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[6] **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[7] leads to pseudo esters that are very labile to basic hydrolysis.[8]

Levulinic anhydride **2** was obtained in quantitative yield by reaction of levulinic acid (20 mmol) with dicyclohexylcarbodide (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 $NaBH_4$ 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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References and Notes

(1) Synthetic Methods, VII. For the previous paper in this series see J. Rasmussen and A. Hassner, *J. Org. Chem.*, **39**, 2558 (1974).
(2) C. B. Reese in "Protective Groups in Organic Chemistry", J. F. W. McOmie Ed., Plenum Press, New York, N.Y., 1973, Chapter 2.
(3) S. M. Kupchan, A. D. J. Balon, and E. Fujita, *J. Org. Chem.*, **27**, 3103 (1962).
(4) R. L. Letsinger, M. H. Caruthers, R. S. Miller, and K. K. Ogilvie, *J. Am. Chem. Soc.*, **89**, 7146 (1967); **91**, 3356 (1969).
(5) A. I. Meyers, A. Nabeya, H. W. Adickes, I. R. Politzer, G. R. Malone, A. C. Kovelesky, R. L. Nolen, and R. C. Portnoy, *J. Org. Chem.*, **28**, 36 (1973).
(6) The applicability to adenine and guanine derivatives is under investigation.
(7) M. S. Newman, N. Gill, and B. Darre, *J. Org. Chem.*, **31**, 2713 (1966).
(8) T. H. Fife, *J. Am. Chem. Soc.*, **87**, 271 (1965).

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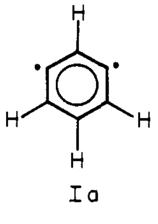
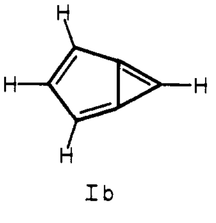
Generation of Bicyclo[3.1.0]hexatriene. A Reactive Intermediate

Sir:

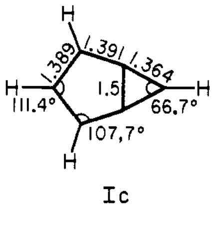
Of the three dehydrobenzenes possible, 1,3-dehydrobenzene or *m*-benzyne (I) has received the least consideration.



Ia

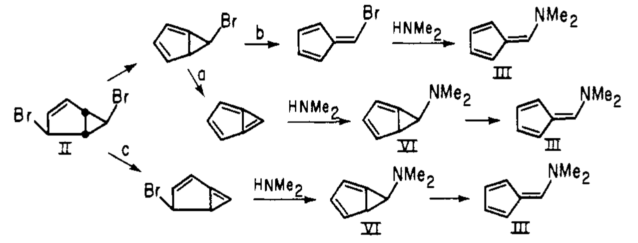


Ib



Ic

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.[1]

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.[2,3] However, MINDO/3 calculations led Dewar to predict, after geometry optimization, the ground state to be represented by structure Ib, in which the C_1–C_5 separation was reduced from 2.41 Å in structure II to 1.97 Å.[4] 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 σ framework. Such a precursor was *exo-exo*-2,6-dibromobicyclo[3.1.0]hex-3-ene (II), readily available from benzvalene.[5] 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_6 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)[6] at −75° under argon after 5 min generated 6-dimethylaminofulvene (III)[7] in 90% yield. In addition, *exo-exo*-2-dimethylamino-6-bromobicyclo[3.1.0]hex-3-ene[9] and 6-*tert*-butoxyfulvene[10] (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_6 of I would form 6-dimethylaminobicyclo[3.1.0]hexa-1,3-diene (VI) after protonation. A [1.5]-sigmatropic shift of C_6 from C_5 to C_1 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.[12]

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_6 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.[14] 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_6 to form a severely distorted 2-halogenated bicyclo[3.1.0]hexa-3,5-diene. Nucleophilic addition of dimethylamine at C_6 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[5] was prepared and found to react sluggishly even at 25° with potassium *tert*-butoxide. Since the inductive effect of an allylic halogen at C_2 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_1–C_5 bond were a weak or nonexistent bond (i.e., structure Ia), hydrogen abstraction would be favored over nucleophilic addition.[16] 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.[18] To simplify the undertaking, I was assumed to possess C_{2v} 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_1–C_5 bond length as it was varied from 1.4 to 2.41 Å.

Only one minimum, Ic, was found in which the C_1–C_5 bond length was 1.5 Å.[19] 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_1–C_5 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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References and Notes

(1) R. S. Berry, J. Clardy, and M. E. Schafer, *Tetrahedron Lett.*, 1011 (1965).
(2) R. Hoffmann, A. Imanura, and W. J. Hehre, *J. Am. Chem. Soc.*, **90**, 1499 (1968).
(3) D. L. Wilhite and J. L. Whitten, *J. Am. Chem. Soc.*, **93**, 2858 (1971).
(4) M. J. S. Dewar and W. Li, *J. Am. Chem. Soc.*, **96**, 5569 (1974).
(5) R. J. Roth and R. J. Katz, *J. Am. Chem. Soc.*, **94**, 4770 (1970).
(6) For the elimination to proceed at −75°, the reaction medium must be completely dry. The THF was distilled from sodium–benzophenone; the potassium *tert*-butoxide was freshly sublimed.
(7) The structure assignment was confirmed by independent synthesis of III.[8]
(8) K. Hafner, K. H. Vopel, G. Ploss, and C. Konig, *Justus Liebigs Ann. Chem.*, **661**, 52 (1963).
(9) The structure assignment was consistent with mass spectral and ^{1}H NMR data.
(10) The structure assignment was confirmed by independent synthesis of 6-*tert*-butoxyfulvene.[11] The two compounds were identical by GC, ^{1}H NMR, and uv.
(11) K. Hafner, W. Bauer, and G. Schulz, *Angew. Chem., Int. Ed. Engl.*, **7**, 806 (1968).
(12) For example, bicyclo[3.2.0]hepta-1,3-diene spontaneously rearranges to spiro[2,4]hepta-4,6-diene.[13]
(13) (a) M. Oda and R. Breslow, *Tetrahedron Lett.*, 2537 (1973); (b) N. K. Hamer and M. E. Stubbs, *ibid.*, 3531 (1972).
(14) 6-Bromofulvene was synthesized by the slow addition of bromoform to potassium cyclopentadienide in petroleum ether at −20°. It is an air-sensitive thermally unstable yellow orange liquid which readily reacts with dimethylamine to form III. Similar reactivity with amines was observed for 6-chlorofulvene.[15]
(15) M. B. D'Amore and R. G. Bergman, *Chem. Commun.*, 461 (1971).
(16) The diradical character of *p*-benzyne was demonstrated by preferential hydrogen abstraction from methanol in lieu of nucleophilic addition.[17]
(17) R. R. Jones and R. G. Bergman, *J. Am. Chem. Soc.*, **94**, 660 (1972).
(18) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind., Program No. 236.
(19) For comparative purposes, the bridging bond of azulene was determined to be 1.484 Å.[20]
(20) J. M. Robertson, H. M. M. Shearer, G. A. Sim, and D. G. Watson, *Acta Crystallogr.*, **15**, 1 (1962).

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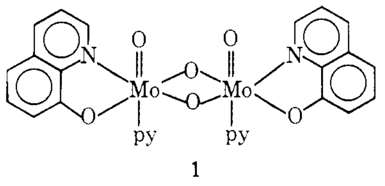
Reactions of Bisoxinato Complexes of $[Mo_2O_4]^{2+}$. I. The Preparation and Structure of the Novel Coordination Compound μ-(2-Mercaptoethanolato-*S:O*)-μ-oxo-bis[oxo-8-hydroxyquinolinatomolybdenum(V)]

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.[1] 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-μ-oxo-bis-[oxo-8-hydroxyquinolinatopyridinemolybdenum(V)] (**1**)[2] with 2-mercaptoethanol produces a novel coordination compound (**2**) in which two $[MoO]^{3+}$ units are bridged by *three* donor atoms.



1

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_2Cl_2 and $CHCl_3$. **2** decomposed at ~200° and upon treatment with strong acids and bases.

Anal. Calcd for $C_{20}H_{16}SN_2Mo_2O_6$: 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_2(oxine)$_2$(mercaptoethanol), but did not