

well as several nucleosides. Of particular interest are the successful protection and deprotection of uridines, **8**, in the presence of the 2',3'-di-*O*-benzoyl function, of a 5'-*O*-trityl protected thymidine<sup>6</sup> **9**, and the fact that the levulinates are stable in 80% acetic acid over a 48-hr period and in trifluoroacetic acid for 20 hr. Furthermore in at least six cases, the borohydride reduction and the consecutive lactonization appeared to be quantitative as determined by TLC. The yields reported are those of recrystallized material.

The levulinates had to be prepared via levulinic anhydride **2** since levulinyl chloride<sup>7</sup> leads to pseudo esters that are very labile to basic hydrolysis.<sup>8</sup>

Levulinic anhydride **2** was obtained in quantitative yield by reaction of levulinic acid (20 mmol) with dicyclohexylcarbodiimide (10 mmol) in 65 ml of ether for 5 hr followed by filtration and evaporation of the solvent. A solution of 10 mmol of **2**, and 5 mmol of **9** in 10 ml of anhydrous pyridine was kept for 24 hr, ice water was added, and the levulinate **3** (100%) crystallized from benzene-hexane mp 143–145° (81%). A solution of 0.25 mmol of the levulinate in 2 ml of dioxane was treated with 37 mg of NaBH<sub>4</sub> in 0.5 ml of water for 20 min, the pH was brought to 5 (HOAc), and the mixture was poured onto ice. 5'-*O*-Tritylthymidine (**9**) was filtered (90%), mp 128°.

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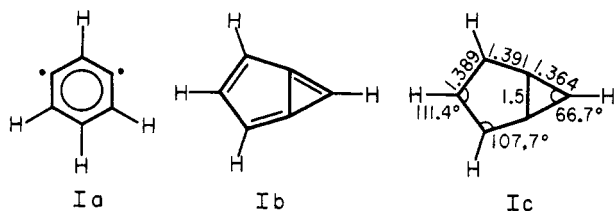
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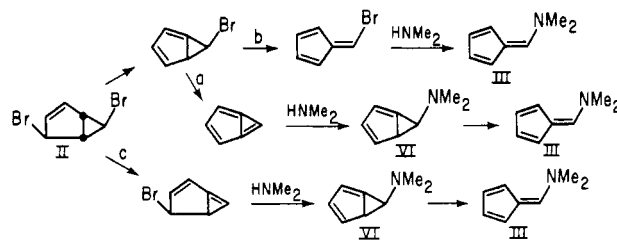
## Generation of Bicyclo[3.1.0]hexatriene. A Reactive Intermediate

Sir:

Of the three dehydrobenzenes possible, 1,3-dehydrobenzene or *m*-benzyne (**I**) has received the least consideration.



Scheme I



We wish to describe the synthesis of **I** and the results of theoretical calculations pertaining to **I**. To date, the only report of **I** is that of Berry detailing the results of the flash pyrolysis of *m*-benzenediazonium carboxylate.<sup>1</sup>

Two distinct geometrical representations are possible for *m*-benzyne: a hexagonal conformation (**Ia**) resembling that of benzene or a bicyclo[3.1.0]hexa-1,3,5-triene (**Ib**). Until very recently all theoretical studies of *m*-benzyne had considered only the hexagonal conformation **Ia** and had consequently focused upon the multiplicity of the ground state.<sup>2,3</sup> However, MINDO/3 calculations led Dewar to predict, after geometry optimization, the ground state to be represented by structure **Ib**, in which the C<sub>1</sub>–C<sub>5</sub> separation was reduced from 2.41 Å in structure **II** to 1.97 Å.<sup>4</sup> Furthermore, his studies represent the first suggestion that *m*-benzyne would be a singlet of stability comparable to that of *o*-benzyne.

In our approach to *m*-benzyne, we sought suitable precursors containing the  $\sigma$  framework. Such a precursor was *exo-exo*-2,6-dibromobicyclo[3.1.0]hex-3-ene (**II**), readily available from benzvalene.<sup>5</sup> **II** was a particularly desirable precursor since the *exo* stereochemistry of the halogens favored the initial 1,4-elimination of HBr to form a cyclopentadiene. Subsequent ionization should be particularly favorable since ring strain would be relieved. Eventual loss of halide from C<sub>6</sub> would generate **I**.

The dropwise addition of **II** to a tetrahydrofuran solution containing 3 equiv of potassium *tert*-butoxide (0.33 *M* in potassium *tert*-butoxide and 0.56 *M* in dimethylamine)<sup>6</sup> at –75° under argon after 5 min generated 6-dimethylaminofulvene (**III**)<sup>7</sup> in 90% yield. In addition, *exo-exo*-2-dimethylamino-6-bromobicyclo[3.1.0]hex-3-ene<sup>9</sup> and 6-*tert*-butoxyfulvene<sup>10</sup> (**IV**) were formed in 7 and 2% yields, respectively.

Any of three pathways can account for the formation of the 6-dimethylaminofulvene (**III**) (Scheme I). Only one, path a, requires the intermediacy of *m*-benzyne. Nucleophilic addition of dimethylamine at the electron deficient carbon C<sub>6</sub> of **I** would form 6-dimethylaminobicyclo[3.1.0]hexa-1,3-diene (**VI**) after protonation. A [1,5]-sigmatropic shift of C<sub>6</sub> from C<sub>5</sub> to C<sub>1</sub> converts **VI** to **III**. **VI** is a logical precursor of **III** since precedence exists for facile 1,5-alkyl migration in ring systems containing a strained cyclopentadienyl ring.<sup>12</sup>

In one alternative pathway, path b, a 6-halogenated fulvene would be an obligatory intermediate. If *m*-benzyne were sufficiently destabilized due to strain, the second HBr elimination need not occur from **II**. Instead, a 1,5-alkyl migration of C<sub>6</sub> in the intermediate 6-bromobicyclo[3.1.0]hexa-1,3-diene results in the formation of 6-bromofulvene which would subsequently react to form **III**.<sup>14</sup> However, the intermediacy of a halogenated fulvene was discredited by treating **II** as above with potassium *tert*-butoxide but in the absence of dimethylamine. In less than 5 min **II** was completely converted to 6-*tert*-butoxyfulvene (**IV**) and several minor products, two of which have been identified as bromobenzene and 6-bromofulvene. 6-Bromofulvene cannot be the precursor of the 6-*tert*-butoxyfulvene since, under

the reaction conditions, 6-bromofulvene was converted very slowly to IV.

A third possible route, path c, to VI entails the cis 1,2-elimination of the halogen at C<sub>6</sub> to form a severely distorted 2-halogenated bicyclo[3.1.0]hexa-3,5-diene. Nucleophilic addition of dimethylamine at C<sub>6</sub> with concurrent loss of halogen would generate VI and subsequently III after an [1,5]-sigmatropic migration. To establish the feasibility of such a cis elimination, *exo*-6-bromobicyclo[3.1.0]hex-2-ene<sup>5</sup> was prepared and found to react sluggishly even at 25° with potassium *tert*-butoxide. Since the inductive effect of an allylic halogen at C<sub>2</sub> is unlikely to so drastically alter the rate of the cis elimination, path c was no longer considered viable.

In the absence of any alternative mechanisms leading to III, or to 6-*tert*-butoxyfulvene itself, path a, entailing the intermediacy of *m*-benzyne, provides the best explanation of these results.

We have attempted to determine the nature of the ground state of *m*-benzyne. If the C<sub>1</sub>-C<sub>5</sub> bond were a weak or nonexistent bond (i.e., structure Ia), hydrogen abstraction would be favored over nucleophilic addition.<sup>16</sup> When II was treated as above but in the presence of cumene (0.4 M) III was isolated in the same yield as in the absence of cumene. These experimental data are consistent with the reaction proceeding via a singlet ground state of *m*-benzyne best represented by structure Ib.

In order to gain some insight into which geometrical conformation best represented singlet *m*-benzyne, we performed ab initio SCF calculations utilizing the minimal STO-3G basis functions in the GAUSSIAN 70 series of computer programs.<sup>18</sup> To simplify the undertaking, I was assumed to possess C<sub>2v</sub> symmetry and carbon-hydrogen bond lengths of 1.08 Å. The total energy was optimized as a function of geometry and bond length. Particular emphasis was placed on the C<sub>1</sub>-C<sub>5</sub> bond length as it was varied from 1.4 to 2.41 Å.

Only one minimum, Ic, was found in which the C<sub>1</sub>-C<sub>5</sub> bond length was 1.5 Å.<sup>19</sup> The calculated difference in energy between Ic and the hexagonal conformation Ia was 54 kcal. Dewar, using a semiempirical approach (MINDO/3), had similarly found one minimum but the C<sub>1</sub>-C<sub>5</sub> separation corresponded to 1.97 Å. For comparative purposes, the total energy of the conformation of I predicted by MINDO/3 to be of lowest energy was calculated using the STO-3G basis set and found to be 21 kcal less stable than Ic.

Our theoretical prediction of a "real" bond as opposed to a reactive weak long bond bridging the dehydrocarbons of I is substantiated by the chemistry of I. In conclusion, we suggest that *m*-benzyne, or 1,3-dehydrobenzene is a misnomer. Instead, bicyclo[3.1.0]hexa-1,3,5-triene more aptly describes the molecule in question. We are continuing our investigations of bicyclo[3.1.0]hexa-1,3,5-triene.

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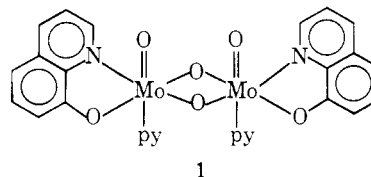
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## Reactions of Bisoxinato Complexes of [Mo<sub>2</sub>O<sub>4</sub>]<sup>2+</sup>. I. The Preparation and Structure of the Novel Coordination Compound $\mu$ -(2-Mercaptoethanolato-S:O)- $\mu$ -oxo-bis[oxo-8-hydroxyquinolinatomolybdenum(V)]

Sir:

A variety of chemical and physical studies suggest that Mo(V) coordinated by one or more S atoms may be an important feature of molybdoenzymes.<sup>1</sup> The current interest in molybdoenzymes and the paucity of data for well-characterized molybdenum complexes of sulfur-containing ligands have led to systematic studies of such complexes in our laboratories. Herein we show that the reaction of di- $\mu$ -oxo-bis[oxo-8-hydroxyquinolinatomolybdenum(V)] (**1**)<sup>2</sup> with 2-mercaptoethanol produces a novel coordination compound (**2**) in which two [MoO]<sup>3+</sup> units are bridged by three donor atoms.



Compound (**1**) (1 mmol in 200 ml of absolute ethanol) was combined with 2-mercaptoethanol (1 mmol in 2 ml of ethanol) and the mixture heated slowly to 75° and stirred for 20 min. The air-stable amber yellow powder (**2**) was filtered and washed with ethanol. Compound **2** was insoluble in water, slightly soluble in DMSO and DMF, and soluble in CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub>. **2** decomposed at ~200° and upon treatment with strong acids and bases.

Anal. Calcd for C<sub>20</sub>H<sub>16</sub>SN<sub>2</sub>Mo<sub>2</sub>O<sub>6</sub>: C, 39.86; H, 2.65; N, 4.65; S, 5.32; Mo, 31.60. Found: C, 39.80; H, 2.67; N, 4.61; S, 5.37; Mo, 31.62

The analyses established that the metal-ligand stoichiometry of **2** was Mo<sub>2</sub>(oxine)<sub>2</sub>(mercaptoethanol), but did not