

either by the cleavage of silicon-carbon ring bond of intermediate oxasilacyclopropane followed by the rupture of carbon-oxygen bond, or by [3 → 2 + 1] cycloelimination to give a primarily phenylmethylcarbene, which rearranges to styrene.<sup>18</sup> The resulting dimethylsilanone could react with dimethyldimethoxysilane to give tetramethyldimethoxysiloxane.<sup>19,20</sup>

In summary the present work demonstrates that silylene could attack on carbonyl to produce oxasilacyclopropane. Thermal cleavage of the silicon-carbon ring bond of oxasilacyclopropane gives a 1,3 diradical or zwitterion which may undergo either intramolecular hydrogen abstraction or addition to the  $\pi$  bond of aromatic ring. The deoxygenation of carbonyl compounds also occurs to give the carbenes.

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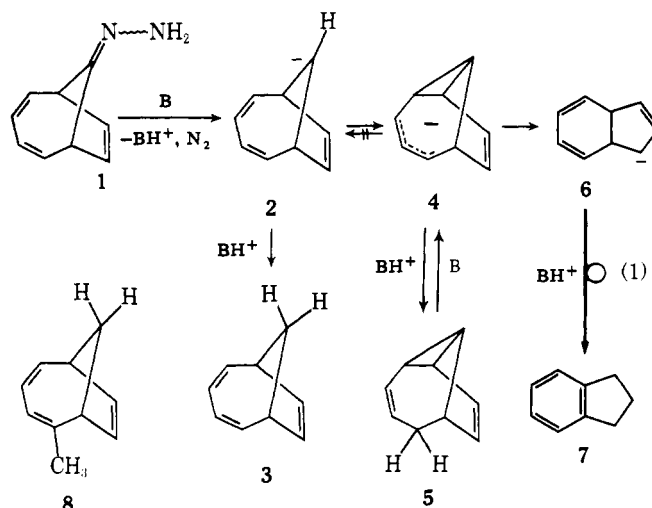
Received May 20, 1977

## Surprises in Base-Catalyzed Decompositions of Bicyclo[4.2.1]nona-2,4,7-trien-9-one Hydrazone

Sir:

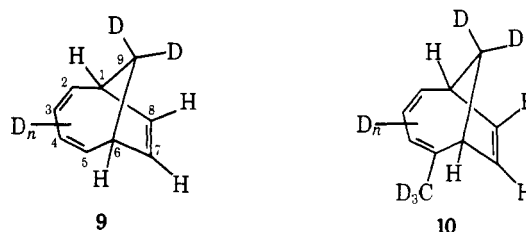
Bicyclo[4.2.1]nona-2,4,7-trien-9-one hydrazone (**1**) is converted by aqueous sodium hydroxide/diethylene glycol at reflux and then at 210 °C to tricyclo[6.1.0.0<sup>4,9</sup>]nona-2,6-diene (**5**, homosemibullvalene; 95%).<sup>1</sup> This excellent synthesis of **5** is presumed<sup>1</sup> to involve Wolff-Kishner conversion<sup>2</sup> of **1** to the bicyclo[4.2.1]nona-2,4,7-trien-9-yl anion (**2**), a supposed bicycloaromatic carbanion,<sup>3</sup> and then the tricyclo[6.1.0.0<sup>4,9</sup>]nona-2,6-dien-5-yl anion (**4**, homosemibullvalenyl anion) which protonates to **5** (eq 1). We now communicate further study of decomposition of **1** in the presence of bases because the system is replete with significant surprises.

In the present investigations in which repetition of the prior



work<sup>1</sup> was attempted, reaction of **1** with aqueous potassium hydroxide/diethylene glycol at reflux to 210 °C is observed to give bicyclo[4.2.1]nona-2,4,7-triene (**3**, 7%) along with **5** (93%).<sup>4a</sup> In subsequent experiments in which enhanced partitioning of **2** to **3** during decomposition of **1** at lower temperatures was the presumed mechanistic objective, potassium *tert*-butoxide/*tert*-butylalcohol (2 equiv)/dimethyl sulfoxide at 74 °C is found to convert **1** to **3** (>69%)<sup>5</sup> and **5** is not obtained.<sup>4a</sup> When added *tert*-butyl alcohol is absent, however, conversion of **1** to **3** is lowered and 2-methylbicyclo[4.2.1]nona-2,4,7-triene (**8**, 10%) is formed.<sup>4a,6a</sup> During the above reactions of **1**, **5** is not isomerized to **3**;<sup>4b</sup> potassium *tert*-butoxide/*tert*-butyl alcohol/dimethyl sulfoxide however does rearrange **5** slowly to indan (**7**) at 74 °C, presumably via **4**<sup>7</sup> and then the dihydroindenyl anion (**6**). Potassium *tert*-butoxide/*tert*-butyl alcohol/dimethyl sulfoxide does not convert **3** nor **5** to **8** nor effect methylation of **1** prior to development of the reduction processes.

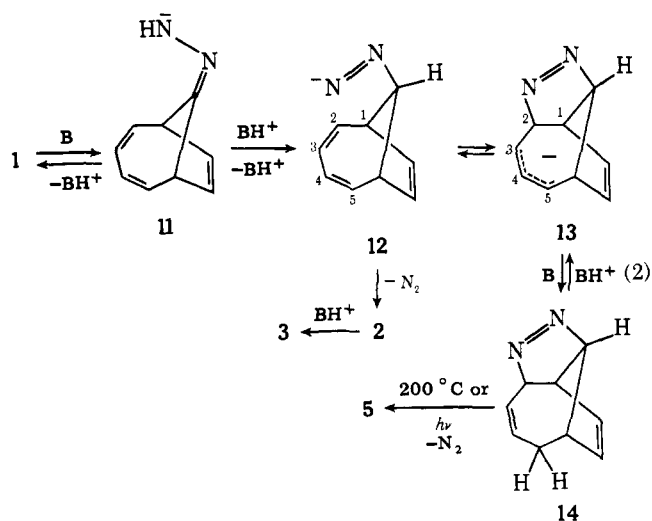
Base-catalyzed decompositions of **1** were then investigated to explain the product differences when the reactions are effected with different bases in dimethyl sulfoxide and in diethylene glycol. Upon determining that potassium *tert*-butoxide (1 equiv)/*tert*-butyl alcohol-*O-d* does not exchange deuterium into triene **3** at 74 °C,<sup>8</sup> it was of interest to demonstrate the intermediacy of anion **2** in the reduction systems of **1** by deuterium capture at C<sub>9</sub>. Bicyclo[4.2.1]nona-2,4,7-trien-9-one hydrazone-*N-d*<sub>2</sub><sup>9</sup> containing 20% **1** does react with potassium *tert*-butoxide/*tert*-butyl alcohol-*O-d*/dimethyl sulfoxide-*d*<sub>6</sub> at 74 °C to give bicyclo[4.2.1]nona-2,4,7-triene (**9**) with ~100% deuterium incorporation at c<sub>9</sub> and no deute-



rium at the bridgehead positions (C<sub>1</sub> and C<sub>6</sub>).<sup>6b</sup> It was of great surprise, however, that **9** forms with ~80% exchange (3.20 D) on its C<sub>2</sub>-C<sub>5</sub> diene bridge and with none on C<sub>7</sub>-C<sub>8</sub>.<sup>6b</sup> Similar results are obtained for methyltriene **10** with the minor difference that exchange of its diene hydrogens is ~83% (2.50 D).<sup>4b</sup> Deuterium exchange into the diene bridge of **1** by potassium *tert*-butoxide/*tert*-butyl alcohol-*O-d*/dimethyl sulfoxide-*d*<sub>6</sub> at 74 °C prior to the supposed Wolff-Kishner reactions could not be determined because of the rapid disappearance of the hydrazone under the conditions. Bicyclo-

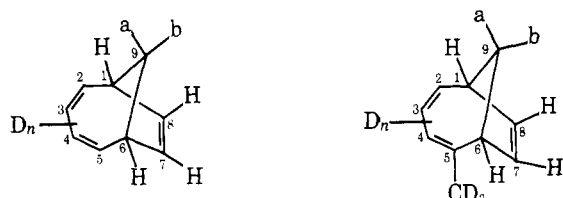
[4.2.1]nona-2,4,7-trien-9-one *N,N*-dimethylhydrazone does not incorporate deuterium, however, into any of its C–H bonds under conditions for conversion of **1** to **3** and thus it is reasonably clear that **1** does not undergo deuterium exchange at C<sub>2</sub>–C<sub>5</sub> before entry into its Wolff–Kishner systems.

Search was then initiated for intermediates in the base-catalyzed reactions of **1** responsible for exchange of the protons of only the diene bridges during formation of **9** and **10**. Surprisingly, bicyclo[4.2.1]nona-2,4,7-trien-9-one<sup>10</sup> reacts with hydrazine hydrate/potassium hydroxide/ethylene glycol at 100–120 °C for 2 h and then extractive workup (not distillation) with petroleum ether gives 2,3-diazatrienylcyclo[6.3.0.0<sup>4,11</sup>]undeca-2,5,9-triene (**14**, >>75%; mp 130–135 °C) as a readily isolable product,<sup>5,11</sup> presumably via **11**–**13** (eq 2). Involvement of **14** as a major intermediate in base-catalyzed decompositions of **1** in dimethyl sulfoxide is also demonstrable by following the reactions in their early stages by thin layer chromatography.



Pyrazoline **14** is stable to potassium hydroxide in diethylene glycol up to 180 °C. In the absence of potassium hydroxide, **14** extrudes nitrogen in diethylene glycol at ~200 °C (30 min) to give **5** (~100%). These experiments thus raise the question that formation and thermal decomposition of **14** is a source of **5** in reactions of **1** in either sodium or potassium hydroxide/diethylene glycol at ~200 °C. Further, **14** photolyzes (Hanovia medium pressure lamp through Pyrex) in pentane to **5** (100%).<sup>5</sup> Pyrazoline **14**, however, decomposes in potassium *tert*-butoxide/*tert*-butyl alcohol/dimethyl sulfoxide at 74 °C to **3** (75%) and **8** (20%); **3** presumably arises from **13**, **12**, loss of nitrogen, and then protonation of **2**. These results are essentially identical with that for reduction of **1** in the potassium dimsyl environment and provide strong support that **14** is an intermediate in the base-catalyzed decompositions of **1** as presently described.

Of additional note is that **14** reacts with potassium *tert*-butoxide/*tert*-butyl alcohol-*O-d*/dimethyl sulfoxide-*d*<sub>6</sub> at 30 °C (14 h) to give bicyclobutienes **15**–**16** (81%) and methylbicyclobutienes (**17**–**18** (18%) with about one deuterium at C<sub>9</sub> (the ratios of **15**/**16** and **17**/**18** are 1.66 and 1.25, respectively) and extensive exchange (3.00 D for **15**–**16** and 2.70 D for **17**–**18**) of the C<sub>2</sub>–C<sub>5</sub> protons.<sup>6b</sup> The selective exchange of diene protons to form **15**–**16** is thus similar to that in Wolff–Kishner reactions of **1**. For transfer of three deuteriums into the diene bridges of **15**–**16**, **13** apparently exchanges at C<sub>5</sub> and/or C<sub>3</sub>, **12** undergoes reversible ring closures at C<sub>2</sub> and C<sub>5</sub>, and deuterium is incorporated at C<sub>2</sub> and/or C<sub>4</sub>. Further, **14** is converted at 30 °C (20 min) by sodium dimsyl-*d*<sub>5</sub>/dimethyl



**15**, a = D; b = H; n = 3.00

**16**, a = H; b = D; n = 3.00

**19**, a = D; b = H; n = 0.00

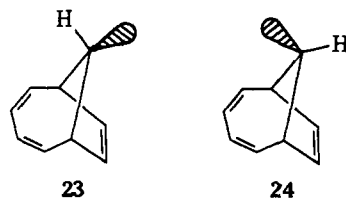
**20**, a = H; b = D; n = 0.00

**17**, a = D; b = H; n = 2.70

**18**, a = H; b = D; n = 2.70

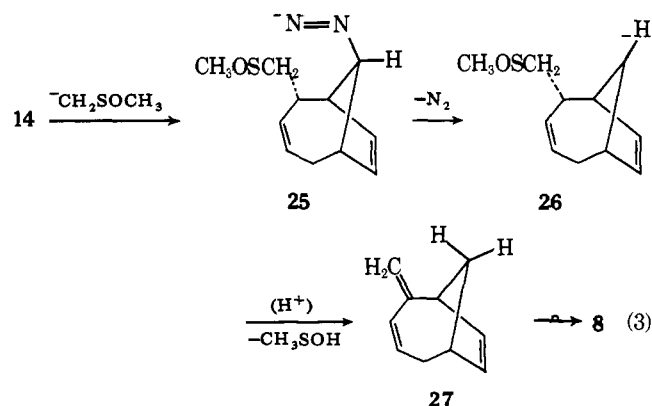
**21**, a = D; b = H; n = 0.00

**22**, a = H; b = D; n = 0.00



sulfoxide-*d*<sub>6</sub> to bicyclobutienes **19**–**20** (30%) with about one deuterium at C<sub>9</sub> (the ratio of **19**/**20** is 1.61) and none in the C<sub>2</sub>–C<sub>5</sub> bridge and to methylbicyclobutienes **21**–**22** (60%) with about one deuterium at C<sub>9</sub> (the ratio of **21**/**22** is 1.50) and no deuterium at C<sub>2</sub>–C<sub>5</sub>.<sup>6b</sup> Sodium dimsyl-*d*<sub>5</sub>/dimethyl sulfoxide-*d*<sub>6</sub>, a much stronger and more aprotic base than potassium *tert*-butoxide/*tert*-butyl alcohol-*O-d*/dimethyl sulfoxide-*d*<sub>6</sub>, apparently does not allow deuterium exchange into **13** and its enantiomer as derived by cyclization of **12** at C<sub>5</sub>. Finally deuterium at C<sub>9</sub> in **15**–**16** and **19**–**20** is strong evidence for generation of deuterated analogues of **2** though the mechanism of formation of **2** is quite different from that initially presumed (eq 1).<sup>1</sup> On the basis of steric effects **2** is expected to deuterate preferentially from the anti direction as **23**. The fact, however, is otherwise in that the ratios of **15**/**16** and **19**/**20** are >1.6 and thus are consistent with the proposition that **24** experiences favorable syn bishomoaromatic (6π) interaction with its C<sub>2</sub>–C<sub>5</sub> diene segment.<sup>12</sup> The extent and significance of the delocalization in **2** remain yet, however, as important mechanistic questions.<sup>3,8</sup>

There is some insight into the origins of methylbicyclobutene **8** and its deuterated analogues **17**–**18** and **21**–**22**. Thus **8** may be formed (eq 3) by displacement of **14** with dimsyl



anion, loss of nitrogen from **25** to give **26** which undergoes protonation and elimination of methanesulfenic acid, and then isomerization of **27**. Base-catalyzed and appropriate deuterium exchange reactions of the **14**–**13**–**12** system and then displacement et cetera as for dimsyl anion and **14** rationalize formation of **17**–**18** and **21**–**22**.

**Acknowledgments.** We gratefully acknowledge support of this research by the National Science Foundation and the Stauffer Chemical Co.

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- (4) (a) These initial experiments were conducted by D. C. Sanders, Ph.D. Dissertation, The Ohio State University, 1972. (b) All subsequent research was carried out by T. V. Rajan Babu, Ph.D. Dissertation, The Ohio State University, 1976.
- (5) The method summarized is superior for preparing the indicated product.
- (6) (a) All new compounds are of proper analysis and mass, NMR, and IR spectra. (b) Deuterated derivatives were assigned by NMR and mass spectral methods. The proton contents at C<sub>2</sub>-C<sub>5</sub>, C<sub>7</sub>-C<sub>8</sub>, and C<sub>9</sub> in **9** and **10** were determined by NMR integration relative to that at C<sub>1</sub> and C<sub>6</sub>.
- (7) Wolff-Kishner reaction of tricyclo[6.1.0.0<sup>4,9</sup>]nona-2,6-dien-5-one (homosembullvalenone) with potassium hydroxide/hydrazine/diethylene glycol at reflux (210 °C) yields **5** (95%) presumably via kinetic capture of **4**,<sup>4b</sup> **3** was not detected.
- (8) (a) The resistance of conversion of **3** to **2** is further revealed by the observation that reaction of **3** with lithium cyclohexylamide in cyclohexylamine-*N*-d<sub>2</sub> gives recovered triene with 89% deuterium on the monoene, 55% on the diene, and 0% at the C<sub>9</sub> positions. (b) A similar result has been reported by R. R. Boettcher, Ph.D. Dissertation, University of Wisconsin, Madison, Wis., 1970.
- (9) Prepared with ~80% deuterium incorporation by treatment of bicyclo[4.2.1]nona-2,4,7-trien-9-one hydrazone with excess deuterium oxide in methylene chloride.
- (10) T. A. Antkowiak, D. C. Sanders, G. B. Trimitsis, J. B. Press, and H. Shechter, *J. Am. Chem. Soc.*, **94**, 3366 (1972).
- (11) (a) It has been previously observed that Wolff-Kishner reduction of bicyclo[4.2.2]deca-2,4,9-trien-7-one by hydrazine/potassium hydroxide/ethylene glycol fails to produce bicyclo[4.2.2]deca-2,4,7-triene.<sup>11b</sup> Under these conditions the decatrienone is converted to 2,3-diazatricyclo[6.3.1.0<sup>4,11</sup>]dodeca-2,5,9-triene.<sup>11b</sup> (b) J. B. Press and H. Shechter, *J. Org. Chem.*, **40**, 2446 (1975). (c) NOTE ADDED IN PROOF. After submittal of this manuscript, M. Kato, T. Chikamoto, and T. Miwa, *Bull. Chem. Soc. Jpn.*, **50** (5), 1082 (1977), reported that benzo[7,8]bicyclo[4.2.1.]nona-2,4,7-trien-9-one hydrazone reacts with potassium *tert*-butoxide/dimethyl sulfoxide to give 9,10-diazabenzocyclo[2,3]tricyclo[6.3.0.0<sup>4,11</sup>]undeca-2,6,9-triene which pyrolyzes at 180°C or photolyzes with a high pressure lamp to yield benzo[6,7]tricyclo[6.1.0.0<sup>4,9</sup>]nona-2,6-diene. These transformations are thus formally analogous to the conversions of **1** to **14** and then **5** in the present communication.
- (12) For related experiments and theory, see J. K. Stille and K. N. Sannes, *J. Am. Chem. Soc.*, **94**, 8489 (1972), and references therein.

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### In Support of Anionic Hyperconjugation. The Versatile Methyl Group

Sir:

The direction of secondary isotope effects on the rates of solvolytic reactions proceeding through carbocationic transition states<sup>1</sup> and on gas phase equilibria involving stable carbocations<sup>2</sup> has been ascribed to hyperconjugation. In the language of perturbation molecular orbital theory,<sup>3</sup> interaction of the highest filled,  $\pi$  symmetry, orbital on a methyl (CD<sub>3</sub>) group with the vacant p function at C<sup>+</sup> results not only in net energetic stabilization but also in significant charge reorganization. Specifically, electron density is removed from the methyl CH linkages, resulting in their weakening. The associated reduction in CH stretching force constants leads directly to the observed kinetic and thermodynamic preference for formation of the light cation.<sup>4</sup>

In this communication we present experimental and theoretical evidence in support of the notion that hyperconjugative factors are also operative in the interaction of anionic centers with alkyl substituents. Our data have led us to conclude that a methyl group attached to a center of negative charge may

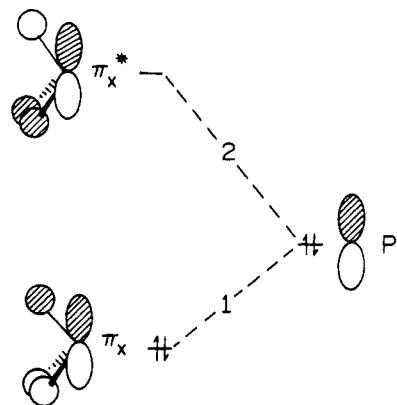
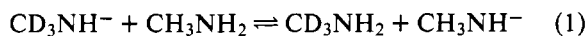


Figure 1. Interaction of a methyl group with the lone pair on an anionic center.

act as an electron acceptor. Furthermore, they indicate that the intrinsic electron-withdrawing ability of a methyl group is comparable with, if not greater than, its ability to donate charge in those instances where it is attached to an electron-deficient center.

We have determined by pulsed ion cyclotron resonance spectroscopy<sup>5</sup> the free energies of the proton transfer equilibria 1, 2, and 3



$$\Delta G^\circ = -0.37 \pm 0.08 \text{ kcal/mol}^{6,7}$$

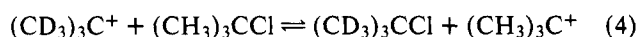


$$\Delta G^\circ = -0.50 \pm 0.10 \text{ kcal/mol}^6$$



$$\Delta G^\circ = -0.30 \pm 0.08 \text{ kcal/mol}^6$$

involving formation, in the gas phase, of the methylamino, methoxy, and thiomethoxy anions. In all three cases equilibrium lies to the right (i.e., favors the formation of the light ion), the same preference which has been observed thermodynamically<sup>2</sup> and kinetically<sup>1</sup> for processes leading to the buildup of positive charge adjacent to a methyl probe (e.g., reaction 4).<sup>2</sup>



$$\Delta G^\circ (\text{per CD}_3) = -0.12 \pm 0.05 \text{ kcal/mol}^6$$

The preferences are also in the same direction, but of far greater magnitude, than secondary effects noted kinetically in solution for reactions leading through what are suspected to be anionic transition states.<sup>8</sup>

The observed isotope effects may be rationalized using the perturbation molecular orbital theory.<sup>3</sup> Interaction of a methyl group with the lone pair on an anionic center to which it is attached through the  $\sigma$  system is describable in terms of stabilizing and destabilizing components (Figure 1). The four-electron term, 1, involving interaction of the methyl  $\pi$  orbital and the lone pair at the anion center, results in net energetic destabilization. Both functions are fully occupied, and little if any redistribution of electron density is to be expected. Significant charge reorganization is to be anticipated as a result of the stabilizing two-electron interaction, 2. Specifically, electron density is shifted away from the nonbonded lone pair at the anion center and directed into a CH antibonding orbital on methyl. As a result the CH bonds should weaken giving rise to the observed isotopic preference for formation of the light anion.

Ab initio molecular orbital calculations at the minimal basis STO-3G level<sup>9,10</sup> concur with the conclusions of the simple