

due to the coupling through nitrogen. This assignment is further confirmed by the large splitting of the  $C_{2,6}$  peak of **3** (12 Hz) where  ${}^3J(C_2-H_6)$  is the only three-bond coupling involved. This enhancement by nitrogen is interesting because it makes a sharp contrast with  ${}^1H-{}^1H$  coupling through nitrogen in pyridine. Thus,  ${}^4J(H_2-H_6)$  is less than one-tenth of  ${}^4J(H_2-H_4)$  or  ${}^4J(H_3-H_5)$ .<sup>8,9</sup>  ${}^3J(C_2-H_4)$  of **2** is small as a three-bond coupling (4 Hz). Any  ${}^3J$  through the substituted carbon (the carbon carrying the cyano group) is generally small. Thus,  $C_4$ , peak c, is a quartet with one normal and one small  ${}^3J$ , i.e.,  ${}^3J(C_4-H_6)$  (6 Hz) and  ${}^3J(C_4-H_2)$  (4 Hz). Although no three-bond coupling is involved, the splitting of the  $C_5$  peak is very large (9 Hz). This should either be  ${}^2J(C_5-H_6)$  or  ${}^2J(C_5-H_4)$ . The last interpretation is incompatible with a very small  ${}^2J$  such as  ${}^2J(C_4-H_5)$  or  ${}^2J(C_4-H_3)$ . If the analogy between  ${}^2J(C-H)$  and  ${}^2J(H-H)$  is taken for granted,<sup>10</sup>  ${}^2J(C_5-H_6)$ , a two-bond coupling constant between  ${}^{13}C$  and  ${}^1H$  adjacent to  $sp^2$ -hybridized nitrogen, can be very large as is  ${}^{gem}J(H-H)$  for the  $H_2C=NR$  system.<sup>11</sup> This large two-bond coupling is characteristic for all pyridine derivatives and has some diagnostic value.<sup>12</sup>

These observations can be summarized as below. (i)  ${}^3J$  is normally in the range of 5–8 Hz; the coupling through nitrogen is enhanced to 12–13 Hz, and the one through the substituted carbon is reduced to 3–5 Hz. (ii)  ${}^2J$  is normally in the range of 1–4 Hz; the coupling between  ${}^{13}C$  and the proton adjacent to nitrogen is remarkably enhanced to 8–9 Hz. (iii)  ${}^4J$  is not larger than 2 Hz.

The multiplets observed for **1** and **3** are interpretable with the aid of these criteria. In Figure 2, a part of the uncoupled spectrum of **1** is reproduced. In this spectrum, the resolution is so good that a number of the small four-bond couplings ( ${}^4J = 1$  Hz) are easily resolved. Here again,  ${}^2J$  with the proton adjacent to nitrogen and  ${}^3J$  through nitrogen are enhanced while other  ${}^2J$  and  ${}^3J$  values are within the range of normal values. Much the same is true for **3**. Thus, both  $C_{2,6}$  and  $C_{3,5}$  signals consist of a pair ( ${}^1J$ ) of a doublet of doublet ( ${}^2J$  and  ${}^3J$ ), while both  $C_4$  and  $C_{CN}$  signals are a triplet (two  ${}^3J$ ).

Previously the assignment of signals of  ${}^{13}C$  spectra of substituted pyridines<sup>5</sup> (and any other aromatic and heteroaromatic compounds) was made by the additivity principle, i.e., by the comparison of observed shifts with those estimated from the appropriate substituent parameters (obtained from  ${}^{13}C$  spectra of monosubstituted benzenes). With this, however, there often remains some uncertainty in the assignment when the estimated (hence observed) chemical shifts are close. In fact such is the case with  $C_3$  and  $C_5$  for **1**, and  $C_2$  and  $C_6$  for **2**. Our assignment based on the coupling constants is unequivocal and completely free from such an ambiguity. We believe that the long-range  ${}^{13}C-{}^1H$  coupling constants are very valuable as a means for the

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structure determination of organic compounds and as the touchstone of the theory of coupling constants.<sup>13</sup>

**Acknowledgment.** We thank Professor A. R. Katritzky and the University of East Anglia for the use of the instrument.

(13) NOTE ADDED IN PROOF. M. Hansen and H. J. Jacobsen (*J. Magn. Resonance*, **10**, 74 (1973)) measured narrow-range proton-noise uncoupled spectra of pyridine and 2-bromopyridine, and determined long-range coupling constants from complete iterative computer analysis. Our values are in good agreement with theirs.

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### Stereochemistry of the Solvolysis of Menthyl Tosylate. An Example of Retained Chair Conformation in the Transition State<sup>1</sup>

Sir:

We wish to report that the solvolysis of menthyl tosylate (**1**-OTs) in both aqueous ethanol (E) and aqueous trifluoroethanol (T) gives hydroxylic substitution products of predominantly retained configuration (58% in E, 83% in T). This result and the observed significantly reduced  $\beta,\beta'$ - $d_3$  isotope effect ( $k_H/k_D = 1.30$ ), which contradict the expected behavior of most cyclohexyl derivatives,<sup>2-6</sup> suggest a retained chair conformation in the rate-determining transition state and the intermediate ion pair(s).

Conformational rigidity has been proposed by Winstein and Holness<sup>7</sup> for transition states in solvolyses of both *cis*- and *trans*-4-*tert*-butylcyclohexyl tosylates. However, in a recent study, Lambert, *et al.*,<sup>8</sup> found that the product distribution in the solvolysis of the unsubstituted conformationally flexible cyclohexyl tosylate is essentially identical with that from the supposedly rigid *trans*-4-*tert*-butylcyclohexyl tosylate. Doubts about the generality of the Winstein and Holness<sup>8</sup> assumption have been repeatedly expressed in the past, but satisfactory explanations were not given.<sup>9,10</sup> Half-chair transition states in solvolyses of uncomplicated

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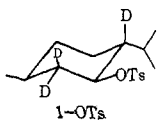
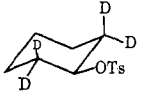
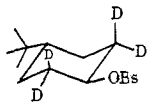
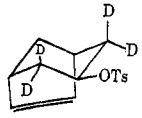
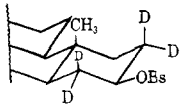
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Table I. Reaction Rates and  $\beta$ -Deuterium Isotope Effects in Solvolyses of Some Cyclohexyl Derivatives

Compound	Solvent <sup>a</sup>	Temp, °C	$10^5 k_H \text{ sec}^{-1b}$	$k_H/k_{D_3}^b$	Ref
 1-OTs	97 T	45	5.52 (2)	1.27 (1) <sup>c</sup>	This work
	70 T	45	7.29 (3)	1.30 (2) <sup>c</sup>	
	AcOH	50	23.9	2.34	2
	50 E	35	3.57	2.425	3
	AcOH	76	0.14	2.16	4
	96 E	60	2.67 (3)	1.29 (2)	5

<sup>a</sup> T = 2,2,2-trifluoroethanol-H<sub>2</sub>O (wt %); E = EtOH-H<sub>2</sub>O (vol %). <sup>b</sup> Uncertainties are given as standard errors; e.g., 5.52 (2) = 5.52 ± 0.02. <sup>c</sup>  $k_H/k_{D_3}$ .

cyclohexyl substrates which facilitate nucleophilic solvent participation have been explicitly proposed by Nordlander.<sup>11</sup> This also seems to be the case in the solvolysis of *trans*-4-*tert*-butylcyclohexyl brosylate as suggested by Shiner and Jewett<sup>3</sup> on the basis of isotope effect studies. Similar conclusions were also reached by others.<sup>6, 10b, 12</sup>

The strong conformational dependence of hyperconjugation<sup>13</sup> which can be best demonstrated by  $\beta$ -secondary deuterium isotope effects<sup>14</sup> and the conformational rigidity of 1-OH<sup>15</sup> makes 1-OTs a good model for stereochemical studies of cyclohexyl solvolysis transition states. The relevant kinetic data are presented in Table I.

Only 3-cholestanyl brosylate<sup>5</sup> shows a similarly small isotope effect as 1-OTs. In all other cases known to us<sup>2-6</sup> (only a few examples are given in Table I)  $\beta$ -effects have been considerably larger. Analyzing the  $\beta$ -effects under the assumption that one hydrogen cis or trans to the leaving group gives rise to an isotope effect of 1.20–1.27<sup>2, 3, 5</sup> and since these effects in the absence of 1,2-hydrogen shifts are cumulative the  $\beta, \beta'$ - $d_3$  effects in 1-OTs should be 1.73–2.04. By taking into account a 1,2-hydrogen shift, as in *cis*-4-*tert*-butylcyclohexyl brosylate,<sup>3</sup> the calculated effect should be  $(2.2) \times (1.07) \times (0.96) = 2.25$ . Since these large effects are best interpreted in terms of a rate determining

hydrogen participation<sup>16</sup> and/or elimination<sup>17</sup> (in addition to hyperconjugation<sup>3</sup>), the significantly smaller effect with 1-OTs is indicative of a chair-like conformation in the transition state. Only in this case are the two axial deuteriums oriented properly for hyperconjugative interaction with the reactive center, but due to an equatorial leaving group unable to participate in the rate-determining step. The resulting effect should be approximately  $(1.20)^2$ , i.e., 1.44. A reduction of this value to the observed magnitude of 1.30 is then probably caused by the inductive effect of the remaining equatorial deuterium atom.<sup>3</sup> An O-S fission in the rate-determining step can be ruled out on the basis of the observed  $\alpha$ -isotope effect ( $k_H/k_D = 1.17$ , 45°, 70 T).

A hydrogen shift cannot be excluded in some of the later steps, but this process cannot contribute significantly in our case as shown by the small amount of the rearranged alcohol among the products.

Further support for a chair-like conformation for the transition state and the subsequently formed intermediate ion pair(s) was obtained from the analysis of the solvolysis products (Table II).<sup>18</sup>

The amount of the substitution product with retained configuration, i.e., menthol, is by far greater than with most other substituted cyclohexyl derivatives<sup>7, 8, 11, 12</sup> and even exceeds (in trifluoroethanol) the stereochemical

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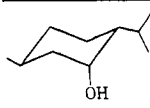
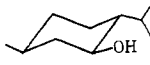

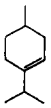
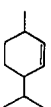
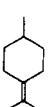
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**Table II.** Product Composition in Solvolysis of Menthyl Tosylate (1-OTs)

Products (mol %) <sup>b</sup>	—Reaction conditions <sup>a</sup> —	
	70 T, 45°	70 E, 70°
	3	13
	30	22
	3 <sup>c</sup>	3 <sup>c</sup>
	27	37
	12	13
	4	0
Ethers	21	12

<sup>a</sup> Initial concentrations 0.06–0.08 mol/l., buffered with 1 equiv of 2,6-lutidine. <sup>b</sup> Rounded off average values of two independent experiments with five–six glc analyses of each product mixture. All products were shown to be stable under the reaction conditions. <sup>c</sup> Stereochemistry at the tertiary carbon atom has not yet been established.

outcome of 2-adamantyl tosylate solvolysis.<sup>19,20</sup> In analogy to adamantyl tosylate front side displacement from the solvent separated ion pair seems to be the preferred substitution path because of the steric hindrance to solvent approach from the rear.<sup>23</sup> This hindrance is apparently operative for the chair-like conformation of the intermediate but not for the half-chair transition state in which nucleophilic solvent participation is facilitated.<sup>11</sup> The necessary condition for the occurrence of this chair-like transition state is in our opinion the presence of substituent(s) in such positions which greatly hinder the formation of bent chair ( $C_2$  symmetry) or half-chair ( $C_s$  symmetry) transition states.<sup>24</sup> These requirements are best met by two bulky equatorial substituents in positions 2,5 and 2,4 relative to the reacting center. With such an arrangement at least one substituent has to assume the unfavorable pseudoequatorial or pseudoaxial orientation if  $C_2$  or  $C_s$  conformations are to be formed. The re-

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sulting nonbonded interactions render this geometry less favorable than a front side displacement on the unperturbed chair form.<sup>25</sup> One substituent cannot prevent distortions of the chair conformation in the transition state as demonstrated in the case of 4-*tert*-butylcyclohexyl derivatives.<sup>3</sup>

**Acknowledgments.** We thank Professor V. J. Shiner, Jr., for stimulating discussions. D. E. S. is grateful for the hospitality of the Department of Chemistry, Indiana University, Bloomington, Ind., in the course of this work.

(25) This might also explain why 1-OTs is, under identical conditions, about 50 times less reactive than cyclohexyl tosylate.

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### Reaction of Diiron Nonacarbonyl with Stereochemically Fixed Divinylcyclopropyl Systems in Norcaradienes

Sir:

Recently several examples of the reaction of diiron nonacarbonyl with various cisoid divinylcyclopropyl systems have been reported.<sup>1</sup> The products are either  $\sigma$ - $\pi$ -allyl complexes or may be considered as resulting from initial formation of such an intermediate.

One example of the behavior of a transoid divinylcyclopropyl system with  $Fe_2(CO)_9$  has been reported; namely, spiro[2,4]hepta-4,6-diene yields 6-methylfulvene diiron hexacarbonyl and an iron tricarbonyl complex of the starting diene.<sup>2</sup>

In order to contrast the behavior of cisoid relative to transoid divinylcyclopropyl systems, the reaction of spironorcaradienes with  $Fe_2(CO)_9$  is particularly relevant because they possess both systems within the same molecule.

Accordingly, the reaction of spiro[2,4-cyclopentadiene-1,7'-norcaradiene-2',4'-diene] (4)<sup>3</sup> and spiro[2,4-cyclopentadiene-2',5'-dimethyl-1,7'-norcaradiene-2',4'-diene] (5)<sup>4</sup> with  $Fe_2(CO)_9$  under various conditions was carried out. The products obtained are as shown in Scheme I.

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(4) Compound 5 is a new compound preparation by the irradiation (medium-pressure 450-W Hanovia mercury lamp) of diazocyclopentadiene in *p*-xylene for 4 hr. It is a low melting yellow crystalline solid which decomposes upon exposure to air: nmr ( $CDCl_3$ ,  $\delta$  ppm) 1.92 (s, 6 H,  $CH_3$ 's), 3.07 (s, 2 H, cyclopropyl protons), 5.81 (s, cyclohexadiene protons), 6.09 (m, 2 H, cyclopentadiene  $\alpha$ -protons), 6.39 (m, 2 H, cyclopentadiene  $\beta$ -protons). Synthesis of 4 and 5 is extremely dangerous. A serious explosion occurred in the distillation at 27° (0.25 mm) of diazocyclopentadiene.