Tetrahedron Vol. 38, No. 6, pp. 853 to 862, 1982
Printed in Great Britain.

0040-4020/82/060853-10$03.00/0
Pergamon Press Ltd.

CROSS-CONJUGATED BIRADICALS

KINETICS AND KINETIC ISOTOPE EFFECTS IN THE THERMAL ISOMERIZATIONS OF *CIS*- AND *TRANS*-2,3-DIMETHYLMETHYLENECYCLOPROPANE, *CIS*- AND *TRANS*-3,4-DIMETHYL-1,2-DIMETHYLENECYCLOBUTANE, AND OF 1,2,8,9-DECATETRAENE

JOSEPH J. GAJEWSKI, CHARLES W. BENNER, BRUCE N. STAHLY, RALPH F. HALL
and RONALD I. SATO
Department of Chemistry, Indiana University, Bloomington, IN 47405, U.S.A.

(*Received in U.S.A.* 16 *March* 1981)

Abstract—*cis*- and *trans* - 2,3 - Dimethylenemethylenecyclopropane (C and T) interconvert at 160.0° with a small normal kinetic isotope effect (KIE) when the *exo*-methylene is deuterated, but the 1,3-shift products, 2-methylethylidenecyclopropane, show a large normal KIE, 1.35 and 1.31, when formed from C and T, respectively. This data can be interpreted in terms of either parallel reactions or a common trimethylenemethane diradical intermediate formed with a normal KIE of 1.11 and closing to 1,3-shift product with a normal KIE of 1.29 due to the effect of deuterium in the required 90° rotation of the *exo*-methylene carbon.

The kinetics of the thermal 1,3- and 3,3-shifts of *cis*- and *trans*-3,4-dimethyl-1,2-dimethylenecyclobutane (CB and TB) were determined in a flow reactor. The first order rate constants are log k_{CB} (sec^{-1}) = 13.7 − 42,200/2.3 RT and log k_{TB} (sec^{-1}) = 13.6 − 41,900/2.3 RT (E_a in kcal/m) which compare favorably to that from the parent hydrocarbon, 1,2-dimethylenecyclobutane, after reasonable correction for dimethyl substitution.

Rearrangement of TB and its bis(dideuteriomethylene) derivative at 230.0° revealed a normal KIE of 1.08. This KIE could be interpreted in terms of either a methylene rotational isotope effect in a concerted reaction or formation of a bisallyl diradical with the expected normal rotational IE on closure to the 1,3-shift product of 1.12 with no IE in the ring opening when the result is corrected for return of the biradical to starting material.

The kinetics of intramolecular 2 + 2 cycloaddition of 1,2,8,9-decatetraene were determined in a flow reactor. The first order rate constant is log k(sec^{-1}) = 9.4 − 30,800/2.3 RT (E_a in kcal/m). These energetics are compared with those of other 2 + 2 cycloadditions. The major product is 3,4-dimethylenecyclooctene (DC) which is also formed from the minor product, *cis*-7,8-dimethylenebicyclo[4.2.0]octane (CO), at higher temperatures. The *trans* isomer, TO, also gives DC at about the same rate as CO.

Cross-conjugated pi-biradicals like trimethylenemethane (TMM) and 2,2′-bisallyl(BA) have challenged experimentalists and theorists.[1] Like carbenes these species can be either singlets or triplets and in addition there is the potential for different geometries and different chemistry in each state. The singlet TMM and BA species are apparently formed upon pyrolysis of methylenecyclopropane (MCP) and 1,2-dimethylenecyclobutane (DMCB), respectively, since each of these hydrocarbons undergoes a first-order scrambling of methylene (CH_2) groups with an Arrhenius preexponential term that is not abnormally low suggesting no intersystem crossing. Furthermore, intramolecular reactions do not seem to be characteristic of triplet states. Through kinetic studies and the use of optically active dimethyl labeled materials the extent of intervention of planar and non-planar species has been bracketed but there are still important questions remaining. Do these singlet biradicals represent intermediates which partition to the various products or are the thermal interconversions involving 1,1-, 1,3- and 3,3-shifts separate pathways? There is stereochemical evidence that the TMM species is an intermediate in the pyrolysis of dimethylcyanomethylenecyclopropanes[2] and kinetic evidence in the trapping of a TMM species confined to a 5-membered ring,[3] but no evidence in the simpler 2,3-dimethylmethylenecyclopropane system where evidence was gathered for planar and orthogonal TMM species. Similarly, little evidence for intermediates in the DMCB degenerate rearrangement has been published.

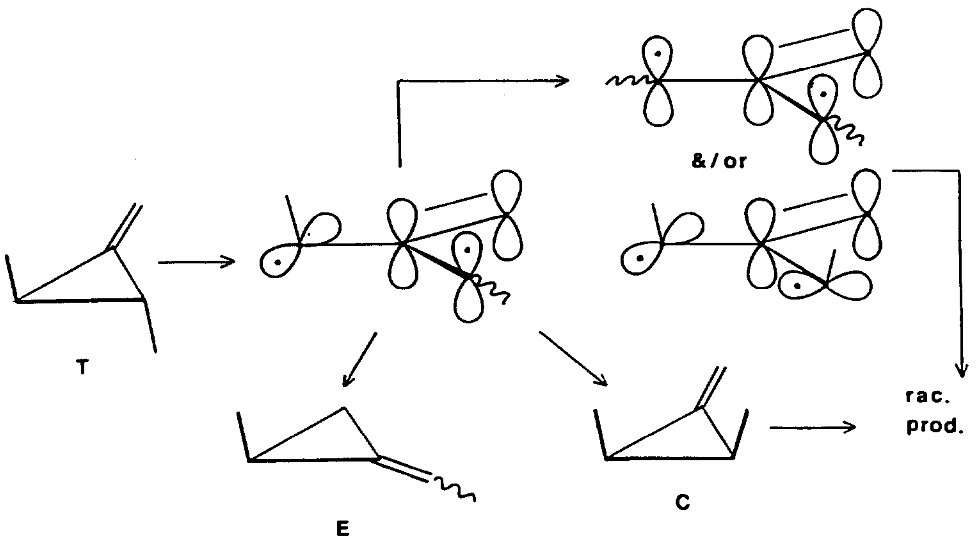
This paper reports attempts to apply the rate vs product determining deuterium isotope effect criteria for intermediates[4] in these rearrangements, and in so doing, analyzes the assumptions of the approach. Also reported are the kinetics of the rearrangement of *cis*- and *trans*-3,4-dimethyl DMCB and a study of the 1,2,8,9-decatetraene intramolecular allene 2 + 2 dimerization.

Methylenecyclopropane to trimethylenemethane

The degenerate rearrangement of MCP was first discovered in the pyrolysis of Feist's ester (*trans*-2,3-dicarbethoxymethylenecyclopropane)[5] whose products were determined by Ettlinger.[6a] Ullman provided evidence that a planar TMM biradical could not be an exclusive intermediate or transition state.[6b]

In 1963 Chesick studied the kinetics of the interconversion of 2-methyl-MCP and ethylidenecyclopropane and found that log $(k_f + k_b) = 14.26 - 40{,}400/2.3\,RT$.[7] While the kinetics do not provide information about the geometry of TMM, the activation energy is roughly ~ 13 kcal/m higher than the estimated BDE of the 2,3-bond assuming the biradical is stabilized only to the extent of a single allyl radical.

In an effort to quantify the stereochemistry of the rearrangement, pyrolysis of optically active *trans*-2,3-dimethylmethylenecyclopropane, T, to low conversions



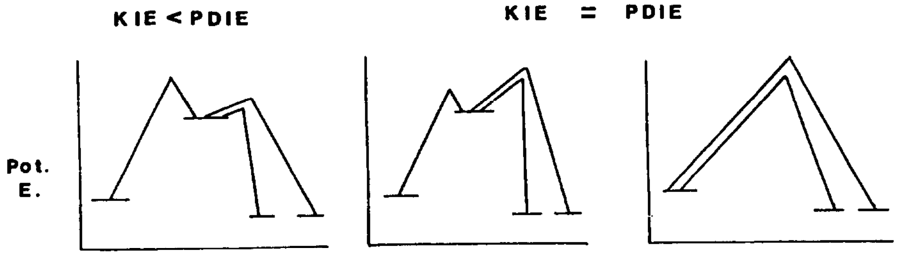
was found to give a 1:2 ratio of *cis*-2,3-dimethyl materials, C, and a mixture of *syn*- and *anti*-2 methylethylidenecyclopropane, E, of opposite rotation to that of starting material.[8] Moreover, T had racemized to twice the extent as was possible by being reformed from achiral C. The sign of rotation of the structurally rearranged ethylidene product was taken as indicating inversion at the remaining chiral ring carbon in the reaction. The geometric isomerization of the starting material indicated incursion of a biradical intermediate which results from at least one 90° rotation around a ring bond after C-2,C-3 bond fission. A parsimonious rationalization for both structural isomerization and rearrangement invokes an orthogonal (face to edge) TMM biradical which closes faster than it undergoes bond rotation. Indeed, whatever TMM species could be responsible for geometric isomerization would seem likely to also close to the structural rearrangement product. The excess racemization of *trans* starting material accounting for 5–10% of the total rearrangement was taken as indication of further rotation in the orthogonal TMM to an achiral planar TMM.

Simultaneously, Doering and H. D. Roth reinvestigated the Feist's ester pyrolysis and reported that there was extensive inversion of configuration of the remaining chiral center in the α,β-unsaturated product.[9] Very slow racemization of starting material was observed and little *cis* diester was formed. The mechanistic scheme offered for the dimethyl MCP system could easily accommodate the Doering results invoking reasonable strain and dipolar effects.

Doering later examined the thermal interconversions of 3-methyl-2-cyanoethylidenecyclopropane.[2] If the structural rearrangement were a $2\pi s + 2\sigma a$ concerted progress then the kinetic product resulting from cyano carbon migration with inversion starting with the *cis,syn* isomer can only be the *trans,anti* isomer by s + a pathway; yet all four isomers were interconverted at similar rates putting to rest the notion of concert in the 1,3-shift here.

In order to tell if the TMM species is an intermediate in this reaction, T and C and their exocyclic methylene deuterated derivatives, T-D_2 and C-D_2, were pyrolyzed in an effort to ascertain the rate and product determining isotope effects. The approach here is that popularized by Dolbier which may prove that the reaction has an intermediate and therefore must be stepwise.[4] Judicious placement of deuterium may result in the substituent altering the product distribution (with isotopic substitution, this is the product-determining isotope effect) without affecting the rate of the reaction (the kinetic isotope effect). If this can be demonstrated, then the reaction is not concerted and the first step is rate determining. However, the converse is not true. If the substituent affects both the product distribution and the rate in the same way, then either the reaction is concerted or it is two step, with the second step being rate determining. Nonetheless, in a two-step process there is the opportunity for the intermediate species to partition to two or more products which might be detected by a positive response to a Dolbier experiment. The figure below shows the possible reaction coordinate diagrams.

Thus the technique requires that the intermediate be formed after the rate determining step and that there is



no (or a known small) isotope effect on the rate determining step.

Previously the kinetics of T, C, and the deuterated derivatives were studied, but due to insufficient gc resolution the kinetics of C and C-D_2 could not be determined with high precision or accuracy.[8c] Further, the rearrangement of T could not be used to apply the Dolbier technique because the two products, C and E, are formed in the rate determining step if there is a TMM intermediate. This can be seen from the pyrolysis of C which gives T and E in a 3 : 2 ratio; thus, an intermediate formed from T reverts to T faster than it gives E. The isotope effect expected is a normal one resulting from retarded rotation of a CD_2 in the formation of E.[4] Indeed, it was found that $k^{H}_{T,E}/k^{D_2}_{T,E} = 1.31$ and $k^{H}_{T,C}/k^{D_2}_{T,C} = 1.0$. These results can be interpreted either in terms of two separate pathways with the usual isotope effect on formation of E and no isotope effect on the formation of C. Alternatively, an intermediate TMM species could be formed which gives E and C in the rate determining step where the IE on formation of E is the usual normal one and where there is no IE on the formation of C or on the formation of the intermediate. Therefore it was necessary to reexamine these reactions focusing on C where reversion of a potential TMM intermediate back to C appears to be slow judging by the fact that T gives C and E in a 1:2 ratio.

RESULTS

Synthesis. The syntheses were performed as described in a previous paper[8c] with the following exceptions. In the preparation of the 1,1-dibromo-2,3-dimethylcyclopropane from 2-butene, bromoform, and potassium t-butoxide, the reaction mixture was diluted with pentane before warming to room temperature. In the coupling reaction with methyl iodide one equivalent of butyllithium (1.55 mM hexane) was added at a rate of 17 mmol/hr. The mixture was stirred at −95° for at least 2.5 hr after this addition was complete. β-elimination was performed with a great excess of potassium t-butoxide in Me_2SO at 60° and the exocyclicmethylene product was immediately trapped in a dry ice-acetone condenser. This reaction was performed for ~6 hr for both the protio and deuterio compounds. The trapped products were purified by VPC and were >99.9% pure. NMR analysis revealed 14% protium incorporation in the *exo*-methylene of T-D_2 and C-D_2.

An alternate synthetic scheme was performed involving carbene formation from 1,1-dichloro-2,2,-trideuterioethane and subsequent addition to either *cis*- or *trans*-2-butene. Overall yield of olefin was sacrificed without any gain in isotopic purity.

Pyrolysis. The pyrolyses of pure T, T-D_2, C and C-D_2 were conducted at 160.0 ± 0.1° in the gas phase in a 2 l. bulb whose surface was treated with dichlorodimethylsilane then with pyrrolidine. This procedure has previously been demonstrated to give a non-catalytic surface.[10] Sample size was ~7 μl and ~100 torr of nitrogen was also added to the bulb. Pyrolyses were conducted for 1.5, 3.0 and 4.5 hr and each was repeated at least once in a random order. Analyses were conducted on a silver nitrate–triethylene glycol capillary gc at least six times per sample. All of the data is given in Table 1 along with the standard deviation in each pyrolysis. On the silver nitrate column the order of retention times is E, T and C, and baseline separation was achieved of all components except of the two ethylidene isomers which were not resolved at all.

In order to obtain rate constants M. Saunder's numerical integration program was used. Here assumed values of the rate constants were input and concentrations of the three components T, C and E were output at the experimental times. After a few trials the best set of rate constants that reproduced the experimental concentrations at each time were obtained, and these were averaged to obtain the rate constants of Scheme 1.

The values of the rate constants for reversion of E to T and C are very small and close to those predicted by

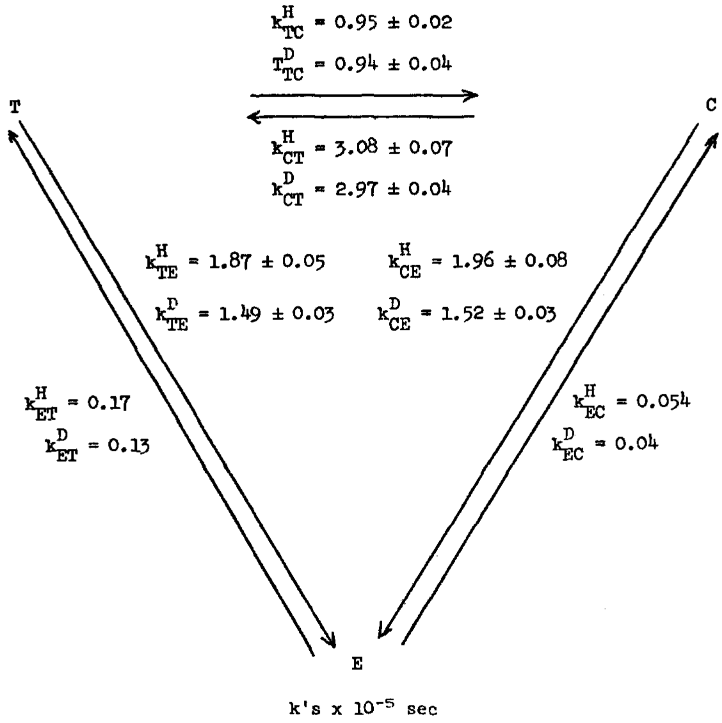
Table 1

Pyrolysis of T and T-D_2

	E	E-D_2	T	T-D_2	C	C-D_2
1.5 hr	.100 ± .003	.076 ± .001	.862 ± .003	.881 ± .002	.038 ± .003	.042 ± .002
	.098 ± .002	.081 ± .003	.858 ± .002	.876 ± .003	.044 ± .002	.044 ± .003
3.0 hr	.185 ± .002	.147 ± .002	.749 ± .002	.785 ± .003	.066 ± .003	.068 ± .001
	.181 ± .002	.149 ± .002	.752 ± .002	.787 ± .002	.068 ± .002	.064 ± .002
4.5 hr	.253 ± .001	.206 ± .002	.659 ± .001	.702 ± .002	.088 ± .002	.092 ± .003
	.248 ± .002	.208 ± .001	.667 ± .004	.698 ± .002	.085 ± .005	.094 ± .002
		.208 ± .001		.701 ± .003		.091 ± .004

Pyrolysis of C and C-D_2

	E	E-D_2	T	T-D_2	C	C-D_2
1.5 hr	.100 ± .003	.079 ± .001	.132 ± .003	.134 ± .004	.767 ± .004	.787 ± .003
	.100 ± .002	.078 ± .001	.136 ± .001	.136 ± .001	.764 ± .002	.786 ± .001
3.0 hr	.195 ± .002	.153 ± .001	.225 ± .002	.228 ± .002	.581 ± .003	.619 ± .003
	.195 ± .001	.145 ± .001	.225 ± .001	.220 ± .002	.580 ± .002	.635 ± .003
		.148 ± .001		.222 ± .001		.630 ± .002
4.5 hr	.252 ± .004	.215 ± .001	.268 ± .002	.284 ± .001	.482 ± .005	.502 ± .001
	.255 ± .002	.214 ± .003	.269 ± .003	.286 ± .002	.477 ± .004	.500 ± .002



Scheme 1.

the equilibrium constants. Furthermore, these could be varied with little effect on the calculated concentrations, nonetheless these were adjusted so that the microscopic reversibility condition was satisfied, namely that $k_{TE} \times k_{EC} \times k_{CT} = k_{TC} \times k_{CE} \times k_{ET}$.

DISCUSSION

Correction for incomplete deuteration. NMR analysis of $\underline{T}$-D_2 and $\underline{C}$-D_2 revealed the presence of 14% protium in the *exo*-methylene of each isomer. If the protium is distributed statistically then the mole fractions of zero, mono, and dideuterated materials are 0.07 : 0.14 : 0.79. The presence of protium will clearly lower the observed KIE's but concern might be expressed about the constancy of rate constants when three different isotopic species are reacting. To assuage these fears consider a first order reaction like the k_{CE} process which is assumed to be irreversible. If $k^H/k^{D_2} = 1.300$ then the observed isotope effect at zero time will be $(k^H/k^D)_{obs} = 0.79 \times 1.30 + 0.14 \times (1.30)^{1/2} + 0.07 \times 1 = 1.256$. At the half-life of loss of the all protio-material, the observed k^H/k^D would be 1.259, the change being due to fractionation of the deuterium species, so the effect of fractionation is minimal. The actual effect from $\underline{C} + \underline{T}$ is even less since these materials also interconvert with little apparent isotopic fractionation so that isotopic fractionation in the $\underline{C}$ to $\underline{E}$ and $\underline{T}$ to $\underline{E}$ process is "diluted".

Correction for incomplete deuteration was therefore made by the following simple equations:

$$(k^H/k^D)_{obs} = \frac{k^{H_2}}{0.79k^{D_2} + 0.14k^{HD} + 0.07k^{H_2}}$$

$$\therefore \frac{1}{(k^H/k^D)_{obs}} = 0.79\left(\frac{k^{D_2}}{k^{H_2}}\right) + 0.14\left(\frac{k^{D_2}}{k^{H_2}}\right)^{1/2} + 0.07$$

Then solving for k^{D_2}/k^{H_2} and multiplying by $k^{H_2}_{obs}$ gives k^{D_2}. The four major rate constants from isotopically pure $\underline{T}$-D_2 and $\underline{t}$-D_2 then are:

$$k^{D_2}_{\underline{T}\underline{E}} = 1.43 \pm 0.03 \times 10^{-5}/\text{sec.}$$

$$k^{D_2}_{\underline{T}\underline{C}} = 0.94 \pm 0.04 \times 10^{-5}/\text{sec.}$$

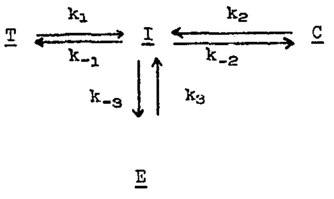
$$k^{D_2}_{\underline{C}\underline{T}} = 2.95 \pm 0.04 \times 10^{-5}/\text{sec.}$$

$$k^{D_2}_{\underline{C}\underline{E}} = 1.45 \pm 0.03 \times 10^{-5}/\text{sec.}$$

Mechanistic analysis. The isotope effects revealed by the rate constants k_{CT} and k_{CE} indicate that the anticipated behavior for reaction of $\underline{C}$ via a common TMM intermediate is not observed. There is the expected normal IE on k_{CE}, but k_{CT} does not have the expected inverse IE. If a common intermediate were formed from $\underline{C}$ in the rate determining step with no IE and if the intermediate partitions to $\underline{E}$ and to $\underline{T}$, then the reduction in the rate constant k_{CE} should be matched by a corresponding increase in k_{CT}. Thus, either the $\underline{C}$ to $\underline{T}$ and $\underline{C}$ to $\underline{E}$ reactions are different paths or the assumption of no IE in the formation of the intermediate is incorrect.

To pursue the latter possibility the mechanistic Scheme 2 might be assumed to apply.

From the steady state treatment of this scheme and identification of the components of the differential rate expressions with those of the phenomenological expres-



Scheme 2.

sions the equations below can be obtained

$$\frac{k^{H}_{TC}+k^{H}_{TE}}{k^{D_2}_{TC}+k^{D_2}_{TE}} = 1.19 \pm 0.05$$

$$= \frac{k^{H}_{1}}{k^{D_2}_{1}}\left(1\Big/\left(1+1\Big/\left(\frac{k^{H}_{-2}}{k^{H}_{-1}}+\frac{k^{H}_{-3}}{k^{H}_{-1}}\right)\right)\right)$$

$$\left(1+\left(1\Big/\left(\frac{k^{D_2}_{-2}}{k^{D_2}_{-1}}+\frac{k^{D_2}_{-3}}{k^{D_2}_{-1}}\right)\right)\right)$$

$$\frac{k^{H}_{CT}+k^{H}_{CE}}{k^{D_2}_{CT}+k^{D_2}_{CE}} = 1.15 \pm 0.05$$

$$= \frac{k^{H}_{2}}{k^{D_2}_{2}}\left(1\Big/\left(1+1\Big/\left(\frac{k^{H}_{-1}}{k^{H}_{-2}}+\frac{k^{H}_{-3}}{k^{H}_{-2}}\right)\right)\right)$$

$$\left(1+\left(1\Big/\left(\frac{k^{D_2}_{-1}}{k^{D_2}_{-2}}+\frac{k^{D_2}_{-3}}{k^{D_2}_{-2}}\right)\right)\right)$$

and

$$\frac{k_{TE}}{k_{TC}} = \frac{k_{-3}}{k_{-2}};\ \frac{k_{CE}}{k_{CT}} = \frac{k_{-3}}{k_{-1}};\ \frac{k_{TE}k_{CT}}{k_{TC}k_{CE}} = \frac{k_{-1}}{k_{-2}}.$$

From the data it follows that

$$\frac{k^{H}_{1}}{k^{D_2}_{1}} = 1.09 \pm 0.06;\ \frac{k^{H}_{2}}{k^{D_2}_{2}} = 1.13 \pm 0.06;\ \frac{k^{H}_{-3}k^{D_2}_{-1}}{k^{D_2}_{-3}k^{H}_{-1}} = 1.29 \pm 0.06;$$

and

$$\frac{k^{H}_{-3}k^{D_2}_{-2}}{k^{D_2}_{-3}k^{H}_{-2}} = 1.29 \pm 0.06$$

where the error limits arrive from a random error analysis using the standard deviation in the rate constants. Thus, the anticipated normal IE on k_{-3} is 1.29 assuming no IE on k_{-1} or k_{-2}, but there must be a substantial, normal IE on k_1 and k_2 if mechanistic Scheme 2 applies.

If on the other hand the geometric and structural isomerization of T and C are separate pathways then the kinetic isotope effects on each path are directly the ratio of phenomenological rate constants:

$$k^{H}_{TC}/k^{D_2}_{TC} = 1.01 \pm 0.03 \quad k^{H}_{TE}/k^{D_2}_{TE} = 1.31 \pm 0.05$$

$$k^{H}_{CT}/k^{D_2}_{CT} = 1.04 \pm 0.03 \quad k^{H}_{CE}/k^{D_2}_{CE} = 1.35 \pm 0.05.$$

The lack of a KIE on geometric isomerization is not unexpected for no change in the number of ligands at the *exo*-methylene throughout. On the other hand the large normal KIE in the formation of the 1,3-shift products might be surprising since there is an increase in the number of bonds to the deuterium bearing carbon which should give rise to an inverse KIE. However, the *exo*-methylene must undergo a 90° rotation in the course of the reaction which requires that a torsion in the starting material be converted to a reaction coordinate motion. The loss in zero point energy difference between H and D in the starting material at the transition state is a reasonable rationalization for this effect and its magnitude is not unreasonable.[8c]

Whether or not Scheme 2 is an appropriate description of the mechanistic path is therefore determined by whether or not the isotope effects on k_1 and on k_2 are reasonable. In all other systems where allyl radicals are generated in the rate determining step by homolytic bond fission in a hydrocarbon with protio or deuterio *exo*-methylene group, no kinetic isotope effect has been observed. These include the allene dimerization[4] and the rearrangement of 1,3-dimethylenecyclopentane.[11] However, small normal KIE's ($k^H/k^D \leq 1.03$) are observed at the newly formed radical site in radical additions to olefins suggesting weaker force constants at a radical site than at a normal double bonded trigonal carbon.[12]

It is not appropriate to decide on the question of mechanism of the MCP rearrangement on the basis of the current data but merely to point out the ambiguity that can arise in the application of the rate and product determining isotope effect criterion for intermediates if the system exhibits both a KIE and a PDIE. The only situation that is unambiguous in favor of an intermediate is when there is no KIE, but one of the products shows a normal IE and the other an inverse IE.

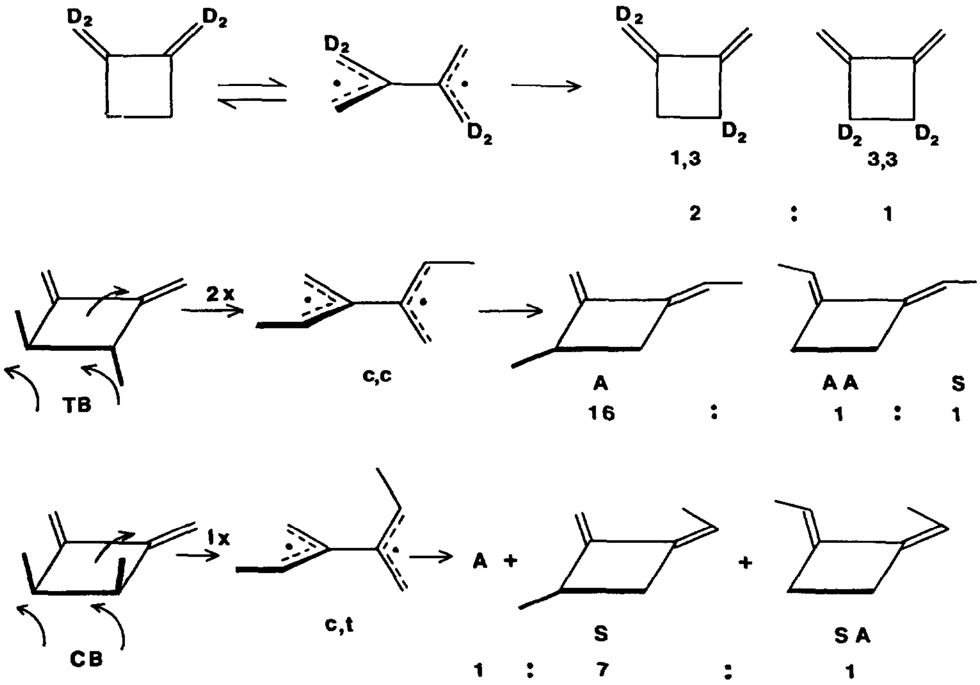
1,2 - Dimethylenecyclobutane to 2,2′ - bisallyl. 1,2 - Dimethylenecyclobutane, DCMB, is the major kinetic product in the thermal dimerization of allene.[4] The presumed intermediate in the reaction, namely the 2,2′-bisallyl diradical, BA, (or tetramethyleneethane) can apparently be generated from DMCB since 1,2-bis(dideuteriomethylene)cyclobutane gives a 2 : 1 ratio of 1,3- and 3,3-shift deuterium isomers[13] upon heating with log k = 14.45 − 46,800/2.3 RT.[14] The near statistical distribution of the products suggests that either a fixed orthogonal and/or a rapidly central bond rotating BA species, presumably as a singlet, is involved. Further, the very high E_a compared with the estimated BDE of C-3, C-4 bond does not suggest concert in this rearrangement.

Despite the suggestion that the rearrangement is nonconcerted, pyrolysis of the *trans*- and *cis*-3,4-dimethyl DMCB's, TB and CB respectively, give very different distributions of the stereoisomers of the 1,3- and 3,3-shift products suggesting conrotatory opening to the dimethyl BA followed by closure without much randomization of the stereochemistry of the trigonal carbons in the intermediate.[15] The further fact that the rate of rearrangement of CB is only half the rate of rearrangement of TB suggests that the conrotatory opening is accompanied by a "bevel" rotation about the C-1,C-2 bond to minimize the steric rate retardation usually associated with conrotatory opening of *cis*-3,4-dimethylcyclobutenes. Finally, optically active TB was pyrolyzed with the results that the major 1,3-shift product was optically inactive and that starting material racemized 2.2 times faster than it undergoes the 1,3-shift.[16] This is consistent with conrotatory-bevel opening to a chiral dimethylbisallyl diradical which undergoes central bond rotation faster than reclosure, and reclosure TB is at least 2.2 times faster than closure to the 1,3-shift product.

The questions to be pursued below are the activation parameters for the isomerizations of TB and CB; the rate effect of deuterium substitution in the *exo*-cyclomethylenes of TB, the kinetics of intramolecular cyclization of 1,2,8,9-decatetraene, and the thermal interconversion of the products of this cyclization.

RESULTS

Kinetics of rearrangement of TB and CB. TB and CB were prepared as described previously[15] and were pyrolyzed in a commercial flow reactor having a thermostated gold reaction tube. The pyrolysate was passed directly into a 200′ capillary gc column for analysis. Rate



constants were determined at 315°, 330°, 345°, 360° and 375° with three different flow rates varying over a factor of 1.5–1.8. The residence times (tr) were calculated from the volume of the reactor and flow rates corrected for temperature. In Tables 2 and 3 is all the data where only the amount of starting material remaining is given. The product distribution from both TB and CB was similar to that reported previously.

Kinetic isotope effect in the pyrolysis of TB. trans - 3,4 - Dimethyl - 1,2 - bis(dideuteriomethylene) cyclobutane, TB-D_4, was prepared from *trans*-3,4-diemthylcyclobutane-1,2-dicarboxylic acid anhydride by $LiAlD_4$ reduction and followed by the usual sequence of derivatization and base-induced elimination.[15] NMR integration revealed the presence of 1% protium on the *exo*-methylene carbons. Two pyrolyses of TB and two pyrolyses of TB-D_4 at 230.0° were conducted alternately for each of three experimental times, 100.0, 200.0 and 300.0 min. The data and isotope effects are presented in Table 4. The pyrolyses were conducted in the static 2 L reactor which was pre-treated with dichlorodimethylsilane.

Intramolecular allene cycloaddition of* 1,2,8,9-*decatetraene and pyrolysis of* cis *and* trans - 7,8 - *dimethylenebicyclo*[4.2.0]*octane. In order to determine the transition state enthalpy for the allene dimerization, the kinetics of the intramolecular cycloaddition of 1,2,8,9-decatetraene, D,[17] were determined. Further impetus for this study derived from the possible products which would be of interest in connection with the question of the stereochemistry of ring openings of DMCB's.

Pyrolysis of D in a laminar flow system at 360°–430° resulted in first order conversion to two major products in a 1 : 3 ratio at conversions up to 80% with $\log k(\text{sec}^{-1}) = 9.4 - 30{,}800/2.3\ RT$ (Table 5). The minor of these two products was 7,8-dimethylene-*cis*-bicyclo[4.2.0]octane, CO, and the major isomer was 3,4-

Table 2. Flow kinetics of rearrangement of TB

Temp. (C°)	Trial	Flow Rate (ml/min)	t_R (sec)	C/Co	k (sec^{-1})
315°	1	6.061	19.52	0.7785	0.0128
	2	5.085	23.26	0.7620	0.0117
	3	4.225	27.99	0.7231	0.0116
330°	1	18.35	6.286	0.8271	0.0302
	2	14.81	7.786	0.7822	0.0316
	3	11.39	10.13	0.7448	0.0291
	4	9.662	11.94	0.7167	0.0279
345°	1	27.03	4.164	0.7693	0.0658
	2	20.28	5.548	0.7129	0.0712
	3	15.63	7.203	0.6195	0.0665
360°	1	33.00	3.330	0.6238	0.1418
	2	28.41	3.868	0.5725	0.1442
	3	23.81	4.615	0.5169	0.1430
375°	1	54.05	1.986	0.4923	0.3568
	2	44.44	2.415	0.4463	0.3340
	3	33.33	3.220	0.3535	0.3230

log k = 13.6-41,900/2.3 RT corr coef = 0.9997

Table 3. Flow kinetics of rearrangement of CB

Temp. (C°)	Trial	Flow Rate (ml/min)	t_R (sec)	C/Co	k (sec^{-1})
315°	1	6.061	19.52	0.8236	0.0100
	2	5.085	23.26	0.7806	0.0106
	3	4.225	27.99	0.7475	0.0104
330°	1	18.35	6.286	0.8449	0.0268
	2	14.81	7.786	0.8066	0.0276
	3	11.39	10.13	0.7832	0.0241
	4	9.662	11.94	0.7879	0.0243
345°	1	27.03	4.164	0.7693	0.0630
	2	20.28	5.548	0.7129	0.0610
	3	15.63	7.203	0.6634	0.0570
360°	1	33.00	3.330	0.6421	0.1331
	2	28.41	3.868	0.6163	0.1251
	3	23.81	4.615	0.5813	0.1175
375°	1	54.05	1.986	0.5276	0.3220
	2	44.44	2.415	0.4966	0.2898
	3	33.33	3.220	0.4056	0.2802

log k = 13.7-42,200/2.3 RT corr coef = 0.9997

Table 4. Pyrolyses of TB and TB–D_4 at 230.0°C

Time(sec)	Cpd	C/Co[a]	$k^H(sec^{-1}) \times 10^5$	$k^{D_4}(sec^{-1}) \times 10^5$		k^H/k^{D_4} [b]
6000.0	TB-D_4	0.879 ± 0.002		2.153 ± 0.02		
	TB	0.870 ± 0.001	2.33 ± 0.02			
	TB-D_4	0.883 ± 0.001		2.074 ± 0.02		
	TB	0.873 ± 0.001	2.27 ± 0.02			
			2.30	2.11	=	1.09 ± 0.02
12000.0	TB	0.754 ± 0.002	2.34 ± 0.02			
	TB-D_4	0.774 ± 0.002		2.13 ± 0.02		
	TB	0.758 ± 0.003	2.31 ± 0.03			
	TB-D_4	0.775 ± 0.002		2.13 ± 0.02		
			2.32	2.13	=	1.09 ± 0.02
18000.0	TB-D_4	0.678 ± 0.002		2.16 ± 0.02		
	TB	0.663 ± 0.001	2.28 ± 0.01			
	TB-D_4	0.673 ± 0.002		2.20 ± 0.02		
	TB	0.654 ± 0.002	2.36 ± 0.02			
			2.32	2.18	=	1.06 ± 0.02
						1.08 ± 0.01

a. Fraction of starting material remaining

b. Uncorrected for 1% protium on the exocyclic methylene carbons.

Table 5. Flow system kinetics of pyrolysis of D

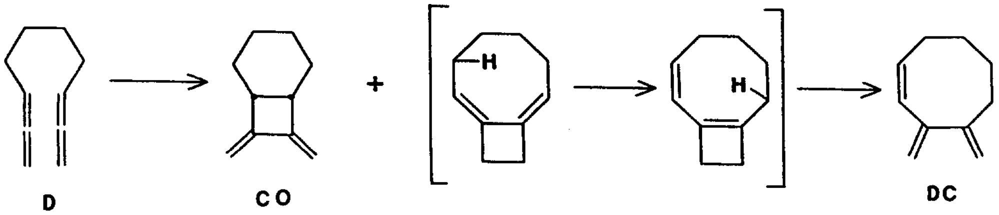
Temp(°C)	t_r(sec)	D/Do	k(sec^{-1})
360°	7.03	0.658	0.0595
379°	5.12	0.513	0.130
400°	2.27	0.540	0.271
420°	2.36	0.310	0.497

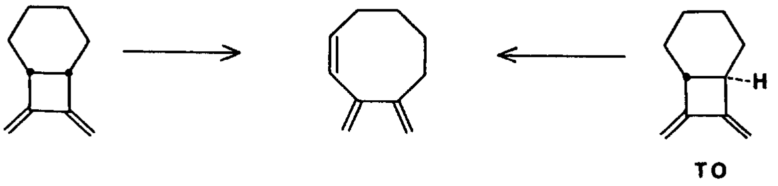
log k = 9.4-30,800/2.3 RT corr. coef = 0.999

dimethylenecyclooctene, DC. CO and its *trans* isomer TO were synthesized from the known photocycloadducts[18] of cyclohexene and maleic anhydride with the assigned stereochemistry being consistent with the large upfield shift of the bridgehead hydrogens in TO relative to CO. Pyrolysis of CO and TO at 475–525° led, with almost equal rates, to triene DC whose structure was assigned from its NMR spectrum when it was isolated from a preparative, static pyrolysis of CO. The CO to DC rearrangement is nearly as fast as the TO to DC conversion and both have activation free energies near 50 kcal/m which is about 8 kcal/m higher than that for ring opening of 3,4-dimethyl-DMCB's.

DISCUSSION

Arrhenius parameters for rearrangement of TB and CB. The kinetics of reaction of TB and of CB are well-behaved and indicate irreversible first order reactions in the laminar flow reactor. The derived Arrhenius parameters (log k_{TB} = 13.5 – 41,500/2.3 RT and log k_{CB} = 13.6 – 41,800/2.3 RT) are not unreasonable in comparison with those for reaction of DMCB itself (log k = 14.45 –





46,800/2.3 RT). As usual, methyl groups lower the E_a in a bond-breaking rate determining or pre-equilibrium step by 2–2.5 kcal/m/methyl.[19] The data indicates that previous assumptions about the steric and electronic effects of methyls in the DMBC rearrangement (Introduction) were not unreasonable.

Kinetic isotope effects in the rearrangement of <u>*TB*</u>. The normal kinetic isotope effect ($k^H/k^{D_4} = 1.08 \pm 0.02$) in the rearrangement of <u>TB</u> and <u>TB-D$_4$</u> is not that expected for a reaction which converts a trigonal carbon bearing deuterium simply to a tetrahedral carbon. However, there must be at least a 90° rotation about one of the *exo*-methylene carbons in the formation of the major product, the 1,3-shift isomer, (Introduction). In other thermal reactions this produces a normal IE since a torsional mode in the starting material (or intermediate) is converted into a reaction coordinate motion with concomitant loss of the zero point energy difference between H and D in the original torsional mode.[4,8] The data cannot answer the question of whether or not there is an intermediate in this reaction since if there were an intermediate, the rate and product determining step are the same. This follows from the previous observation that optically active <u>TB</u> racemizes 2.2 times faster than it undergoes the 1,3-shift to the major product. Thus, if an intermediate bisallyl biradical is generated as in the scheme below k_{-1} is at least 2.2 times faster than k_{-2}. As a result the expected rotational isotope effect on k_{-2} will also affect the overall loss of <u>TB</u>. Here again another limitation on the Dolbier approach[4] to determining if there is an intermediate becomes apparent.

$$\begin{tikzcd}
\underline{\mathrm{TB}} \arrow[r, shift left, "k_1"] & \underline{\mathrm{I}} \arrow[l, shift left, "k_{-1}"] \arrow[r, "k_{-2}"] \arrow[dr, "k_{-3}"] & \text{1,3-shift product} \\
 & & \text{3,3-shift product}
\end{tikzcd}$$

The observed isotope effect then is consistent with either a concerted reaction involving rotation as a reaction coordinate motion whose magnitude cannot easily be estimated or with the two-step process depicted in the scheme above. Remarkably, however, with Dolbier's isotope effect data that demonstrates an intermediate in the allene dimerization which presumably involves a bisallyl biradical,[4] the two-step scheme above correctly predicts the experimentally determined KIE if there is no isotope effect on the ring opening reaction. Thus, application of the steady state approximation to the intermediate and ignoring k_{-3} since it is so small, the observed isotope effect is:

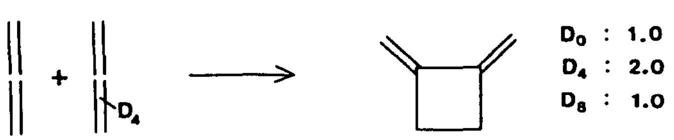
$$k^H/k^{D_4} = \frac{k_1^H}{k_1^{D_4}}\left(\frac{1 + k_{-1}^{D_4}/k_{-2}^{D_4}}{1 + k_{-1}^H/k_{-2}^H}\right)$$

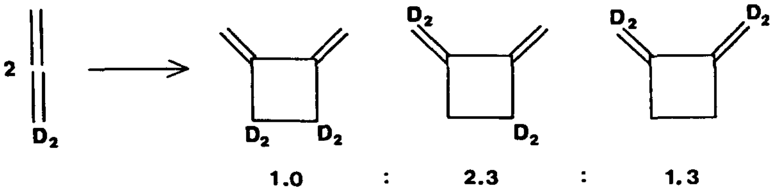
where $k_{-1}^H/k_{-2}^H = 2.2$ and $k_{-1}^{D_4}/k_{-2}^{D_4} = 2.2 \times 1.12$ (1.12 is the temperature corrected isotope effect per methylene group in the closure of the bisallyl diradical from 1,1-dideuterioallene). To review, Dolbier found that at 140°, 1,1-dideuterioallene gave DMCB-D$_4$ with a ring to vinyl proton ratio of 1.14. Degradation and mass spectral analysis of this material by Shih using his well-developed procedure[15] gave the ratios shown in the scheme below which confirms the NMR result. All of the data reveals a 1.15 fold kinetic preference for a CH_2 over a CD_2 group to form a ring sigma bond.

Thus, from the equation above, $k^H/k^{D_4} = 1.08 \pm 0.02 = k_1^H/k_1^{D_4} \times 1.08$. If there is no IE on k_1 then the calculated and observed KIE's are very similar. Whether or not there is an IE on k_1 cannot be determined, and there is precedence for either in related systems. In the allene dimerization a 1 : 1 mixture of D_0- and D_4-allene gives a nearly statistical ratio of D_0-, D_4- and D_8-DMCB's indicating no isotope effect in the rate determining step which indicates that formation of the <u>BA</u> species from allene shows no IE where the hybridization change is similar.[4] However, there may be an IE at the *exo*-methylene in the ring opening of <u>MCP</u> reported earlier in this paper if a common TMM biradical is involved.

Intramolecular cycloaddition of 1,2,8,9-*decatetraene-energetics*. Despite the interest in allene 2+2 cycloadditions the activation energy has not been determined partly due to experimental difficulties. Intramolecular examples have been studied by Roth and others but the small number of methylene carbons (two) between the allenes may prevent attainment of the most stable transition state geometry in these cases. 1,2,8,9-Decatetraene (<u>D</u>) was previously prepared by Skattebøl, but its reaction was not well characterized.[17] In the vapor phase it undergoes moderately clean cyclization in a first order process with log k = 9.4 − 30,800/2.3 RT.

The very low pre-exponentional term is characteristic





of a highly ordered transition state which may not indicate concert but the "freezing" of rotation about four methylene groups in order for the digonal carbons to bond. Indeed, the dimerization of allene itself does not appear to be concerted[4] although it is partly stereospecific.[20]

The activation energy of 31 kcal/m is very similar to that for the allene + ethylene 2 + 2 cycloaddition (33 kcal/m) as calculated from the activation energy for cleavage of methylenecyclobutane and the heats of formation of reactants and products.[18] However, by a similar calculation, the E_a for the 2 + 2 cycloaddition of ethylene is 44 kcal/m.[19] All these cycloadditions are exothermic but to different extents. $\Delta H^{298°}(2 \times C_3H_4) = -39$ kcal/m, $\Delta H^{298°}(C_3H_4 + C_2H_4) = -29$ kcal/m and $\Delta H^{298°}(2 \times C_2H_4) = -19$ kcal/m. The different exothermicities no doubt reflect the instability of pi bonds to digonal centers since the strain energy of the products is similar in every case, but it is interesting that the E_a for the allene dimerization does not reflect this as much as the E_a for the allene + ethylene cycloaddition in comparison to that for the ethylene dimerization. This comparison is noted but speculation on its origin is deferred until all of the energy surfaces can be better characterized.

Product formation. The product distribution from D consists of *cis*-2,8-dimethylenebicyclo[4.2.0]octane (CO) and 3,4-dimethylenecyclooctene, (DC). Moreover, DC is formed from both CO and its *trans* isomer (TO) at 100° higher temperatures than those required for the cyclization of D. Triene CD most likely results from the 3.3-shift isomer of DO and TO, namely bicyclo[6.2.0]deca-1,7-diene, (BD) which undergoes a 1,5-hydrogen shift to a cyclobutene derivative which ring opens (Results). Why D gives only DO and not TO in the intramolecular cyclization is unclear although the sterically most favorable conformation of a concerted 2s + 2a transition state or its alternate, a two step process with disrotatory motions to a biradical followed by controtatory closure, will give CO.

Pyrolysis of both DO and TO affords DC, and the rates of the two reactions are similar with free energies of activation near 50 kcal/m or about 8 kcal/m higher than that for pyrolysis of the two 3,4-dimethyl-1,2-dimethylenecyclobutanes (Table 2). This may reflect more strain energy in the biradical where two partial double bonds are constrained to an eight-membered ring or the possibility that the 3,3-shift isomer BD is less stable than TO or BO. Further work of a quantitative nature is necessary in order to narrow the mechanistic possibilities.

EXPERIMENTAL

Kinetics. All pyrolyses were performed either in a thermostated 2 l. vessel attached to a vacuum line or in a Chemical Data Systems Pyrochrome flow reactor. All analyses were performed on a Varian 1220-2 flame ionization gc with a 200' di-n-butyltetrachlorophthalate capillary column except with T and C where a silver nitrate–triethylene glycol column was used. The signal output was attached to a Vidar Auto Lab Digital Integrator.

The 2 l. vessel, which was pretreated with dichlorodimethylsilane and with pyrrolidine, was immersed in a sodium nitrate–potassium nitrate eutectic mixture whih was thermostated with a Bayley Model 124 temperature controller.

cis- and trans-7,8-Dimethylenebicyclo[4.2.0]octane. A soln of 41.0 g maleic anhydride and 200 ml cyclohexene in 1200 ml Fischer spectroquality EtOAc with 3.0 g redistilled acetophenone as a photosensitizer, was photolyzed at −78° under N_2 with a 450 W medium pressure mercury vapor lamp through a water cooled, vacuum jacketed pyrex well.[18] After 60 hr the solvent and unreacted cyclohexene were removed on a rotary flash evaporator at water aspirator vacuum. The residues were distilled yielding first variable amounts of the unreacted anhydride followed by a mixture of the *cis* and *trans* fused bicyclo[4.2.0]pctane-7,8-dicarboxylate anhydride which at 5 torr and 100° on a spinning band column proved inseparable. IR 3.0(w), 3.5(m), 5.4 (s), 5.7 (m), 10.9 (s). NMR δ 1.3–δ 2.2 ppm (m) 4H, δ 3.3–δ 3.8 ppm 1H, δ 4.2–δ 4.6 ppm 1H.

One ml of conc HCl was refluxed for 6 hr with 1.8 g of the anhydride described above in 50 ml MeOH. Upon neutralization and dilution with water the ester was extracted with ether, dried with Na_2SO_4 and the solvent distilled to yield 2.0 g (89%) of the mixture of esters which was separated into its stereochemical ring fused isomers by preparative gas liquid partition chromatography on a 20 ft by 3/8 in 30% DEGS on 60/80 mesh Chromosorb W column at 200° using a 200 ml/min flow rate of helium as Baltrop and Robson[18] had noted. Assignment of the stereochemistries of the two compounds collected was based on the NMR measurements following the symmetry based arguments of Baltrop and Robson.[18]

Each ester as prepared and separated above, was reduced to the bisdiol with lithium aluminum hydride, then converted to the ditosylate.[8] Each ditosylate was then added to four equivalents of t-BuOK (1 N in dimethyl sulfoxide) while the system was kept at ambient temp. The mixture was quickly quenched by the addition of water. Subsequent pentane extraction provided large amounts of hydrocarbon (*ca* 80% of the theoretical amount) which yielded the desired material on preparative gas chromatography on a 15 ft × 1/4 in. TCEP column at 110°. NMR CO (Varian 220 MHz) in CCl_4: δ 5.00 (s), 2H, δ 4.62 (s) 2H, δ 2.85 (bs) 2H, δ 1.2–δ 1.85 (m) 8H. MS (AEI MS-9) parent calc. 134.1094 fd. 134.1095 also 119, 106, 105, 91, 44, 41, 28. NMR TO (220 MHz) in CCl_4: δ 4.81 (s) 2H, δ 4.53 (s) 2H, 2.08 (bs) 2H, δ 1.84–δ 1.96 (m) 4H, δ 1.39 (m) 4H. MS (AEI MS-9) parent calc. 134.1094 fd. 134.1096.

Acknowledgement—We thank the National Science Foundation for continuing support of this work.

REFERENCES

[1] For overview of these species and other intermediates see J. J. Gajewski, *Hydrocarbon Thermal Isomerizations*. Academic Press, New York (1981).

[2] W. von E. Doering and L. Birladeanu, *Tetrahedron* **29**, 499 (1973).

[3] M. Mazur and J. A. Berson, *J. Am. Chem. Soc.* **103**, 684 (1981).

[4] W. R. Dolbier, Jr. and S.-H. Dai, *Ibid.* **94**, 3946 (1972).

[5] F. Feist, *Ber. Dtsch. Chem. Ges.* **26**, 747 (1893).

[6] E. F. Ullman, *J. Am. Chem. Soc.* **82**, 505 (1960).

[7] J. P. Chesick, *Ibid.* **85**, 2720 (1963).

[8a] J. J. Gajewski, *Ibid.* **90**, 7178 (1968); [b] *Ibid.* **93**, 4450 (1971); [c] J. J. Gajewski and S. K. Chou, *Ibid.* **99**, 5696 (1977).

[9] W. von E. Doering and H. D. Roth, *Tetrahedron* **26**, 2825 (1970).

[10] J. J. Gajewski, R. J. Weber, R. Braun, M. L. Manion and B. Hymen, *J. Am. Chem. Soc.* **99**, 816 (1977).

[11] J. J. Gajewski and J. Salazar, *Ibid.* **101**, 2739, 2740 (1979).

[12] R. W. Henderson and W. A. Pryor, *Int. J. Chem. Kinet.* **4**, 325 (1972) and refs therein.

[13] J. J. Gajewski and C. N. Shih, *J. Am. Chem. Soc.* **89**, 4532 (1967).

[14] W. von E. Doering and W. R. Dolbier, Jr., *Ibid.* **89**, 4534 (1967).

[15] J. J. Gajewski and C. N. Shih, *Ibid.* **94**, 1675 (1972).

[16] J. J. Gajewski, *Ibid.* **97**, 3457 (1975).

[17] L. Skattebøl and S. Solomon, *Ibid.* **87**, 4506 (1965).

[18] J. A. Baltrop and R. Robson, *Tetrahedron Letters* 597 (1963).

[19] S. W. Benson and H. E. O'Neal, *Kinetic Data on Gas Phase Unimolecular Reactions*. NSRDS-NBS 21 (Feb. 1970).

[20] W. R. Moore, R. D. Bach and T. M. Ozretich, *J. Am. Chem. Soc.* **91**, 5918 (1969).