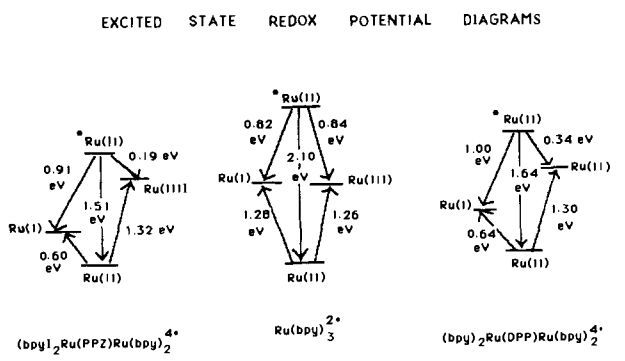

Figure 5. Excited-state potential diagrams comparing $Ru(bpy)_3^{2+}$ (center) to dimeric complexes of dpp (right) and ppz (left). See Table III for reference potentials.

potentials of the bimetallic complexes for the quinoxaline-based ligand complexes (entries 3 to 5) are estimated from the correlation in Figure 4. In spite of these approximations, the excited state potentials listed in Table III clearly indicate that MLCT states of these kinds of binuclear complexes are invariably weaker reductants than their monometallic counterparts. The decrease in MLCT state 2+*/3+ potential arises principally in the decline in energy in the π^* acceptor orbital, since ground-since oxidation potentials of the mono- and bimetallic analogues are the same within experimental error. In contrast, the MLCT states of the bimetallic complexes are stronger oxidants than their corresponding monometallic analogues since the decrease in the energy of the π^* acceptor orbital is more than offset by a decrease in the ground-state reduction potential (i.e., for the bridging ligand). In fact, as illustrated in Figure 5, the bimetallic dpp and ppz complexes are stronger excited-state oxidants than $*Ru(bpy)_3^{2+}$. Also of note, in view of the recognized difficulties in controlling the reversibility of the photoredox chemistry of $Ru(bpy)_3^{2+}$, is the significant reduction in the ground-state reduction potentials, which lowers the driving force for the thermal back reaction. With the appropriate choice of a weak reducing quencher, reductive quenching of these bimetallic complexes can be used to transfer an electron to a second oxidant by means of a second thermal reaction. Although the fraction of radiant energy converted to redox potential is small, the overall reaction, i.e., oxidation of a quencher and reduction of the second oxidant, will not be burdened by an exergonic back reaction. Quenching experiments are in progress to test the calculated MLCT state potentials and the possibility of utilizing the above scheme to reduce viologens or other desirable electron-transfer intermediaries.

Conclusions

The detection of emission from binuclear complexes of Ru(II) of the type $[(bpy)_2Ru\text{-}L\text{-}Ru(bpy)_2]^{4+}$ at room temperature in fluid solution is closely correlated with the energy of the bridging ligand π^* acceptor orbital, which, along with the ground-state oxidation and reduction potentials, is a monitor of the degree of interaction between the two $Ru(bpy)_2^{2+}$ units as moderated by the bridging ligand. The excited-state redox potentials of binuclear complexes with dpp and ppz are luminescent, and their MLCT states are calculated to be weak reductants but surprisingly potent oxidants.

Acknowledgment. H.D.G. gratefully acknowledges the support of the Technology Acquisition Program of the Dow Chemical Company. A.D.B., T.C.S., and H.D.G. acknowledge the support of the City University of New York/Professional Staff Congress research award program.

Unsymmetrically, Chemically Activated 1,2-Dicyclopropylacetylene: An Example of Restricted Energy Flow?

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Abstract: The Doering–Gilbert–Leermakers strategy for revealing chemical reaction possibly more rapid than internal flow of energy is applied to 1,2-dicyclopropylacetylene by examining addition of dideuteriomethylene to 1-cyclopropyl-2-vinylacetylene and of methylene to 1-(2,2-dideuteriocyclopropyl)-2-vinylacetylene in the gas phase. This reduction to practice of the general strategy has three advantages: one of the three isomers of allylcyclopropylacetylene, itself the key product of chemically activated rearrangement, bears internal witness to the achievement of structural symmetry prior to its generation; the long, linear acetylenic linkage precludes internal energy flow by a mechanism of intramolecular collision; and the activation energy of the cyclopropane–propene rearrangement is lowered significantly. Analysis of the experimental results reveals a small amount of rearrangement at high pressures occurring prior to complete symmetrization of structure and/or energy. If this observation can be ascribed to incomplete symmetrization of *energy*, the basic premise of the Rice–Ramsperger–Kassel–Marcus theory—that internal energy flow be so much faster than chemical reaction that a structureless statistical treatment is justified—may require reconsideration.

Rice–Ramsperger–Kassel–Marcus (RRKM) theory of unimolecular, gas-phase processes supposes an internal flow of energy so much faster than chemical reaction that a structure-free, statistical theory is applicable.[1] Efforts to define the experimental limits of this premise begin with the work of Kistiakowsky and Butler[2] and continue into the present era of multiphoton infrared

†This work is dedicated to the late Richard Leopold Wolfgang, July 24, 1928–June 19, 1971; in profound appreciation of his seminal contribution to my awareness of modern kinetic theory and in reaffirmation of lasting loss.

(1) For references to earlier reviews and recent work, see: Holbrook, K. A. *Chem. Soc. Rev.* **1983**, *12*, 163–211. Goodall, D. M.; Cureton, C. G. *Chem. Brit.* **1983**, 493–501.

(2) Butler, J. N.; Kistiakowsky, G. B. *J. Am. Chem. Soc.* **1960**, *82*, 759–765.

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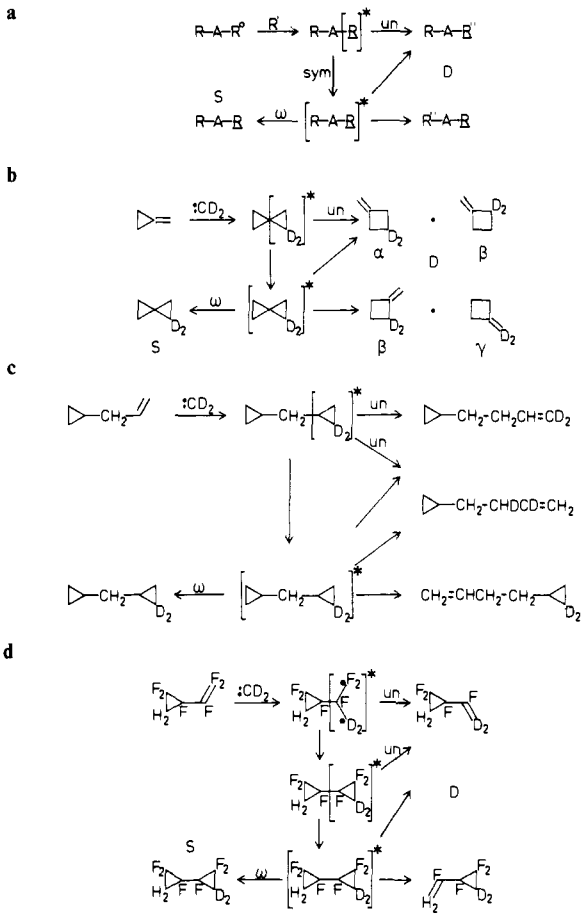
Scheme I



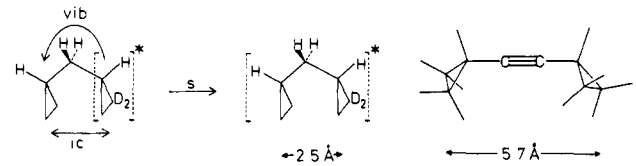
and overtone laser energization.[3-6]

A conceptually unambiguous approach to a test of the validity of the premise, formulated by Doering, Gilbert, and Leermakers,[7] involves generation of an activated species, RA[*R*]*, capable of undergoing rearrangement at the original site of energization to RA*R*″ or, after symmetrization of energy to [RA*R*]* and its remobilization at the remote site R, to R″A*R* (Scheme Ia).

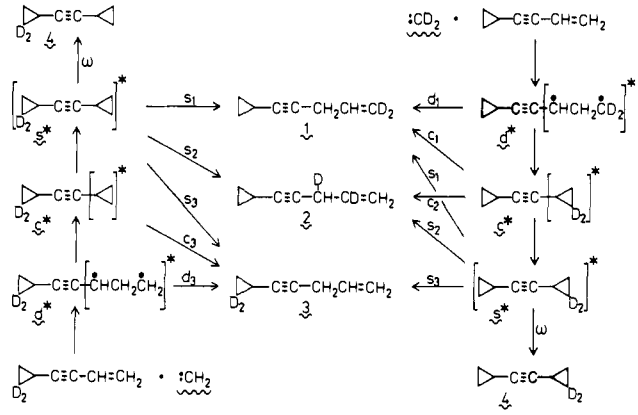
The reactions of methylene with methylenecyclopropane (Scheme Ib), where A is a single carbon atom in common[7] (essentially minus a carbon atom in the general formulation, Scheme Ia), and with allylcyclopropane, where A is a methylene group[8] (Scheme Ic), were examined in these laboratories as initial efforts to apply the new strategy. Both examples showed complete symmetrization of energy, within experimental uncertainties, prior to rearrangement (vinylcyclopropane, in giving mainly cyclohexene, remained stilborn).[7]

In a widely acclaimed application of the strategy, Rynbrandt and Rabinovitch[9] examined the reaction of labeled methylene with hexafluorovinylcyclopropane and reported a small amount (3.5%) of nonrandom reaction (Scheme Id). This elegantly conceived example is not entirely unambiguous, owing to formidable, incompletely resolved experimental difficulties.[10]

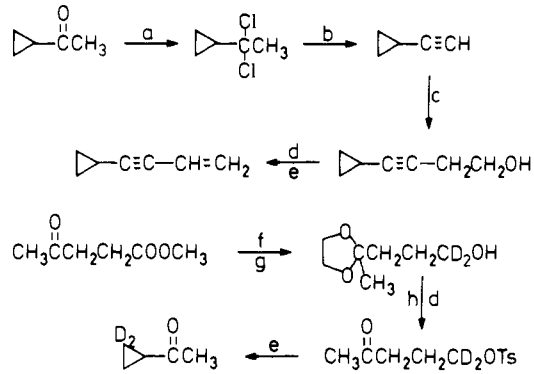
Scheme II



Scheme III



Scheme IV



a) PCl_5, b) KOtBu, c) $LiNH_2$,oxirane, d) $C_7H_7SO_2Cl$, e) 50% KOH, f) $(CH_2OH)_2$, H^+, g) $LiAlD_4$, h) H_2O, H^+.

In view of these reservations and the continuing high level of interest in the problem from both theoretical and practical points of view, we have undertaken a further search for an example in which chemical reaction might be competitive with intramolecular energy flow.

In order for experimental results to bear on the premise of RRKM theory, the mechanism for energy transfer from one part of a molecule to another must be restricted to internal vibrational coupling (vib). To this end, the stategy is extended to the acetylenic linkage as the interposing group,[11] a choice designed to separate an original cyclopropane ring from a neonatal cyclopropane ring by a distance sufficient to prevent transfer of energy by the intramolecular equivalent of intermolecular collision (ic) (see Scheme II).

The acetylenic linkage not only satisfies this requirement convincingly but offers two possible further advantages: first, its fundamental stretching frequency, not being close to any other

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(5) Farneth, W. E.; Thomsen, M. W. *J. Phys. Chem.* **1983**, *87*, 3207–3212. Farneth, W. E.; Thomsen, M. W. *J. Am. Chem. Soc.* **1983**, *105*, 1843–1848.

(6) Jasinski, J. M.; Frisoli, J. K.; Moore, C. B. *Discuss. Faraday Soc.* **1983**, *75*, 289–299.

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(8) Avery, N. L. Ph.D. Dissertation, Harvard University, 1972.

(9) (a) Rynbrandt, J. D.; Rabinovitch, B. S. *J. Phys. Chem.* **1970**, *74*, 4175–4176; **1971**, *75*, 2164–2171. (b) Rynbrandt, J. D. Ph.D. Dissertation, University of Washington, 1970.

(10) These difficulties relate to purification and spectroscopic characterization of starting materials and products and standardization of mass spectra by means of pure reference substances. Replotting log (S/D) of "Figure 3" of ref 9a (see Figure 2, this paper) as (S/D) or S/(S + D) serves to highlight the absence of orderly change in yield of D over the pressure range, 195–3100 torr, where the divergences in *m/e* 95/97 ("Figure 1") and 47/45 ("Figure 2") *are critical to a reliable diagnosis of nonrandom reaction.*

(11) (a) Hutchinson, J. S. *J. Chem. Phys.* **1985**, *82*, 22–30. (b) Hall, R. R. Ph.D. Dissertation, Rice University, 1984. (c) Uzer, T; Hynes, J. T. *J. Phys. Chem.* **1986**, *90*, 3524–3527. (d) Holme, T. A.; Hutchinson, J. S. *Chem. Phys. Lett.* **1986**, *124*, 181–186.

Table I. A Brief Kinetic Study of the Thermal Rearrangement of 1-Cyclopropyl-2-(2,2-dideuteriocyclopropyl)acetylene (**4**) in the Gas Phase

t (s)	T (°C)	p (torr)	**4**	ACA-d_2[a]	C-*t*-PA-d_2[b]	k_1 ($\times 10^6$)[c,d]
3600	340	36	0.972	0.0107	0.0175	7.89
7200	340	36	0.947	0.0198	0.0333	7.56
14400	340	36	0.898	0.0383	0.0644	7.57
480	390	38	0.879	0.0489	0.0724	269
900	390	38	0.790	0.0907	0.1194	262
1800	390	38	0.651	0.1570	0.1920	238

[a] A mixture of dideuterioallylcyclopropylacetylenes **1**, **2**, and **3** (ACA-d_2). [b] A mixture of dideuteriocyclopropyl-*trans*-propenylacetylenes (C-*t*-PA-d_2). [c] First-order rate constants calculated from the usual expression, $\ln [(x_0 - x_t)/x_0] = -k_1 t$. [d] Activation parameters, calculated from average values of k_1 ($7.64 \pm 0.22 \times 10^{-6}$ s^{-1} at 340° and $2.56 \pm 0.16 \times 10^{-4}$ s^{-1} at 390°) and $\ln A = (T_1 \ln k_1 - T_2 \ln k_2)/(T_1 - T_2)$ and $E_a = (\ln A - \ln k)RT$, have values of $E_a = 57 \pm 2$ kcal/mol and $\log A = 15 \pm 0.5$.

frequency in the molecule, may not be conducive to efficient vibrational coupling, but note that recent theoretical analysis by Uzer and Hynes offers no support to this possibility;[11c] and second, the activation energy of the cyclopropane–propene rearrangement should be lowered by some 6.5 kcal/mol by propargyl resonance[12] and thus lead to faster and more competitive rearrangement of chemically activated species.

An overview of the complete system is presented in Scheme III. The rearrangement product of major interest is allylcyclopropylacetylene (A), for it assuredly cannot be produced by direct insertion of methylene into a carbon–hydrogen bond. In order to minimize isotope effects on the interpretation, the study includes the addition of CD_2 and CH_2 to undeuteriated cyclopropylvinylacetylene and to 1-(2,2-dideuteriocyclopropyl)-2-vinylacetylene, respectively. Three dideuterio isomers of allylcyclopropylacetylene, **1**, **2**, and **3**, are expected, and these should be the same in structure, if not in amount, as those obtained by direct thermal rearrangement of 1-cyclopropyl-2-(2,2-dideuteriocyclopropyl)acetylene (**4**).

The two cyclopropylvinylacetylenes required in Scheme III as starting material are prepared in the manner outlined in Scheme IV. The sequence in common is the conversion of acetylcyclopropane to cyclopropylvinylacetylene via cyclopropylacetylene. The task of producing the dideuterio analogue reduces to the preparation of acetyl-2,2-dideuteriocyclopropane.

Thermal activation of dicyclopropylacetylene **4** led mainly to cyclopropyl-*trans*-propenylacetylene and allylcyclopropylacetylene (A) in a ratio of 1.7 ± 0.1 at 340° and 1.3 ± 0.3 at 390°. Samples needed for the development of an analytical method were obtained by heating **4** on a large scale and isolating by preparative gas chromatography.

Kinetics of the rearrangement of **4** were studied in an air-thermostated, 3-L sphere of Corning 0120 lead–potash glass at 340° and 390° ± 0.5°. A slow falloff in first-order rate constants with length of run precluded extraction of accurate kinetics. Because the present purpose would be sufficiently well served by an approximate estimation of activation parameters, the study was truncated (see Table I). The resulting values of E_a and log A were 57 ± 2 kcal/mol and 15.0 ± 0.5, respectively. Thus, the acetylenic linkage lowered the activation energy 7 ± 2 kcal/mol below that for cyclopropane itself.

After much ultimately vain effort had been invested in trying to develop a mass spectrographic method of analysis, ^2H NMR of sufficiently high resolution became available as the method of choice. Isomer **1** revealed its two deuterium atoms as a pair of doublets, D_Z at 5.28 and D_E at 5.08 ppm, isomer **2**, its allylic D_a as a doublet at 2.84 and its vinylic D_v at 5.76 ppm, while isomer **3** showed its two cyclopropyl D_c at 0.70 and 0.61 ppm. Thus, a single measurement established the structure of the allylcyclopropylacetylene as a mixture of **1**, **2**, and **3**, excluded significant contamination by compounds having any other distribution of deuterium, and allowed the relative amounts of the three isomers to be determined within the usual limits of accuracy (ca. ± 2%) of NMR spectroscopy.

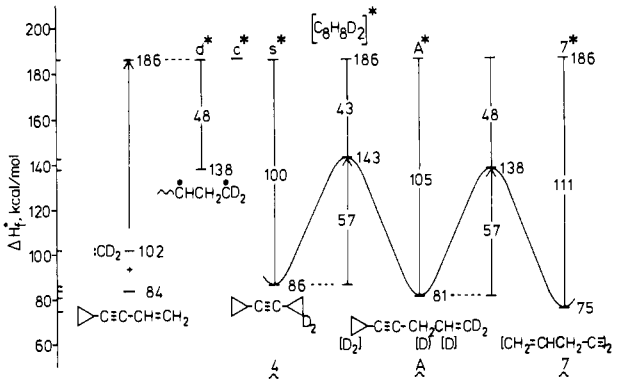

Figure 1. An enthalpy diagram (kcal/mol) of the reactants, products, and chemically activated species depicted in Scheme III. Although shown here for the reaction of dideuteriomethylene with unlabeled 1-cyclopropyl-2-vinylacetylene, it applies as well to the reaction of unlabeled methylene with 1-cyclopropyl-2-(2,2-dideuteriovinyl)acetylene.

Pure samples of A, obtained after thermal rearrangement of **4** in a flow system at 490 ± 10° (seven runs), gave ratios of **1**/**2**, (**1** + **2**)/**3**, and **1**/**3** of 1.60 ± 0.11, 0.74 ± 0.02, and 0.46 ± 0.03, respectively. Rearrangement in a 3-L flask (38 torr) at 390° (two runs) gave corresponding ratios of 1.60 ± 0.03, 0.72 ± 0.01, and 0.45 ± 0.01, respectively. The primary isotope effect (H/D) in the generation of isomer **2** is 1.78 whereas the secondary effect in the formation of isomer **1** is 1.11.

Chemically activated dicyclopropylacetylene (s* of Scheme III) is generated by photolysis of diazomethane in the gas phase and addition of the resultant singlet methylene to cyclopropylvinylacetylene. Although **4** is the major product even at the lowest pressures (longest time between collisions) examined in this work, many other products are observed as the result of insertion into the six types of carbon–hydrogen bonds and as the result of further rearrangement of the initial products while still in chemically activated states. For analytical purposes, capillary gas chromatography suffices to give quantitatively reliable information on the relative amounts of the major product of stabilization (S) (here dicyclopropylacetylene, **4**) and the key product of decomposition (D) (here allylcyclopropylacetylene, A).

The origin of the chemical activation is elucidated by thermochemical analysis. Reasonable estimates can be made for the various species involved in Scheme III based, unless otherwise noted, on heats of formation given in Cox and Pilcher.[13] For cyclopropylvinylacetylene, $\Delta H_f^\circ = +84.3$ kcal/mol can be estimated from the experimental ΔH_f° of propene, methylcyclopropane, and propyne and a conjugative correction of −2.0 kcal/mol; for singlet CH_2, the currently best value for ΔH_f° is 102 ± 1 kcal/mol;[14] for dicylopropylacetylene, $\Delta H_f^\circ = +85.7$ kcal/mol may be estimated from the heats of formation of bicyclopropyl, butyne-2, and ethane; for allylcyclopropylacetylene A and diallylacetylene **7**, group equivalent values[13] give ΔH_f° of 80.8 and 74.9 kcal/mol, respectively; for the thermally equilibrated diradical corresponding in Scheme III to d*, $\Delta H_f^\circ = +138.2$ kcal/mol is obtained by adding the value of $\Delta\Delta H_f^\circ$ involved in breaking a primary CH bond (+48.5 kcal/mol) and a secondary CH bond (+44.8 kcal/mol)[15] in cyclopropyl-*n*-propylacetylene and subtracting the value of 6.5 kcal/mol derived by Schmidt[12]

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(13) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: New York, 1970.

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Table II. Distribution among the Three Isomers, **1**, **2**, and **3**, of 1-(Dideuterioallyl)-2-cyclopropylacetylene[a] Formed in the Reaction of Methylene with 1-(2,2-Dideuteriocyclopropyl)-2-vinylacetylene (CH_2 Series) and Dideuteriomethylene with 1-Cyclopropyl-2-vinylacetylene (CD_2 Series), and in the Thermal Rearrangement of 1-Cyclopropyl-2-(2,2-dideuteriocyclopropyl)acetylene, **4** (Th)

	2		**1**		**3**
conditions	D_a	D_v	D_Z	D_E	D_c
CH_2/1.5 mm	9.55 ± 0.33	9.58 ± 0.28	12.33 ± 0.09	12.73 ± 0.28	
	19.13 ± 0.23		25.06 ± 0.21		55.80 ± 0.40
CH_2/15 mm	9.53 ± 0.19	9.27 ± 0.51	11.50 ± 0.22	11.08 ± 0.19	
	18.80 ± 0.63		22.57 ± 0.17		58.62 ± 0.57
CH_2/47 mm	8.79 ± 0.24	8.65 ± 0.20	10.79 ± 0.14	10.48 ± 0.17	
	17.44 ± 0.37		21.27 ± 0.12		61.30 ± 0.47
CD_2/1.5 mm	10.24 ± 0.49	9.60 ± 0.26	13.79 ± 0.42	13.63 ± 0.35	
	19.84 ± 0.69		27.42 ± 0.64		52.74 ± 0.60
CD_2/15 mm	9.54 ± 0.11	9.51 ± 0.18	17.49 ± 0.10	19.36 ± 0.80	
	19.05 ± 0.13		36.86 ± 0.72 (34.98)[b]		44.09 ± 0.61
CD_2/45 mm	10.30 ± 0.34	9.32 ± 0.32	19.25 ± 0.06	19.14 ± 0.38	
	19.62 ± 0.35		38.39 ± 0.39		41.99 ± 0.32
CD_2/200 mm	8.54 ± 0.12	6.98 ± 0.48	27.47 ± 0.52	27.68 ± 0.36	
	15.52 ± 0.36		55.15 ± 0.47		29.32 ± 0.27
Th/390°	7.93 ± 0.28	8.22 ± 0.51	12.90 ± 0.25	12.92 ± 0.12	
	16.14 ± 0.23		25.82 ± 0.25		58.03 ± 0.21
Th/490°	8.11 ± 0.74	8.24 ± 0.21	13.27 ± 0.22	12.80 ± 0.32	
	16.34 ± 0.91		26.17 ± 0.44		57.48 ± 1.05

[a] Each point is derived from three or more ^2H NMR measurements; given in %. [b] The data at CD_2/15 mm relate to two runs that were combined and subjected to several purification procedures before limitations of quantity required settling on the data reported. The value in parentheses is simply twice the value for the deuterium content of the D_Z position.

for propargyl resonance. These values and the enthalpy of activation of the thermal rearrangement of dicyclopropylacetylene (57 kcal/mol) are collected in the energy diagram of Figure 1.

As initially formed, s* is estimated to have a heat of formation of 186 kcal/mol (Figure 1), which is some 43 kcal/mol above that of the transition state required for its thermal rearrangement to allylcyclopropylacetylene A. Unless collisionally deactivated, s* must therefore rearrange to allylcyclopropylacetylene A*, which in statu nascendi, will have an undiminished heat of formation of 186 kcal/mol and therefore an estimated excess enthalpy of 105 kcal/mol. This enthalpy content exceeds that of the transition state for further rearrangement to decomposition products such as diallylacetylene **7** by 48 kcal/mol. The general qualitites of the reaction are revealed in the ratios of dicyclopropylacetylene, **4** or S, to allylcyclopropylacetylene, A or D, as a function of pressure. The accumulated data from 22 experiments in a range of pressure from 0.05 to 200 torr are graphed in Figure 2 as the plot of log (S/D) vs. log p.

Were it not for the further rearrangement of A* to 1,2-diallylacetylene **7**, which is presumed to proceed more rapidly by a constant factor, a, these data should fall on a line of slope = 1.00. Given this complication, a more elaborate kinetic scheme, such as that developed in Figure 3, is needed. It is analyzed in terms of the usual steady-state assumption. Note that complete randomization of energy is assumed in this scheme; that is, each cyclopropane ring in s* is given the same chance, k_0, of rearranging. Further, the rate of thermal rearrangement of **4** is assumed twice that of A on statistical grounds and not to be influenced by the cyclopropyl or the allyl group. At high pressures, S/(S + D) should approach 1.00 (high rates of collisional deactivation: $\omega = pZ$), while, at low pressures, S/D should approach the value $a/2$ asymptotically.

When the data are plotted as S/D vs. p, it is easy to see how strongly experimental error in the high-pressure region influences the value of the intercept at $p = 0$. When the linear eq 4 is fit to the data by linear regression, quite disparate values of $a/2$ are obtained depending on whether the last high-pressure point or the last two or the last three are included. Consistently, the slope, $(Z/2k_0)$, is only very slightly affected by changes in the value of $a/2$. To pin $a/2$ down with good accuracy would require more data of higher quality at very low pressures, a formidable task at best. We conclude that a reasonable range for $(Z/2k_0)$ is 1.0 ± 0.1 and for a is 9 ± 3. The solid curve in Figure 2 results from incorporating these values into eq 4 of Figure 3.

The magnitude of a falls within the range predicted by RRK theory. If the values for E and E_0 in Figure 1 are inserted in the formula, $k_E = C[(E - E_0)/E]^{s-1}$ and s is set equal to $3(N - 2)/2$, $a = 4.95$.

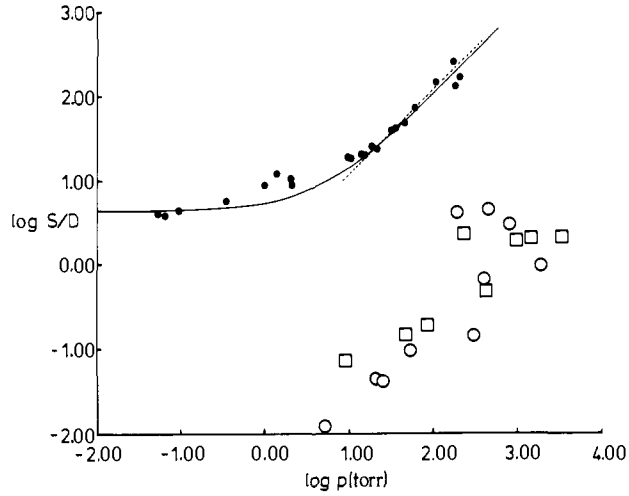
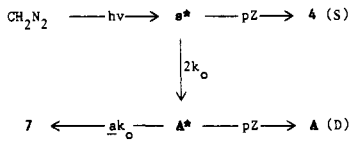


Figure 2. Filled circles show the ratio of dicyclopropylacetylene (S) to allylcyclopropylacetylene (D) observed in the reaction of methylene with cyclopropylvinylacetylene at various pressures. The dotted line shows a slope of 1.00, whereas the solid curve is calculated from eq 4 of Figure 3. The open squares and circles reproduce the results of Rynbrandt and Rabinovitch[9] from their study of the reaction of dideuteriomethylene with 1,2,2-trifluoro-1-(trifluorovinyl)cyclopropane (open squares) and methylene with 3,3-dideuterio-1,2,2-trifluoro-1-(trifluorovinyl)cyclopropane (open circles) (page 65 and 65a[9b]).

Photolyses of diazomethane in cyclopropylvinylacetylene with deuterium-labeled materials are conducted in a 22-L, round-bottomed, thoroughly seasoned, Pyrex flask under irradiation with a G.E. RS sunlamp. In the run at 200 torr, nitrogen is the diluting bath gas. Allylcyclopropylacetylene A as the product of interest is scrupulously purified in a sequence of separations on four GC columns. Distribution of deuterium among its deuteriated isomers **1**, **2**, and **3** is then determined by ^2H NMR with results given in Table II.

Note first that the ratio of vinylic to allylic hydrogen in isomer **2** is 1.0 within the probable uncertainty. From this result, strong argument can be made against an arcane path for the generation of allylcyclopropylacetylene by direct insertion into the carbon–carbon bond linking the acetylenic and the vinylic groups of cyclopropylvinylacetylene. As was also to be expected, the ratio of the two vinylic deuterium atoms in isomer **1** is 1.0 within



$$d[A^*]/dt = 2k_o[s^*] - (\underline{a}k_o + pZ)[A^*] = 0 \quad (1)$$

$$d[A]/dt = pZ[A^*] = (pZ2k_o[s^*]/(\underline{a}k_o + pZ); \quad d[4]/dt = pZ[s^*] \quad (2)$$

$$S/(S + D) = (\underline{a}k_o + pZ)/[(\underline{a} + 2)k_o + pZ] \quad (3)$$

$$S/D = \underline{a}/2 + (Z/2k_o)p \quad (4)$$

Figure 3. The kinetic scheme for the conversion of unlabeled diazomethane and 1-cyclopropyl-2-vinylacetylene to 1,2-dicyclopropylacetylene **4** or (S), 1-allyl-2-cyclopropylacetylene A or (D), and diallylacetylene **7**.

Table III. Data of Table II Presented as Ratios among the Isomers of Dideuterioallylcyclopropylacetylenes **1**, **2**, and **3** at Various Pressures

p (torr)	1/2	2/3	1/3	D/(S + D)
		CH_2 Series[a]		
1.5	1.31	0.34_3	0.44_9	0.08
15	1.20	0.32_0	0.38_5	0.05
45	1.22	0.28_5	0.34_7	0.03
		CD_2 Series[b]		
1.5	1.38	0.37_6	0.52_0	0.08
15	1.84	0.43_2	0.79_4	0.04
47	1.96	0.46_8	0.91_5	0.02
200	3.55	0.53_0	1.88_1	0.01

[a] "CH_2 series": photolyses of diazomethane in 1-(2,2-dideuteriocyclopropyl)-2-vinylacetylene. [b] "CD_2 series": photolyses of dideuteriodiazomethane in 1-cyclopropyl-2-vinylacetylene.

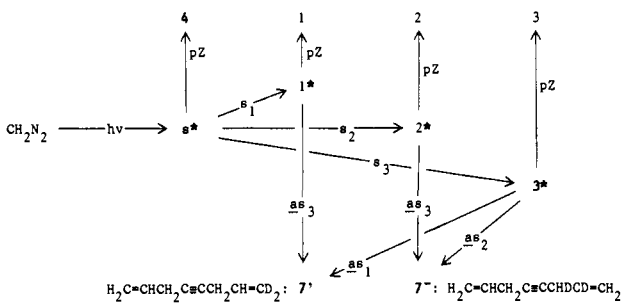
experimental error. In Table III, the data in Table II are presented as ratios in order to highlight trends as a function of pressure.

The most striking feature of the results lies in the nonidentity of the two series. In the CH_2 series, the reaction of unlabeled, photolytically generated methylene with deuterium-labeled cyclopropylvinylacetylene, the three ratios in Table III decrease with increasing pressure, whereas in the CD_2 series (labeled methylene and unlabeled cyclopropylvinylacetylene) the reverse is true: the ratios increase with pressure. No matter how complicated the systems may be, if the same energy-symmetrized, chemically activated species, s*, were the immediate product of the addition in both series, then, within experimental error, the results in the two series would be identical regardless of pressure. Clearly, an element of asymmetry, which makes itself felt more strongly the higher the pressure, biases the system.

That the bias is larger when monitored by **1** than by **2** is easily seen in the ratio, **1/2**, in the CD_2 series. That the biases appear to increase with pressure is caused by a decrease in the importance of s* as the source of **1**, **2**, and **3** (D) as pressure increases. Consistently, the ratio of rearranged product D to the sum of D and stabilized (**4** or S) product [D/(**4** + D)] increases as pressure is lowered.

At the low-pressure limit, the major portion of A stems from s*, which has its excess energy symmetrically distributed among all internal degrees of freedom, and thus requires, according to RRKM theory, the longest time to reorganize its excess energy into the activated complex for rearrangement. As pressure is raised, increasing amounts of internally equilibrated s* suffer collisional deactivation prior to rearrangement and become stabilized as **4**. The yield of **4** therefore rises with increasing pressure at the expense of A. Thus, products of rearrangement prior to symmetrization appear more and more prominent with increasing pressure, because the products of rearrangement *post* symmetrization are increasingly prevented by collisional deactivation from making their appearance and diluting the unsymmetrical component.

Consistently, results in both the CH_2 and CD_2 series seem to converge at the low-pressure limit. Whatever the origin of the high-pressure biases, they represent an increasingly small fraction of total A as pressure decreases and yield increases. The biasing processes are clearly introduced in the short time scale, high-pressure region of the process and play only a passive role in determining the composition of the product at the longer lifetimes associated with lower pressure.



$$d[1^*]/dt = s_1[s^*] - (\underline{as}_3 + pZ)[1^*] \quad (1)$$

$$d[2^*]/dt = s_2[s^*] - (\underline{as}_3 + pZ)[2^*] \quad (2)$$

$$d[3^*]/dt = s_3[s^*] - (\underline{as}_1 + \underline{as}_2 + pZ)[3^*] \quad (3)$$

$$d[1]/dt = pZ[1^*] = (s_1pZ[s^*])/(\underline{as}_3 + pZ) \quad (4)$$

$$d[2]/dt = pZ[2^*] = (s_2pZ[s^*])/(\underline{as}_3 + pZ) \quad (5)$$

$$d[3]/dt = pZ[3^*] = (s_3pZ[s^*]/(\underline{as}_1 + \underline{as}_2 + pZ) \quad (6)$$

$$\frac{[1]}{[2]} = \frac{s_1pZ[s^*]t}{(\underline{as}_3 + pZ)} \cdot \frac{(\underline{as}_3 + pZ)}{s_2pZ[s^*]t} = \frac{s_1}{s_2} \quad (7)$$

$$\frac{[1]}{[3]} = \frac{s_1pZ[s^*]t}{(\underline{as}_3 + pZ)} \cdot \frac{(\underline{as}_1 + \underline{as}_2 + pZ)}{s_3pZ[s^*]t} = \frac{s_1}{s_3} \cdot \frac{(\underline{as}_1 + \underline{as}_2 + pZ)}{(\underline{as}_3 + pZ)} \quad (8)$$

Figure 4. The kinetic scheme for the chemically activated, energetically symmetrized system s*, its rearrangement to **1***, **2***, and **3*** (representing chemically activated **1**, **2**, and **3**, respectively, prior to collisional deactivation), and their further rearrangement to **7'** and **7''**, based on the steady-state assumption (see Scheme III for definition of terms).

More detailed analysis of what would be expected in the deuterium-labeled experiments if all rearrangement were to pass through chemically activated, symmetrized s* parallels that developed above in Figure 3 for unlabeled materials. The relevant equations are based on the reaction scheme in Figure 4 it is assumed that (*a*) the rates of rearrangement of **1***, **2***, and **3*** to **7** are greater by the factor *a* than the rates, s_1, s_2, and s_3, from s* owing to the larger degree of chemical excitation (estimated to be 5 kcal/mol; see Figure 1); (b) all chemically activated molecules are deactivated at the same rate; and (c) the first collision removes enough energy so to slow further rearrangement that contributions from partially deactivated molecules can be neglected in the first approximation and that the rate of deactivation can be equated with the collision frequency, pZ (in a more realistic approach, deactivation would be treated as a stepwise process).

The three differential equations, 1–3, in Figure 4 may each be set equal to zero under the steady-state assumption, solved for [**1***], [**2***], and [**3***], respectively, and used to generate the second set, eq 4–6. These may in turn be integrated and combined to give expressions for the desired ratios, eq 7 and 8.

Equation 7 predicts that the ratio of **1/2** should be invariant with pressure as well as independent of the origin of s*. Equation 8 reveals that the ratio **1/3** has for its high-pressure solution, the expression, s_1/s_3, and a low-pressure solution, $(s_1/s_3)([s_1 + s_2]/s_3)$, in which the ratio is lowered by the sum of the two isotope effects prevailing in s_1 and s_2.

We choose to begin discussion of experimental results in terms of **2**, because **2**, as may be seen in Scheme III, may not be formed in the CD_2 series from d* and can only be formed after the symmetry of a cyclopropane c* has been achieved. The same cannot be said for the formation of **1**. We believe this requirement implies a distribution of the energy of chemical activation prior to generation of **2** at least wide enough to include the internal

degrees of freedom associated with a monosubstituted cyclopropane (but vide infra).

An important consideration concerns the possible involvement of triplet methylene and a corresponding triplet state of d*. No matter how tenable this possibility may be for accommodation of the generation of **1**, it is energetically untenable as a participant in the generation of **2** (vide infra).

Finally, the generation of **2** by some arcane reaction of the acetylenic bond with CD_2 seems far less plausible than might be the generation of **1**. In sum, conclusions about rearrangement prior to energy symmetrization based on monitoring of **2** carry considerably more authority than those based on **1**.

As pressure increases, the values of the ratios **2**/**3** diverge from the "low-pressure" limit of 0.36, decreasing in the CH_2 series and increasing in the CD_2 series. Were **2** to have been produced entirely from energy-symmetrized intermediate s*, no divergence of these ratios with pressure would have been observed at pressures ≥10 torr (vide supra). A conclusion seems firm: rearrangement to **2** occurs in part through an unsymmetrized species, for the structure of which energy-unsymmetrized but structurally symmetrized, chemically activated c* is a strong contender (Scheme III).

These results constitute a demonstration of restricted energy flow if it be accepted that the crucial structural symmetrization of the new cyclopropane has been fully achieved prior to the chemically activated, energetically unsymmetrized transition state (see Scheme Ia). Superficially, the very reaction selected to achieve structural symmetry—the addition of singlet methylene to an olefin—is so widely accepted to proceed on a concerted, "no-mechanism" path to cyclopropane that questioning may seem contrived. The situation remains ambiguous, however, when the available energy is recognized to be sufficient to enable the initially formed 1,3-diradical d* to rearrange to allylcyclopropylacetylene competitively with ring-closure to c*.

Prior to collision with a third body, CH_2 and cyclopropylvinylacetylene lead to chemically activated C_8H_{10}* having $\Delta H_f°$ = +186 kcal/mol regardless of structure. This species lies 100 kcal/mol above thermally equilibrated dicyclopropylacetylene, 43 kcal/mol above the transition state for its thermal rearrangement to allylcyclopropylacetylene and 48 kcal/mol above the $\Delta H_f°$ calculated for a model diradical corresponding to d*. Clearly, there is more than enough enthalpy available to maintain C_8H_{10}* as the open diradical d*.

Whereas this chemically activated diradical d* has two exit channels—ring closure to c* and rearrangement by hydrogen migration to chemically activated **1** (**1***) (we are not concerned here with the branched isomer of d* and its rearrangement to cyclopropyl-*trans*-propenylacetylene)—only rearrangement subsequent to ring closure to c* is unequivocally germane to the demonstration of restricted energy flow.

Witness to that ring closure is provided by the formation of **2** because there is no credible path for its formation from d*. Prior to the availability of ^2H NMR, no analytical method to focus attention exclusively on **2** had been available. The example of Rynbrandt and Rabinovitch[9] suffers from lack of an internal indicator comparable to **2** to bear witness that a hypothetical diradical resulting from bonding CH_2 to the monofluorinated carbon atom of the olefin has indeed closed to the constitutionally symmetrical cyclopropane prior to the ejection of CF_2 (see Scheme Id). Were closure not to occur as the exclusive process, an indefinite amount of a constitutionally *unsymmetrical* intermediate would make loss of CF_2 irrelevant to the question of nonsymmetrization of energy.

The availability of a product like **2** is also helpful in removing the triplet state of d* as the source of an apparent restriction to energy flow. Such an explanation envisions triplet methylene adding to the olefin to generate triplet d* (^{3}d*), which would not be able to undergo ring closure to triplet c*[16] and thence rearrange to **2**. Although ^{3}d* might rearrange to triplet **1*** (or eject triplet difluoromethylene[17] in the Rynbrandt–Rabinovitch example), neither of these processes is energetically attractive.

As an intermediate with a lifetime in the 100–1000 ns range, ^{3}d* would preserve asymmetry until intersystem crossing generated ^{1}d*, but ample opportunity would have been provided for vibrational symmetrization of its 48 kcal/mol of excess energy. Although the resulting c* could rearrange to **2**, its internal distribution of energy would by then be much more akin to that in s* than is implied by energy-unsymmetrized c*.

When attention is shifted to **1** as the monitor, results similar to those seen with **2** as monitor might have been anticipated. In fact, the ratio **1**/**3** diverges from its low-pressure value substantially faster than does **2**/**3**. Equally striking is the divergence of the ratio **1**/**2** in the CD_2 series (Table III). By contrast, this ratio in the CH_2 series does not change with pressure because both **1** and **2** arise only from energy-symmetrized s*.

An explanation of this observation that avoids assigning a role to d* involves increasing the ratio of the deuterium isotope effects operating in c_1 and c_2. In order to assess the magnitude of the isotope effect in c_2 required to develop a successful accommodation, the data in Table III may be translated into relative contributions among the six processes in Scheme III. Two assumptions are made: first, d_1 is set equal to zero; and, second, the ratio c_1/c_2 is set equal to the ratio s_1/s_2 inferred from the data in the CH_2 series by extrapolation to zero pressure.

The experimental ratios, **1**/**3** and **2**/**3** in the CD_2 series, can be written in accord with Scheme III

$$\mathbf{1/3} = d_1/s_3 + c_1/s_3 + s_1/s_3 = r_1 \quad (1)$$

$$\mathbf{2/3} = c_2/s_3 + s_2/s_3 = r_2 \quad (2)$$

In the CH_2 series, the ratios, s_1/s_3 and s_2/s_3, are assumed equal to the low-pressure limits of **1**/**3** and **2**/**3**, respectively

$$(\mathbf{1/3})_{p0} = s_1/s_3 = t_1 = 0.47 \quad (3)$$

$$(\mathbf{2/3})_{p0} = s_2/s_3 = t_2 = 0.36 \quad (4)$$

where s_1/s_2 is taken to be 1.30_6.

It follows that

$$d_1/s_3 + c_1/s_3 = r_1 - t_1 \text{ and } c_2/s_3 = r_2 - t_2 \quad (5)$$

Because d* has been excluded from the scheme and d_1 has been set equal to zero, values of c_1/c_2 can be calculated to fit the experimental data in the CD_2 series from the equation

$$c_1/c_2 = (r_1 - t_1)/(r_2 - t_2)$$

The results are given in the order, pressure and calculated ratio c_1/c_2: 1.5 torr, 3.1; 15 torr, 4.1; 47 torr, 4.1; 200 torr, 8.3.

Although one might rationalize the apparent inconstancy of c_1/c_2 as experimental error, it would be hard to accept a value for c_1/c_2 outside the range 3–7. We argue that c_1/c_2 from the thermal rearrangement of **4** being 1.60 and from the rearrangement of s* being 1.31, it is likely that the ratio from c* would be closer to 1.00, as a consequence of the confinement of the 43 kcal/mol excess energy to a smaller region of the molecule. Conclusion: the hypothesis that d* plays no role ($d_1 = 0$) requires such a large ratio of isotope effects as to be quite untenable.

If the contribution of a hypothetical d_1 process is to be calculated on the assumption that the ratio of isotope effects, $i = c_1/c_2 = 1.30_6$, eq 6 and 7 apply

$$c_1/s_3 = i(c_2/s_3) = i(r_2 - t_2) \quad (6)$$

$$d_1/s_3 = r_1 - t_1 = i(r_2 - t_2) \quad (7)$$

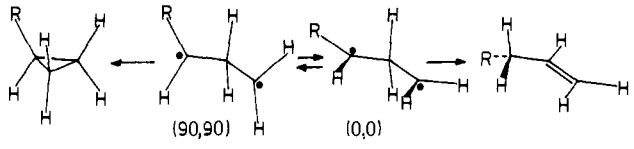
The resulting values of the ratio d_1/s_3 at the four pressures follow: 1.5 torr, 0.03; 15 torr, 0.23; 47 torr, 0.30; 200 torr, 1.19.

On balance, the involvement of a third process in the generation of **1** is strongly implicated. It seems reasonable that process should be represented by d*. As deduced earlier, and summarized in Figure 1, there is approximately 48 kcal/mol more enthalpy available than is required to maintain dicyclopropylacetylene **4**

(16) Cvetanović, R. J.; Avery, H. E.; Irwin, R. S. *J. Chem. Phys.* **1967**, *46*, 1993–1994.

(17) Bauschlicher, C. W., Jr.; Schaefer, H. F. III; Bagus, P. S. *J. Am. Chem. Soc.* **1977**, *99*, 7106–7110.

Scheme V



in its open form, the singlet diradical, d*. For its rearrangement by hydrogen shift to chemically activated **1**, the appropriate geometry is closer to (0,0) than the (90,90) geometry appropriate to ring-closure (see Scheme V). However, note that the activation enthalpy for rearrangement of cyclopropane to propene is 3.7 kcal/mol higher than that for cis–trans isomerization.[18]

If d* is to be a reasonable candidate for delaying attainment of the cyclopropane symmetry represented by c*, then methylene must be able to add to the olefin initially to generate the diradical. Clearly, the exothermicity of the reaction is large enough to tolerate successful bonding through the π-electrons of the olefin over a wide range of angles of attack. Recall that methylene reacts with both sp^2 and sp^3 carbon–hydrogen bonds in a statistically indiscriminate fashion.[19] Ring closure from d* is presumed to have zero enthalpy of activation,[15] but it may be dynamically complicated by the need to redistribute part of the 48 kcal/mol of excess energy to other than the stretching modes of the cyclopropane ring.

Otherwise, the situation could be similar to that prevailing in the collision of two potentially bonding atoms in the absence of a third body: an elastic collision without consummation of bonding. An alternative is coupling the excitation of vibrational modes with ring closure; that is, significantly to dissipate excess energy internally at the moment of closure to the ring. Such a requirement, entropic in nature and dependent on the amount of excess energy in the critical stretching mode, might give sufficient life to d* to allow rearrangement to **1**.

This hypothesis departs widely from the implications of those potential energy calculations which purport to reveal an intricate flight path for the two-point landing of methylene on a double bond.[20] But note that this latter model takes no note of the possible dynamic complications associated with the need to dissipate substantial amounts of exothermicity.

If the conceptual scheme of d* as a chemically activated, structurally unsymmetrical intermediate is valid, then that portion of **1** produced from d* does not relate directly to restriction of energy flow in the RRKM sense. It relates to a different, but not necessarily less interesting, question of how the rate of ring closure of d* to c* and the rate of rearrangement of d* to **1** vary with the excess energy content of d*.

By contrast, c* would satisfy the key requirement of the strategy for investigating restriction of energy flow that structural symmetry be achieved. Thus, that portion of **2** not generated from s* (and that portion of **1** not generated from d* or s*) is validly assigned to rearrangement of c* prior to energy symmetrization to s*. A credible proviso might invoke the transformation of d* in a one-step, ring-closing, ring-opening to a rearranged d* having the same structure as that otherwise accessible through c* or s* as an intermediate, but there is no known basis for supporting such an hypothesis.

As far as we can ascertain, there is no reported investigation of the reaction of ethylene or of a simple olefin with dideuteriomethylene in the gas phase to elucidate the detailed structure of the resulting dideuteriopropenes for evidence of excess formation of an isomer corresponding to **1**. As fascinating as may be the implication of the greater degree of rearrangement seen with **1** as monitor, the fundamental conclusion of this work is based on **2** as monitor and remains unaltered.

To questions about values of k_E (vide supra) for the rearrangement of d* to **1** and of c* to **2**, we have little to offer. In the liquid phase, no allylcyclopropylacetylene is formed. Between 200 torr and the liquid phase there are, presumably, pressures at which the amount of **2** from c* will have been reduced to half its low-pressure limit and the same will be true for **1** from d*. We have not scrutinized pressures high enough to observe competitions between rearrangement and collisional deactivation or partial deactivation of c* to **4** or states less weakly activated than s*.

It has been noted that the ratio d_1/c_2 appears to increase with pressure. If that trend be real, it may indicate preferential deactivation of the longer lived c*, in which event quenching of c* is being encountered in a pressure range corresponding to $\omega = 3.4 \times 10^9\ s^{-1}$. For comparison, k_E for similarly chemically activated cyclopropane and methylcyclopropane are reported[21] to be 45 and $1 \times 10^9\ s^{-1}$, respectively.

Acetylene as the interposing group appears to introduce a structural factor that can retard the rate of energy flow within the chemically activated molecule to a point where a chemical reaction, namely rearrangement of hydrogen, becomes detectably competitive with energy symmetrization. Implications for the prospects of effecting chemical reaction by specific mode excitation and for the basic premise of RRKM theory in its present structureless form are clear.

The present example should serve to stimulate the search—both theoretically and heuristically—for other structural features capable of restraining energy flow. We are currently curious to know how *cis*- and *trans*-vinylene as interposing groups in Scheme I compare to each other—the former as permitting energy flow by the mechanism of intramolecular collision, the latter not; both lowering the activation energy for competing rearrangement by about 14 kcal/mol; and both introducing the ring enlargement as a new following reaction with quite different geometrical requirements from that of hydrogen atom rearrangement.

In view of the qualifications imposed on the interpretation of this work, it is important to substitute ^{13}C as the tracer in a repetition or any extensions in order to minimize the disturbing, unresolved primary deuterium isotope effects.

Experimental Section

Physical chemical measurements were made on the noted instruments as following: infrared spectra on Perkin-Elmer spectrophotometers, Models 598 and 421; mass spectra on double focussing AEI MS9 and Kratos MS50 mass spectrometers; proton NMR spectra on Varian T-60 (60-MHz), Varian CFT20 (80 MHz, Fourier-transform), and Bruker WM300 (300-MHz) instruments, reported in δ units, ppm from Me_4Si.

Deuterium NMR spectra were determined on a Bruker WM300 spectrometer with an Aspect 2000 computer for Fourier-transform and integration: the field was 46.073 mHz; relaxation times for deuterium in **1**, **2**, and **3** were estimated to be <0.5 s; acquisition times of 2 s or greater were used to ensure accuracy of the integrations; receiver gain was set at $^1/_2$ the clipping point for weak samples; resolution usually was better than 1.0 Hz or about 0.02 δ; best integration was achieved when the vinyl, allyl, and cyclopropyl regions were phased individually before recording; signal/noise ratio for the integration was at least 10/1 for the smallest peaks measured and usually much higher.

Gas chromatographic analyses were effected on a Perkin-Elmer 990 gas chromatograph with a Hewlett-Packard 3380S digital recording integrator processing the signal from a flame-ionization detector; the capillary columns used for quantitative analysis were Perkin-Elmer 300-ft Carbowax K20M or Analabs 100-m Carbowax, which afforded comparable separations and statistically indistinguishable, quantitative results.

Gas chromatographic separations were effected on an Aerograph A90P3 gas chromatograph by using the following columns (aluminum tubing): CW1: 12 ft × 1/4 in. i.d., acid-washed 10% CW20M on Chromosorb P 60/80 mesh at 100–140 °C; CW2: 15 ft × 1/4 in. i.d., acid-washed 12% CW20M on Chromosorb P 60/80 mesh at 110–120 °C; Ag: 6 ft × 1/4 in. i.d., 20% $AgNO_3$ in glycerol, 20% on Kieselguhr 40/60 mesh at maximum T of 60 °C (long usable life if kept oxygen-free and stored at 0 °C); Ph: 12 ft × 1/4 in. i.d., acid-washed 10% di-*n*-butyltetrachlorophthalate on Chromosorb P 60/80 mesh at 130 °C.

Recovery of material from preparative GC is highest (80–90% of material injected, depending on the compound and conditions) when the

(18) Waage, E. V.; Rabinovitch, B. S. *J. Phys. Chem.* **1972**, *76*, 1695–1966.
(19) Doering, W. von E.; Buttery, R. G.; Laughlin, R. G.; Chaudhuri, N. Y. *J. Am. Chem. Soc.* **1956**, *78*, 3224.
(20) Bodor, N.; Dewar, M. J. S.; Wasson, J. S. *J. Am. Chem. Soc.* **1972**, *94*, 9095–9102.
(21) Dorer, F. H.; Rabinovitch, B. S.; Placzek, D. W. *J. Chem. Phys.* **1964**, *41*, 3995–3996.

GC effluent is passed through a collector cooled in dry-ice/acetone, containing a porous plug of glass wool wetted with a solvent such as liquid butane, which can be easily removed by evaporation.

Materials. Cyclopropylacetylene is prepared from cyclopropyl methyl ketone (Aldrich Chem. Co.) following a procedure adapted from that of Schobarth and Hanach.[22] Details for this and other preparations described here may be found in Ehlhardt's Ph.D. dissertation.[23]

1-Allyl-2-cyclopropylacetylene. This compound is obtained by an adaptation of a general procedure in Houben-Weyl,[24] in which cyclopropylacetylene is treated with *n*-butyllithium and anhydrous CuCl, followed by allyl bromide: NMR ($CDCl_3$, 80 MHz) 0.65 (m, 2 H), 0.71 (m, 2 H), 1.19 (m, 1 H), 2.84 (d of d, 2 H, J = 1.7, 5.4 Hz), 5.03 (d of m, 1 H, J = 11.6 Hz), 5.26 (d of m, 1 H, J = 17.2 Hz), 5.72 (m, 1 H); IR (neat) 3080, 3010, 2250, 1640 cm^{-1}; MS *m/e* (int) 106 (M, 30), 91 (100), 77, 78, 79 (40), 65 (35).

1-Cyclopropyl-2-vinylacetylene. Preparation is effected by an adaptation of a procedure developed by Link et al.[25] 1-Cyclopropyl-4-hydroxybut-1-yne results from treatment of a solution of $LiNH_2$ and cyclopropylacetylene with ethylene oxide (Matheson Corp.): NMR ($CDCl_3$, 80 MHz) 0.60 (m, 4 H), 1.1–1.3 (m, 1 H), 2.35 (d of t, 2 H, J = 2.0, 6.2 Hz), 3.60 (br t, 2 H), 3.20 (variable br s, 1 H); IR (neat) 3375, 3080, 3010, 2950, 2870, 2245 cm^{-1}.

The alcohol is then treated with *p*-toluenesulfonyl chloride in dry pyridine to afford the tosylate, which is heated with powdered KOH to give 1-cyclopropyl-2-vinylacetylene: NMR ($CDCl_3$, 300 MHz) 0.71 (m, 2 H), 0.77 (m, 2 H), 5.30 (d of d, 1 H, J = 2.4, 10.8 Hz), 5.44 (d of d, 1 H, J = 2.4, 17.3 Hz), 5.65 (m, 1 H); IR (neat) 3080, 3010, 2950, 2310, 2260 cm^{-1}.

1,1-Dideuterio-2-ethynylcyclopropane. Following the method of Bruice and Piskiewicz,[26] itself patterned after the general procedure of Conrad et al.,[27] levulinic acid is heated with absolute ethanol containing concentrated sulfuric acid to give ethyl levulinate, which is refluxed with ethylene glycol in benzene containing *p*-toluenesulfonic acid to give 2-methyl-1,3-dioxolan-2-propanoic acid, ethyl ester. This material is then reduced with lithium aluminum deuteride (99.8% isotopically pure, KOR Isotopes, Inc.) in anhydrous ether.

The resulting alcohol is hydrolyzed with 0.1 N HCl to 5,5-dideuterio-5-hydroxy-2-pentanone: NMR ($CDCl_3$, 80 MHz) 1.75 (br t, 2 H), 2.11 (s, 3 H), 2.50 (br t, 2 H), 3.10 (variable br s, 1 H); ^2H NMR (CCl_4) 3.45 (br s, 2 D). Treatment with *p*-toluenesulfonyl chloride in dry pyridine affords the tosylate which is converted to cyclopropyl methyl ketone-d_2 following the method of Curtius et al.[28] by addition to hot (80 °C) 50% NaOH solution: NMR (CCl_4, 80 MHz) 0.7 (br m, 2 H), 1.5–1.7 (br m, 1 H), 2.1 (s, 3 H); ^2H NMR (CCl_4) 0.73 (br d, 1 D), 0.87 (m, 1 D); IR (neat) 3050, 3010, 2980, 2210 (C–D), 1710, 1695, 1475, 1390, 1180 cm^{-1}; MS (int), *m/e* 86 (M, 45), 85, 84, 71 (100), 43, 42, 41, 40.

Isotopic purity follows from examination of *m/e* 69 ($C_3H_5O^+$), which has no measurable peaks immediately above or below. Thus, fragment peaks 71 (d_2), 70 (d_1), and 69 (d_0) are used for analysis. The average of four traces gave relative amounts, 100.0:1.2:0.9, respectively, corresponding to isotopic purity of 98.5 ± 0.4%.

Conversion of cyclopropyl methyl ketone-d_2 into 1,1-dideuterio-2-ethynylcyclopropane is accomplished exactly as for unlabeled cyclopropyl methyl ketone: NMR ($CDCl_3$, 80 MHz) 0.6 (br m, 2 H), 1.25 (br m, 1 H), 1.55 (d, 1 H); IR (CCl_4) 2250 (C–D), 2210 (triple bond) cm^{-1}.

1-Butenynyl-2,2-dideuteriocyclopropane (Cyclopropylvinylacetylene-d_2). This compound is prepared from cyclopropylacetylene-d_2 by using the same procedures as for the unlabeled compounds: NMR ($CDCl_3$, 80 MHz) 0.7 (br, m, 2 H), 1.3 (br m, 1 H), 5.25–5.75 (m, 3 H); ^2H NMR (CCl_4) 0.71 (br, d, 1 D), 0.77 (br, t, 1 D); IR (neat) 2260 (C–D), 2230 (triple bond) cm^{-1}.

1-Allyl-2-(2,2-dideuteriocyclopropyl)acetylene. This compound is prepared from cyclopropylacetylene-d_2 in the same manner as the unlabeled substance: NMR ($CDCl_3$, 80 MHz) 0.6–0.7 (br m, 2 H), 1.1–1.3 (br m, 1 H), 2.90 (m, 2 H), 5.0–6.5 (m, 3 H); ^2H NMR (CCl_4) 0.63 (m, 1 D), 0.71 (m, 1 D); MS, *m/e* 109 (10), 108 (M, 100), 107, 93 (65), 92 (60), 91 (35), 81 (25), 80 (40), 79 (40), 78 (40), 77 (20).

1,2-Dicyclopropylacetylene. This material is prepared by the method of Köbrich et al.[29] Raman spectroscopy (neat) shows intense bands at 2250 (triple bond), 1186, and 3015 cm^{-1}; NMR (CCl_4, 60 MHz) 0.65 (m, 2 H), 0.70 (m, 2 H), 1.0–1.4 (m, 1 H); IR (neat) 3080, 3000, 1230, 1060, 1045, 1010 cm^{-1}; MS *m/e* 106 (M, 40), 91 (100), 79 (80), 78, 77.

1-Cyclopropyl-2-(2,2-dideuteriocyclopropyl)acetylene. This compound is isolated from the mixture of products obtained in gas- and liquid-phase photolyses of CD_2N_2 with cyclopropylvinylacetylene or of CH_2N_2 with cyclopropylvinylacetylene-d_2 (vide infra) by preparative GC by using column CW1 (He flow 60 mL/min, column 110 °C, retention time 55–60 min). If necessary, it is further purified by passing through column CW2 (He flow 60 mL/min, column 140 °C, retention time 50 min), leading to material greater than 99% of purity, as measured by capillary GC. Its isotopic purity depends on the isotopic purity of the CD_2N_2 or cyclopropylvinylacetylene-d_2 used and is thus reported in the results for each experiment (Tables IV and V, Ehlhardt[23]): ^2H NMR (CCl_4) 0.65 (m, 1 D), 0.68 (m, 1 D).

Diazomethane. A 50% KOH solution (100 mL) is placed in a 250-mL, round-bottomed flask having 3 ⅋ 19/30 female, polished-glass joints (West Glass Inc.) with magnetic stirrer, 100-mL addition funnel, condenser, and a capillary tube connected to a tank of argon so that gas can be bubbled slowly through the solution. Polished-glass joints are used exclusively in the apparatus. A saturated solution of Diazald (Aldrich Chem. Co.) in diglyme is added very slowly to the stirred and heated (80 °C) KOH solution, the resulting diazomethane being carried past the condenser with the argon stream into a trapping solution of 40 mL of diglyme, decalin, or *tert*-butyltoluene cooled to −40 °C. From 0.1 mol of Diazald, about 0.05 mol of diazomethane is obtained. The solution is dried over KOH at 0 °C.

With diazomethane, being explosive and highly poisonous, no ground-glass joints are used, and preparations must be conducted in a hood protected against explosion by a shield.

Diazomethane-d_2. The procedure is adapted from that of Gassman and Greenlee.[30] A solution of approximately 0.05 mol of diazomethane in 40–50 mL of diglyme is placed in a dried, 250-mL Erlenmeyer flask under argon and stirred at 0 °C. It is treated with 10–12 mL of 1 N NaOD in D_2O (99.7% isotopically pure, KOR Isotopes Inc.) and lightly stoppered (caution must be exercised because CH_2N_2 is released during exchange). After 45 min, stirring is discontinued, and the solution is allowed to separate into two layers, from which the D_2O layer is removed by pipet. The exchange is repeated 2–3 times, each time using 10–12 mL of $NaOD/D_2O$, at which point the solution contains an estimated 0.025–0.030 mol of CD_2N_2 and some D_2O.

Analysis of Diazomethane-d_2. Quantitative analyses are effected by the method of Avery.[8] Approximately 1 mL of solution of diazomethane is titrated with a dried, saturated solution of iodine in ether until a faint, residual red color persists. For gas-phase work, 10–20-mg samples are distilled into a vacuum line system from a reservoir of CD_2N_2 in diglyme and condensed into an ampoule containing 1–2 mL of a dried, saturated solution of iodine in ether, which is warmed to room temperature to effect reaction. The resulting CD_2I_2 is isolated by washing the ether solution with 1–2 mL of saturated aqueous sodium thiosulfate and 2 mL of saturated aqueous NaCl and then removing the ether by distillation. Analysis by mass spectroscopy (MS9 or MS50) gives the relative amounts of CH_2I_2, $CDHI_2$, and CD_2I_2 (*m/e* 268, 269, and 270, respectively) directly from the mass spectral trace (range 0–120 mm, measured to ±0.5 mm). At 12 eV, there are no fragmentation peaks, and relative amounts can be measured directly. At 60 eV only the CDI_2^+ fragment (M − 2) interferes. After correction for its abundance, analyses at 12 and 60 eV gave identical results within experimental error. Measurements from 5–10 traces led to a standard deviation for the calculated isotopic purities of less than ±0.2%.

High-Temperature Rearrangement of Dicyclopropylacetylene. A 10 in. tube of 1 in. i.d. is packed with Pyrex helices and wrapped with heating tape (maximum temperature 650 °C). Seasoned by soaking for 2 days in concentrated NH_4OH, it is washed with water until neutral, dried, evacuated, and heated at 350 °C for 2–4 h. Attached to one end is a 5-mL tapered flask and, to the other end, a trap, connected via a vacuum line system to a rotary pump and a reduction manometer. Dicyclopropylacetylene is frozen in the flask at −196 °C, and the tube is evacuated to less than 0.01 torr and closed to the vacuum. After the trap has been cooled to −190 °C, the tube is heated to 490–510 °C, the flask

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is warmed to room temperature in order to evaporate the sample quickly, and the products are trapped.

Dicyclopropylacetylene reacts to give mainly two products when thermolyzed at 490–510 °C. At any given pressure, a narrow temperature band (±2–3 °C) allowed reasonable formation of the two products with little polymerization or formation of side products. Typically, 12 passes led in about 40% conversion to approximately equal amounts of allylcyclopropylacetylene and cyclopropylpropenylacetylene, with about 20% conversion to other products.

Analysis by capillary GC (column 55 °C, head pressure 35 psi) revealed allylcyclopropylacetylene, cyclopropylpropenylacetylene, and dicyclopropylacetylene of retention times of 34.1, 36.5, and 49.4 min, respectively. The main products were separated (≥98% of purity) by preparative GC on column CW1 (He flow 60 mL/min, column 110 °C): retention times of 30, 33, and 55 min for allylcyclopropylacetylene, cyclopropylpropenylacetylene, and dicyclopropylacetylene, respectively. Allylcyclopropylacetylene is identified by comparison of its IR and NMR spectra with those of an authentic sample. Cyclopropyl-*trans*-propenylacetylene is characterized: NMR ($CDCl_3$, 80 MHz) 0.70 (m, 2 H), 0.75 (m, 2 H), 1.29 (m, 1 H), 1.80 (d of d, 3 H, J = 1.8, 3.0 Hz), 5.35 (d of t, 1 H, J = 11 Hz), 5.70 (m, 1 H); IR (neat) 3090, 3020, 2900, 2250, 1630, 1520, 1460 cm^{-1}; MS, m/e 106 (M, 25), 91 (100), 77, 78, 79 (80), 65, 66, 67 (60).

High-Temperature Rearrangement of Dicyclopropylacetylene-d_2. In the same manner as above, 1-cyclopropyl-2-(2,2-dideuteriocyclopropyl)acetylene is heated leading to allylcyclopropylacetylene-d_2 and to cyclopropyl-*trans*-propenylacetylene-d_2. The ^2H NMR ($CDCl_4$) spectrum of allylcyclopropylacetylene-d_2 consists of a composite of the spectra of three isomers: ^2H NMR (CCl_4) (**1**) 5.06 (d, 1 D, J = 1.5 Hz, *trans*-vinyl), 5.27 (d, 1 D, J = 2.6 Hz, *cis*-vinyl); (**2**) 2.83 (d, 1 D, J = 2.9 Hz, methylene), 5.79 (m, 1 D, vinyl); (**3**) 0.67 (m, 1 D, *trans*-cyclopropyl), 0.71 (m, 1 D, *cis*-cyclopropyl); MS m/e, 108 (M, 100), 91, 92, 93 (80), 77–81 (60).

Cyclopropyl-*trans*-propenylacetylene-d_2 is also a mixture of three isomers: ^2H NMR (CCl_4) (a) 0.70 (m, 1 D, *trans*-cyclopropyl), 0.78 (m, 1 D, *cis*-cyclopropyl); (b) 1.81 (m, 2 D, methyl); (c) 1.81 (t, 1 D, methyl), 5.84 (m, 1 D, vinyl).

Gas-Phase Rearrangement of Dicyclopropylacetylene 4. The apparatus is an air-thermostat constructed by Beasley[31] after a design of Clark.[32] At the operating temperature (340 and 390 °C), the variance is ≤0.2°. The reaction vessel is a 3-L, round-bottomed flask of Corning 0120 lead–potash glass attached to the vacuum line by a graded seal from soft glass to Pyrex of 5 mm i.d. and a high-vacuum Teflon O-ring stopcock (Ace Glass). The reactant, 1-cyclopropyl-2-(2,2-dideuteriocyclopropyl)acetylene (10 mg; ≥98.5% of purity; 98.5% of 2 D), and *tert*-butylbenzene or cycloheptane (1–2 mg) as internal standards along with enough cyclohexane to bring the total mass of the solution to 400 mg are transferred to a small cold finger on the vacuum line. The contents are degassed, warmed to 40–50 °C and admitted to the previously evacuated reaction flask (10^{-4} torr). Evaporation of the solution is assisted by a heat gun (80 °C). After 10 s, the transfer is complete, pressure is measured, and the valve to the reaction flask is closed. At the end of a run, the flask is opened to a trap cooled to −196 °C at 10^{-4} torr. Introduction and removal of weighed samples shows that greater than 95% of the material can be recovered in the trap. Evacuation of the flask is complete within 5 s. Neither introduction nor removal of the reaction mixture causes a change in the temperature of the air thermostat.

Analysis of starting material and products is effected by capillary GC. The standard deviation for the ratios is within 0.1% as determined by 3 or 4 GC injections. At the pressures and temperatures used, the formation of side products is low, being less than 10% of total for the 30-min run at 390 °C. For purposes of spectroscopic analysis by ^2H NMR, a mixture of 60 mg of **4** and 340 mg of cyclohexane is heated in the manner above for 45 min at 390 °C and 35 torr. Owing to the increased amount of starting material, 4–5 min are required to transfer the solution completely into the reaction flask. The rate of conversion to the two main products (45%) is consistent with the results of the kinetic runs at 390 °C. Formation of byproducts amounts to 10% of theory.

The resulting allylcyclopropylacetylene-d_2 is isolated by preparative GC by using column CW2, followed by column Ag. Approximately 8–10 mg of this material is collected and shown by capillary GC to be 100% of purity with respect to other known deuterium-containing compounds. The relative amounts of isomers **1**, **2**, and **3** in the mixture are measured by ^2H NMR integration and are given in Table II (Th/390° and Th/490°).

Photolysis of Diazomethane in Cyclopropylvinylacetylene (Liquid). The photolysis is carried out in a 5-mL Pyrex tube fitted with a dry-ice/acetone condenser, irradiated by a General Electric RS sunlamp (Pyrex filter, $\lambda > 310$ nm), and cooled by a water jacket. Through an inlet valve, attached by tubing to a flask containing a solution of diazomethane in decalin at 0 °C, a stream of CH_2N_2 in argon is bubbled through 1 mL of neat cyclopropylvinylacetylene in the photolysis cell, while the solution is being photolyzed. The process is continued until about 50% of the starting material is converted into products, as measured by capillary GC (about 5 h). Diazomethane is introduced at approximately the rate at which it reacts.

After vacuum transfer of volatile material, a light yellow liquid is collected. Analysis by capillary GC (Perkin-Elmer; column head 35 psi; column 65°) reveals dicyclopropylacetylene (87%, retention time 30.34 min), cyclopropyl-*trans*-propenylacetylene (2%, retention time 23.12 min), and four other compounds A–D (1–2% each, retention time 15.03, 17.37, 21.14, and 34.40 min, respectively) making up all but 1% of the rest, which is a mixture of numerous unidentified substances. Cyclopropylvinylacetylene, cyclopropyl-*trans*-propenylacetylene, dicyclopropylacetylene, and compounds A–D are separated, purified by preparative GC by using column CW1, and isolated in greater than 90% of purity.

The first three are identified by comparison of their NMR and IR spectra with those of authentic materials. Compounds A–D corresponded to C–H insertion products of cyclopropylvinylacetylene and dicyclopropylacetylene; their retention times on the capillary column, NMR spectra (80 MHz, $CDCl_3$), and IR spectra (neat) follow: A (15.03 min) NMR 0.90–1.20 (m), 1.55 (s), 1.60 (s), 5.20–5.70 (m); IR 3090, 3010, 2960, 2220, 1550 cm^{-1}. B (17.37 min) NMR 0.60–1.50 (m), 1.75 (s), 5.00–5.70 (m); IR 3100, 3010, 2960, 2220, 1620, 1550 cm^{-1}. C (21.14 min) NMR 0.50–1.70 (m), 5.10–5.70 (m); IR 3080, 3010, 2950, 2240, 1560 cm^{-1}. D (34.40 min) NMR 0.50–1.50 (m); IR 3090, 3010, 2950, 2210, 1580, 1550 cm^{-1}.

Allylcyclopropylacetylene (retention time 22.20 min) was coinjected with the photolysis mixture on the capillary GC and did not give rise to a coincident peak. By using the measured amount of the smallest peak noted on the capillary GC trace as a guide, it was estimated that no more than 0.2% of this compound could have been formed, relative to dicyclopropylacetylene.

Photolysis of Diazomethane in Cyclopropylvinylacetylene (Vapor). The apparatus consists of a vacuum line equipped with an oil-diffusion pump system capable of producing a vacuum below 10^{-6} torr (pressure is measured with a mercury reduction manometer below 10^{-4}–5 torr and a normal mercury bar manometer above 10 torr). Four male ₹ 19/38, polished joints of the O-ring type are used for attachments. A 22-L, Pyrex flask with cold finger and a 10-mm, O-ring Teflon stopcock is attached via a female ₹ 19/38 polished glass joint. A 125-mL, two-necked, round-bottomed flask, containing solutions of diazomethane (d_0 or d_2) in *tert*-butyltoluene or diglyme, is attached to another joint in the same way, the second neck being sealed by a septum. The entire vacuum line is seasoned with diazomethane at 10 torr for 3 days before initial use. The pump exhaust is vented to the outside.

Gas-phase photolyses involving the photoaddition of CD_2 to cyclopropylvinylacetylene and CH_2 to 1-(2,2-dideuteriocyclopropyl)-2-vinylacetylene are all effected in identical manner. Diazomethane (d_0 or d_2) is distilled directly into the vacuum line from degassed reservoirs in *tert*-butyltoluene (mp −54 °C, bp 185 °C) or bis(2-methoxyethyl)ether (diglyme, mp −64 °C, bp 162 °C) until the desired pressure is reached. Cyclopropylvinylacetylene (d_0 or d_2) is weighed in a small ampoule with a female ₹ 19/38 polished glass joint, placed on the vacuum line, degassed, and transferred to the reaction vessel by evaporation. Its vapor pressure at room temperature is 10–12 torr, and the reduction manometer is not reliable above 5 torr. At higher pressures, the standard bar manometer is used instead and checked against the weighed amount of material by using the ideal gas law and known volume of the flask. All pressures noted are those actually measured manometrically. The accuracy of the pressure measurements is approximately ±10% below 20 torr, and ±1 torr at higher pressures. In photolyses carried out at total pressures greater than 15 torr, nitrogen, dried and oxygen-free (catalyst R3-11, Chemical Dynamics Corp., heated to 100 °C), is bled into the system from an attached reservoir to reach the desired pressure. The mixture is then condensed into the cold-finger at −196 °C, and the residual pressure is noted. It is well below 1% of the total pressure (except in runs with added nitrogen).

The flask is then isolated, and the mixture in the cold-finger is evaporated and irradiated for 1.5–2.0 h with 4 GE RS sunlamps positioned 1–4 in. outside the flask. At the end of the photolysis, product is condensed at −196 °C in the ampoule at the bottom of the reaction flask, the residual pressure is noted, and the flask is evacuated to less than 10^{-3} torr. The condensed product is then warmed and vacuum-transferred on the vacuum line to another ampoule, which is removed and warmed to room temperature carefully to release any volatile side products and

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remaining diazomethane. It may be stored for several days under argon or sealed under vacuum, but a change in composition is noted by capillary GC after a few weeks. Pressures, amounts of materials, irradiation times, etc., for each photolysis are given in Ehlhardt's dissertation[23] (for the results of photolyses involving unlabeled materials, see Figure 2 and Ehlhardt's Table III; for photolyses with dideuteriodiazomethane, Ehlhardt's Table IV; and for photolyses of diazomethane in labeled 1-(2,2-dideuteriocyclopropyl)-2-vinylacetylene, Ehlhardt's Table V).

The mixtures are analyzed by capillary GC by using either Carbowax column. A sample trace from a photolysis at 15 torr of unlabeled materials can be seen in Ehlhardt's[23] Figure 16. Peaks corresponding to allylcyclopropylacetylene and cyclopropyl-*trans*-propenylacetylene are first identified by coinjection of authentic materials. Amounts of allylcyclopropylacetylene (D) vary from 0.4–25.0% of the main product, dicyclopropylacetylene (S), in photolyses carried out between 200 and 0.06 torr, respectively. Reproducibility of the integrations is within 0.2–0.3% for the ratios of products. The measured ratios tend to rise or fall if the amounts of material injected are much greater or smaller than the normal injection (0.5 μL of a 10% solution of the photolysis mixture in ether). Overall, the photolysis produces about 100 products in quantity greater than 0.01% of the starting material. Solvents used for the diazomethane solutions are present in amounts of less than 0.5% of the total and do not interfere with the measurement of any of the products.

Isolation of Allylcyclopropylacetylene (d_0 or d_2) and Cyclopropyl-*trans*-propenylacetylene (d_0 or d_2) from Gas-Phase Photolyses. Allylcyclopropylacetylene-d_2 is isolated and purified by preparative GC in four stages, except where otherwise noted. First, column CW1 is used to separate the main components (He flow 60 mL/min, column 110 °C). Unreacted cyclopropylvinylacetylene (retention time 22 min) and dicyclopropylacetylene (retention time 55 min) are recovered in greater than 95% purity, as assessed by capillary GC. Allylcyclopropylacetylene (retention time 30 min) and cyclopropyl-*trans*-propenylacetylene (retention time 33 min) are collected as a single fraction containing all materials eluting between cyclopropylvinylacetylene and dicyclopropylacetylene. In the second stage, column CW2 is used (He flow 60 mL/min, column 100 °C) to separate allylcyclopropylacetylene and cyclopropyl-*trans*-propenylacetylene (retention time 40 and 45 min, respectively), each as mixtures containing 2–3 other main components. Third, impure allylcyclopropylacetylene is enriched to 90–95% of purity by chromatography on column Ag (He flow 120 mL/min, column 55 °C, retention 5.5 min). Fourth, chromatography on column Ph (He flow 60 mL/min, column 130 °C, retention time 25 min) allows isolation of allylcyclopropylacetylene in 98% of purity, most of the impurity being butyl alcohol from the column. This material is suitable for ^{2}H NMR analysis and shows peaks for isomers **1**, **2**, and **3** only.

Two photolyses, carried out at 15 torr with CD_2N_2 and cyclopropylvinylacetylene, were processed by using the first three steps of the above preparative GC separation procedure and yielded allylcyclopropylacetylene-d_2 in 94% of purity in one experiment and 93% of purity in another. To remove the impurity, the two samples were united after measurement of ^{2}H NMR spectra (each 2–4 mg in 2 mL of CCl_4), concentrated by distilling CCl_4 slowly (over 5 h) through a 30 in. Vigreux column until 0.5 mL of solution remained, and rechromatographed on column Ag to give A in 98% of purity.

The mixture from the series of photolyses carried out at 1.5 torr using CD_2N_2 and cyclopropylvinylacetylene was separated by the procedure consisting of the first three steps outlined above. The resulting material was 92% pure and contained an impurity interfering with the ^{2}H NMR analysis. The ^{2}H NMR sample (5 mg in 2 mL of CCl_4) was concentrated by removing CCl_4 by slow distillation (over 5 h) through a 30 in. Vigreux column, leaving 0.3 mL of solution, which was chromatographed by using column Ph and afforded material 100% of purity with respect to known deuterium-containing compounds and 98% of purity overall (capillary GC). The results are recorded in Table II.

A sample of allylcyclopropylacetylene (d_0 from photolyses with unlabeled materials was isolated by preparative GC by using the first three steps of the procedure outlined above. The resulting material was 93–96% of purity (capillary GC) and served in identification of samples of allylcyclopropylacetylene produced in gas-phase photolyses by comparison of IR and NMR spectra.

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Studies on the Synthesis of the Antitumor Agent CC-1065. Synthesis of the Unprotected Cyclopropapyrroloindole A Portion Using the 3,3′-Bipyrrole Strategy

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Abstract: The total synthesis of the unprotected A portion of the potent cytotoxic agent CC-1065 **1** using the 3,3′-bipyrrole strategy is described. Treatment of ethyl sorbate with (*p*-tolylsulfonyl)methyl isocyanide (TosMIC)/NaH gave the pyrrole **7**, which was *N*′-phenylsulfonated and treated again with TosMIC/NaH/HMDS to give the 3,3′-bipyrrole **11**. Through a sequence of transformations involving the Mannich reaction and standard homologation, the bipyrrole **11** was converted into the carboxylic acid **18**, which was readily induced to undergo intramolecular cyclodehydration to give the tricyclic phenol **20**. Alternative methods for converting **11** into **20** were examined, but the sequence described above was the most efficient. The 2,3-double bond in **20** was selectively reduced by using $HSiEt_3$/TFA to give **33**, after acetylation during the workup. Reduction of the ester **33** gave **34**, which upon exposure to the Mitsunobu conditions, namely, $EtO_2CN{=}NCO_2Et/Ph_3P$/THF, gave the cyclopropapyrroloindole **35**. Deprotection of **35** to give first **36** and subsequently **2** was achieved by treatment with MeONa/MeOH. The substrate **35** was exposed to *p*-ClC_6H_4SH to give **37** and *p*-TsOH to give **38**. Initially, coupling studies demonstrated that the sodium salt of **2** on treatment with indole-2-carbonyl chloride gave **41**, albeit in low yield.

The potent cytotoxic agent CC-1065 has the unusual triindole structure **1**.[1] It is more active than actinomycin, vinblastine, or maytansine. The overall molecule has a helical topology, and as such, is able to bind into the minor groove of DNA, where the

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