Tetrahedron, Supplement No. 7, pp. 397 to 414. Pergamon Press Ltd. Printed in Northern Ireland

DEGENERATE REARRANGEMENT OF METHYLENECYCLOBUTANE[1]

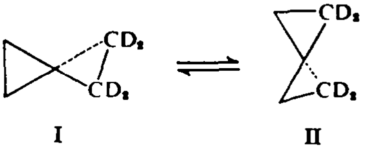
W. von E. DOERING and J. C. GILBERT[2]
Kline Chemistry Laboratory, Yale University, New Haven, Connecticut

(*Received* 25 *March* 1966)

Abstract—The failure of spiropentane to suffer a degenerate scrambling rearrangement is established by the synthesis and pyrolysis of 1,1,2,2-tetradeuteriospiropentane. A new degenerate rearrangement, that of methylenecyclobutane, has been demonstrated by the synthesis and heating of dideuteriomethylenecyclobutane. The activation energy of the rearrangement has been determined.

PREPARATORY to the investigation of the photochemical reaction of methylenecyclopropane and dideuteriodiazomethane, it was necessary to know whether spiropentane and one of the products of its thermal rearrangement, methylenecyclobutane, might undergo degenerate rearrangements on thermal activation.[3] Without this knowledge, interpretation of the behaviour of chemically activated 1,1-dideuteriospiropentane would be severely limited.

The hypothetical, degenerate rearrangement of spiropentane would result in the exchange of methylene groups between the two three-membered rings. It is illustrated in the potential interconversion of 1,1,2,2-tetradeuteriospiropentane (I) and its 1,1,4,4-isomer (II), the example actually investigated:



1,1,2,2-Tetradeuteriospiropentane (I) was prepared from diethyl cyclopropane-1,1-dicarboxylate[4] in a sequence of steps which involved reduction with lithium aluminum deuteride,[5] conversion of the resultant diol to the dibromide with bromine and triphenyl phosphite,[6] and removal of bromine with zinc dust.[7] The NMR spectrum[8] consists of a sharp singlet at $\delta = 0{\cdot}767$ ppm and a ^{13}C satellite spectrum ($J_{C-H} = 80$ c/s) itself split into a pair of crude doublets of $J = 8{\cdot}5$ and $5{\cdot}5$ c/s. The spectrum is identical in every

---

[1] Taken from a dissertation submitted to Yale University, October 1965, in partial fulfillment of the requirements for the Degree of Doctor of Philosophy. This work was supported in part by grants G-11378 and G-0959 of the National Science Foundation (U.S.A.).

[2] Award of a National Science Foundation Cooperative Fellowship (1961–62) and National Science Foundation Graduate Fellowships (1962–65) is gratefully acknowledged.

[3] J. P. Chesick, *J. Phys. Chem.* **65**, 2170 (1961).

[4] A. W. Dox and L. Yoder, *J. Amer. Chem. Soc.* **43**, 2097 (1921).

[5] H. O. House, R. C. Lord and H. S. Rao, *J. Org. Chem.* **21**, 1487 (1956).

[6] G. A. Wiley, R. L. Hershkowitz, B. M. Rein and B. C. Chung, *J. Amer. Chem. Soc.* **86**, 964 (1964).

[7] D. E. Applequist, G. F. Fanta and B. W. Henrikson, *J. Org. Chem.* **23**, 1715 (1958).

[8] NMR spectra were measured on a Varian A-60 Analytical NMR Spectrometer, the gift of the National Science Foundation (grant 22689), and are reported in the δ scale as described in Ref. 9, p. iii.

respect to that of pure spiropentane.[9] From the mass spectrum[10] obtained at low ionizing voltage (9·5 ev), I is seen to consist of 92·5% of tetradeuteriospiropentane and 7·5% of the trideuterio isomer.

The other isomer, 1,1,4,4-tetradeuteriospiropentane (II), was synthesized by the double addition of methylene to tetradeuterioallene, itself prepared by reduction of hexachloropropene with zinc and deuterium oxide[11] and shown by mass spectrometric analysis at low ionizing voltage (9·5 ev) to consist of 91·2% tetradeuterio, 6·7% trideuterio and 2·2% dideuterio-allene. The NMR spectrum of II consisted of a pentuplet centered at $\delta = 0{\cdot}767$ ppm ($J_{H-D} = 1{\cdot}1$ c/s). The IR spectra of I and II differ quite markedly (Table 2) and sufficiently to permit the facile detection of 5% of either isomer in the presence of the other. The bands at 857 cm^{-1} in I and 832 cm^{-1} in II are particularly suitable for this purpose.

Favorable circumstances for detection of the interconversion of I and II involved heating until a significant portion had decomposed to ethylene and allene and rearranged to methylenecyclobutane.[12,13] After being heated for 27 hr at 355° and 300 mm, I could still be recovered in substantial amount (18·3%) while a large amount (79·7%) had rearranged to tetradeuteriomethylenecyclobutane and a trace (2·0%) had decomposed to allene and ethylene.

The recovered spiropentane had NMR, IR and mass spectra identical to those of the starting material, I. Quantitative analysis of the region at 832 cm^{-1} in the infrared spectrum indicated that *no more* than 5% of II could have been formed. The hypothetical interconversion of I and II therefore fails to occur.

Further search for the interconversion might involve much higher temperatures and correspondingly shorter reaction times or irradiation in the vacuum ultraviolet, where Hoffmann has predicted a planar geometry for the lowest $\sigma \rightarrow \sigma^*$ excited state, and relative rotation of the two three-membered rings on excitation.[14] The search for degenerate reactions of spiropentane should clearly include a study of the *cis-trans* interconversion, characteristic of cyclopropane and some of its derivatives.[15,16] The question is the more interesting in spiropentane, owing to the presence of a significant incremental strain (+8·8 kcal/mole)[17] and its possibly selective effect on the relative rates of *cis-trans* isomerization and rearrangement.

The second hypothetical rearrangement involves methylenecyclobutane and a possible exchange of methylene groups between the two allylic positions and the exocyclic position of methylenecyclobutane (IIIa → IIIb). Chesick[3] is responsible for the suggestion that labelling of the exocyclic methylene group with deuterium might reveal such a novel, degenerate rearrangement of methylenecyclobutane. This suggestion

---

[9] *NMR Spectra Catalog* combined Vol. I and II. Varian Associates, Palo Alto, Calif. (1962 and 1963).

[10] Mass spectra were obtained on a Consolidated 20-103C Mass Spectrometer, the gift of the National Science Foundation (grant GP-1442).

[11] A. T. Morse and L. C. Leitch, *J. Org. Chem.* **23**, 990 (1958).

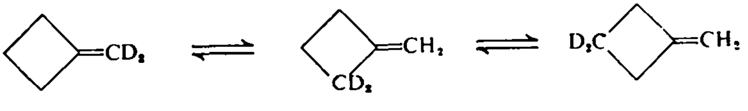
[12] M. C. Flowers and H. M. Frey, *J. Chem. Soc.* 5550 (1961).

[13] P. J. Burkhardt, *The Kinetics of the Thermal Decomposition of Spiropentane and Methylenecyclobutane.* Ph.D. Dissertation, University of Oregon, 1962 (Thesis Director, D. F. Swinehart). Dissertation 62-4938, University Microfilms, Inc., Ann Arbor, Michigan.

[14] R. Hoffmann, *Tetrahedron Letters* 3819 (1965).

[15] B. S. Rabinovitch, E. W. Schlag and K. B. Wiberg, *J. Chem. Phys.* **28**, 504 (1958).

[16] D. W. Setser and B. S. Rabinovitch, *J. Amer. Chem. Soc.* **86**, 564 (1964); *q.v.* for references to other work in this field.



IIIa IIIb IIIc

has now been taken up and has indeed revealed a rearrangement in which the exocyclic methylene group mixes with the two allylic methylene groups.

An attempt to prepare dideuteriomethylenecyclobutane (IIIa) from cyclobutanone and dideuteriomethylenetriphenylphosphorane was structurally a success but isotopically a failure. Mass spectrometric analysis of the resultant methylenecyclobutane showed species labelled with as many as six deuterium atoms. Apparently exchange of the α-hydrogen atoms of the ketone with the deuterium atoms of the phosphorane proceeds more rapidly than the Wittig reaction. This limitation might well be added to the lore of the Wittig reaction.[21]

The method of Conia and Gore[22] for the preparation of methylenecyclobutane was easily turned to a successful synthesis of dideuteriomethylenecyclobutane (IIIa). Beyond replacement of LAH by the deuteride in the reduction of N,N-dimethylcyclobutane carboxamide, little change in procedure was required. The NMR spectrum of the product was entirely consistent with that expected of essentially pure IIIa. The NMR spectrum of non-deuteriated III is reported[23] to consist of a narrow pentuplet centered at 4·67 ppm arising from the olefinic exocyclic methylene group coupled ($J = 2$ c/s) to the two methylene groups at positions 2 and 4, a triplet (of which each part is further split into a narrow triplet) at 2·67 ppm arising from the two pairs of allylic hydrogen atoms and a pentuplet ($J = 7{\cdot}5$ c/s) centered at 1·90 ppm arising from the aliphatic methylene groups at position 3. The sample of IIIa, as expected, showed no absorption at 4·67 ppm and therefore conservatively contained less than 3% of protons in the olefinic methylene groups; the absorption at 1·90 ppm (2·00 protons) consisted of a pentuplet while the absorption at 2·67 ppm (3·90 protons) consisted of a triplet.

The behaviour of IIIa on heating cannot be examined under conditions more drastic than those which cause the decomposition to allene and ethylene (ca. 400° for 24 hr).[3,13,24] Fortunately, temperatures as low as 250° effect noticeable change in IIIa, while heating at 342° for 47 hr completes the change and leads to the establishment of a new equilibrium. The resultant change is reflected in altered IR and

---

[17] From their determination of the heat of combustion of spiropentane,[18] Fraser and Prosen derive a heat of formation of gaseous spiropentane at 25° of +44·23 kcal/mole. This value is to be compared with a heat of formation (gas phase at 25°) calculated by the group equivalent method of Franklin[19] for a strain-free assembly of four CH_2 groups and one C group. This calculated value (−18·90 kcal/mole) differs by +63·13 kcal/mole from the experimental value and is customarily identified with the total strain in the molecule. Since the total strain in cyclopropane when derived in the analogous way[20] is +27·15 kcal/mole, the total estimated strain in spiropentane is greater than twice the total estimated strain of cyclopropane (+54·30 kcal/mole) by +8·83 kcal/mole.

[18] F. M. Fraser and E. J. Prosen, *J. Res. Nat. Bur. Stand.* **54**, 143 (1955).

[19] J. L. Franklin, *Ind. Eng. Chem.* **41**, 1070 (1949).

[20] J. W. Knowlton and F. D. Rossini, *J. Res. Nat. Bur. Stand.* **43**, 113 (1949).

[21] S. Trippett, *Quart. Rev.* **17**, 406 (1963); J. G. Atkinson *et al.*, *Can. J. Chem.* **43**, 1614 (1965).

[22] J. Conia and J. Gore, *Bull. soc. chim. Fr.* 735 (1963).

[23] See Ref. 9, spectrum 109.

[24] L. L. Brandauer, B. Short and S. M. E. Kellner, *J. Phys. Chem.* **65**, 2269 (1961).

NMR spectra, but unchanged mass spectrum, and can be interpreted as an intramolecular isomerization.

Most significantly, the mass spectrum is not changed in the region, $m/e = 66$ to 71. Therefore, heating has not changed either the total deuterium content or the relative proportions of deuteriated species.

Whereas the IR spectrum of IIIa is dominated by two intense bands at 1645 and 695 cm^{-1}, new bands have appeared at 1665 and 875 cm^{-1} in the equilibrated sample. These are closely related to the bands at 1670 and 880 cm^{-1} in methylenecyclobutane itself and may be ascribed to the deformation mode of olefinic methylene groups.[25] The emergence of these bands supports the hypothesis that protons have migrated to the exocyclic methylene group in the equilibrated product.

The most revealing change is in the NMR spectrum. Where there was no absorption in the region, 4·67 ppm, in IIIa, there is now significant absorption in the form, however, of a *triplet*, instead of a pentuplet characteristic of deuterium-free III. This evidence not only confirms the presence of an exocyclic protonated methylene group, but also allows the inference that this group has, not two, but only one allylic protonated methylene group with which to couple. Accordingly, little, if any dideuteriated methylene has migrated to the aliphatic 3-position with consequent formation of molecules containing *two* pairs of protonated allylic methylene groups. The pentuplet at 1·90 ppm remains, but has suffered further fine splitting consistent with replacement of some of the adjacent allylic protonated methylene groups by deuteriated methylene groups. No change is to be seen in the triplet at 2·67 ppm, associated with the allylic methylene groups.

Quantitative description of the nature of the rearrangements rests on the ratios of the three types of methylene groups: olefinic, allylic and aliphatic. The experimental equilibrium ratios of 1·32:2·64:2·04 are in very close agreement with the theoretical values of 1·33:2·67:2·00 expected if the rearrangement were to involve equilibration between IIIa and IIIb (with a statistical weight of two), but without the participation of IIIc. Were all three isomers to be set in equilibrium, the expected ratios would be 1·50:3·00:1·50.

The kinetic order and temperature dependence of the new rearrangement were investigated, once it had been established that the reaction was homogeneous and unaffected by a large increase in the ratio of surface to volume. The rate followed the expression associated with a reversible first-order reaction: $\text{IIIa} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{IIIb}$. For such a reaction $(k_1 + k_{-1})t = \ln\{k_1a/[k_1a - x(k_1 + k_1/K)]\}$ where a = initial concentration of IIIa, x = amount of IIIb at time, t, and $K = k_1/k_{-1} = 2$. The results are shown in Table 1.

An Arrhenius plot of the data gives a temperature dependence of the following form:

$$\log(k_1 + k_{-1}) = (14{\cdot}77 \pm 0{\cdot}3) - (49{,}500 \pm 1000/2{\cdot}303RT).$$

Translated into terms of transition state theory, these data correspond to an enthalpy of activation, $\Delta H^{\ddagger} = +48{\cdot}8 \pm 1$ kcal/mole and an entropy of activation, $\Delta S^{\ddagger} = +\,5{\cdot}3$ e.u.

The behaviour of spiropentane and methylenecyclobutane on heating has been the

---

[25] L. J. Bellamy, *The Infra-red Spectra of Complex Molecules* (2*nd* Edition) Methuen, London (1957).

TABLE 1. RATE CONSTANTS FOR THE EQUILIBRATION OF 1-DIDEUTERIOMETHYLENECYCLOBUTANE (IIIa) AND 2,2-DIDEUTERIO-1-METHYLENECYCLOBUTANE (IIIb)

T(°C)[a]	t(sec)	rel. areas[b]	IIIb (%)	$10^5(k_1 + k_{-1})$
287·5[e]	18060[d]	7·2:102·4:54·8	13·1	1·215
287·5[c]	35880[d]	10·5: 76·7:43·6	24·1	1·249
301·5[e,f]	19200	19·9: 85·8:56·8	37·3	3·899
305·9[g]	6780[d]	14·0:126·3:70·3	19·6	5·233
305·9[g]	14580[d]	26·0:114·5:70·2	37·0	5·563
321·3[e]	4000	18·0: 94·7:56·0	33·1	16·45
321·3[e]	10800	32·7: 87·4:60·0	54·5	15·78
339·5[e]	800	15·8:112·9:64·4	24·5	57·36
339·5[e]	2200	34·8:112·8:72·9	47·8	56·11
354·3[e]	900	35·3:111·1:73·4	48·1	141·8
354·3[e]	1080	29·7: 83·1:56·2	52·9	145·4
354·8[e]	400	19·3:102·3:60·8	31·7	161·6

[a] Uncorrected temp.

[b] Experimental areas are corrected so that sum of vinylic and allylic areas is 4·0 when area of homoallylic hydrogens is taken as 2·0; relative areas are reported in the order, vinylic, allylic and homoallylic.

[c] Hexadecane, b.p. 286·8°, used as solvent.

[d] Time corrected for thermal equilibration by 120 sec.

[e] Run made in tube furnace.

[f] Surface: volume ratio increased by loosely packing the 600-ml ampoule with Pyrex glass wool.

[g] Benzophenone, b.p. 305·9°, used as solvent.

subject of several independent investigations which have had as their common mechanistic goal the definition of the energy surface which relates spiropentane, methylenecyclobutane and the pair of molecules, allene and ethylene.

Flowers and Frey[12] reported the predominant product of the pyrolysis of spiropentane to be methylenecyclobutane, accompanied by small amounts of allene and ethylene and recorded an activation energy of 57·6 kcal/mole for the first-order process. Chesick[3] and Brandauer, Short and Kellner[24] reported activation energies of 63·3 and 61·5 kcal/mole, respectively, for the first-order transformation of methylenecyclobutane to allene and ethylene. Burkhardt (and Swinehart)[13] have determined these values more accurately by conventional extrapolation to infinite pressure as well as by evaluation of the Kassel integral. They find an activation energy of 55·50 kcal/mole for the first-order reaction of spiropentane and 63·50 kcal/mole for the first-order decomposition of methylenecyclobutane.

Knowledge of the heats of formation of the four stable molecules in the system allows five points on the energy surface to be fixed: that for spiropentane, the transition state of its further transformation, methylenecyclobutane, the transition state of its decomposition and the ultimate products, allene and ethylene.

The heat of formation of spiropentane is reported to be +44·23 kcal/mole.[18] That of methylenecyclobutane cannot be assigned with the same degree of reliability, but it can be estimated from the experimental heat of hydrogenation of methylenecyclobutane[26] and either the reported heat of combustion of methylcyclobutane[27] or

---

[26] R. B. Turner, *Theoretical Organic Chemistry, The Kekulé-Symposium*, 1958, Butterworths, London (1959).

[27] G. L. Humphrey and R. Spitzer, *J. Chem. Phys.* **18**, 902 (1950).

its calculated heat of formation. Values of +26·7 kcal/mole[28] and +30·7 kcal/mole,[31] respectively, are obtained. For the purposes of completing arguments which can be changed quantitatively whenever more reliable values for the heat of formation of methylenecyclobutane appear, we shall use the average value, +28·7 kcal/mole. The sum of the heats of formation of allene (+45·9 kcal/mole[34]) and ethylene (+12·5 kcal/mole)[34] is +58·4 kcal/mole.

These three points are located in Fig. 1. On this same figure, the transition state for the first-order reaction of spiropentane (+44·2) is to be found at +99·7 kcal/mole and that for the transformation of methylenecyclobutane (+28·7) to ethylene (+12·5) and allene (+45·9) at +92·2 kcal/mole.

From the present contribution, the transition state for the newly uncovered degenerate rearrangement of methylenecyclobutane may be located at +78·2 (+28·7 + 49·5) kcal/mole. Embarrassingly less accurate than some of its other more elegantly evaluated coinhabitants of the figure, this point in multidimensional energy space is doubtless not identical with any of the other five points. Its numerical value is too far removed for it not to represent the rate-determining transition state of a distinct reaction.

Does this point represent the transition state, TS-III°, of the one-step, concerted rearrangement of IIIa to IIIb and vice versa? We believe not. First, the entropy of activation ($\Delta S^{\ddagger} = +5{\cdot}3$ e.u.) is positive and therefore suggestive of a state in transition

---

[28] A heat of combustion of liquid methylcyclobutane of −801·1 kcal/mole is reported by Humphrey and Spitzer[27] along with a heat of combustion of liquid spiropentane of −778·7 kcal/mole (the heat of combustion of the gas, −785·3 kcal/mole, may be compared with the value, −787·8 kcal/mole, reported by Fraser and Prosen five years later[18]). The heat of vaporization of methylcyclobutane can be estimated by Trouton's rule to be 6·8 kcal/mole at 25° (taking b.p. 309°K and 22 kcal/mole as the constant) or by comparison with cyclobutane to be 6·4 kcal/mole (ΔH_V of cyclobutane at its b.p. is 5·7 kcal/mole;[29] in cyclopentane and cyclohexane the addition of one methyl group increases ΔH_V at the b.p. by 0·39 kcal/mole;[30] correction from the b.p. to 25° would add an additional 0·3 kcal/mole). Taking 6·6 kcal/mole as the estimated ΔH_V at 25°, one derives −807·7 kcal/mole as the vapor-phase heat of combustion of methylcyclobutane at 25° or a heat of formation of −4·15 kcal/mole (this value compares with −25·99 kcal/mole calculated by Franklin's method for a strain-free methylcyclobutane: the low value of the strain, +21·84 kcal/mole, cries for further experimental verification). The heat of hydrogenation of liquid methylenecyclobutane is −29·43 kcal/mole,[26] from which a somewhat higher vapor-phase heat of hydrogenation is expected, say −30·9 kcal/mole. The estimated $\Delta H^{\circ}_{f,25^{\circ}}$ of gaseous methylenecyclobutane is thus +26·7 kcal/mole.

[29] G. W. Rathjens, Jr. and W. D. Gwinn, *J. Amer. Chem. Soc.* **75**, 5629 (1953).

[30] American Petroleum Institute Research Project 44, Texas Agricultural and Mechanical University, College Station, Texas.

[31] On the assumption (the more deplorable that it begs the question of how methyl groups interact with small rings) that the strain energy of methylcyclobutane be equal to that of cyclobutane (+25·75 kcal/mole),[32] the method of Franklin's group equivalent values[19] leads to a calculated gas-phase heat of formation of methylcyclobutane of −0·24 kcal/mole or a heat of formation of methylenecyclobutane of +30·66 kcal/mole (compare the calculated strain-free value of +2·11 kcal/mole for an estimated strain of +28·55 kcal/mole).

[32] Estimated in the usual way (see reference 17) from the reported heat of formation of cyclobutane[33] and the calculated strain-free value.[19]

[33] S. Kaarsemaker and J. Coops, *Rec. Trav. Chim.* **71**, 261 (1952).

[34] American Petroleum Institute Research Project 44, Texas Agricultural and Mechanical University, College Station, Texas. Heat of formation of ethylene [Table 8p (Part 1)] and allene [Table 11p (Part 1)].

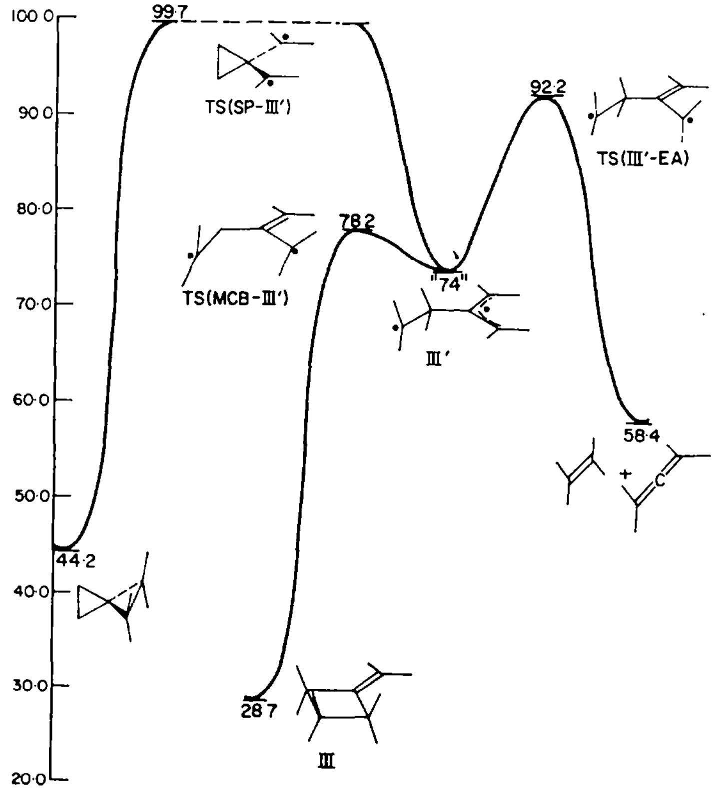
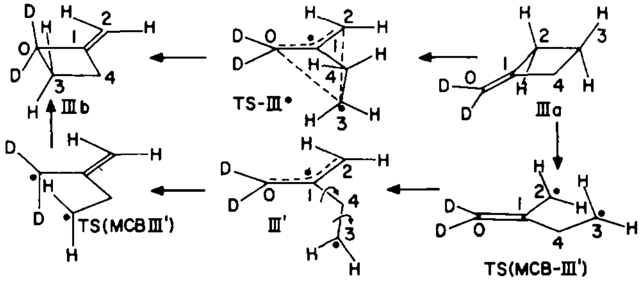


FIG. 1. The heats of formation of several geometrically isomeric assemblies of composition, C_5H_8, in kcal/mole.

to a product of fewer restrictions and more degrees of freedom, not of a state proceeding to a product of identical entropy. Second, the structure of such a concerted transition state, TS-III°, is in conflict with orbital symmetry rules since the second π orbital of the allyl radical, having a node at its central carbon, has opposite symmetries at its terminal carbon atoms.[35] Accordingly, these atoms can not be bonded simultaneously to a single sp^3 orbital or to a single lobe of a 2p orbital. (This restriction would not apply if the two hydrogen atoms of the trigonal methylene group, number 3,



[35] R. B. Woodward and R. Hoffman, *J. Amer. Chem. Soc.* 87, 2511 (1965).

lay in the plane defined by carbon atoms 3, 4 and 1; and each lobe of the 2p orbital could overlap with that portion of the lower half of the π orbital of the allyl radical of appropriate symmetry). Third, the distances C_3–C_0 and C_3–C_2 are too long for significant bonding when, at best, bonding between half orbitals does not amount to a great deal.[36,38]

In a preferable analysis this energy point, +78·2 kcal/mole, is described as the transition state, TS(MCB-III′), between methylenecyclobutane (IIIa) and a hypothetical intermediate, III′, achievement to which permits reversion of the starting molecule or conversion through a similar transition state, in fact identical to TS(MCB-III′) but for the position of the deuterium label, to the rearranged methylenecyclobutane, IIIb.[41] This intermediate, III′, differs from the previously discussed hypothetical transition state, TS-III°, in that there is no appreciable bonding between C_3 and C_0, and C_3 and C_2, and essentially complete freedom of rotation about the carbon bonds, C_1–C_4 and C_4–C_3. The condition of a positive entropy of activation is thereby accommodated in a plausible manner. This state, TS(MCB-III′), is envisioned as the transition from methylenecyclobutane, in which the planes occupied by the methylene groups at C_0 and C_2 are mutually perpendicular, to the intermediate III′, in which these methylene groups are coplanar and the full energy of allylic delocalization has been realized. On the energy surface, III′ is then assigned a value somewhat below +78·2 kcal/mole, quite arbitrarily taken to be +74 kcal/mole.

The transition state at +92·2 kcal/mole is the top of the pass separating methylenecyclobutane and the dissociated pair, allene and ethylene [TS(III′-EA)]. Many rest stations on the way down to allene and ethylene may await identification, but presently available experimental observations suggest nothing but a smooth slide. On the other side, up from methylenecyclobutane, complications may be considered. Establishment of the rate-determining transition state, TS(MCB-III′) at +78·2 kcal/mole in the methylenecyclobutane rearrangement taken with the *assumption* of an intermediate III′, is equivalent to the conclusion that methylenecyclobutane and III′ are in a state of pre-equilibrium relative to any transition state of higher energy, such as TS(III′-EA). It is possible to conclude that III′ is the immediate precursor of TS(III′-EA), the structure of which would then have to be chosen to reflect its immediate origin and

[36] For example, the highly favorable overlap between two allyl radicals in the four-centered transition state of the Cope rearrangement leads to bonding worth about 12 kcal/mole [the difference between the activation energy for the breaking of hexadiene-1,5 into free allyl radicals (46·5 kcal/mole) and the activation energy for the Cope rearrangement of 1,1-dideuteriohexadiene-1,5 (35·5 kcal/mole)].[37]

[37] W. von E. Doering and V. Toscano, unpublished results.

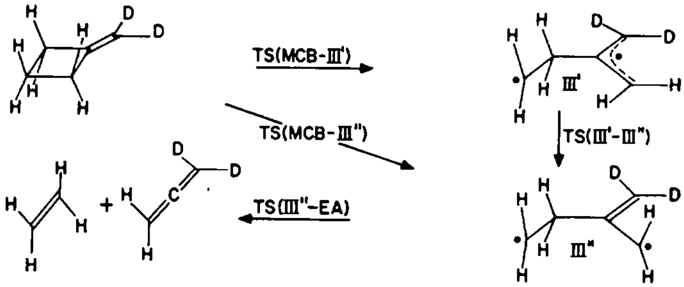
[38] As another example, note that the activation energy for the exo-endo interconversion of 2-methylbicyclo[2.1.0]pentane is 38·9 kcal/mole.[39] The activation energy predicted on a model in which the total strain (53·6 kcal/mole)[40] less the residual strain in cyclopentane (6·2 kcal/mole) contributes to the lowering, would amount to 31·6 kcal/mole. Since the predicted value is lower than the experimental value, there is no need to assume additional lowering from 1,3-(2p–2p) overlap.

[39] J. P. Chesick, *J. Amer. Chem. Soc.* **84**, 3250 (1962).

[40] R. B. Turner *et al.*, in preparation, deduce a strain of 53·6 kcal/mole for bicyclo[2.1.0]pentane.

[41] Such an intermediate could also serve to rationalize the formation of dienes in the pyrolysis of substituted methylenecyclobutanes.[42]

[42] J. J. Drysdale, H. B. Stevenson and W. H. Sharkey, *J. Amer. Chem. Soc.* **81**, 4908 (1959).



destination.[43] Formulated in this way, TS(III′-EA) must be in the process of establishing the perpendicular arrangement of methylene groups demanded by allene and of drastically rehybridizing the orbitals of the central atom of the allylic system, C_1, and the attached carbon atom, C_4 or C_2 (which owe their indistinguishability to the pre-equilibrium). Establishment of perpendicularity must be accompanied by loss, to a greater or lesser extent, of the energy of allylic delocalization. Whether this loss would be more than compensated by the energy of ethylene and allene delocalization cannot be decided. That such an hermaphroditic state should be higher in energy than III′ is not unreasonable, but it can only be ruled necessary by *de novo* quantum mechanical calculations. An appropriately designed study of the reverse reaction,[44] the formation of methylenecyclobutane from ethylene and allene, could resolve the question in much the same way as the Bartlett study[46] resolved the similar question of the involvement of an intermediate diradical, 1,4-tetramethylene, in the cyclo-addition reaction.

In a piece on steric inhibition of resonance in the formation of radicals, Nangia and Benson[47] note that the activation energy (63·5 kcal/mole)[13] of the thermolysis of methylenecyclobutane to ethylene and allene is identical with the activation energy required to cleave cyclobutane (63·2 kcal/mole)[48] and its principal derivatives by way of a 1,4-diradical. On the assumption that the total strain in methylenecyclobutane essentially equals the total strain in cyclobutane,[31] they conclude from this identity that allylic assistance is completely barred by the perpendicular relationship of the two planes of the relevent methylene groups. The weakness in the argument lies in the further assumption that rupture of the ring is the rate-determining feature revealed in the transition state for the decomposition. The weakness of this assumption is foreshadowed by Chesick[3] who noted that "a primary reversible ring opening might be easier because of the extra ring-strain energy [in methylenecyclobutane over cyclobutane], but the resulting species [III′] might be more stable than the tetramethylene analog and would require greater energy for complete dissociation to allene and

---

[43] Discussions of this sort do no more than indicate structurally and energetically compatible pathways and, to the extent that they involve selections among various plausible possibilities, reflect prejudices and preferences among working hypotheses.

[44] Such an experiment would involve, for example, examination of the methylenecyclobutane generated from ethylene and optically active allene (e.g. 1,3-dideuterioallene) for induced optical activity. It might also be explored by study of the stereochemistry of the products of reaction of allene with dimethylfumarate and dimethylmaleate; but these examples seem not to be among those reported in the discovery of the general cycloaddition.[45]

[45] H. N. Cripps, J. K. Williams and W. H. Sharkey, *J. Amer. Chem. Soc.* **81**, 2723 (1959).

[46] P. D. Bartlett, L. K. Montgomery and B. Seidel, *J. Amer. Chem. Soc.*, **86**, 616 (1964).

[47] P. Nangia and S. W. Benson, *J. Amer. Chem. Soc.* **84**, 3411 (1962).

[48] R. W. Vreeland and D. F. Swinehart, *J. Amer. Chem. Soc.* **85**, 3349 (1963).

ethylene, giving a larger net activation energy." And, so indeed it has turned out: rupture of the ring to give III′ is measured by the methylenecyclobutane rearrangement (E_{act} 49·5 kcal/mole) and not by the cleavage to ethylene and allene (E_{act} 63·5 kcal/mole). The ring-opening is thus markedly assisted by allylic delocalization and has certainly not been completely inhibited sterically.

Evaluation of the quantitative extent of allylic assistance and therefore of the degree, if any, to which contribution of the allylic delocalization energy has been sterically inhibited depends on what assumptions are made. An evaluation free of assumptions is not possible. At the least assumptions have to be made about the energy of a hypothetically unassisted transition state.

One simple assumption is the same as Nangia and Benson's: that the strain energy in cyclobutane (+25·75 kcal/mole)[32] and methylenecyclobutane (+28·55 kcal/mole)[31] being essentially equal, the ring-opening of cyclobutane to tetramethylene and the unassisted ring-opening of methylenecyclobutane would have similar energy requirements. On the basis of this assumption the hypothetical energy level of TS(MCB-III″), the transition state for the unassisted rupture, would be 63·2 kcal/mole (or not less than 60·4 kcal/mole if the apparent, but experimentally far from certain, extra strain (2·8 kcal/mole) of methylenecyclobutane is allowed to operate fully) and allylic assistance in the actual transition state for rupture [TS(MCB-III′)] would amount to 13·7 kcal/mole (or no less than 10·9 kcal/mole).

Alternatively, we may assume as, in fact, did Nangia and Benson, that the actual transition state [TS(III′-EA)] for the decomposition of methylenecyclobutane to ethylene and allene (ΔH_f° + 92·2 kcal/mole; E_{act} 63·5 kcal/mole) is close in geometry to III″, the expected result of rupture of the methylenecyclobutane ring without assistance from allylic delocalization. This assumption leads to 14·0 kcal/mole as the measure of allylic assistance.

Another way of developing the conclusion recognizes that the transition state for rupture [TS(MCB-III′); ΔH_f° 78·2 kcal/mole] is assisted by allylic delocalization while the transition state for decomposition to ethylene and allene [TS(III′-EA); ΔH_f° 92·2 kcal/mole] has lost most, if not all, of its allylic delocalization owing to its need to assume the perpendicularity of methylene groups demanded by one of its products, allene. In this analysis the difference between the heats of formation of TS(MCB-III′) and TS(III′-EA) is equated with the partially sterically inhibited energy of allylic delocalization (14 kcal/mole).

These estimates of the magnitude of the possibly partially sterically inhibited assistance by allylic delocalization may be compared with the various estimates of the energy of full allylic delocalization, here listed in part and without critical comment. A value of 20 kcal/mole is derived from the activation energy for the cleavage of butene-1 to methyl and allyl radicals;[49,50] a value of 19 kcal/mole from the activation energy for the homolysis of allyl bromide;[51,52] a value of 12 kcal/mole from the activation energy for the iodine-catalyzed positional isomerism of butene-1;[53] a value of 18 kcal/mole from the activation energy for the cleavage of hexadiene-1,5 to two

[49] M. Szwarc and A. H. Sehon, *Proc. Roy. Soc.* **A202**, 263 (1950).

[50] J. A. Kerr, R. Sencer, and A. F. Trotman-Dickenson, *J. Chem. Soc.* 6652 (1965).

[51] A. Maccoll, *J. Chem. Phys.* **17**, 1350 (1949).

[52] M. Ladacki and M. Szwarc, *Proc. Roy. Soc.* **A219**, 341 (1953).

[53] K. W. Egger, D. M. Golden and S. W. Benson, *J. Amer. Chem. Soc.* **86**, 5420 (1964).

allyl radicals;[36] a value of 15·5 kcal/mole from the activation energy of the vinylcyclopropane rearrangement;[54,55] a value of 25 kcal/mole from consideration of several bond energies;[56] and finally a value of 17–18 kcal/mole calculated by Franklin and Field.[57] It may be noted safely that the 10·9–14 kcal/mole estimated as the contribution of allylic delocalization to the methylenecyclobutane rearrangement is surprisingly large in comparison to the various estimates of sterically allowed allylic delocalization.

As a further remark on the subject of steric inhibition of allylic assistance, Nangia and Benson[47] note that "the very low E_{act} of 32·5 kcal/mole observed[58] for the first order isomerization of cyclobutane to butadiene cannot be reconciled" with the assumption of steric inhibition of resonance "unless one assumes that the strain energy in cyclobutene exceeds that in cyclobutane by about 10–20 kcal/mole" which "seems rather unreasonable." Perhaps it is more profitable to note that the enthalpy of the rearrangement of cyclobutene to butadiene is exothermic and that the activation energy would be zero were it not for the partial inhibition of butadiene delocalization in the transition state. In fact, when the conrotatory process has reached the transition state, about 45% of the 53 kcal/mole, which represents the estimated difference between *cis*-butadiene and but-2-ene-1,4-diyl, has been made available. To have been unable to predict even approximately that this butadiene assistance should have amounted to 20 kcal/mole and not 10 kcal/mole or 50 is to emphasize the extraordinarily primitive control theoretical organic chemistry exercises over the subject of activation energies.

Chesick has already pointed out that methylenecyclopropane[59] is another example which might have shown complete steric inhibition of resonance but actually does not. In general, a thesis opposite to that of Nangia and Benson must be advanced: whenever an apparently one-step reaction requires a large change in geometry to accommodate rehybridization in the immediate product or intermediate, some, but neither all nor none, of the exothermicity of the immediate product is available for lowering the energy of the transition state.

Elucidation of the methylenecyclobutane rearrangement is relevent to the extraordinary features of the pyrolysis of spiropentane uncovered in the superlative study of Burkhardt (and Swinehart).[13] In addition to having determined the activation parameters of the transformations of spiropentane and methylenecyclobutane with high accuracy, they discovered two first-order pressure-dependent paths for the thermal reorganization of spiropentane. At high pressure rearrangement to methylenecyclobutane is the exclusive path, while at low pressure decomposition to ethylene and allene becomes the predominant reaction. At a pressure of 150 microns the two paths are of equal importance. More surprisingly the ratio of these two paths at constant pressure is independent of temperature.

These phenomena must be interpreted in terms of a common, *excited* intermediate which of necessity suffers unimolecular decomposition unless it is collisionally (bimolecularly) deactivated. In structural terms, this intermediate may be described as excited methylenecyclobutane, excited ethylene-allene, excited intermediate III′ or

[54] H. M. Frey and D. C. Marshall, *J. Chem. Soc.* 3981 (1962).

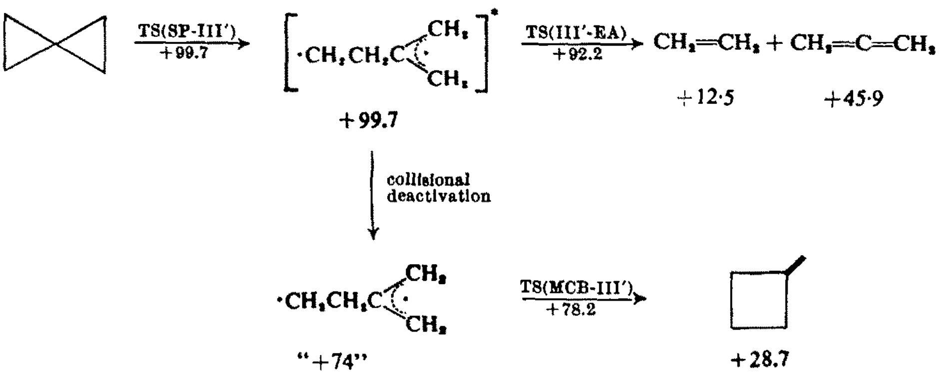
[55] R. J. Ellis and H. M. Frey, *J. Chem. Soc.* 959 (1964).

[56] C. Walling, *Free Radicals in Solution* Chap. 2. Wiley, New York, N. Y. (1957).

[57] J. L. Franklin and F. H. Field, *J. Amer. Chem. Soc.* **75**, 2819 (1953).

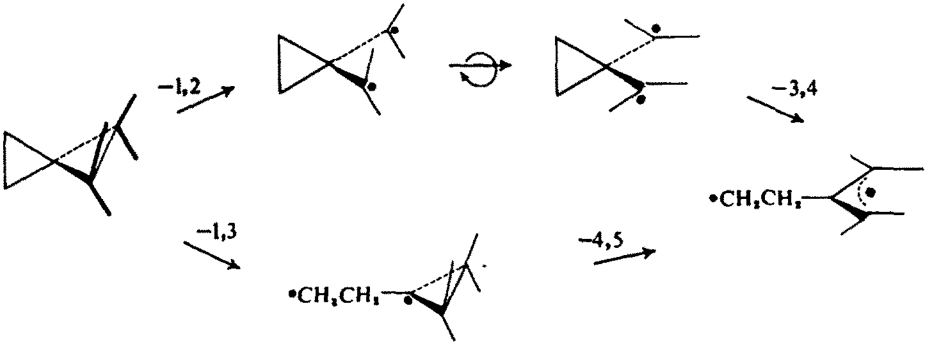
[58] W. P. Hauser and W. D. Walters, *J. Phys. Chem.* **67**, 1328 (1963).

[59] J. P. Chesick, *J. Amer. Chem. Soc.* **85**, 2720 (1963).



TS(SP-III'), the transition state for the transformation of spiropentane. The important feature of this excited intermediate is its energy: having a heat of formation of +99·7 kcal/mole, it lies above the transition states for the decomposition to ethylene and allene (heat of formation of +92·2 kcal/mole) and rearrangement to methylenecyclobutane (+78·2 kcal/mole). It has no choice but to decompose to an excited mixture of ethylene and allene unless it is deactivated to an energy level below 92·2 kcal/mole. Such a deactivation is normally considered to require only a single collision and must lead to methylenecyclobutane, either directly or indirectly by way of intermediate, III'. Although it is possible to imagine the excited intermediate being deactivated to spiropentane, nothing in the present work bears on this point.[60] From the composite description given to the excited intermediate no specific structural assignment is meaningful. Nonetheless, as a short-hand representation, an excited version of the intermediate III' may be helpful.

In the hypothetical sequence of bond-breaking steps by which spiropentane is transformed to the excited intermediate, initial rupture of the 1,2-bond seems to be more attractive than rupture of the 1,3-bond. The resulting 1,3-diradical can assume by free rotation[15] a coplanar conformation within which rupture of the 3,4-bond could lead, with a minimum of further readjustment, to III' in its most stable configuration. On the assumption that little or no activation energy is required in this terminal phase



---

[60] W. von E. Doering and J. C. Gilbert have unpublished work on the behavior of chemically excited spiropentane generated by the reaction of CD_2 with methylenecyclopropane (estimated heat of formation 120 kcal/mole), in which both spiropentane and methylenecyclobutane appear as products.

of the transformation, the observed activation energy would be associated to a first approximation with the initial opening of the cyclopropane ring. The experimental E_{act} of 55·5 kcal/mole falls close to the activation energy for the rupture of the bond in cyclopropane itself (64 kcal/mole)[15] lowered by the estimated extra strain in spiropentane (+8·8 kcal/mole).[17] Although the agreement is doubtlessly fortuitously good, it makes this sequence more attractive than the alternative in which rupture of the 1,3-bond is followed by rupture of the 4,5-bond. In this process the methylene groups cannot have attained in the transition state the coplanarity required for realization of the full allylic delocalization.

EXPERIMENTAL[61]

1,1,2,2-*Tetradeuteriospiropentane* (I)

(a) 1,1-*Dicarboethoxycyclopropane*. This substance was prepared according to the procedure of Dox and Yoder[4] and had an NMR spectrum consisting of a quartet at 4·15 ppm (4 protons) and a singlet at 1·31 ppm superimposed on a triplet centered at 1·26 ppm (total of 10 protons).

(b) 1,1-bis(*Hydroxydideuteriomethyl*)*cyclopropane*. For the reduction of the ester by the procedure of House, Lord and Rao,[5] 22·5 g 1,1-dicarboethoxycyclopropane and 6·0 g LAD (Metal Hydrides, Inc.) was employed. The resulting diol, 11·1 g, b.p. 96–98°/3 mm, had an NMR spectrum[62] from which absorption at 3·56 ppm, the region in which the methylene protons appear in 1,1-*bis*-hydroxymethylcyclopropane, was missing. The IR spectrum is available.[62]

(c) 1,1-bis(*Bromodideuteriomethyl*)*cyclopropane*. Following the method of Wiley *et al.*,[6] the diol (11·1 g), triphenylphosphite (76 g) and anhydrous N,N-dimethylformamide (130 ml) were placed in a 500-ml, three-necked flask fitted with a dropping funnel, mechanical stirrer, thermometer and a condenser equipped for introduction of dry N_2. To the stirred solution, blanketed with N_2 and held at 55° or below throughout the reaction, Br_2 (36·0 g) was added over 0·5 hr. The resulting orange-red solution was stirred at room temp for 3 hr and distilled *in vacuo* into a receiver cooled in Dry-Ice until b.p. reached 67°/3 mm. The distillate was poured into 400 ml cold water, shaken and separated. The upper, aqueous layer was centrifuged to facilitate isolation of additional dibromide. The crude dibromide in an equal volume of ether was dried over Na_2SO_4. Filtration, concentration and distillation afforded 15·5 g colorless dibromide; b.p. 80–85°/13 mm; reported[63] b.p. 63·7–64·0°/5·1 mm. The product was contaminated with a small amount of N,N-dimethylformamide. Analysis of the integrated NMR spectrum[62] showed an absence of absorption at 3·49 ppm, the region in which the methylene protons of 1,1-*bis*(bromomethyl)cyclopropane absorb. The IR spectrum is available.[62]

(d) 1,1,2,2-*Tetradeuteriospiropentane* (I). The procedure devised by Applequist *et al.*[7] for the conversion of pentaerythrityl tetrabromide to spiropentane was used here. A 500-ml, three-necked flask was equipped with a high-speed stirrer, N_2 inlet, apparatus for the addition of solids and a West condenser fitted with a Claisen head to which was attached a spiral condenser linked, in turn, to two receivers cooled in Dry-Ice-acetone. A mixture of 24·2 g NaOH pellets, 30·5 g ethylenediaminetetraacetic acid, 0·6 g NaI, 40 ml water and 64 ml 95% EtOH was placed in the flask, brought to reflux, and treated with 8·7 g Zn dust. 1,1-*bis*(Bromodideuteriomethyl)cyclopropane (15·5 g) was added to the stirred, refluxing slurry over a 1-hr period by means of a dropping funnel which had replaced the solids-addition apparatus. After having been refluxed under a steady stream of N_2 for 1 hr, a distillate had condensed in the cooled receivers (Dry-Ice). Br_2 was slowly added to the distillate until an orange color persisted in the solution for 20 min. Excess Br_2 was destroyed by dropwise addition of cyclohexene. The colorless solution was cooled to −80° and separated. The upper layer was distilled to give 4·5 g I; b.p. 33·0–34·5°/760 mm; reported[7] b.p. 36·5–37·5°/760 mm. Final purification was achieved by glpc on a 4-meter 1/4″ column of 40–60 mesh firebrick containing 20% β,β'-oxydipropionitrile.

---

[61] M.ps and b.ps are not corrected. IR spectra were obtained with a Perkin–Elmer model 221 spectrometer while NMR[8] and mass spectra[10] are obtained as noted.

[62] This spectrum is fully reproduced in the dissertation of J. C. Gilbert.[1]

[63] D. E. Applequist and J. D. Roberts, *J. Amer. Chem. Soc.* **78**, 874 (1956).

The NMR spectrum[62] of I consisted of a singlet of width at one-half height of 1·5 c/s at δ = 0·767 ppm. The ^{13}C—H satellites are a crude pair of doublets with $J_{^{13}C-H}$ of 5·5 and 8·5 c/s. The IR spectrum[62] is tabulated in Table 2.

1,1,4,4-*Tetradeuteriospiropentane* (II)

(a) 1,1,3,3-*Tetradeuterioallene*. By the procedure of Morse and Leitch[11] a mixture of allene-d_4 and propyne-d_4 was prepared. The propyne was removed by passing the mixture through two gas washing bottles, both of which contained a solution formulated from 4 g $CuSO_4$ in 40 ml water, 60 g NH_4Cl, 160 ml conc NH_4OH, 120 g $NH_2OH{\cdot}HCl$ made up to 1000 ml with water.[64] The purified allene-d_4 was collected in a receiver cooled in a bath of Dry-Ice and acetone. IR analysis showed the absence of propyne-d_4 while low voltage mass spectrometry at an ionizing voltage of 9·50 ev indicated the presence of 91·2% tetradeuterio-, 6·7% trideuterio- and 2·2% dideuterioallene.

(b) 1,1,4,4-*Tetradeuteriospiropentane* (II). A 15-ml tube was equipped with a gas-inlet tube, a cooling jacket and a cold finger containing MeOH and a cooling coil. The apparatus was cooled by circulation of MeOH at −55° (passed continuously through a heat transfer coil immersed in acetone and Dry-Ice) through the cooling jacket and coil. After 2 ml allene-d_4 had been distilled into the cooled tube, diazomethane[65] from 4 g N-nitrosomethylurea was swept into the hydrocarbon over a 1-hr period. The resulting yellow solution was photolyzed 2 hr with two G. E. sunlamps (low-press, Pyrex-filtered Hg lamp). The addition of diazomethane and the photolysis were repeated two more times (diazomethane from a total of 12 g N-nitrosomethylurea). The reaction mixture was distilled from the tube by warming the apparatus to room temp under a stream of N_2 and collecting the distillate in a receiver cooled in acetone and Dry-Ice. The colorless mixture was then distilled into two fractions, b.p. −30 to 25° and b.p. 25–40°. Compound II in the higher boiling fraction was isolated and purified by glpc on a 4 meter, 1/4″ column of kieselguhr containing 20% Dow-Corning 710 silicone oil and the previously described oxydipropionitrile column. The IR spectrum[62] is tabulated in Table 2.

Table 2. IR spectra of 1,1,2,2-tetradeuteriospiropentane (I) and 1,1,4,4-tetradeuteriospiropentane (II)

Frequency in cm^{-1}	% Transmission[a]			Frequency in cm^{-1}	% Transmission[a]		
	II[b]	I[c]	I[b,d]		II[b]	I[c]	I[b,d]
3072	(30)	11	2	1065	(60)	37	37
3065	12	(25)	(22)	1047	55	13	10
3000	16	8	0	1020	11	(32)	(30)
2312	28	20	17	1011	(50)	7	4
2220	45	38	35	960	74	25	20
2203	(68)	39	35	895	56	(89)	(87)
2192	47	(55)	(52)	872	49	79	79
1435	74	(77)	(74)	857	(79)	26	22
1420	(84)	56	50	832	17	(74)	(70)
1402	76	(82)	(78)	808	(79)	47	43
1152	(90)	59	50	765	7	(7)	(9)
1130	64	(78)	(73)	760	(35)	3	1
1110	45	81	74	747	47	(55)	(53)

[a] All values, except those in parentheses, pertain to absorption maxima.

[b] Neat in a 0·028-mm cell.

[c] Neat in a 0·025-mm cell.

[d] Recovered from the heating at 355° for 27 hr.

---

[64] D. M. Sharefkin, R. Sallé and L. Pichat, *Radiochimica Acta* **1**, 87 (1963).

[65] Diazomethane is prepared and handled according to the procedure of Doering and Roth.[66]

[66] W. von E. Doering and W. R. Roth, *Tetrahedron* **19**, 715 (1963).

Compound II could also be prepared by catalytic decomposition of diazomethane with CuCl. To a small reaction vessel, cooled to −80°, equipped with a stirring bar, gas-inlet tube, and a spiral condenser connected to a Dry-Ice condenser, and containing 1 ml allene-d_4 and 4 ml decalin, 50 mg freshly prepared CuCl was added. Diazomethane from 30 g N-nitrosomethylurea was bubbled into the resulting slurry and held at −30° for 5 hr. The distilled reaction mixture was purified by glpc as described above. This sample of II had IR and NMR spectra identical to those of II prepared above.

The NMR spectrum[42] of II, like that of I, consisted of a band centered at $\delta = 0{\cdot}767$ ppm, which in II is a pentuplet of width at one-half height of 3·0 c/s instead of a singlet. The coupling constant, $J_{D\text{-}H}$, is 0·75 c/s.

(c) 2,2-*Dideuterio*-1-(*dideuteriomethylene*)*cyclopropane*. The low-boiling fractions from the preparations of II were combined and purified by glpc on the two columns employed in the purification of II. Mass spectrographic analysis at an ionizing voltage of 9·50 ev indicated the presence of the tetradeuterio species (79·0%), the trideuterio (16·0%) and the dideuterio (5·0%). Analysis of the integrated NMR spectrum[42] showed the presence of no more than 4·3% of H_2 in the vinyl positions. The IR spectrum is available.[42]

Rearrangement of 1,1,2,2-*tetradeuteriospiropentane* (I)

A 600-ml Pyrex tube equipped with a vacuum stopcock was conditioned by thermolysis at 360° of two 30-microliter samples of I for a 24-hr period. Compound I (ca. 300 microliters) was then heated 27 hr at 355° in the seasoned vessel. The products were analyzed and purified by glpc on the 4-m column of 20% β,β′-oxydipropionitrile. They consisted of ethylene-d_x in unknown amount of relative retention time 1·00, allene-d_x (2·0% and rel. ret. time 9·02), spiropentane-d_x (18·3% and rel. ret. time 23·2) and methylenecyclobutane-d_x (79·7% and rel. ret. time 30·4; NMR and IR spectra are available[42]). The NMR spectrum of recovered spiropentane was identical with that of starting I.

TABLE 3. MASS SPECTRA OF 1,1,2,2-TETRADEUTERIOSPIROPENTANE (I) AND 1,1,4,4-TETRADEUTERIOSPIROPENTANE (II)

m/e	Intensities[a,b]			m/e	Intensities[a,b]		
	I	I[c]	II		I	I[c]	II
72	11·4	12·5	9·3	46	4·8	4·7	4·2
71	56·7	65·0	46·8	45	12·0	12·0	13·9
70	33·6	41·3	31·7	44	39·6	41·3	22·2
69	2·7	2·9	3·7	43	19·5	19·7	30·1
68	2·7	2·9	2·3	42	100·0	100·0	100·0
67	1·8	2·0	1·4	41	38·2	38·2	76·4
				40	65·8	65·8	63·9
				39	43·5	43·6	21·3
				38	11·4	10·8	9·3
				37	4·5	4·3	4·2
57	6·9	7·4	4·2	33	1·8	2·0	1·9
56	17·7	18·9	16·2	32	5·4	5·4	3·7
55	18·9	20·1	18·1	31	4·2	2·9	4·6
54	8·1	13·7	6·0	30	15·0	14·2	15·3
53	3·3	3·6	3·7	29	16·8	17·7	31·0
52	4·2	4·3	4·6	28	27·3	30·0	35·6
51	4·5	4·3	4·6	27	13·8	13·4	14·2
50	2·1	2·1	1·9	26	3·9	5·1	5·7

[a] Intensities relative to that of m/e 42 as 100 at an ionizing voltage of 68 ev.

[b] Those ratios of mass to charge associated with a relative intensity less than 2·0 are omitted from the Table.

[c] Recovered from the heating at 355° for 27 hr.

The mass spectrum, shown in Table 3, is virtually unchanged from that of starting material. Tabulation of the IR spectra of samples of starting I and recovered I show essential identity (Table 2). Analysis of the IR spectra of I and II at 832 cm^{-1} indicated that no II had been formed and that the detection of more than 5% would have been assured, while the detection of as little as 3% was probable.

1-(*Dideuteriomethylene*)*cyclobutane* (IIIa)

(a) *From cyclobutanone.* An attempted application of the Wittig reaction[21] failed to yield isotopically homogeneous IIIa. Methyltriphenylphosphonium bromide, (15·0 g) prepared according to Wittig and Schöllkopf,[67] was converted to trideuteriomethyltriphenylphosphonium bromide, after the general method of Bestmann *et al.*,[68] by treatment with 30 ml D_2O (99·8% D) in a stoppered 125-ml Erlenmeyer flask equipped with a stirring bar, and a catalytic amount of NaOD. After the solution had been stirred at 25° for 4 hr, NMR analysis indicated that the Me group had been at least 96% deuterated. Concentration and recrystallization from chloroform–dioxan gave trideuteriomethyltriphenylphosphonium bromide: 15·0 g; m.p. 232–235°; reported[69] m.p. 230–231°.

In accord with the procedure of Wittig and Schöllkopf,[67] a 250-ml, three-necked flask, supplied with a stirring bar and containing 21·6 g trideuteriomethyltriphenylphosphonium bromide and 3·0 g 50% NaH dispersed in mineral oil (Metal Hydrides, Inc.), was attached to a vacuum line and degassed. Degassed benzene (100 ml) was then distilled into the flask, and the resulting slurry was stirred at 25° for 6 days, by which time the benzene solution was reddish-brown and ca. 90% of the theoretical quantity of H_2 had been evolved. The flask was removed from the vacuum line under a positive press of N_2, fitted with an inlet for N_2 and a reflux condenser linked to a receiver cooled in a bath of Dry-Ice and acetone. Cyclobutanone (3·0 g; Columbia Organic) was added in one portion under a blanket of N_2. The color disappeared rapidly and the resulting slurry was stirred at 25° for 0·5 hr. The mixture was refluxed 3 hr under a stream of N_2 to give a distillate of methylenecyclobutane-d_x (48% of theory). Analysis by NMR indicated deuterium in both the allylic and the vinylic positions. Mass spectrographic analysis at an ionizing voltage of 68 ev confirmed the presence of species up to and including methylenecyclobutane-d_6. Ratios of mass to charge and intensities relative to *m/e* 69 as 100 are given: 74–4; 73–9; 72–35; 71–57; 70–87; 69–100; 68–87.

(b) *From cyclobutane carboxylic acid by way of acetoxydideuteriomethylcyclobutane.* To a solution of 11·0 g cyclobutane carboxylic acid for the generous gift of which we are indebted to Mr. John Hiatt of Yale University, in 50 ml anhydrous ether in a 125-ml Erlenmeyer flask, cooled in an ice-bath, a solution of diazomethane in ether was slowly added until the yellow color persisted. The resulting solution was warmed to room temp. After 2 hr, the excess diazomethane was destroyed by cautious addition of AcOH. The ethereal solution was dried over Na_2SO_4 and concentrated to yield 11·4 g 1-carbomethoxycyclobutane: b.p. 131–134°/760 mm; reported[70] b.p. 134·5°/754 mm.

Conversion to acetoxydideuteriomethylcyclobutane was effected by the procedure of Conia and Gore[22] with the replacement of LAH by the deuteride. The acetate which was isolated by distillation, b.p. 93–95°/60 mm, had NMR and IR spectra[62] consistent with the expected structure.

Pyrolytic decomposition followed the procedure of Conia and Gore.[22] The labeled acetate was passed at the rate of 0·5 g/hr into a 1-m Pyrex tube of 10-mm diameter packed with Pyrex helices and heated at 480°. The apparatus was continuously flushed with dry N_2 at the rate of 10 ml/min which afforded a contact time of 4 min. The pyrolysis mixture was collected in a receiver cooled in acetone and Dry-Ice. Under these conditions the acetate was converted to methylenecyclobutane-d_2 in 74% of theory, based on recovered acetate. IR and NMR analyses showed the hydrocarbon to be a nearly equilibrated mixture of IIIa and IIIb. Pyrolyses involving contact times of 1–2 min not only produced lower conversions, but still yielded the undesired equilibrated mixture.

(c) *By way of the* N-*oxide of* N,N-*dimethylaminodideuteriomethylcyclobutane*. This oxide was prepared according to the procedure of Conia and Gore[22] by the sequence in which cyclobutane carbonyl chloride (prepared according to the procedure of Applequist and Greer:[71] b.p. 125–128°/760 mm; reported[71] b.p. 130–140°/760 mm) is converted to the N,N-dimethylamide which is then

---

[67] G. Wittig and U. Schöllkopf, *Chem. Ber.* **87**, 1318 (1954).

[68] H. J. Bestmann, O. Kratzer and H. Simon, *Chem. Ber.* **95**, 2750 (1962).

[69] M. Schlosser, *Chem. Ber.* **97**, 3219 (1964).

[70] G. H. Jeffery and A. I. Vogel, *J. Chem. Soc.* 1804 (1948).

[71] D. E. Applequist and D. E. Greer, *J. Amer. Chem. Soc.* **82**, 1965 (1960).

reduced by LAD in place of LAH and oxidized with H_2O_2. The concentrated N-oxide, not otherwise purified, was heated at 150–180° at atm press to afford a 33% yield of IIIa. Analysis by glpc (β,β'-oxydiproprionitrile column) showed the hydrocarbon to be at least 99% pure after one distillation at atm press. NMR and IR spectra[22] were consistent with the structural assignment. Analysis of the integrated NMR spectrum showed no detectable absorption in the region, 4·6–4·8 ppm, of vinylic hydrogen. The mass spectrum is tabulated in Table 4.

Rearrangement of dideuteriomethylenecyclobutane (IIIa)

(a) *Thermal stability of methylenecyclobutane.* Purified methylenecyclobutane (Columbia Organic) was found, by glpc analysis, to be unchanged after 24 hr at 290° in an evacuated ampoule at 60 mm. After 56 hr at 380°, allene (11·2%), identified by retention time on the silicone column, and a more rapidly eluting substance, presumably ethylene, were observed in addition to unchanged starting material.

(b) *Pyrolysis of* 1-*(dideuteriomethylene)cyclobutane* (IIIa). A 600-ml ampoule was conditioned by prior decomposition of equilibrated methylenecyclobutane-d_2 obtained from the pyrolysis of acetoxydideuteriomethylcyclobutane (*vide supra*). Samples of IIIa were heated at 290° in the seasoned ampoule for various periods of time. The change in IIIa upon thermolysis was monitored by IR spectroscopy. After 24·0, 52·0, 77·5 and 133·0 hr, the ratio of the % transmission at 1665 cm^{-1} (IIIb: $C{=}CH_2$) and 1645 cm^{-1} (IIIa: $C{=}CD_2$) was 0·91, 0·96 and 1·01 and 1·42, respectively. In the 52·0- and 77·5-hr runs, less than 0·5% allene was produced. The mass spectrum (ionizing voltage of 68 ev) of material recovered from the 133·0-hr run was essentially identical with that of starting material (Table 4).

TABLE 4. MASS SPECTRA OF DIDEUTERIOMETHYLENECYCLOBUTANES IIIa AND IIIb

m/e[a]	Intensities[b]		*m/e*[a]	Intensities[b]	
	IIIa	IIIa and b[c]		IIIa	IIIa and b[c]
71	4·8	4·5	44	8·6	8·4
70	85	82	43	18	16
69	100	100	42	90	71
68	25	25	41	70	51
67	5·7	5·5	40	81	83
66	3·2	3·1	39	28	39
65	1·7	1·5	38	9·4	9·7
64	2·4	2·0	37	4·7	4·7
63	2·5	2·4			
62	2·0	1·8			
55	19	19			
54	22	22			
53	11	9·7	30	2·6	3·2
52	4·5	4·1	29	7·9	7·9
51	5·7	5·1	28	16	16
50	3·6	3·8	27	23	17

[a] Those ratios of mass to charge associated with a relative intensity less then 2·0 are omitted from the Table.

[b] Intensities relative to that of *m/e* 69 as 100 at an ionizing voltage of 68 ev.

[c] Mixture obtained by heating IIIa 133 hr at 290° is 80% equilibrated.

(c) *Equilibrium beteeen* IIIa *and* IIIb. A 130-microliter sample of a partially equilibrated mixture of IIIa and IIIb was heated 47 hr at 342° in a seasoned 600-ml ampoule. The average of five integrations of the NMR spectrum of the recovered material gave a ratio of the areas of vinylic: allylic: homoallylic protons of 1·29:2·59:2·00.

(d) *Determination of rate constants and activation energy for the equilibrium.* Rate constants for the conversion of IIIa to IIIb were determined over the range 287·5–354·3°. The temp was measured with an uncalibrated chromel-alumel thermocouple coupled to a Leeds and Northrup potentiometer and is estimated to be within ±1·0° of the absolute value. For kinetic runs in which refluxing liquids were utilized for heating the ampoules, the fluctuation of the temp during any one run was less than ±0·5°, while thermal homogeneity, determined by measuring the temp at the extremes of the ampoule, was better than ±0·25°. When a tube furnace was used for heating, fluctuation of the temp was less than ±0·25° during any one run while thermal homogeneity was better than ±1·0°.

For kinetic runs in which the 600-ml ampoule was utilized, the run was begun by expansion of ca. 100 microliters IIIa from a 20-ml bulb into the ampoule. The ampoule was heated in a tube furnace. Each kinetic run was terminated by expanding the mixture from the ampoule into an evacuated bulb cooled in liquid N_2.

For the runs in which a refluxing liquid was employed as the constant-temp bath, the liquid was contained in a 1000-ml flask equipped with a 50-cm neck of 38-mm o.d. insulated with glass wool. The system was blanketed with N_2 at all times. The sealed 50-ml ampoule containing 50 microliters IIIa, was suspended in the vapors of the refluxing liquid, care being taken that the ampoule did not touch the surface of the liquid itself. The temp at the upper extreme of the ampoule did not reach the equilibrium value for approximately 90 sec after suspension of the ampoule in the apparatus. Consequently, a correction of 120 sec was made in the time measurement for each run as compensation for the time required for thermal equilibration of the ampoule. The exact value for the correction is not critical owing to relatively long duration of each run. Runs were terminated by cooling the ampoule in a stream of air.

The amount of rearrangement to IIIa was determined by integration of the NMR spectrum of the recovered methylenecyclobutane-d_2. A minimum of ten integrations was averaged to obtain the ratio of vinylic: allylic: homoallylic protons. The value for the area assigned to homoallylic protons was then adjusted until the area of the vinylic and allylic protons equaled 4·00. This adjustment was made because, within experimental error, there is no deuterium in the homoallylic position after equilibration. This observation requires that 2·0 of the 6·0 hydrogens present in IIIa and IIIb be in the homoallylic position with the remaining 4·0 hydrogen atoms in the vinylic and allylic positions The normalized integral was used to calculate the percentage of IIIb:

% IIIb = 100 (area of vinylic hydrogen/area of homoallylic hydrogen). The calculated rate constants are given in Table 1.