

The mass spectrum of I was remarkable in the relative intensity of the parent/base peak at  $m/e$  240. Besides the  $C_{18}H_{23}^+$  peak (39%), the next most intense fragmentation peak at  $m/e$  91 ( $C_7H_7^+$ ) was only 9% of the base! This pronounced resistance toward fragmentation is a characteristic of adamantanoid molecules.<sup>3,10,11</sup> Besides the usual 2900- and 1450- $cm^{-1}$  hydrocarbon bands, there are only six other peaks of moderately weak intensity in the infrared spectrum of I. This is consistent with a structure of high symmetry, such as I (point group  $C_{2v}$ ).

Four separate resonances are observed in the 100-MHz nmr spectrum of I (Figure 1) at 1.82 (area 2), 1.65 (16), 1.40 (2), and 1.24 ppm (4). When it is recalled that adamantane (II) (CH protons at 1.88 and  $CH_2$  protons at 1.78 ppm)<sup>12</sup> and diamantane (III) (all three kinds of protons at  $\delta = 1.68$  ppm)<sup>3</sup> give essentially a single line in the nmr, the multiplicity of bands displayed by I seems surprising, despite the eight different kinds of protons in the molecule. However, II and III are poor models for I, since the structure of the latter alone is "folded back" upon itself and C-C bond anisotropies can produce chemical shift differences. As shown in VII, a 1-ethyl group in adamantane shields the adjacent methylene groups and deshields the bridgehead protons.<sup>12</sup>

The methylene groups marked a in Ic should mutually shield one another. They have no counterpart in II or III, but are analogous to the indicated ring methylenes in VII. The observed shielding effect of signal a in Figure 1 is 0.41 ppm, measured from the resonance of the main body of protons, c. The methylene groups a (Ic) are unique in that there is but one adjacent proton. A doublet with area four and coupling constant  $2.6 \pm 0.2$  Hz<sup>12</sup> would be predicted for their resonance, and this is exactly what is found.

The bridgehead protons marked d should be deshielded by the presence of the third adamantanoid ring (compare VII). The observed magnitude of this deshielding is 0.17 ppm (d, Figure 1). Bridgehead proton resonances in adamantane appear as featureless, broad ( $w_h = ca. 10$  Hz) bands.<sup>12</sup> Because of the six adjacent hydrogens, the same appearance would be expected for the protons d, as found. The area measurement (two protons) also corresponds. More direct confirmation of the assignments of a and d was achieved by spin-decoupling experiments. Irradiation of resonance d collapses resonance a to a singlet. In addition, the two downfield peaks of the large c absorption are also collapsed, suggesting that the eight protons (labeled c' in Ic) are responsible for this feature. Irradiation of a does not affect b.

The two bridgeheads b (Ic) have no counterpart in II or III, and they can be considered to be centrally a part of the two diamantane systems which comprise I (compare Ic and III). Since a bridgehead proton in adamantane (1.88 ppm) shifts upward in going to diamantane (1.68 ppm) by 0.20 ppm, there should be a comparable shift of protons b in Ic. The shift to higher fields of resonance b (Figure 1) (area two protons) is 0.18 ppm, consistent with the assignment proposed. Further, the breadth of this band ( $w_h = ca. 5$  Hz)

(11) Z. Dolejšek, S. Hála, V. Hanuš, and S. Landa, *Collection Czech. Chem. Commun.*, **31**, 435 (1966).

(12) R. C. Fort, Jr., and P. von R. Schleyer, *J. Org. Chem.*, **30**, 789 (1965).

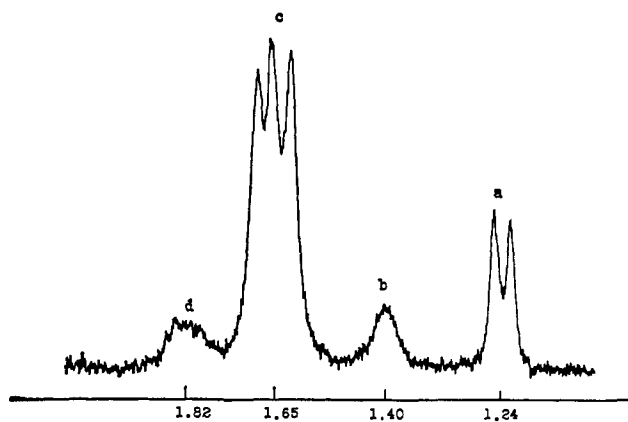


Figure 1. The 100-MHz nmr spectrum of triamantane (I); solvent  $CDCl_3$ ,  $\delta$  in parts per million from tetramethylsilane.

is smaller than that generally found for bridgehead resonances, but this is because protons b have only two adjacent neighbors each, and a narrower line than that from protons d is observed.

The mode of preparation employed would be expected<sup>2,3,8-10,13</sup> to lead to the thermodynamically most stable  $C_{18}H_{24}$  isomer. Triamantane (I) is that molecule. All of the spectral properties of the substance obtained are in complete agreement with those expected of triamantane, although the information supplied is not really sufficiently detailed to establish the structure with absolute certainty. Accordingly, we have submitted the material for X-ray analysis. Nevertheless, we regard the degree of uncertainty in the structural assignment at present to be so low as to warrant our claim of synthesis of triamantane.

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(13) P. von R. Schleyer, G. J. Gleicher, and C. A. Cupas, *ibid.*, **31**, 2014 (1966).

(14) National Science Foundation Undergraduate Research Participant, summer 1965.

(15) Alfred P. Sloan Foundation Fellow, 1962-1966.

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

Van Zandt Williams, Jr.,<sup>9,14</sup> Paul von Ragué Schleyer<sup>15</sup>  
Gerald Jay Gleicher, Lynn B. Rodewald<sup>16</sup>

Department of Chemistry, Princeton University  
Princeton, New Jersey 08540

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### Vinyl Proton Abstraction during Base-Catalyzed Exchange of 2,3-Dihydrothiophene 1,1-Dioxide

Sir:

The role of carbanionic intermediates in base-catalyzed tautomerism of allylic systems is an area of high

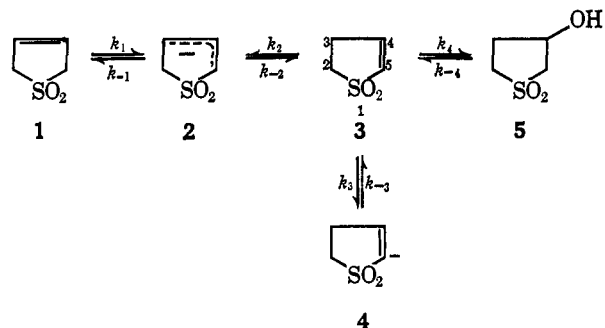


Figure 1.

current interest.<sup>1-5</sup> Previous studies with unsaturated sulfoxides<sup>6</sup> and ethers<sup>7</sup> have shown that relative reactivities cannot be related to the ground-state stabilities of the isomers involved.

In a continuation of these studies, deuterium exchange of the unsaturated cyclic sulfones (**1** and **3**) shown in Figure 1 has now been examined. The establishment of the relative rate values as  $k_1 > k_2$  and  $k_{-1} > k_{-2}$  and the relative ground-state energies as **1** > **3** is discussed below; however, the surprising feature arising from this work concerns the strong evidence for rapid proton abstraction at the vinylic 5 position of 2,3-dihydrothiophene 1,1-dioxide (**3**).

The unsaturated sulfone **1** (2,5-dihydrothiophene 1,1-dioxide) is commercially available.<sup>8</sup> Isomer **3** was obtained by liquid chromatography<sup>9</sup> of a mixture of **1** and **3** produced by heating a basic solution of **1** to 50° for 30 min followed by extraction of the sulfolenone<sup>10</sup> isomers with chloroform. This operation gives a rather clean separation of **1** and **3** from the Michael addition product, 2,3,5-trihydro-4-hydroxythiophene 1,1-dioxide (compound **5** in Figure 1).

The nmr spectrum of **3** in D<sub>2</sub>O shows multiplets centered at 7.55, 7.3, 3.8, and 3.45 ppm downfield from an external tetramethylsilane standard in a ratio of 1:1:2:2. These signals can be assigned to the 4, 5, 2, and 3 positions, respectively, based on the splitting pattern of an approximate ABR<sub>2</sub>X<sub>2</sub> system with  $J_{2,4}$  and  $J_{2,5} \approx 0$ . Recording the nmr spectrum of **3** after 22 min in -OD-D<sub>2</sub>O at room temperature shows the relative areas to be 1.0:0.08:2.04:2.0 in the order given. Additionally, a singlet at 6.6 ppm (see nmr discussion of **1** below) with a relative area of 0.014 is observed. These observations then clearly show that deuterium exchange at the vinylic 5 position is rapid relative to exchange at the allylic 3 position.<sup>11</sup> After 67 min the

relative areas of these signals are 1.0 (7.55 ppm), ~0 (7.3 ppm), 0.46 (6.6 ppm), 2.0 (3.8 ppm), and 2.08 (3.45 ppm).

Systems have been reported<sup>2</sup> previously in which vinylic exchange was rapid compared to allylic; however, in those cases it was proposed that rapidly reversible Michael addition accounted for this observation. This explanation, if extended to the present system, would require that the steps shown as  $k_4$  and  $k_{-4}$  be rapid compared to proton abstraction at the allylic position, *i.e.*,  $k_2$ . Strong evidence has been obtained that formation of **5**, while occurring,<sup>12</sup> is slow relative to the proton exchange reactions shown in Figure 1. Perhaps the most simple and direct observation bearing on the question of rapid reversibility is the failure of alcohol **5** to regenerate sulfolenone **3** under the exchange reaction conditions. Thus, the alcoholic product was isolated from a reaction conducted at 50° and subjected to exchange conditions. No evidence for the formation of **3** was obtained, indicating that the addition reaction is slowly reversible or irreversible. One is then left with the conclusion that the rapid exchange at the vinylic position of **3** is due to a simple vinyl proton abstraction mechanism ( $k_3/k_{-3}$  of Figure 1).

As mentioned in the opening statement, relative rates have been established as  $k_{-1} > k_{-2}$ ;  $k_1 > k_2$ . Also good evidence has been obtained that an equilibrium mixture of these isomers consists of ~42% **1** and ~58% **3**. Deuterium exchange of **1** shows that  $k_{-1} > k_{-2}$ . Thus, the nmr spectrum of **1** in D<sub>2</sub>O shows singlets at 6.6 and 4.2 ppm in a ratio of 1:2 which can be assigned to the vinylic and allylic protons, respectively. Upon including potassium acid phthalate as an internal standard in an -OD-D<sub>2</sub>O solution of **1** and recording the spectrum after 10 min it was seen that the signal due to the allylic protons had decreased by ~95% while the vinylic signal had undergone essentially no diminution. This is clearly consistent with  $k_{-1} > k_{-2}$ , which conforms to the generalization that protonation occurs more rapidly at the allylic position adjacent to an electron-withdrawing substituent.<sup>6</sup>

To establish that  $k_1 > k_2$  a mixture<sup>13</sup> consisting of 38% **1** and 62% **3** was subjected to exchange conditions. It was found that the signal due to the allylic positions of **1** disappeared rapidly compared to the allylic position of **3**.

Equilibration in a system such as this can be approached if the interconversion of isomers is rapid compared to the removal of one of the isomers (removal in this case occurring by the Michael addition reaction). The data shown in Table I indicate that this situation prevails. Thus, an identical ratio of 1:3 is obtained from both sides of the equilibrium (compare entries 1-4 to entry 5) and a constant ratio of 1:3 is maintained with time as the total amount of **1** and **3** decreases through formation of alcohol **5**. These observations lend strong support to the conclusion that vinyl exchange of **3** must be accounted for by proton abstraction rather than rapid addition-elimination of deuterium oxide.

Factors which could enter into this inordinate reac-

(12) R. C. Krug and D. E. Boswell, *J. Org. Chem.*, **27**, 95 (1962), have reported an analogous alcoholic product formed by treatment of 3-methyl-2,3-dihydrothiophene 1,1-dioxide with base.

(13) Obtained as an intermediate liquid chromatographic cut during separation of **1** and **3**.

(1) (a) D. J. Cram and R. T. Uyeda, *J. Am. Chem. Soc.*, **84**, 4358 (1962); (b) D. J. Cram and R. T. Uyeda, *ibid.*, **86**, 5466 (1964); (c) D. J. Cram and R. D. Guthrie, *ibid.*, **87**, 397 (1965).

(2) J. Warkentin and L. K. M. Lam, *Can. J. Chem.*, **42**, 1676 (1964).

(3) G. Bergson, *Acta Chem. Scand.*, **17**, 2691 (1963).

(4) S. Bank, C. A. Rowe, Jr., and A. Schriesheim, *J. Am. Chem. Soc.*, **85**, 2115 (1963).

(5) For studies with dienes see R. B. Bates, R. H. Carnighan, and C. E. Staples, *ibid.*, **85**, 3032 (1963).

(6) D. E. O'Connor and C. D. Broaddus, *ibid.*, **86**, 2267 (1964).

(7) C. D. Broaddus, *ibid.*, **87**, 3706 (1965).

(8) Obtained from Shell Development Co.

(9) The mixture was chromatographed over silica gel using benzene-ether solutions as eluent.

(10) **1** will be referred to as  $\beta,\gamma$ -sulfolenone and **3** as  $\alpha,\beta$ -sulfolenone.

(11) The signal due to the 5 position has been reduced by 92% during a time interval in which 7%  $\beta,\gamma$ -sulfolenone (**1**) is formed, as evidenced by the singlet at 6.6 ppm. Since  $k_{-1} > k_{-2}$  and  $k_1 > k_2$  (see below), only the vinylic signal of  $\beta,\gamma$ -sulfolenone is observed.

**Table I.** Variation of Isomer Distribution<sup>a</sup> in Sodium Hydroxide Solution at 50°

Entry	Compd	Time, min	% 1	% 3	Wt 1 + 3 recovered, <sup>b</sup> g
1	1	10	43	57	1.7
2	1	20	41	59	1.4
3	1	40	43	57	1.2
4	1	60	41	59	1.0
5	3	15	41	59	0.8 <sup>c</sup>

<sup>a</sup> Analysis by integration of nmr curves. <sup>b</sup> Entries 1-4 were obtained by removing 10-ml aliquots from a solution of 10.0 g (0.085 mole) of  $\beta,\gamma$ -sulfolene in 47 ml of 2 *N* sodium hydroxide. The weights recorded are those of the chloroform extracts of these basic solutions. Combining the water layers of the four aliquots followed by treatment with dimethyl sulfate provided 5.7 g of ether arising from alcohol 5. These results account for 88% of the material used. <sup>c</sup> Recovered ~0.8 g of the sulfolene mixture from a run in which 1.0 g of 3 was used.

tivity are the inductive effect of the sulfone group, the state of hybridization of the carbon atom, and 3d-orbital stabilization of the transition state leading to 4. Since the 3d-orbital factor could also be operative, and possibly more effectively, in the transition state leading to the allylic species 2,<sup>14</sup> inductive and hybridization effects are favored as an explanation for the rapid vinyl proton abstraction.

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(14) H. P. Koch and W. Moffitt, *Trans. Faraday Soc.*, **47**, 7 (1951).

Charles D. Broaddus

The Procter & Gamble Company, Miami Valley Laboratories  
Cincinnati, Ohio 45239

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### Azoalkenes as Intermediate Compounds in the Formation of Osazones from $\alpha$ -Acetoxy Ketones

Sir:

The formation of phenylazoalkenes from the alkaline decomposition of phenyltosylhydrazones was reported in a recent paper<sup>1</sup> and the mechanism shown in Figure 1 (left) was suggested.<sup>1</sup>

This "push-pull" system can proceed in either direction; the treatment of the  $\alpha$ -acetoxy cyclohexanone phenylhydrazone (II; obtained from the reaction between  $\alpha$ -acetoxy cyclohexanone (III) and phenylhydrazine) with LiH in warm benzene leads to the formation within a few minutes of 1-(phenylazo)cyclohexene (I) in a quantitative yield (Figure 1, right). The formation of I from II occurs spontaneously, even in the cold. If II is dissolved in methanol or another solvent, the colorless solution rapidly becomes yellow and thin-layer chromatography of this solution shows that variable amounts of I are being formed.<sup>2</sup>

Compound I has been isolated in significant amounts (35-50%).

(1) L. Caglioti, P. Grasselli, and G. Rosini, *Tetrahedron Letters*, 4545, (1965).

(2) For the formation of aryl- and alkylazoalkenes from analogous reactions see (a) B. T. Gillis and J. D. Hagarty, *J. Am. Chem. Soc.*, **87**, 4575 (1965); (b) F. Ramirez and A. F. Kirby, *ibid.*, **75**, 6026 (1953); (c) J. van Alphen, *Rec. Trav. Chim.*, **64**, 305 (1945).

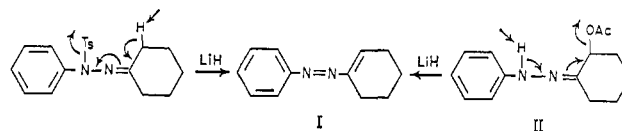


Figure 1.

The formation of II (mp 87-90°, infrared: 3300 and 1720  $\text{cm}^{-1}$ . *Anal.* Calcd for  $\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}_2$ : C, 68.27; H, 7.37; N, 11.37. Found: C, 68.60; H, 7.75; N, 11.40) from the reaction of  $\alpha$ -acetoxy cyclohexanone (III) with 1 mole of phenylhydrazine is very rapid.<sup>3</sup> If III is allowed to react with an excess of phenylhydrazine in benzene or in methanol and the mixture maintained at room temperature for several hours, the 1,2-cyclohexanedione bisphenylhydrazone (IV)<sup>4</sup> is obtained.

The formation of osazones from  $\alpha$ -hydroxy ketones is a well-known reaction which has been studied intensively.<sup>5</sup> The formation of osazones from  $\alpha$ -halo or  $\alpha$ -acetoxy ketones has been reported occasionally, but its mechanism has not yet been elucidated.<sup>2b</sup> To obtain information about the formation of osazones from  $\alpha$ -acetoxy ketones we allowed III to react with phenylhydrazine under different experimental conditions. The course of the reaction was followed by means of thin-layer chromatography. There was an immediate formation of II, which was then rapidly transformed into I. If an excess of phenylhydrazine was present, I was first transformed into compound V, which then formed the osazone IV. The three compounds, I, IV, and V, were isolated from the reaction mixture.

If II is allowed to react with phenylhydrazine under certain conditions, V precipitates<sup>6</sup> as a white yellowish solid, and on standing in the reaction mixture is slowly converted to IV. The analytical data (mp 133-34°; infrared: 3300 and 1640  $\text{cm}^{-1}$ ; ultraviolet: maximum at 208  $\text{m}\mu$  ( $\epsilon$  23,000); 252  $\text{m}\mu$  ( $\epsilon$  19,000); 276  $\text{m}\mu$  ( $\epsilon$  20,000). *Anal.* Calcd for  $\text{C}_{18}\text{H}_{22}\text{N}_4$ : C, 73.43; H, 7.53; N, 19.03. Found: C, 73.43; H, 7.53; N, 19.12) and the nmr spectrum of V<sup>7</sup> suggest that its structure is that of a phenylhydrazone of 2-( $\beta$ -phenylhydrazine)-cyclohexanone (Figure 2). The formation of V can be explained if one assumes a 1:4 addition of phenylhydrazine to the conjugated system of I<sup>8</sup> (Figure 2). To verify this conclusion, we treated I with 1 mole of phenylhydrazine in a concentrated methanolic solution in the cold; V precipitated from the solution in high yield (70-80%).

The transformation of V into IV implies an oxidation. In order to obtain information about this step of the reaction, a series of experiments was undertaken. In neutral solutions V is relatively stable. It remains

(3) Full details of this work will be given elsewhere.

(4) G. J. Bloink and K. H. Pausacker, *J. Chem. Soc.*, 1328 (1950).

(5) I. Dijong and F. Micheel, *Ann.*, **684**, 216 (1965); M. M. Shem-jakin, V. I. Mamind, K. M. Ermolaev, and E. M. Bamdas, *Tetrahedron*, **21**, 2775 (1965), and references.

(6) At this stage, V could be isolated in a yield of 60-70%.

(7) The spectrum shows a large absorption between  $\delta$  1.3 and 2.3 (7 H), a triplet (1 H) at  $\delta$  4.38 ( $\text{CH}_2\text{C}(\text{N})\text{H}$ ), a one-proton signal at  $\delta$  2.75 attributed to the allylic  $\text{H}_{\text{eq}}$  ( $J_{\text{gem}} \cong 13$  cps,  $J_{\text{eq,ax}} \cong J_{\text{eq,eq}} \cong 3$  cps); the allylic  $\text{H}_{\text{ax}}$  is at a higher field overlapped by the methylene absorption. The  $-\text{NH}-\text{NH}-\text{Ph}$  group lies at  $\delta$  3.1-3.9 (2 H, broad); the  $=\text{NNHPh}$  is obscured by the aromatic protons ( $\delta$  6.5-7.5).

(8) For 1:4 additions on analogous system see H. Beyerand and G. Badicke, *Ber.*, **93**, 826 (1960).