucidate the energetics of this remarkable process and to reexamine under more favorable experimental circumstances earlier conclusions concerning the mechanism of 1,3-sigmatropic migrations in such systems.

**Table I. Average Rate Constants for the Rearrangement of 3**

temp, <sup>a</sup> °C	rate constant <sup>b</sup>
178	$(8.79 \pm 0.15) \times 10^{-6}$
188	$(2.11 \pm 0.02) \times 10^{-5}$
199	$(6.46 \pm 0.06) \times 10^{-5}$
210.5	$(1.61 \pm 0.01) \times 10^{-4}$

<sup>a</sup> Maintained at  $\pm 0.5$  °C. <sup>b</sup> Average of duplicate determinations. Reported error range is the deviation from the average.

**Table II. Comparison of Kinetic Parameters**

reactant	$E_a^a$	log A
3	39.4	13.6
1a	46.8 <sup>b</sup>	13.7 <sup>b</sup>
1b	48.6 <sup>c</sup>	14.8 <sup>c</sup>

<sup>a</sup> In kilocalories/mole. <sup>b</sup> Reference 4b. <sup>c</sup> Reference 5, for total disappearance of starting material.

**Table III. Calculated Heats of Formation**

compound	$\Delta H_f^\circ$ <sup>a</sup>	compound	$\Delta H_f^\circ$ <sup>a</sup>
1b	28.1	5	37.4
2b	19.3	6	16.8 <sup>c</sup>
3	-48.1 <sup>b</sup>	7	-68.2 <sup>b</sup>
4	-60.4 <sup>b</sup>		

<sup>a</sup> In kilocalories/mole. <sup>b</sup> Average of syn and anti epimers. <sup>c</sup> Average for syn and anti conformations.

### Results and Discussion

The kinetics of the rearrangement of 3 in decalin were conveniently followed by <sup>1</sup>H NMR by periodic integration of the vinyl region (see Experimental Section). Duplicate determinations were made at each of four different temperatures over a range of 35 °C, and the reactions were followed to over 70% completion. Rate constants were then calculated from kinetic plots and averaged at each temperature. Table I summarizes the results.

An Arrhenius plot made by using these rate constants was found to be linear, and the activation energy for the rearrangement was thus determined. Table II compares the kinetic parameters of this reaction with those of related processes reported earlier.

In order to gain further insight into the nature of energy changes in these rearrangements, enthalpies of reaction were determined from heats of formation calculated by using Allinger's MM2 molecular mechanics program.<sup>7</sup> The results are summarized in Table III. It was thus found that the rearrangement of 1b was exothermic by 8.8 kcal/mol, while the rearrangement of 3 was exothermic by 12.4 kcal/mol. For purposes of comparison, all of the energies determined for these rearrangements are combined in Figure 1.

Berson has pointed out<sup>4</sup> that the anticipated difference in activation energies between concerted and diradical pathways for the rearrangement of 1a is quite small and that the distinction between the two on this basis is not straightforward. The high stereospecificity of the rearrangement of 3 as in the case of 1a argues strongly for a concerted mechanism in both cases, however. Molecular mechanics calculations for the rearrangement of 3 provide additional support for this conclusion. A diradical intermediate formed by homolytic cleavage of the 4,5 bond in 3 could close either to 4 or to 7, the *endo,cis* isomer of 3. The calculated heats of formation of the isomeric systems

(1) (a) Presented at the 18th Central Regional Meeting of the American Chemical Society, Bowling Green, Ohio, June, 1986. (b) Part 3 of this series: Clemans, G. B.; Samaritoni, J. G.; Holloway, R. J.; Edinger, W. *J. Org. Chem.* 1984, 49, 3457.

(2) Dreyfus Undergraduate Research Student, Summer 1985.

(3) For a review, see: Spangler, C. W. *Chem. Rev.* 1976, 76, 187.

(4) (a) Berson, J. A. *Acc. Chem. Res.* 1968, 1, 152. (b) Berson, J. A. *Acc. Chem. Res.* 1972, 5, 406.

(5) Cocks, A. T.; Frey, H. M. *J. Chem. Soc. A* 1971, 2564.

(6) Clemans, G. B. *J. Org. Chem.* 1973, 38, 3459.

(7) (a) Program no. 395 available from QCPE, Department of Chemistry, Indiana University, Bloomington, IN 47450. (b) Burkert, U.; Allinger, N. L. *Molecular Mechanics*; ACS Monograph 177; American Chemical Society: Washington, DC, 1982.