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SYMMETRICAL DISTRIBUTION OF ENERGY IN INITIALLY UNSYMMETRICALLY EXCITED PRODUCTS

REACTION OF DIDEUTERIODIAZOMETHANE WITH ALLENE,* METHYLENECYCLOPROPANE† AND VINYLCYCLOPROPANE†

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Abstract—When spiropentane is formed in the gas-phase through the addition of dideuteriomethylene to methylenecyclopropane, the enthalpy of reaction must be unsymmetrically distributed at the instant of reaction. Nonetheless, the methylenecyclobutane, which is a secondary product of rearrangement of the initially formed excited spiropentane, manifests a statistically random distribution of deuterium, consistent with rapid flow of vibrational energy through a molecule. The lower homologue of this reaction, the addition of dideuteriomethylene to allene, also leads to a product, methylenecyclopropane, in which deuterium is randomly distributed (in pairs). An attempt to extend the study to the higher homolog, vinylcyclopropane, failed to produce significant results since the product of further rearrangement was the symmetrical molecule, cyclohexene.

IN STATU NASCENDI the product of the reaction of methylene (generated photochemically from diazomethane) with an organic molecule is vibrationally excited by an amount of energy at least equal to the exothermicity of the reaction. In the gas-phase such chemically excited states have a lifetime dependent on pressure; that is, on the frequency of collisions and the efficiency of the removal of excitation by collision. Since organic molecules are subject to decomposition or thermal reorganization, the possibility of further chemical change exists whenever the excitation in the initial product exceeds the activation energy for bond-breaking or rearrangement. Reactions with methylene are among the very few which occur in the gas-phase with such a high exothermicity that further transformation of the initial product is almost always a possibility.

Butler and Kistiakowsky[1] and Knox and Trotman-Dickenson[2] were the first to apply this method to the generation of one molecule, methylcyclopropane, in two different ways and therefore in two initially different vibrationally excited states.[1] These initially different states underwent identical further reaction in accord with the hypothesis in the Rice–Ramsberger–Kassel–Marcus theory of collisional activation

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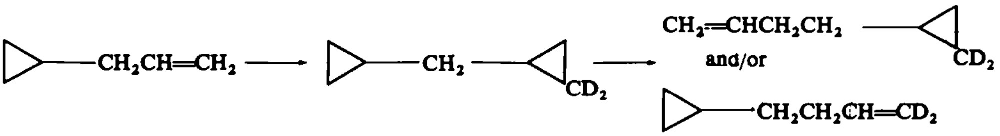
that energy introduced by collision becomes randomly distributed through the molecule before being reconcentrated in a reaction coordinate.

The present study is designed to probe the rate of flow of energy through a molecule by a process in which an initially structurally symmetrical product is generated in an energetically unsymmetrical way and is so chosen that subsequent rearrangement products may be examined for evidence of unsymmetrical reaction. The idea is best illustrated in a hypothetical example, still under investigation. The addition of dideuteriomethylene to allylcyclopropane would generate the symmetrical (but for deuterium labelling) bis-cyclopropylmethane in a sufficiently excited state to rearrange one of the cyclopropyl rings to propenyl and allyl. By examination of the distribution of deuterium in the rearranged products it would be possible to determine (but for the isotope effect) whether rearrangement had occurred immediately

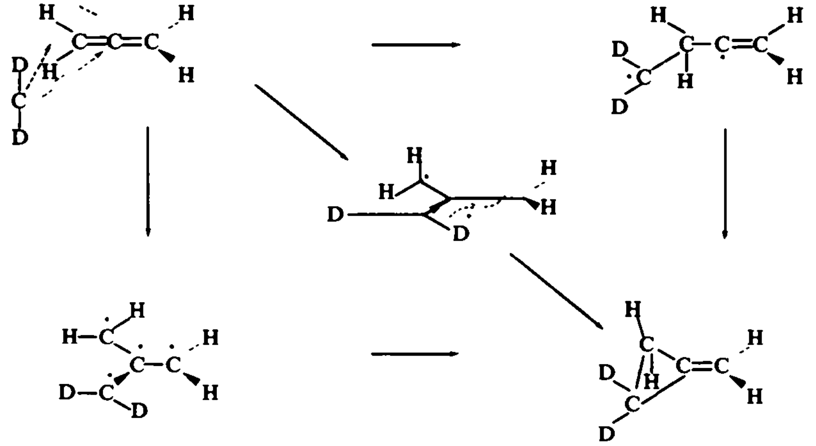


and preferentially in the just-formed ring or whether the excess energy had first been distributed symmetrically and only later had been remobilized to effect the cyclopropane-propylene rearrangement. Were the dideuterated cyclopropyl ring to rearrange in preference to the originally present cyclopropyl ring, then, in principle, an investigation of the change in ratio with pressure could afford a measure of the rate of flow of energy through the system. In this paper we report the investigation of three reactions. The first is the addition of dideuteriomethylene to allene, a reaction which has already been found by Frey[3] to lead in the gas-phase to methylallene and methylenecyclopropane, which decomposes to acetylene and ethylene in amounts depending on pressure. This example brings to light a degenerate rearrangement of methylenecyclopropane, which follows initial addition of methylene to the double bond of allene.

The second reaction, the addition of dideuteriomethylene to methylenecyclopropane, illustrates the new approach to the question of energy flow through an excited molecule. The initially formed spiropentane rearranges to methylenecyclobutane with deuterium distributed randomly in pairs.

Finally, we describe the addition of methylene to vinylcyclopropane as a potentially second example, which fails as an illustration because the major product of rearrangement, cyclohexene, is a symmetrical molecule.

When allene and methylene react in the liquid-phase, methylenecyclopropane is the major product.[4] Carried out with diazomethane and tetradeuterioallene, either photochemically or by copper catalysis, fewer than 4·3% of hydrogen atoms can be found in the exocyclic olefinic methylene group.[5] This result establishes simple addition as the course of the reaction and excludes any intermediate in which the three methylene groups become indistinguishable. A direct one-step addition to one of the double bonds of allene in analogy to the *cis*-stereospecific addition of methylene to olefins is a consistent mechanism, requiring little readjustment of bond angles. A two-step mechanism involving attack at carbon atom 1 is also consistent, but the formation of a two-fold or three-fold symmetrical intermediate such as trimethylenemethane is excluded.



In contrast, in the gas-phase at a total pressure of about 350 mm, the addition of dideuteriomethylene to allene results in methylenecyclopropane having a statistical distribution of deuterium. Analysis of the NMR spectra of the product of two different runs indicates a ratio of allylic to vinylic hydrogen equal to 2·07 and 2·00 to 1·00. These values clearly correspond to that expected of random distribution of deuterium in pairs. They are significantly different from the ratio of 1·00 to 1·00 expected of simple addition without equilibration which is observed in the liquid phase or the ratio 3·00 to 1·00 expected of a possible two-fold symmetrical intermediate. The gas-phase reaction clearly involves a symmetrical intermediate or its equivalent. More complete analysis requires an examination of energy relationships.

The heat of formation of the initial product of the addition of methylene and allene can be estimated to be 138 kcal/mole, the sum of the heats of formation of allene (+45·9° kcal/mole)[6] and methylene (+92 kcal/mole).[7] This estimate suffers from lack of accuracy in the heat of formation of methylene and an inability to estimate that portion of the photochemical energy, above the minimum required to decompose diazomethane to nitrogen and methylene, which remains with the methylene as translational and vibrational excitation.[8,9] The estimate of the heat formation of the product of addition of methylene and allene is therefore almost certainly low.

Trimethylenemethane in its lowest singlet state is an attractive structure for the symmetrical intermediate and is easily visualized as the immediate product of the attack of singlet methylene on carbon atom 2 of allene.

However, Dowd's analysis of the ESR spectrum of the product of photolysis of either 4-methylene-1-pyrazoline[10] or 3-methylenecyclobutanone[11] at low temperature leaves no doubt that triplet trimethylenemethane is more stable than singlet. Whereas this observation would exclude the singlet form as a long-lived intermediate, it is no obstacle to its role as an initial transient intermediate. Indeed the singlet form has been advanced to rationalize the conversion of 4-methylene-1-pyrazoline to methylenecyclopropane at ambient temperatures.[12]

In order to be a credible intermediate, singlet trimethylenemethane must have a heat of formation below that estimated above for the initial product of the addition of allene and methylene. One value can be based on a model in which the activation energy of the opening of cyclopropane to trimethylene (65·1 kcal/mole)[13] is added to the heat of formation of methylenecyclopropane (+45·6 kcal/mole or +48 kcal/mole).* The resultant heat of formation, about 112 kcal/mole, is a maximum value not only because the value of 65·1 kcal/mole does not reflect the entire strain available in cyclopropane for release, let alone the extra strain in methylenecyclopropane, but also because the π-electron delocalization energy of singlet trimethylenemethane is doubtless greater than zero. A lower, more realistic value is obtained from a heat of formation of +7·0 kcal/mole calculated for strain-free methylenecyclopropane,* and a bond strength of 82 kcal/mole for two sp^3 bonded methylene groups.[17] This heat of formation of 89 kcal/mole would presumably be lowered by the energy of π-electron delocalization, estimated by the Hückel method to be 1·46 β (the triplet would be lower by an indeterminant amount).[18] Since both estimated values of the heat of formation of trimethylenemethane are lower than the estimated heat of formation of the initial product of the addition of methylene to allene, trimethylenemethane is an acceptable structure.

The random distribution of deuterium may be explained alternatively by an excited methylenecyclopropane which undergoes multiple rearrangements prior to collisional deactivation. The required rearrangement is illustrated by the thermal interconversion of methylmethylenecyclopropane and ethylidenecyclopropane, for which Chesick found an activation energy of +40·4 kcal/mole.[19] From this value and the heat of formation of methylenecyclopropane (+45·6 or +48 kcal/mole) the heat of formation of the transition state for the rearrangement of methylenecyclopropane can be estimated to be +86·0 or +88·4 kcal/mole. Since this value is much lower than the minimum estimated heat of formation of the immediate product of the addition of singlet methylene to allene, it is energetically acceptable to propose excited methylenecyclopropane as the initial intermediate.

Although it is attractive to propose that the degenerate rearrangement of methylenecyclopropane might also involve singlet trimethylenemethane, this rearrangement must have a concerted mechanism, if Ullman's investigation of the stereochemistry of the rearrangement of Feist's ester[20] can be extended to the rearrangement of methylenecyclopropanes in general.

In descriptions of the behavior of a vibrationally excited assembly of atoms in which there is already enough energy to effect any one of several reactions, the problem of mechanism is concerned with the relative probabilities of moving from one geometrical arrangement to another and not with differences in energy of activation. In the present instance two initial geometries are energetically acceptable: a vibrationally excited trimethylenemethane or a vibrationally excited methylenecyclopropane, which then may move either to trimethylenemethane or to a rearranged methylenecyclopropane. A distinction between these two alternative geometries could be made

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* The first value is calculated from the heat of formation of strain-free methylenecyclopropane (+7·0 kcal/mole) calculated by the Franklin method of group equivalent values[14] and the total strain estimated for methylmethylenecyclopropane (+36·6 kcal/mole) from heats of hydrogenation.[15] The second value is derived directly from the heat of combustion.[16]

by examination of the effect of pressure on distribution of deuterium. If trimethylenemethane were the initial intermediate, deuterium distribution in the final methylenecyclopropane would be independent of pressure, whereas, if excited methylenecyclopropane were the intermediate, distribution of deuterium would be pressure-dependent. To the extent that reaction in solution can be regarded as a reaction at infinite pressure, the presently available results point to vibrationally excited methylenecyclopropane as the description of the immediate product of the addition.

Methylenecyclopropane is the smallest olefin in which the question of energy flow can be examined by the addition of methylene to a double bond. In the liquid phase this reaction leads to spiropentane (73%), the product of addition, and to 2-methyl-1-methylenecyclopropane (17%) and ethylidenecyclopropane (10%), products of insertion. Spiropentane can rearrange thermally to methylenecyclobutane[21,22] and may also decompose to ethylene and allene.[22] The addition of methylene to methylenecyclopropane is thus able to furnish a symmetrical product, spiropentane, which, if sufficiently vibrationally excited, might be expected to rearrange to methylenecyclobutane.

Were methylenecyclobutane in fact a product of the gas-phase reaction, the use of deuterium labelled methylene would provide the opportunity to determine whether a symmetrical intermediate had been involved. At the instant of addition of CD_2 to the double bond the distribution of the exothermicity of the reaction would be unsymmetrically concentrated in the newly formed ring. Were the rearrangement to methylenecyclobutane to occur essentially instantaneously, a non-statistical distribution of deuterium might be expected (however, see below). Were the vibrational excitation to distribute itself symmetrically through the spiropentane *prior* to rearrangement, deuterium would be statistically distributed in the final product.

When the reaction is carried out in the gas-phase, methylenecyclobutane does become one of the products. At a total pressure ranging from 150–300 mm, the photolysis of dideuteriodiazomethane in the presence of methylenecyclopropane produces spiropentane-d_2 (24%), 2-methyl-1-methylenecyclopropane-d_2 (41%) and ethylidenecyclopropane-d_2 (17%) and methylenecyclobutane-d_2 (18%). The methylenecyclobutane appears to be formed at the expense of spiropentane and must have been produced by rearrangement of an excited intermediate. The distribution of deuterium in the methylenecyclobutane was determined by integration of the NMR spectrum. The ratio of vinylic, allylic and homoallylic protons is 1·11:2·01:1·00. This distribution of protons and consequently of deuterium appears to be statistical within experimental error.

In this reaction, spiropentane *in statu nascendi* is sufficiently excited to rearrange to methylenecyclobutane. The heat of formation of the initially formed product is at least 137·5 kcal/mole; i.e. the sum of the heats of formation of methylenecyclopropane* and methylene,[12] and may be considerably higher for reasons referred to earlier. The heat of formation of the rate-determining transition state for the rearrangement of spiropentane to methylenecyclobutane is 99·7 kcal/mole [the sum of the activation

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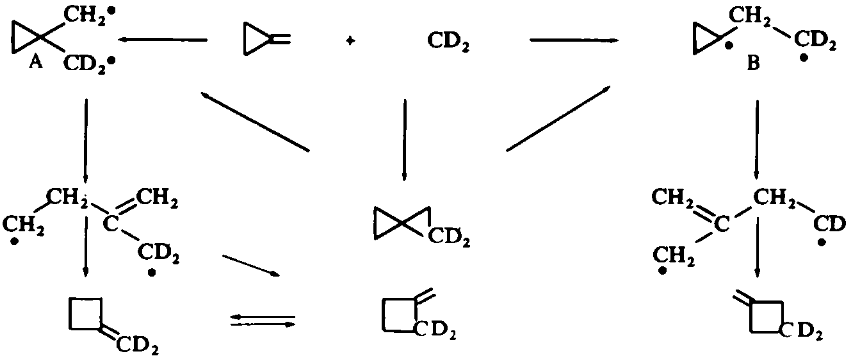
* See footnote * on p. 6866

energy of the rearrangement (55·5 kcal/mole)[22] and the heat of formation of spiropentane (44·2 kcal/mole)][23] There is clearly more than enough energy available for the rearrangement, provided the energy is mobilized faster than it is lost by collisional deactivation. Since the lifetime of excited intermediates in the gas-phase is dependent on pressure, higher pressures should lead to a higher ratio of spiropentane to methylenecyclobutane, whereas lower pressures should lead to a higher ratio of methylenecyclobutane and ultimately to ethylene and allene.[22]

In terms of this picture, the statistical distribution of deuterium observed in methylenecyclobutane is consistent with the hypothesis that the heat of the addition, originally concentrated unsymmetrically as vibrational excitation in the newly formed ring becomes symmetrically distributed before being reconcentrated along the coordinate of the spiropentane-methylenecyclobutane rearrangement.

The existence of a hidden rearrangement of spiropentane to itself, which would also provide an explanation for the statistical distribution, has been excluded with a high degree of certainty.[5] 1,1,2,2- and 1,1,4,4-Tetradeuteriospiropentane were synthesized and found not to be interconverted thermally under the most drastic conditions which did not cause complete rearrangement to methylenecyclobutane.

Another explanation depends on a highly improbable coincidence, but cannot be excluded. Were the initially unsymmetrically excited spiropentane to rearrange through diradicals A and B (or their concerted equivalent) in the ratio of 3:1 and were the still excited molecules of methylenecyclobutane to suffer the methylenecyclobutane rearrangement[5] to equilibrium, a statistical distribution of deuterium would be observed in the final sample of methylenecyclobutane.* The formation of either A or B alone as the initial C_5H_8 which does not proceed to energetically symmetrical spiropentane prior to rearrangement is excluded.



An attempt was made to extend the investigation to vinycyclopropane. The addition of dideuteriomethylene in the gas-phase was expected to form unsymmetrically vibrationally excited bicyclopropyl which, as a "hot" molecule, might undergo the cyclopropane-propene rearrangement before being collisionally deactivated.

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* An equivalent explanation involves diradicals A and B in the ratio 3:1 as the initial products of the addition of methylene to methylenecyclopropane. Either A or B or both are energetically acceptable since their heats of formation are estimated to be about 90 kcal/mole (44 kcal/mole, the heat of formation of spiropentane plus 82 kcal/mole, the bond dissociation energy of 1°-1° carbon–carbon bond, minus 27 kcal/mole, the strain energy of cyclopropane, minus 9 kcal/mole, the extra strain in spiropentane. See footnote 17 of Ref. 5.

From the determination of the distribution of deuterium in either 1- or 3-cyclopropylpropene, evidence of the achievement of a symmetrical distribution of the excess energy in the initial bicyclopropyl could be obtained.

Although bicyclopropyl does undergo thermal rearrangement[24] to the desired olefins, the major product of rearrangement in the addition of methylene to vinylcyclopropane is cyclohexene. Its symmetry precludes the detection of any unsymmetrical element in the rearrangement of the initially formed "hot" bicyclopropyl.

EXPERIMENTAL

NMR spectra were measured on a Varian A-60 Analytical NMR spectrometer, the gift of the National Science Foundation (grant 22689). Mass spectra were obtained on a Consolidated 20-103 C Mass Spectrometer, the gift of the National Science Foundation (grant GP-1442).

The following columns were employed in an Aerograph A-90-P gas chromatographic apparatus:

Column A: 4-m, 20% β,β'-oxydipropionitrile on 40/60 mesh fire brick.
Column B: 4-m, 20% Dow-Corning 710 Silicone Oil on 40/60 mesh kieselguhr.
Column C: 6-m, 20% Dow-Corning 710 Silicone Oil on 40/60 mesh firebrick.
Column D: 4·5-m 20% N,N,N',N'-tetrakis[2-cyanoethoxypropyl]ethylenediamine on 40/60 mesh kieselguhr.

Deuteriodiazomethane

For this work deuterated diazomethane was prepared from normal diazomethane by base-catalyzed exchange. Solns of diazomethane in Decalin were prepared from N-methyl-N-nitrosourea and stored at 4°. Exchange was effected by shaking diazomethane in Decalin with D_2O containing 20% NaOD at 0° for 10 hr. A given sample was normally exchanged 2 or 3 times and analysed by mass spectroscopy at 70 eV. From the normal distribution of masses relative to *m/e* 42 = 100 (39:1·3; 40:6·3; 41:10·1; 42:100·0; 43:3·8; 44:1·3), an exchanged sample showing the following *m/e* (40:8·1; 41:0·0; 42:5·1; 43:8·2; 44:73·5; 45:2·0) could be estimated to consist of CD_2N_2 (90%) and $CHDN_2$ (10%).

Allene and deuteriodiazomethane

In a typical run a 5000-cc Pyrex round-bottom flask was charged by means of a vacuum system with diazomethane (20 mm), allene (120 mm; Columbia Organic Chemical Corp.) and N_2 (210 mm) and irradiated for 5 hr with a G.E. sunlamp. Pure methylenecyclopropane was isolated by GLPC (Column A) and identified by comparison with the reported IR spectrum[25] and from its NMR spectrum: δ = 1·02 ppm (triplet; J = 2·6 Hz) and 5·33 ppm (quintet; J = 2·6 Hz). The ratio of allylic protons to vinylic was determined by measurement of area under each signal. In this run, the ratio was 2·00 and in a duplicate run (500 mm N_2), it was 2·07.

Methylenecyclopropane

(a) 3-Chloro-2-chloromethylpropene-1 was prepared by the procedure of Gragson *et al.*[25] In a 2-liter, 3-necked flask equipped with a mercury-sealed stirrer, gas-dispersion tube, gas outlet and a thermometer and cooled with a stream of tap water, 3-chloro-2-methyl-1-propene (1 kg, 11·0 moles; Matheson, Coleman and Bell) was placed. Under continuous irradiation from two G.E. sunlamps, 850 g (12·0 moles) Cl_2 was bubbled in over a 36-hr period at a rate sufficient to maintain the temp between 30–35°. The resulting soln was poured into cold water to separate a lower, organic phase which was washed with ice water until the washes were only weakly acidic and then with sat NaCl aq. The organic layer was dried over Na_2SO_4 and distilled to yield three fractions: b.p. 40–50°/40 mm; and b.p. 65–80°/38 mm. Analysis of the NMR spectra indicated the first two fractions to be approximately 40:60 mixtures of starting material and 3-chloro-2-chloromethylpropene-1 and the third fraction to be mainly 1,2,3-trichloro-2-methylpropane. The lower boiling fractions (334 g) were combined and used in the next step on the assumption that they contained 1·6 moles 3-chloro-2-chloromethylpropene-1.

(b) In a 2-l., 3-necked flask equipped with an addition funnel fitted with a gas-inlet tube, a stirrer, and a condenser linked to a receiver cooled in dry-ice–acetone were placed 70 g (2·8 g-atom) mg turnings and 20 ml dry THF. A soln of the crude 3-chloro-2-chloromethylpropene-1 in 750 ml dry THF was added dropwise under N_2. Upon completion of addition, the reaction mixture was refluxed 3·5 hr under a stream of N_2.

The distillate obtained from the reaction was separated into two fractions by distillation: b.p. 0–7°/760 mm and b.p. 7–8·2°/760 mm. The IR spectrum of the higher boiling fraction (10 g, 185 mmoles) coincided with the published spectrum of methylenecyclopropane.[25] Analysis by GLPC (column A) indicated 90% of purity for this sample of methylenecyclopropane.

Reaction of diazomethane and methylenecyclopropane in the liquid phase

A soln of 2·5 ml heptane and 1·0 ml methylenecyclopropane was placed in the low-temp irradiation apparatus previously employed in the preparation of 1,1,4,4-tetradeuteriospiropentane.[5] To this soln diazomethane from 4 g N-nitrosomethylurea was introduced. The resulting yellow mixture was irradiated with two G.E. sunlamps. The addition of diazomethane and subsequent irradiation was repeated 3 times.

The products of the photolysis were isolated by a combination of distillation and GLPC (columns A and B) and are listed in Table 1.

TABLE 1. PRODUCTS OF THE LIQUID-PHASE PHOTOLYSIS OF DIAZOMETHANE AND METHYLENECYCLOPROPANE

Product	Rel. Amt. in %	Rel. Ret. Time[a]
2-Methyl-1-methylenecyclopropane[b]	17·6	1·00
Spiropentane[c]	72·7	1·16
Methylenecyclobutane	—[d]	1·63
Ethylidenecyclopropane	9·7	2·10

[a] Relative retention time on column B.

[b] Characterized by comparison of its IR spectrum with that of an authentic sample generously provided by Prof. Chesick.[19]

[c] Characterized by comparison of its retention time and IR spectrum with those of an authentic specimen.

[d] A substance having the same retention time as methylenecyclobutane was observed, but its IR spectrum was significantly different from that of methylenecyclobutane. It is estimated that 5% methylenecyclobutane would have been detected by analysis of the IR spectrum with certainty and 2% with reasonable probability.

Reaction of diazomethane-d_2 and methylenecyclopropane in the gas-phase

Methylenecyclopropane was introduced by means of a vacuum system into a 5-l. evacuated Pyrex bulb until a pressure of 100 mm was attained, and then condensed in the bulb by cooling with dry-ice. Diazomethane-d_2, which had previously been distilled on the vacuum line from decalin soln into a 20-ml receiver cooled in liquid N_2, was then distilled into the 5-l. bulb. For reasons of safety the partial press of diazomethane-d_2 in the bulb was not allowed to exceed 60 mm. The bulb was removed from the vacuum line, cooled by a stream of water and irradiated with two G.E. sunlamps for 4 hr. The bulb was reattached to the vacuum line and cooled in liquid N_2, and any noncondensable gases were removed by pumping. Additional diazomethane-d_2 was introduced and subsequently photolysed until a total of 200 mm diazomethane-d_2 had been consumed.

The products of photolysis were separated and purified by GLPC on Column C. The C_5 compounds are given in Table 2. Twelve integrations of the NMR spectrum of the purified methylenecyclobutane-d_2 gave as the average relative ratio of the vinylic, allylic, and homoallylic protons 1·11 : 2·01 : 1·00.

Reaction of diazomethane and vinylcyclopropane in the gas-phase

The apparatus and techniques outlined for the gas-phase reaction of diazomethane-d_2 and methylenecyclopropane were utilized. A total of 70 mm diazomethane, in 10-mm portions, was photolysed in 10 mm vinylcyclopropane. The reaction mixture was crudely separated by GLPC on column B, and those fractions having retention times corresponding to 3-cyclopropyl-1-propene, bicyclopropyl and cyclohexene were

TABLE 2. PRODUCTS OF THE GAS-PHASE PHOTOLYSIS OF DIDEUTERIODIAZOMETHANE AND METHYLENECYCLOPROPANE

Product	Rel. Amt. in %[a]	Rel. Ret. Time[b]
2-Methyl-1-methylenecyclopropane-d_2[c]	41	1·00
Spiropentane-d_2[d]	24	1·36
Methylenecyclobutane[e,f]	18	1·63
Ethylidenecyclopropane-d_2[c]	17	1·94

[a] These figures are only approximate since peak overlap and the presence of small amounts of other C_5 isomers preclude exact measurement of peak areas.

[b] Relative retention time on column C.

[c] Characterized by comparison of retention time with that of the perhydro compound obtained by reaction of diazomethane and methylenecyclobutane in the gas-phase. The perhydro compound was identified by its NMR and IR spectra.

[d] Characterized by comparison of its retention time with that of spiropentane and by its NMR spectrum.

[e] Characterized by comparison of its retention time with that of methylenecyclobutane and by its IR and NMR spectra.

[f] This isomer was further purified using columns B, A and D in that order.

further purified by GLPC on column A. Within an experimental error estimated to be 2%, no 3-cyclopropyl-1-propene was obtained. Authentic material was prepared from pentadiene-1,4 and diazomethane and had a retention time on column B relative to bicyclopropyl and cyclohexene of 1·00. Bicyclopropyl was the main product (41·5% of the crude C_6 fraction; rel. ret. time 1·54) and was characterized by comparison of its IR spectrum with that of an authentic sample. Cyclohexene was a minor product (3·5%; rel. ret. time 1·93).

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