the deuterated compound IIIb was studied and the results obtained are shown in Table I. Compound VII showed by nmr integration the deuterium equally distributed in the exo and endo positions of the cyclopropane ring, thus confirming the hydrogen shift mechanism. On the other hand, I showed all of the deuterium located at the cyclopropyl-allylic position establishing carbomethoxy migration as the sole route to form I.[9] Even more surprising was the dramatic change in product ratio in the deuterated *vs.* the undeuterated III. While VII was the major product from IIa, I was the major product from IIb. Assuming a negligible secondary deuterium isotope effect, the change in product ratio indicates a minimum primary isotope effect of 3.7.[11]

Table I. Photolyses of IIIa, IIIb, and VIIb[a]

Starting	% (d_1)		
material (% d_1)	I	VII	II
IIIa	35	51	14
IIIb (78)	64 (81)	31 (74)	6
IIIc (94)	67 (96)	27 (87)	5 (72)
VIIb (87)			90 (87)[b]

[a] The deuterium content was determined by nmr. [b] The 90% yield was that for VIIa as determined by vpc.

The effects of isotopic substitution noted here are particularly large and suggest that isotope effects may serve as a useful mechanistic probe for reactions other than those involving hydrogen abstraction. Furthermore, the discovery of competing hydrogen and carbomethoxy migrations in this system suggests that 7-substituted 3,4-benzotropilidenes may serve as a useful model for establishing photochemical migratory aptitudes for various functional groups. This point is under further study.

Acknowledgment. We gratefully acknowledge support from the Merck Company, Rahway, N. J.

Denise M. Madigan,[12] John S. Swenton*
Department of Chemistry, The Ohio State University
Columbus, Ohio 43210
Received August 21, 1970

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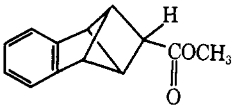
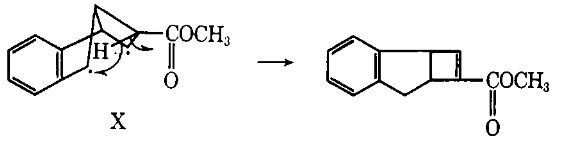
(6) Two pathways which can be envisioned for conversion of III to II involve hydrogen transfer in diradical X as depicted below. The diradical, X, could either be generated by 1,5 bonding in excited III or by thermolysis of IX formed in a photochemical step from III.



IX



X

II

(7) For leading references see H. E. Zimmerman and C. O. Bender, *J. Amer. Chem. Soc.*, 92, 4366 (1970). The complete absence of the di-π-methanevinylcyclopropane route in the parent benzotropilidine suggests the hydrogen shifts in these systems must be of high efficiency.

(8) P. J. Kropp, *Tetrahedron Lett.*, 3647 (1964).

(9) One could consider the photochemistry of III as a competition between (a) hydrogen shift to give VII, (b) an oxa di-π-methane[10] rearrangement to give I, and (c) the unobserved carbo di-π-methane reaction. It is apparent then that the importance of the processes is in the order a > b ≫ c.

(10) (a) Reactions emanating from carbonyl–vinyl bridging[10b,c] have been recognized as general processes and termed the oxa di-π-methane rearrangement;[10d] (b) J. S. Swenton, *J. Chem. Educ.*, **46**, 217 (1969); (c) R. S. Givens and F. W. Oettle, *Chem. Commun.*, 1164 (1969); (d) W. G. Dauben, M. S. Kellogg, J. J. Seeman, and W. G. Spitzer, *J. Amer. Chem. Soc.*, **92**, 1787 (1970).

(11) For a brief discussion of the possible origin of isotope effects in photochemical systems, see D. R. Coulson and N. C. Yang, *ibid.*, **88**, 4511 (1966).

(12) NDEA Fellow, 1968–1969.

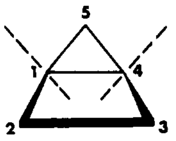
* To whom inquiries should be addressed.

The Stereochemistry of Thermal Isomerizations of 2,3-Dimethylbicyclo[2.1.0]pentanes to 2,5-Heptadienes[1]

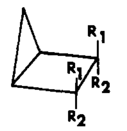
Sir:

To achieve conrotation in a concerted [$2_s + 2_a$] cycloreversion[2] to a butadiene, the two methylene carbon atoms of a cyclobutene each must turn through roughly 90°, so that the axes of the basis set atomic orbitals making up the breaking σ bond (C(3)–C(4)) rotate from an originally orthogonal to a finally parallel relationship to those making up the π bond (C(1)–C(2)). In simple cases, there are no major steric constraints, and the reaction is facile and highly stereospecific. This contrasts with the concerted [$2_s + 2_a$] cycloreversion of a cyclobutane to two ethylenes, where although two of the carbons destined to be π-bonded partners require little or no relative rotation, the other two require roughly 180°. The latter condition imposes severe distortion on the transition state, and convincing examples of this reaction are rare.[3,4]

Naively, one might expect that in a case where the geometric relationship of the axes of the reacting orbitals is intermediate between the extremes represented by cyclobutane and cyclobutene, it might be possible to observe the concerted [$2_s + 2_a$] cycloreversion, albeit with a conrotatory preference less than that of the cyclobutene reaction. The bicyclo[2.1.0]pentane molecule (**1**), in which the cyclopropane orbital axes (dashed lines) are canted with respect to the breaking C(2)–C(3) bond, provides a test of this notion. Pyrolyses of three stereochemically labeled derivatives of the system, *syn-cis-*, *anti-cis-*, and *trans-*2,3-dimethylbicyclo[2.1.0]pentane (**2**, **3**, and **4**) give

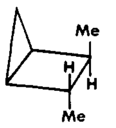


1



2: R$_1$ = Me, R$_2$ = H

3: R$_1$ = H, R$_2$ = Me



4

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(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. We are also grateful for support given by AFOSR(SRC)-OAR, U. S. Air Force, through Grant No. AFOSR-66-1006A, and by the National Science Foundation through institutional Grant No. GU-3282.

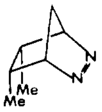
(2) *Cf.* R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, p 38 ff, and references cited therein.

(3) A. T. Cocks, H. M. Frey, and I. D. R. Stevens, *Chem. Commun.*, 458 (1969).

(4) J. E. Baldwin and P. W. Ford, *J. Amer. Chem. Soc.*, **91**, 7192 (1969).

small but analyzable amounts of the isomeric 2,5-heptadienes, the ratios of which measure the stereospecificity of the cycloreversion.

Synthesis of a mixture of **2** (41%) and **3** (59%)[5] by pyrolysis (190°, gas phase) of the azo compound **5** follows procedures used for the parent compound **1**[6] and several derivatives.[7,8] The route to azo compound **5** *via* the previously reported[9] substance **6** is facilitated by the present finding that separation of **6** from the mixed adducts **6**, **7**, and **8** (X = CO_2Me), obtained from dimethyl azodicarboxylate and the dimethylcyclopentadienes, is readily achieved by selective removal of **7** and **8** with aqueous silver nitrate.



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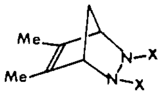

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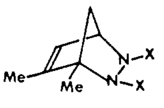

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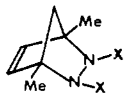
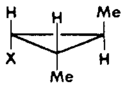
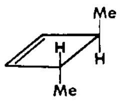


8

Synthesis of the trans hydrocarbon **4** starts with a convenient stereospecific preparation of the precursor *trans*-3,4-dimethylcyclobutene (**12**)[10a] from *trans*-2-butene *via* the known[10b] 1-chloro-*trans*-2,3-dimethylcyclopropane (**9**). Sodium methoxide in diethylene glycol diethyl ether converts the hydrazone **11** (obtained in several steps from **9** *via* the aldehyde **10**) to a mixture of **12**, *trans,trans*-2,4-hexadiene, *trans*-2-butene, and (presumably) acetylene.[11,12] In the presence of cuprous chloride, diazomethane cyclopropanates **12** to give **4**.[13]



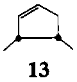
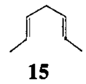
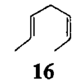
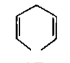
9: X = Cl
10: X = CHO
11: X = CHNNHTs



12

The syn–anti interconversion first observed by Chesick[13a] in the 2-methylbicyclo[2.1.0]pentanes also occurs in the pyrolysis of the cis compounds **2** and **3**, about 10% of either of which is converted to the other (but not to trans compound **4**) after 24 hr at 160° in the gas phase. At 310°, the temperature of the pyrolyses summarized in Table I, the **2** ⇌ **3** interconversion is so rapid that the product mixture is independent of which of the two is used as reactant. The table also gives the results of control experiments on the pyrolytic behavior of most of the products of interest, the 3,4-dimethylcyclopentenes (**13** and **14**) and the 2,5-heptadienes (**15**, **16**, and **17**).

Table I. Pyrolysis Products

	Products, % yield[a]				
	—Absolute—		—Relative[d]—		
					
Reactant	**13**	**14**	**15**	**16**	**17**
cis (60% **2** + 40% **3**)[e,i]	96[b]	0	13	83	4
trans (**4**)[f]	0	96[c]	92	8	0
13	>99.9	0	<0.01[j]	0	0
15	0	0	100	0	0
16[g]	0	0	0	94	6
17[h]	0	0	0	18	82

[a] Reactions for 5 hr at 310° and 0.5–1 atm. [b] Determined using cyclohexane as internal standard and corrected for *ca.* 9% recovered starting material. [c] Determined from **14**:**15** ratio. [d] Based on diene products only unless otherwise indicated. [e] A component with the same vpc retention time as 1,2-dimethylcyclopentene was formed in 0.04% yield. [f] A component with the same retention time as 1,5-dimethylcyclopentene was formed in 0.06% yield. [g] Conversion to **17** reached 9% after 12.5 hr and 12% after 15.8 hr. [h] Conversion to **16** reached 45% after 12.5 hr. The rate was unaffected by added glass wool. [i] In the presence of glass wool **15**, **16**, and **17** were formed in the ratio 33, 61, 6. [j] Relative to **13**.

The only significant interconversion of products is that between *cis,trans*- and *cis,cis*-2,5-heptadienes (**16** and **17**). This is presumably a further example of a well-known type of 1,5-hydrogen shift,[14] which probably proceeds by way of *cis*-1-vinyl-2-ethylcyclopropane. The cyclopropane intermediate is sterically inaccessible from *trans,trans*-2,5-heptadiene (**15**), and consequently the reactions **15** ⇌ **16** and **15** ⇌ **17** do not occur.

The rate of the **16** ⇌ **17** reaction is sufficient to indicate that virtually all of the *cis,cis*-diene **17** observed in the pyrolysis of cis reactants **2** and **3** arises from the *cis,-trans*-diene **16**. Products **16** and **17** therefore are combined in calculating the stereospecificity of the ring opening.

Table I shows that opening of the bicyclo[2.1.0]-pentane nucleus from both the cis (**2** and **3**) and trans (**4**) systems occurs with a conrotatory/disrotatory preference of about 10. This ratio[15] is 10–30 times greater than the corresponding $(2_s + 2_a)/(2_s + 2_s)$ ratio in cyclobutanes[3,4] but at least five orders of magnitude less than that of a cyclobutene,[16] in agreement with the naive analysis based on orbital geometry.

In a subtly different alternative hypothesis, diene formation might occur by way of a true intermediate, the frequently discussed[13a,17–19] cyclopentane-1,3-diyl diradical **18**. Although the conrotation observed in

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(5) Preparative vapor chromatographic (vpc) separation is achieved with a 20 ft × $^3/_8$ in. β,β′-oxydipropionitrile column.

(6) R. Criegee and A. Rimmelin, *Chem. Ber.*, **90**, 414 (1957).

(7) W. R. Roth and M. Martin, *Justus Liebigs Ann. Chem.*, 702, 1 (1967); *Tetrahedron Lett.*, 4695 (1967).

(8) E. L. Allred and R. L. Smith, *J. Amer. Chem. Soc.*, **91**, 6766 (1969).

(9) J. Wagner, W. Wojnarowski, J. E. Anderson, and J. M. Lehn, *Tetrahedron*, **25**, 657 (1969).

(10) (a) For an alternative preparation, see R. E. K. Winter, *Tetrahedron Lett.*, 1207 (1965); (b) G. L. Closs and L. E. Closs, *J. Amer. Chem. Soc.*, **82**, 5723 (1960).

(11) For comparable results in the case of the parent cyclopropanecarboxaldehyde derivative, see L. Friedman and H. Shechter, *ibid.*, **82**, 1002 (1960).

(12) The highly stereospecific formation of *trans*-2-butene suggests the possibility that decomposition of an intermediate gives this product and acetylene in a concerted, disrotatory, nonlinear cheletropic[1] process.

(13) For close analogies, see (a) J. P. Chesick, *J. Amer. Chem. Soc.*, **84**, 3250 (1962); (b) V. Z. Williams, Ph.D. Thesis (with K. B. Wiberg), Yale University, 1968.

(14) W. R. Roth and J. Koenig, *Justus Liebigs Ann. Chem.*, **688**, 28 (1965).

(15) The decreased stereospecificity observed in the presence of glass wool (Table I) is not caused by selective instability of the products. This suggests that there may be a surface-catalyzed component of the pyrolysis that has a stereospecificity lower than that of the homogeneous reaction. Since we cannot guarantee that we fully suppress the heterogeneous reaction even in the absence of deliberately added surface, the factor of 10 should be taken as a lower limit for the specificity of the homogeneous reaction.

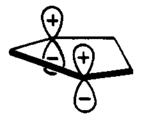
(16) *Cf.* G. A. Doorakian and H. H. Freedman, *J. Amer. Chem. Soc.*, **90**, 5310, 6896 (1968).

(17) C. Steel, R. Zand, P. Hurwitz, and S. G. Cohen, *ibid.*, **86**, 679 (1964).

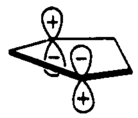
(18) R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, Jr., and M. Pomerantz, *ibid.*, **90**, 4315 (1968).

(19) R. Hoffmann, personal communication cited in ref 8.

18



18S



18A

the pyrolysis of bicyclo[2.2.0]hexanes[20] (a result superficially similar to that found here for bicyclo[2.1.0]pentanes) can be interpreted on purely conformational grounds with the aid of a hypothetical chair-like cyclohexane-1,4-diyl intermediate,[20] it would seem difficult to extend this rationalization to the case of the rather rigid and nearly planar intermediate **18**. Orbital correlation diagrams, however, predict conrotatory opening of **18**, provided the highest occupied molecular orbital is symmetric (**18S**) rather than antisymmetric (**18A**).

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(20) L. A. Paquette and J. A. Schwartz, *J. Amer. Chem. Soc.*, **92**, 3215 (1970).

(21) Supported by a NATO Fellowship and grant-in-aid administered by the Deutscher Akademischer Austauschdienst, 1969–1970.

* Address correspondence to this author.

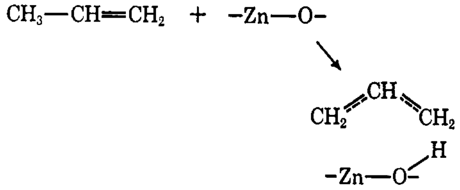
Jerome A. Berson,* Wolfgang Bauer[21]
Malcolm Murray Campbell
Department of Chemistry, Yale University
New Haven, Connecticut 06520
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

Received October 9, 1970

Intermediates in Allene–Acetylene Isomerization over Zinc Oxide

Sir:

Infrared studies[1] reveal that propylene adsorbs on zinc oxide *via* rupture of the methyl carbon–hydrogen bond. This process can be represented by the equation

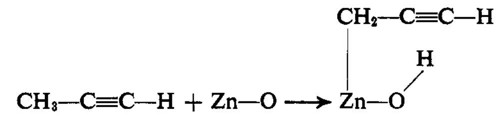


$$CH_3-CH{=}CH_2 + -Zn-O- \longrightarrow \underset{-Zn-O-H}{CH_2{\cdots}CH{\cdots}CH_2}$$

where Zn—O represents a limited number of active-pair sites similar to those responsible for dissociative adsorption of hydrogen.[2,3] Data for various adsorbed, deuterium-labeled propylenes[1] show that the hydrogen removed is attached to an oxide ion; the hydrocarbon fragments yield spectra expected for a symmetric π-allyl complex, and it was concluded[1] that this species is probably bound to the zinc half of the active site. Inasmuch as the zinc and oxide ions of the active site are Lewis acids and bases, respectively, we can expect the allyl species to have anionic character and the abstracted hydrogen to have protonic character. Thus, dissociative adsorption of propylene can be viewed as an acid–base reaction involving heterolytic fission of the acidic, allylic hydrogen. From this standpoint, the interactions of hydrocarbons with zinc oxide should resemble the interactions of hydrocarbons with bases in homogeneous systems. Support for this view is offered by recent studies of butene interactions with and isomerization over zinc oxide.[4]

If, indeed, zinc oxide plays the role of a base with propylene, this role should be even more apparent for the more acidic acetylenes. Adsorbed acetylene on zinc oxide[5] is more strongly bound than olefins, and, in contrast to olefins, acetylene is only partially recovered, as such, even after degassing at 300°. Nevertheless, addition of small amounts of acetylene gives rise to the immediate appearance of a band at 3550 cm^{-1}, a region characteristic of an O–H bond, together with bands expected for the hydrocarbon moiety. Adsorption of perdeuterioacetylene gives rise to no new bands in the OH region; hence, the band at 3550 cm^{-1} is *not* due to hydrogen-bonding shifts of the surface hydroxyls evident in the background spectrum.[6] Perdeuterioacetylene does, however, give rise to an OD band at 2622 cm^{-1}, a position very close to that expected (2623 ± 3 cm^{-1}) for a normal[7] isotope shift of the 3550-cm^{-1} band. Thus, it seems clear that the expected dissociative adsorption of acetylene on zinc oxide does occur.

Adsorption of methylacetylene, as expected, gives rise to an OH band (at 3515 cm^{-1}). *Adsorption of $CH_3-C\equiv C\cdot D$, however, also gives rise to an OH band at 3515 cm^{-1} and* (at least initially) *no corresponding (2598 cm^{-1}) OD band is observed.* This result suggests that the following process occurs



$$CH_3-C\equiv C-H + Zn-O \longrightarrow \underset{Zn-O-H}{CH_2-C\equiv C-H}$$

If, however, the hydrocarbon fragment is essentially the propargyl anion, there are two contributing forms to the resulting resonance hybrid[8]

$$\bar{C}H_2-C\equiv C-H \longleftrightarrow CH_2{=}C{=}\bar{C}-H$$

Then one might expect that the spectrum of adsorbed allene would be essentially the same as that of adsorbed methylacetylene. In fact, the initial spectra of adsorbed methylacetylene and allene are essentially indistinguishable and markedly different from that of either of the parent molecules.[9] Thus, it seems likely that methylacetylene (and allene) adsorbs on zinc oxide to form a propargyl anion.

The propargyl anion is the presumed intermediate in the homogeneous, base-catalyzed, allene–acetylene isomerization.[10] Thus, if the above view is correct, one would expect zinc oxide to be an effective catalyst for isomerization of allene to methylacetylene. In line

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(1) A. L. Dent and R. J. Kokes, *J. Amer. Chem. Soc.*, **92**, 6709, 6718 (1970).

(2) R. P. Eischens, W. A. Pliskin, and M. J. D. Low, *J. Catal.*, **1**, 180 (1962).

(3) A. L. Dent and R. J. Kokes, *J. Phys. Chem.*, **73**, 3772, 3781 (1969).

(4) (a) A. L. Dent and R. J. Kokes, *J. Phys. Chem.*, in press; (b) W. C. Conner and R. J. Kokes, unpublished results.

(5) Experimental procedures for the spectroscopic measurements and the pretreatment of the zinc oxide (Kadox 25, New Jersey Zinc Co.) were those given in ref 1. All experiments reported herein were carried out at room temperature.

(6) D. J. C. Yates and P. J. Lucchesi, *J. Chem. Phys.*, **35**, 243 (1961).

(7) The "normal" isotope shift is that observed when surface hydroxyls are exchanged with deuterium.

(8) As written, the two forms imply different nuclear geometries. Clearly, a common compromise geometry is required if this is resonance rather than tautomerism.

(9) We cannot rule out rapid surface isomerization of allene to methylacetylene, but details of the spectra make this unlikely.

(10) I. Iwai in "Mechanisms of Molecular Migrations," Vol. 2, B. S. Thyagarajan, Ed., Wiley, New York, N. Y., 1969, p 73.