

$$2V_{SVFF} = \sum_{i=1}^3 K_{CC} \Delta R_i^2 + \sum_{i=1}^3 k_{CX} \Delta r_i^2 + \sum_{i=1}^3 H_{CCC} (R \Delta \alpha_i)^2 + \sum_{i=1}^3 H_{CCX} (r \Delta \beta_i)^2$$

and for UBFF

$$2V_{UBFF} = 2V_{SVFF} + 2 \sum_{i=1}^3 K_{CC'} R \Delta R_i + 2 \sum_{i=1}^3 K_{CX'} r \Delta r_i + 2 \sum_{i=1}^3 H_{CCX'} r^3 \Delta \beta_i + \sum_{i=1}^3 F_{CX} [(\Delta q_{C_i X_{i+1}})^2 + (\Delta q_{C_i X_{i-1}})^2] + 2 \sum_{i=1}^3 F_{CX'} [q_{CX} (\Delta q_{C_i X_{i+1}} + \Delta q_{C_i X_{i-1}})] + \sum_{i=1}^3 C_{XX} (\Delta q_{X_i X_{i+1}})^2 + 2 \sum_{i=1}^3 C_{XX'} (q_{XX} \Delta q_{X_i X_{i+1}})$$

where K and H have their usual meanings of stretching and bending force constants, respectively, X denoting halogen. F_{CX} and C_{XX} are geminal and *cis* repulsion terms, respectively, between nonbonded atoms; q is the distance between nonbonded atoms. The linear terms are indicated with a prime.

In the calculation the usual assumption was made that the linear terms are -0.1 of the corresponding quadratic terms. Bond lengths are not available for these ions, and so distances $R_{CC} = 1.39$ Å, $\gamma_{CCl} = 1.79$ Å, and $r_{CBr} = 1.90$ Å were assumed. Force constants were refined by iterative calculation using a Consolidated Data Corp. 1604 electronic digital computer.

In the SVFF calculation, the observed frequencies were all equally weighted except for the band at 200 cm^{-1} , which was given a weighting one-half as large as the others. The agreement of the calculated and observed frequencies were within $\pm 0.4\%$ except for the 200-cm^{-1} band, which showed a deviation of -5.1% .

Acknowledgments. We thank the National Science Foundation for partial support of this work, and the National Institutes of Health for a predoctoral fellowship to S. W. T. We are indebted to the Argonne National Laboratory for making Raman equipment available to us, to Mr. Joseph Wheeler for constructing the special Raman tubes, and to Mr. Paul Kwitowski for the preparation of $\text{C}_3\text{Cl}_4 \cdot \text{GaCl}_3$.

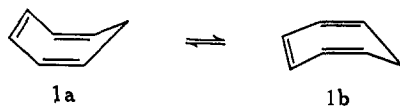
Thermally Induced Skeletal Rearrangements of Tropilidenes¹

Jerome A. Berson and M. Robert Willcott, III²

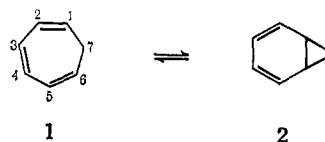
Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin. Received February 4, 1966

Abstract: 3,7,7-Trimethyltropilidene heated at 300° in the gas phase gives a mixture containing recovered starting material, 2,7,7- and 1,7,7-trimethyltropilidenes, 3- and 6-isopropenyl-1-methyl-1,4-cyclohexadienes, and *m*- and *p*-cymenes. The nonaromatizing rearrangements are reversible. Under the same conditions, 1,5-dideuterio-3,7,7-trimethyltropilidene gives the corresponding dideuterated products, in each of which the alternating pattern (D, H, lone methyl, H, D) of substitution characteristic of the starting material is preserved. The rearrangement is therefore one in which the carbons 1-6 of the starting material remain in the same sequence, while C-7 and its geminal methyls are allowed to wander and reattach between any adjacent pair.

Tropilidene (**1**) is perhaps the most intensively studied member of the class of odd-numbered cyclic polyenes $\text{CH}_2(\text{CH}=\text{CH})_n$ ($n = 1, 2, \dots$). Its response to thermal energies over the temperature range from -150 to above 400° has been examined by a variety of techniques. The most facile change is the conformational ring inversion (*e.g.*, **1a** \rightleftharpoons **1b**) of two nonplanar isomers revealed by the low-temperature nmr spectrum of the parent compound ($E_a = 5.7\text{--}6.3$ kcal/mole)³ and the 2-*t*-butyl-3,7,7-trimethyl derivative.⁴ At a perhaps slightly higher level of activation energy



may lie the much discussed⁵⁻⁸ cycloheptatriene-norcaradiene (**2**) interconversion. From bond-energy



tables, a rough value of 11 ± 4 kcal/mole is calculated⁹ for the endothermicity and hence for the minimum activation energy of the **1** \rightarrow **2** reaction. In the range of temperatures high enough to overcome an activation energy of about 31 kcal/mole, the hydrogens of tropilidene spread over the carbon framework by successive C-7 \rightarrow C-3 jumps, as is observed in the behavior of 7-deuterated derivatives.^{10a} This epidermal rearrangement

(1) (a) We are indebted to the Camille and Henry Dreyfus Fund and to the Army Research Office (Durham) for support of this work. (b) For preliminary reports, see J. A. Berson and M. R. Willcott, III, *J. Am. Chem. Soc.*, **87**, 2751, 2752 (1965).

(2) National Institutes of Health Postdoctoral Fellow, 1964-1965.

(3) (a) F. A. L. Anet, *J. Am. Chem. Soc.*, **86**, 458 (1964); (b) F. R. Jensen and L. A. Smith, *ibid.*, **86**, 956 (1964).

(4) K. Conrow, M. E. H. Howden, and D. Davis, *ibid.*, **85**, 1929 (1963).

(5) Cf. W. von E. Doering and M. R. Willcott, III, *Tetrahedron Letters*, 663 (1962), and references cited therein for earlier literature.

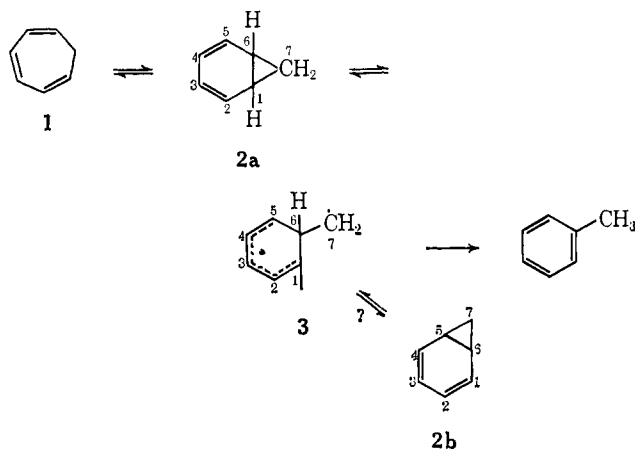
(6) E. Ciganek, *J. Am. Chem. Soc.*, **87**, 1149 (1965).

(7) J. Schreiber, W. Leimgruber, M. Pesaro, P. Schudel, and A. Eschenmoser, *Angew. Chem.*, **71**, 637 (1959).

(8) E. Vogel, *ibid.*, **74**, 829 (1962).

(9) W. von E. Doering and M. R. Willcott, III, unpublished; M. R. Willcott, III, Ph.D. Dissertation, Yale University, 1963.

also occurs with other 7-substituted tropilidenes.^{10b,c} In the case of tropilidene itself, it effects, at equilibrium, the complete structural interchange of all eight hydrogens,^{10a} but presumably leaves the carbon skeleton undisturbed. A large gap intervenes between 31 kcal/mole and the next higher level of activation energy (ca. 50 kcal/mole) at which changes occur. At sufficiently high temperature, tropilidene gives toluene,¹¹⁻¹⁵ and 7-methyltropilidene gives ethylbenzene.¹⁶ The aromatization reaction producing toluene does not go by dissociation to CH₂ and benzene followed by C-H insertion, since it is entirely intramolecular.¹¹ The mechanism proposed¹¹ involves initial valency tautomerism to norcaradiene, rupture of one of the cyclopropane bonds, and hydrogen shift in the resulting diradical.



We were interested in the possibility that recyclization of **3** to norcaradiene might occur at a rate competitive with the hydrogen-transfer rate. This situation obtains in the 1,3-diradical from the pyrolysis of cyclopropane,^{17,18} which can be considered to be the simplest model for this system. Were the **3** → toluene and **3** → **2** rates comparable, it would in principle be possible to observe a new rearrangement of the tropilidene skeleton. Experimentally, the detection of such rearrangements is made difficult by the epidermal hydrogen shifts, which occur at a much faster rate. These can be blocked by 7,7-substitution. Because of its ready accessibility,¹⁹ we chose to work with 3,7,7-trimethyltropilidene (**4**). Although, as will become clear, it is not without its own complications as a system for discerning the skeletal rearrangement, this compound avoids the above difficulty and, in addition,

(10) (a) A. P. ter Borg, H. Kloosterziel, and N. van Meurs, *Proc. Chem. Soc.*, 359 (1962); *Rec. Trav. Chim.*, **82**, 717 (1963), and references therein cited; (b) G. Büchi and E. M. Burgess, *J. Am. Chem. Soc.*, **84**, 3104 (1962); (c) E. Weth and A. S. Dreiding, *Proc. Chem. Soc.*, 59 (1964).

(11) W. G. Woods, *J. Org. Chem.*, **23**, 110 (1958).

(12) W. M. Halper, G. Gaertner, E. W. Swift, and G. E. Pollard, *Ind. Eng. Chem.*, **50**, 1131 (1958).

(13) J. H. Birely and J. P. Chesick, *J. Phys. Chem.*, **66**, 568 (1962).

(14) K. N. Klump and J. P. Chesick, *J. Am. Chem. Soc.*, **85**, 130 (1963).

(15) W. C. Herndon and L. L. Lowry, *ibid.*, **86**, 1922 (1964).

(16) A. G. Harrison, L. R. Honnen, H. J. Dauben, Jr., and F. P. Lossing, *ibid.*, **82**, 5593 (1960).

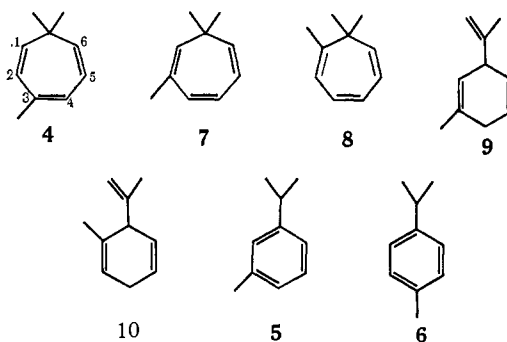
(17) B. S. Rabinovitch, E. W. Schlag, and K. B. Wiberg, *J. Chem. Phys.*, **28**, 504 (1958).

(18) S. W. Benson, *ibid.*, **34**, 521 (1961).

(19) (a) E. J. Corey, H. J. Burke, and W. A. Remers, *J. Am. Chem. Soc.*, **78**, 180 (1956); (b) J. R. B. Campbell, A. M. Islam, and R. A. Raphael, *J. Chem. Soc.*, 4096 (1956).

provides a rewarding microcosm of thermal reactions for study.

Products from Pyrolysis of 3,7,7-Trimethyltropilidene (4). Pyrolysis of compound **4** at or above 300° in the gas phase proceeds at a convenient rate. Aromatization is the thermodynamic terminus of the system; *m*- and *p*-cymene (**5** and **6**) are minor products at short reaction times but accumulate at the expense of nonaromatic materials if pyrolysis is prolonged. The nonaromatic products include, in addition to recovered starting material, two new tropilidenes, 2,7,7- (**7**) and 1,7,7-trimethyltropilidene (**8**), and two new 1,4-cyclohexadienes (**9** and **10**). Under properly controlled conditions, virtually no gas, tar, or carbonaceous material is formed, and the mass balance in terms of these seven identified C₁₀H₁₄ compounds is, except for 1-2% of still uncharacterized products, essentially quantitative.



The assignments of structure to the new tropilidenes rest on spectroscopic criteria. The ultraviolet spectra of all three compounds **4**, **7**, and **8** (Table I) show a medium-intensity band which corresponds in location and strength to those shown by other tropilidenes. Further, the effect of the position of alkyl substitution shown in the series 1-methyl-, 2-methyl-, 3-methyltropilidene (Table I) is virtually duplicated in the series **8**, **7**, and **4**. In both series, the main band suffers a pronounced hypsochromic shift by the structural alteration 1-methyl to 2-methyl but is essentially insensitive to the change 2-methyl to 3-methyl.

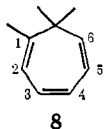
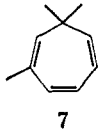
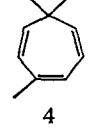
Table I. Ultraviolet Spectra of Tropilidenes^a

Tropilidene	λ_{\max} , m μ	Log ϵ
1-Me ^b	269	3.53
2-Me ^b	258	3.42
3-Me ^b	260	3.58
1,7,7-TriMe (8)	278	3.64
2,7,7-TriMe (7)	270	3.56
3,7,7-TriMe (4)	268 ^c	3.61 ^d

^a Solvent ethanol. ^b N. H. Nelson, J. H. Fassnacht, and J. V. Piper, *J. Am. Chem. Soc.*, **83**, 206 (1961). ^c Reported in ref 4 as 269. ^d Reported in ref 4 as 3.55.

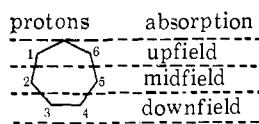
More definitive evidence on the structures of the tropilidenes **7** and **8** comes from the 60-Mc nuclear magnetic resonance (nmr) spectra, which are given in Table II. Like the starting material **4**, both **7** and **8** show six-proton singlets at 1.0 ppm attributable to the gem-dimethyl group and three-proton absorptions as slightly broadened singlets at 2.0 ppm (allylic methyl). The absorption of the remaining five protons in the

Table II. Nmr Absorptions of Trimethyltropilidenes (δ Units)^a

Compd	<i>gem</i> -Me ₂	Allylic Me	C-3-C-4	Olefinic C-2-C-5	C-1-C-6
 8	1.0 (6) s	1.9 (3) bs	5.7-6.4 (4) m		4.8-5.2 (1) m
 7	1.0 (6) s	1.9 (3) bs	6.2-6.4 (2) m	5.8-6.2 (1) m	4.8-5.2 (2) m
 4	1.0 (6) s	2.0 (3) bs	6.1-6.3 (1) m	5.8-6.1 (2) m	4.9-5.2 (2) m

^a Relative intensities are shown in parentheses. The multiplicity is shown by the symbols s (singlet), bs (broadened singlet), and m (multiplet).

compounds **4**, **7**, and **8** falls in the olefinic region and is in each case subdivided into three more or less distinct bands at approximately 6.2-6.4, 5.7-6.2, and 4.8-5.1 ppm downfield from tetramethylsilane, although the separation between the two lowest field bands is incomplete in **8**. Prior studies^{4,9} of many tropilidenes of known structure indicate a characteristic separation of the 1-6, 2-5, and 3-4 pairs of olefinic proton absorptions, respectively, into upfield, midfield, and downfield regions, as in the generalized structure shown. The spectra of compounds **4**, **7**, and **8** (Table II) show that they are the three possible *x*,7,7-trimethyltropilidenes. The detailed structures follow from the intensity ratios of the olefinic proton absorptions, which (reading upfield) are 4:1 for **8**, 2:1:2 for **7**, and 1:2:2 for the starting material (**4**).



The structures of the cyclohexadienes **9** and **10** are not immediately apparent from the spectroscopic data. Quantitative catalytic hydrogenation and empirical composition show that these compounds each contain three double bonds and are monocyclic. The double bonds in each case, however, are unconjugated since both compounds show only end absorption in the ultraviolet. The infrared and nmr spectra are remarkably similar, and both clearly indicate a terminal methylene group (ν_{\max} 890 cm^{-1} , broadened two-proton singlet near 4.7 ppm). Both nmr spectra show three other olefinic protons, two allylic methyl groups (three-proton doublets at 1.6 and 1.7 ppm), a doubly allylic methylene group (two-proton absorption near 2.5 ppm), and a triply allylic methine group (one-proton absorption near 3.3 ppm). Although relatively few formulas incorporating these features can be written, the presence of a 1,4-cyclohexadiene system is not obvious, and the structural clue is provided by mechanistic considerations to be described. This guess suggests that it might be possible to hydrogenate the

terminal methylene double bond selectively and leave the 1,4-cyclohexadiene system intact. In fact, interruption of the catalytic hydrogenation (ethyl acetate or dioxane solvent, 5% palladium on barium carbonate) of either of the trienes **9** or **10** after consumption of 1 mole gives a mixture containing a dihydrocymene. Aromatization is achieved by tetracyanoethylene treatment²⁰ of the hydrogenation reaction mixture. In this way, **9** is converted to *m*-cymene and **10** to *o*-cymene in 30-50% yield. Thus, **9** is 3- and **10** is 6-isopropenyl-1-methyl-1,4-cyclohexadiene.

The Mechanism. The structures of the products from the pyrolysis of **4** establish the occurrence of nonaromatizing skeletal transformations leading to rearranged tropilidenes and to 1,4-cyclohexadienes. Two simple but important features of the mechanism are readily established.

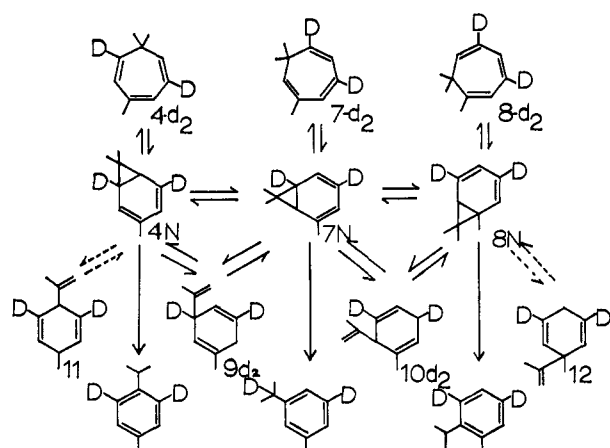
(1) Both kinds of nonaromatizing rearrangement are reversible. When either 2,7,7-trimethyltropilidene (**7**) or 6-isopropenyl-1-methyl-1,4-cyclohexadiene (**10**) is isolated and resubjected to the pyrolysis conditions, it reverts to the typical mixture of pyrolysis products obtained from (and including) **4**.

(2) The rearrangements do not involve intermolecular hydrogen transfers. When 4-*d*₂ is pyrolyzed, the distribution of deuterated species *d*₂, *d*₁, *d*₀ in the rearrangement products is the same as in the starting material. Although one might imagine some kind of intermolecular radical chain process that would account for the structural changes, it would require a scrambled distribution of labeled species in each product. Beyond this, an examination of the behavior of 4-*d*₂ provides (see below) a more detailed picture of the process.

The observations so far permit the construction of a working hypothesis of the mechanism which incorporates the major structural changes, the intramolecularity, and the reversibility. This is illustrated in Scheme I, which also shows the predicted location of deuterium label in each of the products derived from 1,5-dideuterio-3,7,7-trimethyltropilidene (4-*d*₂) by the proposed mechanism.

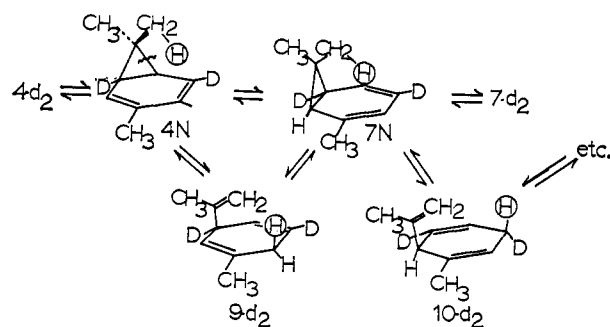
(20) Cf. D. T. Longone and G. L. Smith, *Tetrahedron Letters*, 205 (1962).

Scheme I



The basic assumption of the scheme is that the interconversions of the three tropilidenes **4**, **7**, and **8** occur by way of the corresponding norcaradienes **4N**, **7N**, and **8N**. The carbon skeletal rearrangement can be described *formally* by breaking one of the cyclopropane ring bonds to the *gem*-dimethylated carbon and reforming it at a ring site two atoms removed.

A subtle ambiguity arises in attempts to push the description to a more detailed level, since the $4N \rightleftharpoons 7N$ interconversion might in principle take place by an "all-carbon" process (*i.e.*, directly) and/or by way of



the hydrogen-shifted intermediate cyclohexadiene **9**.²¹ A decision between these possibilities is not easily available by experiment, and even conceptually, the distinction is very fine. An inspection of models shows that in a hypothetical "all-carbon" transition state for the direct $4N \rightleftharpoons 7N$ reaction, the circled hydrogen occupies a position only about 1.5 Å removed from that of the (same) circled hydrogen which is temporarily deposited at C-6 in the cyclohexadiene **9**.

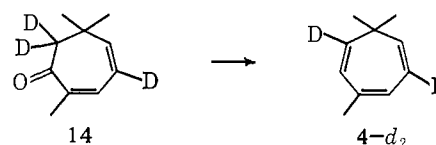
The scheme predicts the formation of two more cyclohexadienes (**11** and **12**) and of one more aromatic compound (*o*-cymene). These may well be present in the 1–2% of uncharacterized material.

Leaving aside for the present the delicate question of whether the cyclohexadienes are necessary or merely permissible intermediates in the norcaradiene rearrange-

(21) For analogous hydrogen shifts in 1-alkyl-2-vinylcyclopropanes, see (a) W. von E. Doering and W. Grimme, cited by W. von E. Doering and W. R. Roth, *Angew. Chem.*, **75**, 27 (1963); W. Grimme, *Chem. Ber.*, **98**, 756 (1965); (b) W. R. Roth, *Ann.*, **671**, 10 (1964); (c) D. S. Glass, J. Zirner, and S. Winstein, *Proc. Chem. Soc.*, 276 (1963); (d) R. J. Ellis and H. M. Frey, *ibid.*, 221 (1964); (e) G. Ohloff, *Tetrahedron Letters*, 3795 (1965); *Chem. Ber.*, **93**, 2673 (1960); (f) W. R. Roth and J. König, *Ann.*, **688**, 28 (1965), and references cited there; (g) strictly speaking, direct hydrogen shift in the nonplanar form of the tropilidene **4** itself to give **9**, while requiring an unusual sp^2-sp^3 bond cleavage and therefore unlikely, cannot be ruled out as an alternative to the mechanism passing through **4N**.

ments, there is a more practical issue which is raised by the hydrogen shifts and is of crucial importance to any attempt to validate the proposed scheme by the indicated deuterium tracer experiment. Since the formation of the cyclohexadienes is reversible, it is essential that the step in which hydrogen is transferred from methyl to a deuterium-bearing carbon ($7N \rightleftharpoons 10-d_2$) be completely stereospecific; that is, only *hydrogen* must make this trip, not deuterium. Any event in which an (originally) methyl hydrogen and an (originally) C-4 deuterium in **7N** interchange their identity in the CHD group generated at C-3 of **10** jeopardizes the whole experiment, for the return to **7N** then allows deuterium to escape from the ring into the *gem*-dimethyl group, and the integrity of the labeling pattern is destroyed. *A priori*, there are grounds to hope that the hydrogen transfer in the $7N \rightleftharpoons 10-d_2$ reaction would be stereospecific. It is intramolecular, and if it occurs by the mechanism shown, the transferred hydrogen and the newly generated isopropenyl group in **10-d₂** are thereby locked in a *cis* relationship to each other. Microscopic reversibility requires that return of the hydrogen occurs in the desired way. Only in the unlikely event of some kind of configurational inversion at C-6 or C-3 could the isopropenyl group and the C-3 deuterium become *cis*. Even this remote possibility is ruled out by the observation that pyrolysis of **10-d₂**, obtained as described below, regenerates the starting material **4-d₂** with complete retention of the labeling pattern; that is, the recovered **4-d₂** is 1,5-dideuterio-3,7,7-trimethyltropilidene, free of other isomers. The integrity of the labeling pattern is established by comparison of the nmr spectra of the starting and recovered **4-d₂** and especially by the superimposability of the infrared spectra, which are quite detailed and characteristic and furthermore entirely distinct in the fingerprint region from that of unlabeled **4**. It seems likely that even small amounts of other deuterium position isomers would have been readily apparent. Consequently, the hydride shifts are completely stereospecific.

Eucarvone, which exchanges three hydrogens for deuterium in basic deuterioxylic medium to give eucarvone-*d*₃ (**14**),^{19a} serves as starting material for the preparation of **4-d₂**. The positions of the deuterium atoms in **14** previously assigned^{19a} are confirmed by the nmr spectrum, which is described in the Experimental Section. Conversion of **14** to 1,5-dideuterio-3,7,7-trimethyltropilidene (**4-d₂**) is achieved by the sequence used¹⁹ in the unlabeled series (lithium aluminum hydride reduction to the alcohol followed by distillation of the latter from a trace of concentrated sulfuric acid).



The mass spectrum of the deuterated **4** shows the distribution 85.4% *d*₂, 10.6% *d*₁, and 4.0% *d*₀ species. If it is assumed that half of the *d*₁ species are C-1 deuterated and half C-5 deuterated, the intensity ratio (reading from downfield to upfield) in the olefinic region of the nmr spectrum should be 1.00:1.05:1.05, in good agreement with the observed ratio 1.00:1.04:1.00.

Table III. Predicted and Observed Nmr Spectra of Tropilidenes from 1,5-Dideuterio-3,7,7-trimethyltropilidene $4-d_2$

Chemical shift, δ							
4.8-5.2							
5.8-6.1							
6.1-6.4							
	$4-d_2$		$7-d_2$		$8-d_2$		
δ	Rel intensity		Rel intensity		Rel intensity		
	Predicted	Found ^{a,b}	Predicted	Found ^b	Predicted	Found ^{b,c}	
4.8-5.2	1	1.00	1	1.04	1	1.0	
5.8-6.1	1	1.04	1	1.16	1	1.0	
6.1-6.4	1	1.00	1	1.15	1	1.0	

^a Same pattern found in starting material. ^b Lone methyl taken as 3. ^c Small sample precluded observation of intensities to better than about 10-12%.

Table IV. Predicted and Observed Nmr Spectra of Aromatic Products from 1,5-Dideuterio-3,7,7-trimethyltropilidene ($4-d_2$)

Chemical shift, δ							
1.2							
2.4-3.1							
7.0							
2.3							
	6		5				
δ	Rel intensity ^a		Rel intensity				
	Predicted	Found	Predicted	Found			
1.2	6 (d)	6.00 (d)	6 (s)	6.00 (s)			
2.4-3.1	1 (sept)	0.82 (m)	0	0			
7.0	2	2.30	3	2.70			
2.3	3	3.00	3	3.00			

^a Lone methyl absorption taken as 3.

Table V. Predicted and Observed Nmr Spectra of Cyclohexadienes of 1,5-Dideuterio-3,7,7-trimethyltropilidene ($4-d_2$)

Chemical shift, δ							
4.7-4.8 ^a							
3.3							
5.3-5.6 ^a							
2.5							
	$9-d_2$		$10-d_2$				
δ	Rel intensity ^b		Rel intensity ^b				
	Predicted	Found	Predicted	Found			
4.7-4.8	2	1.86	2	2.07			
3.3	0	0	1	0.83			
5.3-5.6	2	2.07	2	2.19			
2.5	2	2.03	1	0.98			

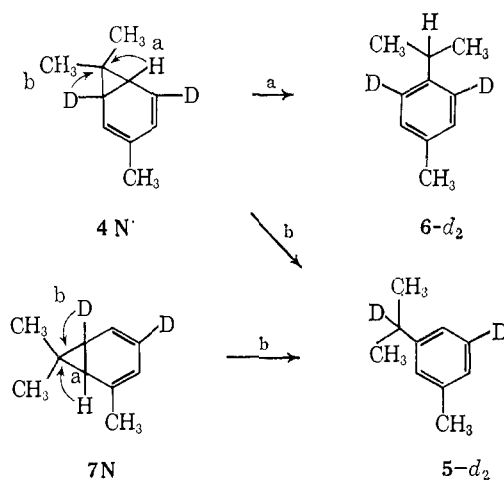
^a Refers to olefinic protons. ^b Methyl group absorption taken as 6.

Pyrolysis of this sample of $4-d_2$ under the conditions used in the unlabeled series, isolation of the deuterated products by preparative vapor chromatography, and

determination of the nmr spectra give the results shown in Tables III, IV, and V.

The mechanism of Scheme I predicts that the alternating pattern (D, H, lone methyl, H, D) characteristic of the starting $4-d_2$ will be preserved in the rearranged tropilidenes $7-d_2$ and $8-d_2$. Thus, the olefinic proton nmr intensity ratios of the three unlabeled tropilidenes 4 (1:2:2), 7 (2:1:2), and 8 (2:2:1) should be replaced in each member of the deuterated series ($4-d_2$, $7-d_2$, $8-d_2$) by an intensity ratio 1:1:1. As Table III shows, this prediction is confirmed.

Scheme I proposes that the formation of the aromatic products occurs by a mechanism formally analogous to that proposed¹¹ for the tropilidene \rightarrow toluene reaction. Thus, *p*-cymene $6-d_2$ is formed from $4N$, which must transfer the bridgehead hydrogen to the sidechain a, but *m*-cymene $5-d_2$ is formed from $4N$ or $7N$, in each case by transfer of bridgehead deuterium to the side chain b. This predicts that the *p*-cymene- d_2 isolated from the pyrolysis should have an intact isopropyl group but that two of the four aromatically bound protons of the unlabeled compound should be replaced



by deuterium. These predictions are confirmed (Table IV). The characteristic isopropyl pattern, a six-proton doublet at 1.2 ppm and a one-proton multiplet extending from 2.4 to 3.1 ppm, is clearly evident, but the relative intensity of the aromatic absorption near 7 ppm is approximately half that in the unlabeled compound. The scheme further predicts that the labeled

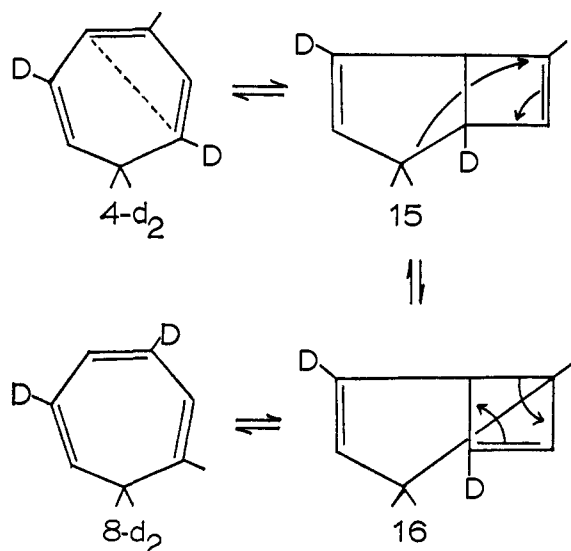
m-cymene should show a three-proton absorption in the aromatic region, but the isopropyl group pattern should be replaced by that of a $(\text{CH}_3)_2\text{CD}$ group, that is by a six-proton singlet. The benzylic hydrogen absorption should disappear. These predictions are again confirmed (Table IV).

As is the case with the rearranged tropilidenes, the labeling results in the aromatic series identify the structural features of the mechanism and are noncommittal with regard to the detailed nature of the intermediates. In particular, the *p*-cymene and *m*-cymene data permit but do not require that diradical intermediates¹¹ be involved in the aromatizations, since they are also compatible with a direct, concerted reaction.

The cyclohexadienes **9-d₂** and **10-d₂** each are expected to show absorption for only two downfield olefinic protons rather than the three each shown by the parent compounds, but the two upfield (terminal methylene) protons should remain intact. In **9-d₂** the triply allylic methine absorption at 3.3 ppm should vanish while the doubly allylic methylene at 2.5 ppm remains, but in **10-d₂**, the reverse should be the case, that is, absorption is expected for one proton at 3.3 ppm and for only one (instead of two) at 2.5 ppm. The predictions are fully confirmed (Table V).

Discussion

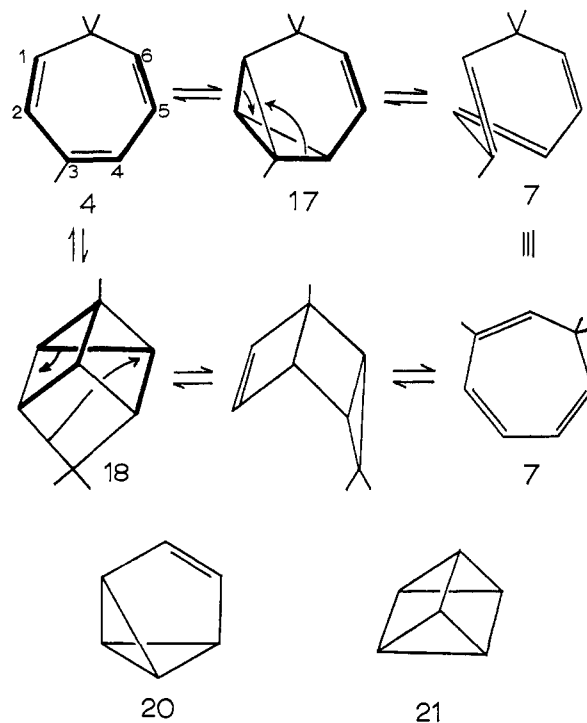
It is not easy to devise alternatives to Scheme I that are compatible with the whole of the interlocked framework of data. Perhaps the most obvious way to replace parts of the scheme involves valency tautomers other than norcaradienes. For example, ring closure of **4-d₂** along the dotted line would lead to the bicyclo[3.2.0]heptadiene (**15**), which is structurally related to **4-d₂** as "Dewar benzene"^{22a} is to benzene. Ring closure of this type has photochemical analogy in the forward direction^{22b} and thermal precedent in the reverse.^{22b-f} Allylic carbon rearrangement of **15** would give **16**, which might well produce the rearranged tropilidene **8-d₂**. This mechanism has the disadvantage



(22) (a) Cf. E. E. van Tamelen, *Angew. Chem.*, **77**, 759 (1965); (b) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **12**, 186 (1961); (c) M. V. Evans and R. C. Lord, *J. Am. Chem. Soc.*, **83**, 3409 (1961); (d) W. G. Dauben, K. Koch, S. L. Smith, and O. L. Chapman, *ibid.*, **85**, 2616 (1963); (e) E. Vogel, *Ann.*, **682**, 1 (1965); (f) R. Criegee and H. Furrer, *Chem. Ber.*, **98**, 2327 (1965).

that it does not lead to the second rearranged tropilidene, the 2,7,7-trimethyl compound (**7**), and must therefore be combined with some other hypothetical process to account for the products.

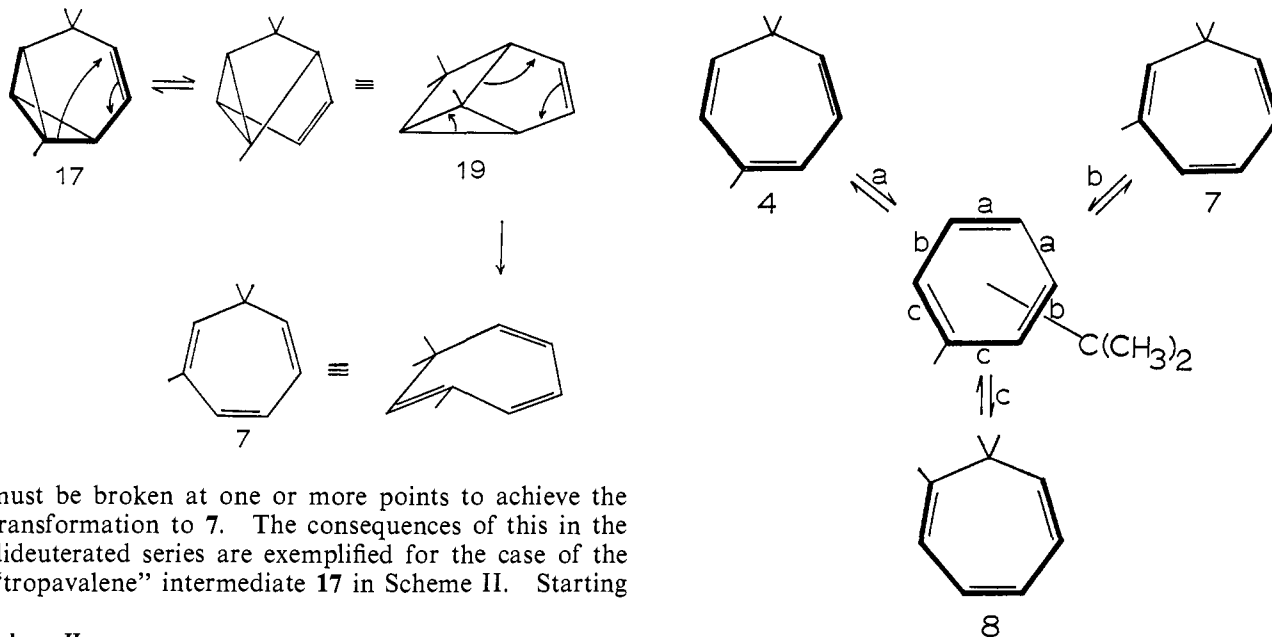
Conversion of **4** to 2,7,7-trimethyltropilidene (**7**) might be imagined to result from reversible formation of "tropavalene" (**17**) or "homoprismane" (**18**) valency



tautomers, analogous to the "benzvalene" (**20**) and "prismane" (**21**) intermediates suggested to account for some photochemical rearrangements of benzene derivatives.^{23a-d} Another conceivable intermediate is the tricyclic one **19**, derived by vinylcyclopropane rearrangement of the "tropavalene" **17**. This type has no direct analog in the series of benzene valency tautomers, where vinylcyclopropane rearrangement of "benzvalene" (**20**) merely converts it into itself.^{23d} (The hypothetical bond shifts in all these processes are shown as mere structural formalisms without implications as to possible diradical intermediates.)

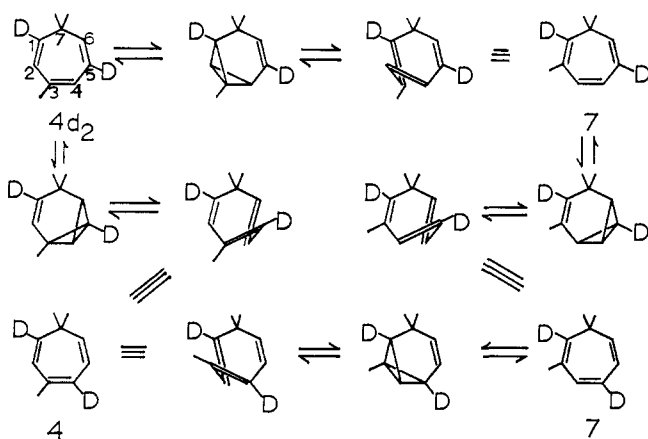
None of these alternatives to Scheme I is compatible with the isotopic marking experiments. The data with respect to the tropilidenes are most readily interpreted as showing that carbons 1-6 of the starting 3,7,7-trimethyltropilidene (**4**) remain sequentially arranged throughout. A characteristic feature of the alternatives to Scheme I is that this chain (shown in heavy outline)

(23) (a) A. W. Burgstahler and P. Chien, *J. Am. Chem. Soc.*, **86**, 528 2940 (1964); (b) E. M. Arnett and J. M. Bollinger, *Tetrahedron Letters*, 3803 (1964); (c) K. E. Wilzbach and L. Kaplan, *J. Am. Chem. Soc.*, **86**, 2307 (1964); L. Kaplan, K. E. Wilzbach, W. G. Brown, and S. S. Yang, *ibid.*, **87**, 675 (1965); (d) for an isolable "benzvalene" and a discussion of benzene valency tautomers, see H. G. Viehe, R. Merenyi, J. F. M. Oth, and P. Valange, *Angew. Chem.*, **76**, 888 (1964); H. G. Viehe, *ibid.*, **77**, 768 (1965); (e) for a related photochemical "bond-crossing" reaction, see R. Srinivasan, *J. Am. Chem. Soc.*, **85**, 4045 (1963); (f) for thermal "uncrossing" processes (bicyclobutane \rightarrow butadiene), see D. M. Lemal, F. Menger, and G. W. Clark, *ibid.*, **85**, 2529 (1963); W. von E. Doering and M. Pomerantz, *Tetrahedron Letters*, 961 (1964); W. von E. Doering and J. F. Coburn, Jr., *ibid.*, 991 (1965); J. P. Chesick, *J. Phys. Chem.*, **68**, 2033 (1964); K. B. Wiberg, G. M. Lampman, R. P. Ciula, D. S. Connor, P. Schertler, and J. Lavanish, *Tetrahedron*, **21**, 2749 (1965); (g) for a thermal rearrangement that appears to proceed by a reversible "bond-crossing" in the dibenzocyclooctatetraene series, see M. Stiles and U. Burckhardt, *J. Am. Chem. Soc.*, **86**, 3896 (1964).



must be broken at one or more points to achieve the transformation to **7**. The consequences of this in the dideuterated series are exemplified for the case of the "tropavalene" intermediate **17** in Scheme II. Starting

Scheme II

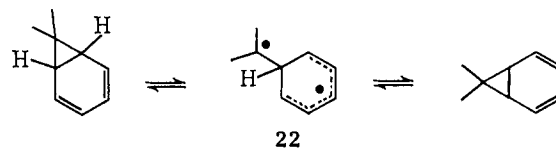


with $4-d_2$ (upper left) with deuterium exclusively at C-1 and C-5, such processes would spread the C-5 deuterium to C-4 until at equilibrium the distribution would be C-1 fully deuterated and C-4 and C-5 each 50% deuterated. The 2,7,7-isomer (**7**) formed early in the conversion (upper right) would have C-1 and C-5 fully deuterated instead of C-4 and C-6, where the label is actually found. At equilibrium, **7** would reach the same kind of distribution as **4**, namely C-1 fully deuterated and C-4 and C-5 each 50% deuterated. The new marking pattern also would produce corresponding changes in the predicted sites of labeling in the cyclohexadienes and aromatic products. None of these predictions is in accord with the observations. Consequently, the "tropavalenes" of Scheme II cannot be sources of the 2,7,7-trimethyltropilidene product, and, furthermore, cannot occur to any appreciable extent even in side reactions. Similar objections apply to intermediates **18** and **19**.

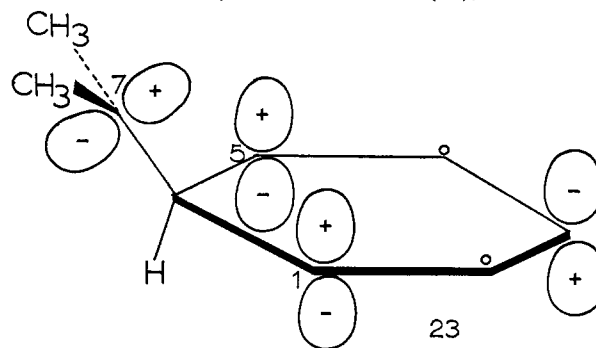
The simplest *formal* representation of the interconversion of the three tropilidenes **4**, **7**, and **8** is one in which C-1 and C-6 of **4** are joined, and C-7 and its attached pair of methyl groups are allowed to wander over the quasi-toluene ring. Readdition at **a** leads to **4**, at **b** to **7**, and at **c** to **8**. This preserves the sequential arrangement of C-1–C-6 required by the experimental observations.

One cannot yet eliminate rigorously the possibility that the detailed mechanism of this process may actually involve an intermediate in which *both* isopropylidene ring bonds are weakened (for example, some kind of complex between dimethylcarbene and the aromatic ring) rather than the succession of interconverting norcaradienes shown in Scheme I. In this connection, Woods¹¹ has considered and ruled out the possibility that the tropilidene \rightarrow toluene aromatization may involve dissociation to benzene and CH_2 followed by C–H insertion. It seems clear that the $4 \rightarrow 7$ and **8** reaction does not involve *free* dimethylcarbene, since propylene should then have been a side product.²⁴

Presently, no experimental basis is available for deciding whether the interconversions of Scheme I proceed *via* diradical intermediates, e.g., **22**, or by *concerted* 1,5-carbon shifts without intermediates. The latter kind of process is permitted (but not re-



quired) by considerations of orbital symmetry,²⁵ since the highest occupied molecular orbital of pentadienyl radical, an electronic model of the conjugated system in the transition state, has two nodes (**23**), and the mi-



(24) Cf. W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964, p 47 ff.

(25) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 2511 (1965).

grating carbon presumably must stay on a given side of the six-membered ring. Concerted migration of C-7 from C-1 to C-5 requires, however, that the new bond C-5-C-7 be formed on the *same face* of C-7 as was originally bonded to C-1. In principle, this is experimentally distinguishable from bonding to the opposite face and from a two-step diradical mechanism (*via* intermediates like **22**) by an examination of the rearrangements of appropriately substituted optically active tropilidene derivatives. This experiment is now in progress.²⁶

Experimental Section²⁷

Pyrolyses were carried out in sealed Pyrex tubes of 150-ml capacity. Before charging, the tube was washed with concentrated ammonia water, rinsed thoroughly with distilled water, and dried in an oven. In a typical run, a sample of 750 μ l was placed in the vessel which was then cooled, evacuated to 10^{-4} mm, and sealed. This was heated in a furnace at $300 \pm 5^\circ$ for 40 min. The contents was then collected by removing the vessel from the furnace, immersing a narrow end in liquid nitrogen, and driving any material from the walls with a heat gun.

Analysis of the bomb contents was carried out by vapor phase chromatography on two columns.

Column A (4.5 m \times 5 mm UCON-HB-2000, 20% on hexamethyldisilazane-treated 60-80 mesh Chromosorb P) was used at 140° and a 100-150-ml/min helium flow. This showed peaks with retention times of 14.4, 15.8, 19.5, 20.2, and 21.8 min. These were identified by collection as (1) mixture, (2) 3-isopropenyl-1-methyl-1,4-cyclohexadiene (**9**), (3) *m*-cymene, (4) *p*-cymene, and (5) 1,7,7-trimethyltropilidene (**8**).

Column B (10 m \times 5 mm tricyanoethoxypropane (TCEP) on 60-80 mesh Chromosorb P) was used at 130° and a 60-ml/min helium flow. This separated peak 1 from the A separation into three components: (6) 6-isopropenyl-1-methyl-1,4-cyclohexadiene (**10**), (7) 2,7,7-trimethyltropilidene (**7**), and (8) 3,7,7-trimethyltropilidene (**4**). These had retention times of 20.6, 21.4, and 22.2 min. In addition, several small peaks totaling less than 2% of the reaction mixture were not further investigated. The composition of the pyrolysis mixture from this run was 35% **4**, 25% **7**, 2% **8**, 20% **9**, 16% **10**, and 2% each of *m*- and *p*-cymene.

The collection was facilitated by decreasing the carrier gas flow rate during emergence of a peak. In most cases, two passes sufficed to produce a component with less than 1% contamination. In the case of 2,7,7-trimethyltropilidene (**7**), however, which stubbornly emerged as an "inside" peak (closely surrounded) on both columns, purification beyond about 85% homogeneity was difficult. The only contaminant in this sample was the immediate gas chromatographic neighbor **4**, the presence of which was easily recognized by its retention time and its nmr spectrum, in which the lone methyl absorption occurs about 0.1 ppm downfield from that of **7**.

The nmr and ultraviolet spectra of compounds **4**, **7**, and **8** are given in Tables I and II. The nmr spectra of **9** and **10** are as described in the text. Both of these compounds showed only end absorption in the ultraviolet. Microanalytical data for all the new compounds are given in Table VI.

m-Cymene (**5**) was identified by comparisons of infrared, ultraviolet, and mass spectra with those (no. 1641, 535, and 461) of an authentic sample.²⁸ *p*-Cymene (**6**) was identified by gas chro-

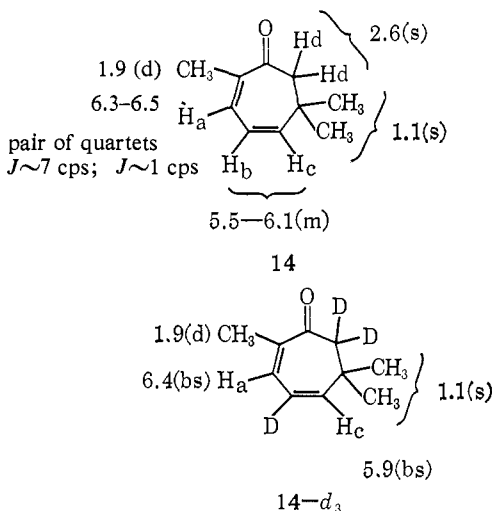
Table VI. Microanalytical Data for New C₁₀H₁₄ Hydrocarbons

Compd	C, %	H, %
C ₁₀ H ₁₄ (calcd)	89.49	10.51
7	89.15	10.70
8	89.49	10.50
9	89.25	10.26
10	89.16	10.70

matographic retention time and infrared, ultraviolet, mass, and nmr spectral comparisons with those of a gas chromatographically purified sample prepared from a commercial product (Eastman practical grade).

The mass spectra of all the C₁₀H₁₄ isomers show medium to strong parent peaks at *m/e* 134. The base peak occurs at 119 (*M* - 15) for all three tropilidenes (**4**, **7**, and **8**) and the other strong peak in these three spectra is at *m/e* 91 (*M* - 43). The *M* - 15 peak is also strong in the dideuterated tropilidenes (*m/e* 121) and is apparently due to loss of methyl from the parent ion. The *M* - 43 peak is empirically accounted for by loss of isopropyl from the parent ion, but the mechanism of its formation is presently unknown. Strong parent, *M* - 15, and *M* - 43 peaks are also present in the mass spectra of *m*-cymene, *p*-cymene, and the two cyclohexadienes **9** and **10**.

The nmr spectrum of eucarvone (**14**)¹⁹ shows the proper intensity ratios for the indicated structure. The description and interpretation of the spectrum is given in the formulas. The spectrum in the olefinic region of **14-d₃** strongly suggests that H_a and H_c remain while H_b is replaced by D. Thus had H_a been replaced, the allylic methyl doublet probably would have collapsed to a singlet. Had H_c been replaced, H_a would have been a multiplet. The intensity of the H_a signal in **14-d₃** indicates that deuteration at the α -carbonyl position is about 95% complete.



1,5-Dideuterio-3,7,7-trimethyltropilidene (4-d₂) was prepared by lithium aluminum hydride reduction of eucarvone-d₃ (**7** g) followed by distillation of the crude alcohol from 20 μ l of concentrated sulfuric acid under water pump vacuum at a bath temperature of 120° . Drying and redistillation gave 2.5 g of pure **4-d₂**, bp $63-65^\circ$ (25 mm). The mass spectrum indicated the composition 85.4% *d₂*, 10.6% *d₁*, and 4.0% *d₀* species.

Pyrolysis of **4-d₂** and isolation of the products was carried out as for **4**. The nmr spectra of the products are recorded in Tables III-V.

The infrared spectra show striking differences in the fingerprint region from those of the undeuterated materials. A very strong band in the long wavelength region for **4**, **7**, and **8** occurs at 720, 715, and 705 cm^{-1} , respectively. In addition, each of these compounds shows a medium intensity band, which occurs at 750, 765, and 780 cm^{-1} , respectively. In the dideuterated series these bands are absent in all of the compounds, which now show medium intensity bands in the 630-680- cm^{-1} region. Compound **9** shows a strong band at 680 and medium bands at 855 and 925 cm^{-1} , while **9-d₂** shows only a weak absorption at 925 cm^{-1} . Compound **10** shows a strong band at 680 and medium intensity bands at 715,

(26) (a) That "all-carbon" rearrangement of norcaradienes can occur independent of a hydrogen-transfer mechanism is indicated by the thermal interconversions of 1-, 2-, and 3-methyl-7,7-dicyanonorcaradienes;^{26b} (b) J. A. Berson, P. W. Grubb, R. A. Clark, and M. R. Willcott, III, unpublished observations.

(27) Infrared spectra of neat samples were obtained with a Beckman IR-8 spectrometer. Ultraviolet spectra (Table I) of solutions in solvent 95% ethanol were determined with a Cary Model 15 spectrophotometer. Nmr spectra (Tables II-IV) of carbon tetrachloride solutions with tetramethylsilane as internal reference were obtained with a Varian A-60 instrument. Chemical shifts are given in ppm downfield. Mass spectra were obtained with a Consolidated Engineering Co. Model 21-103C instrument. We are indebted to Professor Paul Bender for advice on its use. Gas chromatographic analyses were carried out with Wilkens Aerograph A-90 and Hy-Fi instruments. Microanalyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich.

(28) Catalogs of Infrared Spectrograms, Ultraviolet Absorption Spectrograms, and Mass Spectral Data, American Petroleum Institute Research Project 44, Carnegie Institute of Technology, Pittsburgh, Pa.

842, and 950 cm^{-1} , while **10-d₂** shows a strong band at 630 and medium intensity bands at 830 and 925 cm^{-1} . All of the cyclohexadienes, deuterated and undeuterated, show a medium intensity band at 1640 ($\text{C}=\text{C}$ stretching), a strong band at 890 ($=\text{CH}_2$ hydrogen deformation), and a richly detailed series of eight or nine well-resolved bands in the 3000- cm^{-1} region ($\text{C}-\text{H}$ stretching).

Compounds **7-d₂** and **8-d₂** isolated from pyrolysis were analyzed mass spectrometrically and showed the compositions 85.5 and 82.7% *d*₂, 11.2 and 13.4% *d*₁, and 3.4 and 4.0% *d*₀, respectively.

Pyrolyses of **7-d₂** or **10-d₂** regenerated **4-d₂**, isolated and identified by its nmr and infrared spectra. The other six pyrolysis products corresponded in gas chromatographic retention times to those obtained from **4**.

Conversion of **9** to *m*-cymene and **10** to *p*-cymene was effected as follows. A solution of 20 μl (18 mg) of **9** in 5 ml of dioxane con-

taining a suspension of 15 mg of 5% palladium-on-calcium carbonate was stirred under hydrogen in a quantitative microhydrogenation apparatus until 1.2 molar equiv of gas had been absorbed. The catalyst was filtered off, and the solution was treated with 17 mg of tetracyanoethylene. After 6 hr vapor chromatographic analysis showed 50% conversion to *m*-cymene. Five milliliters of water was added, the mixture was extracted with pentane, and the pentane layer was dried and carefully concentrated to a volume of 400 μl with an efficient fractionating column. The residue was preparatively vapor chromatographed to give 4.5 μl of *m*-cymene, identified by its retention time and infrared spectrum.

Similarly, 25 μl of crude **10** (containing 20% of **7**) gave a 20% conversion to *o*-cymene, isolated (2 μl) and identified by comparison of its infrared and ultraviolet spectra with those of authentic materials (ref 27, no. 1640 and 534).

Ketimine Intermediates in Amine-Catalyzed Enolization of Acetone^{1a}

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Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. Received January 14, 1966

Abstract: Catalysis of the enolization of acetone by amines was followed by determining iodination or deuterium exchange of the ketone. Catalysis by free amine, ammonium ion, and the product of amine and ammonium ion was found. Enolizations catalyzed by a series of (free) amines fit the Brønsted relationship between $\log k$ and $\text{p}K_a$ established for the base-catalyzed enolization of acetone by carboxylate anions and pyridine derivatives. The ammonium ion catalyzed enolizations do not fit the Brønsted relationship for catalysis by carboxylic acids, deviating by as much as 10^6 . The conjugate acids of primary and secondary but not tertiary amines show this catalysis. It is suggested that the latter reactions proceed *via* the formation of a protonated ketimine (Schiff base) which then undergoes proton abstraction to give an enamine. This hypothesis is supported by the variation of the enolization rate constant with varying ratios of amine/ammonium ion. The hypothesis is further supported by the observation of kinetic terms involving an acid-base pair, the acid component of which is an ammonium ion. The ammonium ion catalyzed enolization by glycine is kinetically no better than that by methylamine, indicating that intramolecular catalysis by the internal carboxylate ion in the protonated Schiff base formed from glycine and acetone does not occur. The failure to observe such a reaction may be explained by the low value of the Brønsted β for the removal of a proton from protonated Schiff bases. The relative rates of enolization of protonated acetone, the protonated ketimine of acetone, and acetone are 10^{11} , 10^8 , and 1, respectively. From the composite of two model systems, a calculation has been made indicating that an intramolecular catalysis of the enolization of a protonated ketimine intermediate will account for the enolization rate constant in catalyses by the enzyme aldolase.

The enzyme aldolase catalyzes the reaction between fructose 1-phosphate and glyceraldehyde plus dihydroxyacetone phosphate. Likewise, transaldolase catalyzes the transfer of a dihydroxyacetone molecule from one acceptor to another. A ketimine (Schiff base) formed from dihydroxyacetone and enzyme has been implicated in the mechanism of both these enzymatic catalyses, by experiments on the inactivation of the enzyme-substrate compound with sodium borohydride and isolation of the lysine derivative, $(\text{CH}_2\text{OH})_2\text{CHNH}-\text{lysine}$.^{2,3} These enzymatic results have been interpreted to mean that the chemical steps in the aldolase reaction, starting with dihydroxyacetone phosphate, include: (1) ketimine formation, (2) enolization of the ketimine (enamine formation), and (3) condensation of enamine with glyceraldehyde 1-phosphate to

give an enamine of the product. The isolation of a compound related to a ketimine does not, of course, prove that the ketimine is part of the catalytic pathway.

Aldimines and ketimines have been postulated as reaction intermediates in a number of reactions, including condensation and decarboxylation reactions. As a model for possible ketimine formation in the enzymatic catalytic pathway, we have investigated the enolization of acetone in the presence of amines. Some of these amines contain no other groups. Other amines such as glycine contain in addition to the amino group a secondary base, such as the carboxylate ion, which could serve as an intramolecular general basic catalyst of enolization after ketimine formation. Alternatively, the bifunctional amine could react with acetone to form a tetrahedral adduct such as a carbinolamine which then would undergo intramolecular general basic catalysis. Suggestions that the latter pathway is operative in the enolization of acetone in the presence of various amino acids has been made recently.⁴ It is the purpose of this paper to determine

(1) (a) This research was supported by a grant from the National Science Foundation; (b) University of Oxford, Oxford, England.

(2) B. L. Horecker in "Comprehensive Biochemistry," Vol. 15, M. Florkin and E. H. Stotz, Ed., Elsevier Publishing Co., New York, N. Y., 1964, p 48.

(3) J. C. Speck, Jr., P. T. Rowley, and B. L. Horecker, *J. Am. Chem. Soc.*, **85**, 1012 (1963).