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Gas-Phase Addition of [^{13}C]Methylene to Ethene: Rearrangement of Chemically Excited Propene

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Abstract: Reaction of ethene with singlet [^{13}C]methylene, generated photochemically from [^{13}C]diazomethane at four pressures in the range 35−800 Torr, reveals rearrangement of excited [3-^{13}C]propene (**3**), the product of insertion, to [1-^{13}C]propene (**1**) and [2-^{13}C]propene (**2**). This previously unrecognized reaction is formulated as the reverse of the thermal rearrangement of cyclopropane to propene, well known in both thermal and chemically excited modes. The origin of a small excess of **1** over **2** is discussed. Mercury sensitization does not alter the observations at 820 Torr.

The quite unexpected appearance of a small amount of [3-^{13}C]-penta-1,4-diene in the reaction of buta-1,3-diene with [^{13}C]-methylene generated photochemically from [^{13}C]diazomethane[1] has prompted a look at ethene in the same reaction. From an abundant prior literature on the reaction of singlet methylene and ethene in the gas phase,[2,3] four primary products are expected: [^{13}C]cyclopropane by addition (**4**); [1-^{13}C]propene (**1**), [2-^{13}C]propene (**2**) and [3-^{13}C]propene (**3**) (in equal amount in neglect of isotope effects)[4] by pressure-dependent rearrangement (r) of chemically activated **4** (**4***) prior to collisional deactivation; and an additional portion of **3** by insertion (i) into the H−C bonds of ethene. This expectation is pictured in the top and bottom lines of Scheme 1.

Below the high-pressure limit, ratios among the isotopically labeled propenes **1**, **2**, and **3** are expected to be $r{:}r{:}(r + i)$, respectively, on the basis of the prior literature. At the high-pressure limit of this nine-atom system (ca. 30 000 Torr), Rowland, McKnight, and Lee have predicted by extrapolation that **4** would be the major product (78%) by addition and propene the minor product (22%) by insertion.[5] In principle and in neglect of isotope effect, monotritiated methylene CHT as used by Rowland and his colleagues could have led to a complete resolution of the course of the two reactions by which propene is formed. In practice, analysis by chromatography enabled the separation quantitatively of [3-^{3}H]propene, corresponding to **3**, from an otherwise inseparable mixture of [1-^{3}H]- and [2-^{3}H]propene, corresponding to **1** and **2**. No analytical method for the bisection of the latter mixture was discussed. Coupled with scavenging of triplet methylene by triplet dioxygen, these experiments, by convincing extrapolation to the high-pressure limit, gave a reliable estimate of the relative amounts of reaction of singlet methylene with ethene to **4** by addition and to **3** by insertion (the top row of Table 1). In neglect of the secondary isotope effect of tritium, the π-bond is 14 times more reactive than one olefinic C−H bond of ethene. Were the present investigation to offer ^{13}C in place of tritium for the purposes of achieving more nearly complete freedom from primary and secondary isotope effects and confirming the 1:1 ratio expected of isomers **1** and **2** by rearrangement of chemically excited cyclopropane, a shrug in response would suffice.

Table 1. Normalized Yields of Cyclopropane (**4**) and Propenes **1**, **2**, and **3** from the Photochemical Decomposition of [^{13}C]Diazomethane in Ethene at Various Total Pressures

pressure[a]	**4**[b]	**1**[c]	**2**[c]	**3**[c]
[30 000	0.780	0.000	0.000	0.220][d]
820[e]	**0.286**	**0.210** (1.09)[f]	**0.192** (1.00)[f]	**0.312** (1.62)[f]
		[0.165[g]	0.165	0.385 (2.33)[h]]
		+0.045[i]	+0.027	−0.073
800	**0.264**	**0.218** (1.12)	**0.195** (1.00)	**0.323** (1.65)
		[0.172	0.172	0.392 (2.28)]
		+0.046	+0.022	−0.069
287	**0.114**	**0.268** (1.10)	**0.245** (1.00)	**0.373** (1.52)
		[0.222	0.222	0.442 (1.99)]
		+0.046	+0.023	−0.069
100	**0.064**	**0.293** (1.08)	**0.271** (1.00)	**0.372** (1.37)
		[0.253	0.253	0.473 (1.87)]
		+0.053	+0.030	−0.101
35	**0.025**	**0.317** (1.09)	**0.291** (1.00)	**0.367** (1.26)
		[0.252	0.252	0.472 (1.87]
		+0.065	+0.039	−0.105
[0	0?	0.333	0.333	0.333 (1.00)[j]]
[0	0?	0.260	0.260	0.480 (1.85)[j,k]]

[a] Total pressure in Torr of ethene and diazomethane. [b] Analysis of **4** (**1** + **2** + **3**) is by GC. [c] Uncertainty in the NMR analyses for ^{13}C is 2%. [d] These fractions are the high-pressure limits proposed by Rowland et al.[5] [e] Radiation at 253.7 nm in a 5-L quartz flask containing a drop of liquid mercury. [f] Numbers in parentheses are ratios of **1**/**2**, **2**/**2**, and **3**/**2**, respectively. [g] Fractions in the second row are, for **1** and **2**, the fraction of **4** rearranged [e.g., (0.780 − 0.286)/3] and, for **3**, that fraction plus the amount estimated to be formed at the start by insertion [e.g., 0.165 + 0.220]. [h] The ratio **3**/**2** expected on the model of stable **3***. [i] The third row in a listing is the discrepancy between observation and expectation [e.g., 0.210 − 0.165]. [j] The ratio **3**/**2** expected at zero pressure on the model of a **3*** that rearranges to **4*** and then to **1***, **2***, and **3***. [k] This value is sensitive to the chosen composition at the limit of high pressure; had the fractions of **4** and **3** been 0.800 and 0.200, respectively, this ratio would have been 1.75, for example.

The experimental results recorded in Table 1 (in visual form in Figure 1) are not that simple. The change in yield of **3** with pressure, expected to parallel that of **1** and **2**, is clearly behaving strangely. At the 800-Torr point, for example and in conventional terms, **3** is expected to have been accreted by one-third

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Table 2. Analysis by ^{1}H NMR of ^{13}C-Labeled 1,2-Dibromopropane Resulting from the Photolysis of [^{13}C]Diazomethane in Ethene in a 5-L Pyrex Flask at 350 nm[a]

pressure[b]	$I_2(^1H)$[c]	$I_2(^{13}C)$[d]	$I_1(^1H)$[c]	$I_1(^{13}C)$[d]	$I_3(^1H)$[c]	$I_3(^{13}C)$[d]	**1/2**[e]	**3/2**[e]
800	5.67[f]	2.09	11.06	4.75	12.51	10.36	1.14	1.65
	5.80	2.10	11.34	4.65	12.67	10.15	1.11	1.61
	5.51	2.05	10.81	5.58	12.31	10.42	1.12	1.69
287	5.07[f]	2.01	9.87	4.45	11.98	9.20	1.11	1.53
	5.04	1.99	9.73	4.31	11.85	9.05	1.08	1.52
100	4.67[f]	2.02	9.02	4.36	11.66	8.36	1.08	1.38
	4.61	2.01	8.90	4.34	11.40	8.20	1.08	1.36
35	4.38[f]	1.98	8.57	4.33	11.51	7.47	1.09	1.26
	4.43	1.99	8.61	4.38	11.59	7.51	1.10	1.26
820[a]	5.32[f]	1.99	10.31	4.32	12.01	9.70	1.09	1.62
	5.36	2.00	10.35	4.35	12.05	9.73	1.09	1.62

[a] With the exception of the last experiment, which involves irradiation at 253.7 nm in a 5-L quartz flask containing a drop of mercury. [b] Total pressure in Torr of ethene and [^{13}C]diazomethane, the partial pressure of which was 8−10 Torr, except in the 287-Torr experiment where it was 4 Torr. [c] $I_2(^1H)$ is the integral of H-2 at 4.25 ppm; $I_1(^1H)$, H-1 at 3.86 and 3.56 ppm; $I_3(^1H)$, H-3 at 1.83 ppm (none of which is split by ^{13}C coupling). [d] These are the integrals of the ^{13}C sidebands: $I_2(^{13}C)$ for H-2, J = 156 Hz; $I_1(^{13}C)$ for H-1, J = 157 and 155 Hz; $I_2(^{13}C)$ for H-3, J = 102 Hz. [e] **1/2** = 1/2[$I_1(^{13}C)/I_2(^{13}C)$]; **3/2** = 1/2[$I_3(^{13}C)/I_2(^{13}C)$]. [f] Each row at a given total pressure represents a separate analysis of the same sample; the values, not being normalized, are arbitrary measures of area.

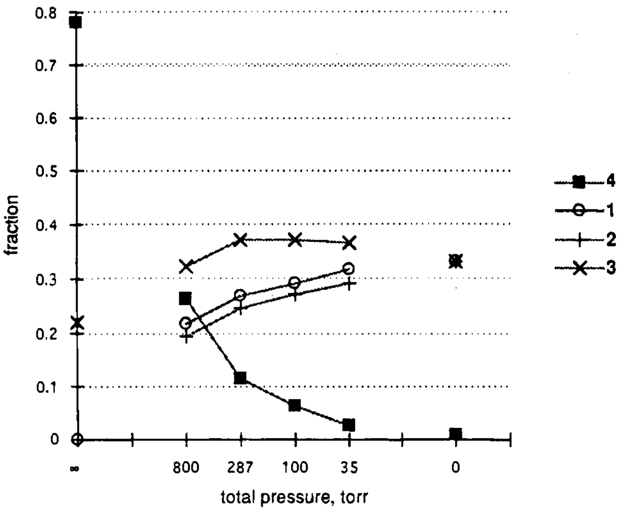

Figure 1. Visualization of the composition of the products from the reaction of ethene and $^{13}CH_2$ at the four pressures shown. The compositions at very high pressure are taken from ref 5, while those at very low pressure are speculative.

of the amount of **4*** that is presumed to have rearranged in equal amount to **1**, **2**, and **3**. In the conventional picture, it has never been doubted that **3***, the precursor of **3**, is stable during its lifetime before collisional deactivation and that the fraction of **3** formed at time zero by insertion remains unchanged regardless of pressure. If the fraction of **2** (0.195) produced be taken as the measure of the amount of **4*** rearranged and the Rowland fraction, 0.220, shown bracketed in the top row of Table 1, be accepted as the measure of initial insertion, total **3** should have amounted to 0.415. Instead there is a shortfall of 0.092 (0.415 − 0.323). The shortfall is the same, 0.092, at 287 Torr, increases to 0.119 in the 100-Torr run and is 0.144 at 35 Torr. Instead of rising from 0.220 in parallel with the formation of **1** and **2** and approaching 0.480 in the low-pressure limit, **3** has not only fallen short but has begun to turn down *as if* headed for the same end point as **1** and **2** (see Figure 1). Such behavior strongly implies an instability of **3***, which can economically be formulated as a reverse rearrangement to **4***, via **dr-1,3***. This addition to the pool of **4*** then joins in the rearrangement to **1***, **2***, and **3***. Thus, at the 800-Torr point, 0.046 of the 0.195 fraction of **2** (and **1** in equal measure) is hypothesized to have originated at the expense of **3**.

Rephrased in terms of **3**:**2**, this ratio is presumed to start at infinity at the highest pressures because **3*** has been produced by insertion alone and there has been no time for rearrangement of **4*** to **1***, **2***, or **3***. At 800 Torr, of the estimated, high-pressure fraction of 0.780, only 0.264 of **4** remains, the rest presumably having rearranged to **1***, **2***, and **3*** in equal parts. Were **3*** (and, of course, **1*** and **2*** as well) stable, the fraction of **3** would have been increased by 0.172 [(0.780 − 0.264)/3] and the expected ratio of **3** to **2** would have had the value 2.28 instead of that observed, 1.65. This construct is to be seen in the second row of each of the experimental entries in Table 1. The expected ratios approach 1.85 in the low-pressure limit, whereas the observed ratios fall significantly below, and might be headed for, 1.00.

In summary, the fraction of **3** that would have been thought set initially by insertion (*i*) appears to be dependent on pressure. The pressure-dependent decrease in **3** is rationalized as the reverse of the rearrangement of cyclopropane to propene.[6] Is this a thermochemically reasonable proposition? The enthalpy of activation of the forward reaction is 63.5 kcal/mol[7] and the heat of formation of cyclopropane is 12.74 kcal/mol,[8] hence the heat of formation of the transition state is 76.2 kcal/mol. With the heat of formation of propene being 4.78 kcal/mol,[8] the enthalpy of activation of the rearrangement of propene to cyclopropane is 71.4 kcal/mol. Taking this enthalpic disadvantage and the entropic together ($S°_{300}$: cyclopropane, 56.8 eu; propene, 63.8 eu)[9] more than suffices to explain the consistent failure to detect cyclopropane among the myriad products of the conventional pyrolysis of propene.[10]

However, the rearrangement is thermochemically allowed whenever propene is excited to a level of energy significantly above the heat of formation of its transition state to cyclopropane. Indeed, when excited propene is prepared by mercury-photosensitization[11] or by photolysis of diazo-*n*-propane,[12] a small amount of cyclopropane has been reported: at 20 Torr, ~ 1.2% of propene is transformed under the latter conditions; ~0.2% under the former. In both investigations, it is hypothesized that there is sufficient excess energy in the propene as initially generated to allow transformation to trimethylene by a 1,2 hydrogen shift (from C3 to C2: cf. **3*** → **dr-1,3*** → **4*** in Scheme 1) but no clue to the partitioning of excited trimethylene between closure to excited cyclopropane and return to excited propene emerges from either study (**dr-1,3*** → **4*** + **1***). In the present study, the products of reaction of singlet $^{13}CH_2$ with ethene prior to collisional deactivation, be they **3***, **dr-1,3***, or **4***, have as a minimum heat of formation the sum of the heats of formation of singlet methylene, 102.6 kcal/mol,[13] and ethene,

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(6) The first synthesis of cyclopropane ("trimethylene") by August Freund (*J. Prakt. Chem.* **1882**, *26*, 367−377) is followed by Berthelot's comparison (Berthelot, M.; Matignon, C. *Bull. Soc. Chim. Paris* **1884**, *11*, 738−741) of its heat of formation (−17.1 kcal/mol) [− according to contemporary convention] with that (−9.4 kcal/mol) of propene (the difference, 7.7 kcal/mol, comparing well with the current best, 8.0 kcal/mol). With penetrating insight, Tanatar (Tanatar, S. *Ber.* **1896**, *29*, 1297−1300) inferred and demonstrated that cyclopropane would rearrange to propene on heating (therewith initiating the field of thermal rearrangements!).

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(8) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: London, 1986.

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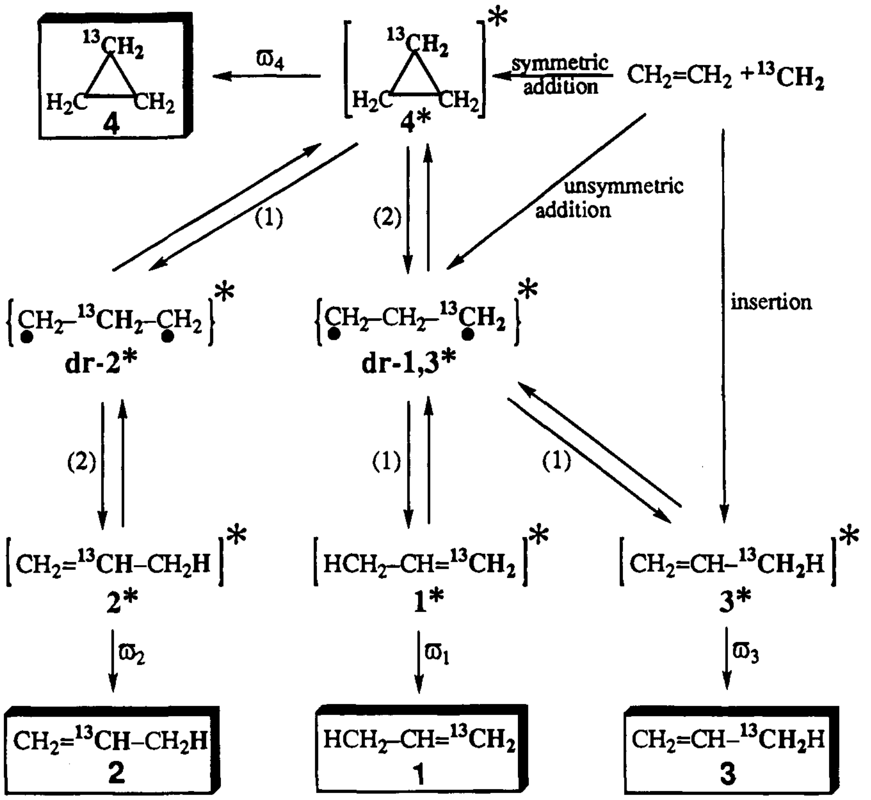
Scheme 1



12.55 kcal/mol;[8] that is, 115.2 kcal/mol. This value exceeds the heat of formation of the transition state as defined above for the interconversion of cyclopropane and propene by 39.1 kcal/mol. Not only does that excess more than suffice to accommodate the extensively studied, fast, pressure-dependent conversion of cyclopropane to propene but it accommodates its reverse as well. At zero pressure and infinite time prior to the onset of stepwise collisional deactivation, in a hypothetical act of instantaneous removal of excess energy, **4*** (and probably **dr-1,3*** as well) would appear as **4**, while **3*** would appear as **3**. The ratio of **3** to **4** will be determined by the ratios of their state densities and is expected to be considerably greater than one.

Under this scheme, at pressures below the high-pressure limit, the composition will be eroded by the rearrangement of **4*** to essentially equal parts of **1***, **2***, and **3*** and, at the same time, **3*** will be rearranging at a slower rate to **4*** and **1***. At the low-pressure limit, the product should be composed of essentially equal parts of **1**, **2**, and **3** and little or no **4**. At intermediate pressures an approximate analysis can be made. Refinement requires the set of differential equations corresponding to the kinetic model given in Scheme 1. Between the high-pressure limit and 800 torr, where our observations commence, 0.516 parts of initially formed **4*** has rearranged to 0.172 parts each of **1***, **2***, and **3***. Meanwhile some fraction of **3***, 0.220 (if Rowland's value for the high-pressure limit be taken) + 0.172 − 0.323, has rearranged to **4*** and **1***. Of this accretion to **4***, a part, 0.022, has contributed to the observed fraction of **2** (0.195) and presumably in like amount to **1** (and **3**).

The second unexpected observation emerging from this labeling study is the consistent small excess of **1** over **2**. Their ratio, instead of being 1.00, hovers around 1.09 (see Table 1 or Figure 1). That the method of determining the ^{13}C content at the three positions, which involves application of NMR to the product of addition of bromine to propene, is not responsible is confirmed by finding the natural abundance ratios of **1**:**2**:**3** to be 1.00. The *speculative* explanation we offer involves trimethylene, **dr-1,3***, excited by at least 39.1 kcal/mol (*vide supra*). There is nothing new about invoking trimethylene as a go-between in the various thermal changes undergone by cyclopropanes.[2,3,14] What is new is the suggestion that excited **dr-1,3*** may possibly assume the role of an intermediate and have more than one exit channel, in this instance, closure to isoenergetic cyclopropane **4*** and rearrangement to **1*** and **3***. As its enthalpy content is increased above the minimum threshold needed to realize stereoisomerization (the "continuous diradical"),[15] it will change in terms of RRKM theory from a structure with a very low density of states and therefore a steady state concentration essentially zero relative to that of equienthalpic cyclopropane and propene to an "intermediate", the relative steady state concentration of which is given by the ratios of its density of states to those of **4***, **1***, and **3***. In this scheme, excited trimethylene, **dr-1,3***, encompasses all those states in which the energy levels of the carbon−carbon stretching modes are above the threshold activation enthalpy for stereoisomerization and below the energy levels of those carbon−hydrogen bending modes associated with the rearrangement of cyclopropane to propene. According to Waage and Rabinovitch,[3c] the enthalpy of activation for this latter process lies about 3.7 kcal/mol above the enthalpy of activation for stereoisomerization. The only theoretical calculation possibly to shed light on the ratio of branching to cyclopropane and propene expected of highly excited trimethylene is that of Doubleday, McIver, and Page.[16] By application of canonical variational transition state

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theory, they predict the appearance of a *free energy* minimum for singlet trimethylene at temperatures above 2000 K. This minimum increases with increasing temperature but has not exceeded *RT* at 4000 K.

In the commonly accepted mechanism proposed by Skell,[17] singlet methylene approaches in a plane that includes the two carbon atoms of ethene and is perpendicular to the plane occupied by ethene. The reaction leads directly to cyclopropane with no role for trimethylene. This mechanism has been supported and elaborated in the theoretical calculations of the potential energy surface (to be sure at 0 K) by Hoffmann at the extended Hückel level,[18] by Bodor, Dewar, and Wasson at the MINDO/2 level,[19] and by Zurawski and Kutzelnigg at the *ab initio SCF* level.[20] The actual process in the gas phase being adiabatic and highly exothermic as noted above, the step from extracting an Eyring type of transition state to a description of the real reaction is highly problematic. In particular, the path of lowest enthalpy extracted from the calculated potential energy surface, in being highly restricted geometrically, is possibly the least probable. Owing to the adiabaticity and high exothermicity, bonding of the two components is more likely to occur over a wide range of angles of approach. Only when attack comes close to the plane occupied by the hydrogen atoms of ethene must the prospect of insertion over addition be entertained. We believe the Skell–Hoffmann formulation does not constitute an argument against initial generation in the gas phase of excited singlet trimethylene but rather that processes like this one are to be handled by RRKM theory, under which time-consuming redistribution of excess energy into other vibrational modes is likely to be required for transmutation into excited cyclopropane. We accept the original picture offered by DeMore and Benson[21] of trimethylene as intermediate and join Zurawski and Kutzelnigg: "...along the minimum energy path, several geometrical parameters vary considerably in the course of the reaction. Although these variations are easily interpreted in terms of chemical concepts, one should resist the temptation to believe that the reaction follows this path. Among the possible reactive trajectories on the potential energy surface, the ones that are close to the minimum energy may be rather unlikely due to dynamic reasons, in particular if this path corresponds to a rather complicated motion."

Triplets? Although we see no necessity to invoke triplet methylene to accommodate the two new observations in this work, the possibility has been explored. However, there is a long history supporting the thesis that singlet methylene is the immediate product of the photochemical decomposition of diazomethane (and ketene) and a recent theoretical paper consistent with no primary role for the triplet state.[22] Involvement of triplet cyclopropane seems securely excluded by its high energy, the lowest suggested spectroscopic assignment being 150 kcal/mol above cyclopropane.[23] Triplet trimethylene is an energetically viable candidate, having a calculated heat of formation 0.8 kcal/mol below that of singlet trimethylene.[24] On the assumption that the experimental enthalpy of activation for geometrical isomerization of cyclopropane approximates the difference in heats of formation of cyclopropane and singlet trimethylene,[25] the heat of formation of triplet trimethylene is estimated to be 71.7 kcal/mol. This value is ~34 kcal/mol below the sum (~106 kcal/mol) of the heats of formation of ethene (12.55 kcal/mol)[8] and triplet methylene (94 kcal/mol).[13] If triplet trimethylene be a player, the work of Cvetanović, Avery, and Irwin[26] proves that it cannot achieve the symmetry of cyclopropane, either via triplet cyclopropane, as suggested by Bell,[27] or by being in equilibrium with it. Finally, triplet propene, having a heat of formation of 102.8 kcal/mol, 98.0 kcal/mol[28] above that of propene (4.78 kcal/mol),[8] might also be an energetically viable player.

In the event, reaction by mercury-sensitized decomposition in a quartz flask with a low-pressure mercury lamp (253.7 nm) produces little change but for the formation of more (unidentified) byproducts (see Table 1, the 820-Torr run).

Conclusion

Further experiments at pressures substantially higher than 800 Torr offer the opportunity of checking the high pressure limiting values proposed by Rowland, but more importantly of seeing whether the initial concentration of **1** is zero or whether some might have been produced from initially generated **dr-1,3***. Experiments at pressures below 35 Torr would show whether the prediction that **1**, **2**, and **3** are formed in equal amount at very low pressures were correct and whether **4*** indeed falls to zero or a small constant value.

It would also be informative to enter the hypothetical manifold by generating excited diradical **dr-1,3*** photochemically from [3-^{13}C]-1-pyrazoline[29] and excited propenes **1*** and **3***, from [1-^{13}C]- and [3-^{13}C]-1-diazopropane,[12] respectively (Scheme 2). When entered from the latter, the slight excess of **1** is expected to vanish if the back rearrangement of **3*** proceeds homogeneously to **4*** by way of **dr-1,3***. If it were to proceed by way of a two-step process in which **dr-1,3*** rearranges in part to **1*** and in part closes to **4***, an excess of **1*** over **2*** would result (in either case, **4*** rearranges to **1***, **2***, and **3*** in equal parts).

Experimental Section

General Methods. NMR spectra were measured in $CDCl_3$ solution on a Bruker AM-500 instrument: ^1H NMR at 500 MHz in ppm (δ) from $CDCl_3$ (7.26) and ^{13}C NMR at 125.76 MHz in ppm (δ) from $CDCl_3$ (77.0). Gas chromatographic analyses were effected on a Hewlett-Packard HP5890A gas chromatograph (flame ionization detector) with a Hewlett-Packard 3393A integrator. The capillary column used for quantitative analysis was 100% methylpolysiloxane (J & W Scientific DB-1) (30 m × 0.523 mm i.d.) with a He flow of 2.0 mL/min, initially at 35 °C for 10 min followed by heating at a rate of 4 °C/min to 250 °C over a 15-min period. Ethene, propene, and cyclopropane eluted at 3.1, 3.3, and 3.5 min, respectively. Compounds with greater retention time than 3.8 min were not identified. Response factors of propene and cyclopropane were assumed to be equal.

Materials. Ethene (Aldrich, >99%) and methylamine-^{13}C hydrochloride (Cambridge Isotope Laboratory, 99 atom % ^{13}C) were used without further purification.

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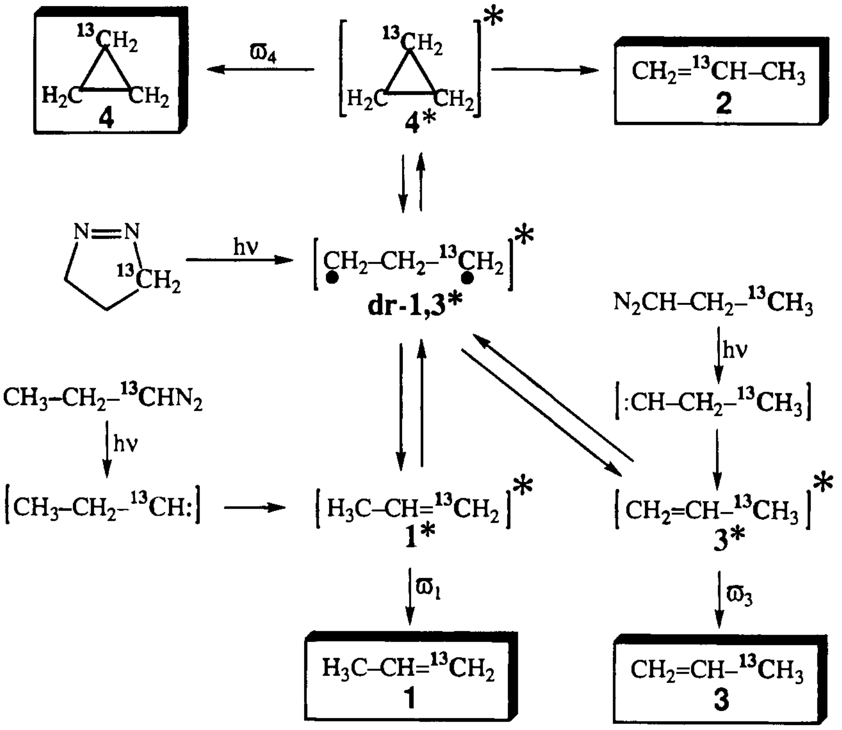
Scheme 2



Diazomethane. Diazomethane, both labeled and unlabeled, was prepared from methylamine hydrochloride by way of 1-methyl-1-nitrosourea (NMU) by a procedure adapted from that of Yates and Betts.[30] A 50% aqueous solution of KOH (10 mL) and decalin (10 mL) were placed in a plastic bottle with a magnetic stirring bar and a small tube, by means of which nitrogen gas was bubbled slowly through the solution. The reaction bottle was connected to eight glass traps in series by means of Tygon tubing (i.d. $^1/_4$ in.). Each trap contained 5 mL of decalin and was cooled in a dry ice/acetonitrile bath at −41 °C. NMU was added in one portion to the plastic bottle, which was cooled in an ice/water bath. The solution became yellow immediately and was stirred for 10 min. Nitrogen was then passed through at the rate of 10 bubbles every 6 s. Stirring in an ice/salt bath was continued for 50 min and thereafter for a further 60 min without cooling. The yellow decalin solutions in the first four traps (the last two traps were colorless) were combined and dried over solid KOH overnight at −78 °C. Diazomethane-^{13}C was prepared from 500 mg of methylamine-^{13}C hydrochloride.

Photolysis of Diazomethane in Ethene. The procedure was adapted from that of Doering and Ehlhardt.[31] The apparatus consisted of a vacuum line equipped with an oil diffusion pump, pressure being measured with a McLeod gauge from 10 to 10^{-4} torr and with a normal mercury-bar manometer above 10 Torr. Three male ₮ 19/38, fire-polished, glass joints of the O-ring type were used for attachments. A 5-L Pyrex flask with a cold finger at the bottom and a 10-mm, O-ring Teflon stopcock at the top was attached via a female, ₮ 19/38, fire-polished glass joint.

A 40-mL Pyrex tube (i.d. 19 mm) containing the solution of diazomethane in decalin was attached to the vacuum line by means of joints. The third joint of the vacuum system was connected to a lecture bottle containing ethene. The entire vacuum line was seasoned with 10−15 Torr of diazomethane for 3−4 days before use. The pump exhaust was vented to a fumehood. The solution of diazomethane in decalin was degassed by three−four freeze−pump−thaw cycles. Diazomethane was evaporated from its initially deep yellow solution in decalin into the 5-L flask through the vacuum line until the decalin solution had become light yellow. Ethene was then introduced into the 5-L flask through the vacuum line until the desired pressure was reached. The accuracy of the pressure measurement was reported to be ±10% below 20 Torr and ±2 Torr at higher pressure.

Light sources were eight RPR 2537A or 3500A lamps in a Rayonet photochemical reactor. After photolysis was complete, the gaseous sample was analyzed by GC to obtain relative yields of cyclopropane and propene. Then the condensable products were collected in a cold trap at −196 °C and mixed with a dichloromethane solution of bromine in slight molar excess. The resultant brown solution was washed with aqueous $NaHSO_3$, $NaHCO_3$, and water and dried over $CaCl_2$ at −10 °C overnight. Dichloromethane was evaporated by bubbling nitrogen through the solution for 1 h at room temperature. The crude 1,2-dibromopropane was held at −10 °C for several hours to precipitate part of the 1,2-dibromomethane (mp 10 °C) and then purified and isolated by GC.

Photolysis of ^{13}C-Diazomethane in Ethene. As an example following the general procedure above, [^{13}C]diazomethane (4 Torr) and ethene (31 Torr) were irradiated at 350 nm at 30 °C for 20 h. In addition to ethene (t_R 3.13 min), propene (3.31 min), and cyclopropane (3.52 min), small unidentified peaks at 3.80, 3.87, 4.96, and 7.50 min were observed by analytical GC. Although these minor peaks were also detected in smaller amount in the reactions at total pressure of 100 and 287 Torr, they were no longer observable in the run at 800 Torr.

Mercury-Sensitized Photolysis of ^{13}C-Diazomethane in Ethene. When [^{13}C]diazomethane (10 Torr) and ethene (810 Torr) were irradiated at 253.7 nm at 30 °C for 20 h in a 5-L quartz flask containing one drop of mercury, small unidentified peaks at 3.77, 3.83, and 4.92 min were observed by analytical GC in addition to **1**−**4**. These peaks were no longer seen when a reaction with mercury identical but for the substitution of a 5-L Pyrex flask was irradiated at 350 nm.

Isolation and NMR Analysis of [^{13}C]-1,2-Dibromopropanes. Preparative GC separations were effected on an Aerograph A 90-P3 gas chromatograph using a column, 20 ft × $^1/_4$ in. i.d., of 20% SE-30 on Chromosorb P 60/80 mesh at 75 °C and a He flow of 80 mL/min. 1,2-Dibromoethane (t_R 63 min) was discarded while [^{13}C]-1,2-dibromopropane (t_R 75 min) was collected by passing the effluent through a collector cooled in a liquid nitrogen bath: ^{1}H NMR 1.83 (m, 3H, H-3, $J_{^{13}\mathrm{C,H}}$ = 102.4 Hz), 3.56 (m, 1H, H-1, $J_{^{13}\mathrm{C,H}}$ = 155.5 Hz), 3.86 (m, 1H, H-1, $J_{^{13}\mathrm{C,H}}$ = 157.0 Hz), 4.25 (m, 1H, H-2, $J_{^{13}\mathrm{C,H}}$ = 156.3 Hz).

For quantitative analysis of [1-^{13}C]−, [2-^{13}C]-, and [3-^{13}C]-1,2-dibromopropane, the proton signals with the longest T_1 (5.8 s) are those at 3.56 and 3.86 ppm (H-1). FID was accumulated (NS = 64−88) with RD = 35 s (>5 T_1).

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Quantitative ^{13}C NMR analyses of [^{13}C]-1,2-dibromopropane were made in 0.4 mL of a $CDCl_3$ solution, 0.1 M in chromium tris(acetylacetonate), in a tube, which was degassed and sealed under vacuum. Values of T_1 were measured using the inversion–recovery method.[32] The longest, 0.26 s, originated in C-2. Spectra were taken using the inverse-gated decoupling method in order to eliminate nuclear Overhauser effects.[33] The proton decoupler was on during the acquisition periods and off during the relaxation-recovery periods of 2.0 s, which was five times longer than the longest T_1 (for C2, about 0.26 s). The region from 80 to 10 ppm was covered, 10 000 scans being made in order to improve the signal-to-noise ratio.

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