Excellent yields are obtained when dry THF is used, and in this case 1.2 equiv of the halide is sufficient for optimal reaction. For instance, the reaction of 2-bromopropene with hexanal gives the expected allylic alcohol in 91% isolated yield.

It is not yet possible to interpret the effect of ultrasounds on the formation of organometallic reagents. However, the mechanical effects can produce some alterations at the metal surface: it has recently been shown that lattice defects such as dislocations are important factors in the initiation of the Grignard reaction.[11] It can also be supposed that ultrasound energy keeps the metal surface free from the derived species (organolithium, lithium halides, or hydroxide) in such a way that it remains highly activated. Further work concerning the extension of this reaction to various substrates and metals is currently under way.

Acknowledgment. Useful discussions with Dr. A. E. Greene are warmly acknowledged.

---

(11) Hill, C. L.; Van der Sande, J. B.; Whitesides, G. M., *J. Org. Chem.* **1980**, *45*, 1020.

† Deceased June 8, 1980.

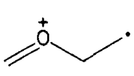
Jean-Louis Luche,* Jean-Claude Damiano†
Laboratoire de Chimie Organique—CERMO
Université Scientifique et Médicale
38041 Grenoble, France

Received July 9, 1980

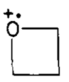
Experimental Proof for the Gas-Phase Existence of the C···C Ring-Opened Trimethylene Oxide Cation: A New Stable $C_3H_6O^{+\cdot}$ Isomer

Sir:

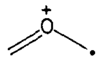
In a recent paper,[1] we presented ab initio theoretical predictions of the structures and stabilities of 17 possible $C_3H_6O^{+\cdot}$ (*m/z* 58) isomers. In addition to those that had been well established by experimental techniques,[2] we identified a number of low-energy, potentially observable structures. One of these, the C···C ring-opened isomer **1** of the trimethylene oxide radical cation **2**, was shown to lie slightly lower in energy than **2** and represents a higher homologue of the stable C···C ring-opened ethylene oxide ion **3**.[3]



1



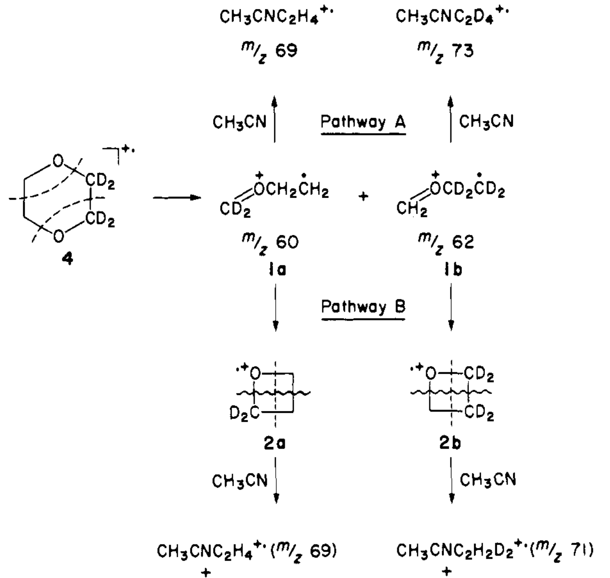
2



3

By analogy with ion **3**, which transfers $CH_2^{+\cdot}$ to a variety of neutral substrates,[3] ion **1** would be expected to show a $C_2H_4^{+\cdot}$ transfer to similar substrates. Indeed, both the *m/z* 58 ion generated by ionization of trimethylene oxide and the *m/z* 58 ion formed from ionized 1,4-dioxane by loss of formaldehyde showed a transfer of $C_2H_4^{+\cdot}$ to neutral acetonitrile when mixtures of these compounds were investigated by ICR spectrometry.[1] This observation did not in itself, however, rule out the possibility that $C_2H_4^{+\cdot}$ transfer could occur from ion **2**. From collisional activation studies, McLafferty[2a] had proposed that the $C_3H_6O^{+\cdot}$ ions from trimethylene oxide and 1,4-dioxane were identical and possessed the closed-ring structure **2**. We therefore set out to determine whether the *m/z* 58 ion from 1,4-dioxane, which showed $C_2H_4^{+\cdot}$ transfer to acetonitrile in the ICR spectrometer, had the open-ring structure **1** or the closed-ring structure **2**.

Scheme I



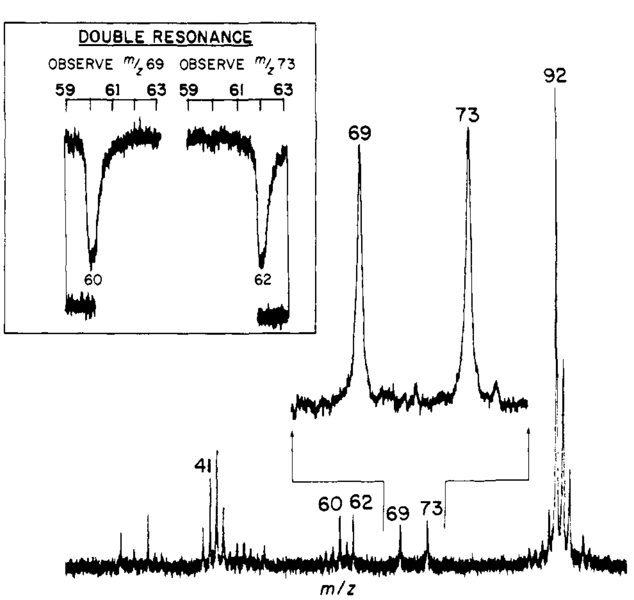


Figure 1. ICR spectrum of a mixture of 2,2,3,3-$[^2H_4]$-1,4-dioxane and acetonitrile.

2,2,3,3-$[^2H_4]$-1,4-Dioxane (92% d_4, 5% d_8, 3% d_0) was synthesized by the method of Jensen and Neese.[4] In the ICR spectrometer[5] its molecular ion **4** showed about equal losses of CH_2O and CD_2O to give ions at *m/z* 62 and 60, respectively (Scheme I). If, in reactions of these ions with acetonitrile, transfer of the ethylene radical cation proceeds without prior cyclization of **1a** and **1b** and without H/D scrambling, then pathway A would be followed and two product ions observed at *m/z* 69 and 73. Alternatively cyclization of **1a** and **1b** to **2a** and **2b**, respectively (pathway B), renders one CH_2 and one CD_2 group equivalent in each case and therefore in the absence of H/D scrambling would be expected to lead to product ions at *m/z* 69, 71, and 73 in a ratio of ~1:2:1 (Scheme I).[6]

The ICR spectrum of a mixture of 2,2,3,3-$[^2H_4]$-1,4-dioxane ($M^{+\cdot}$ *m/z* 92, 1×10^{-5} torr) and acetonitrile (5×10^{-6} torr) is shown in Figure 1. Product ions at *m/z* 69 and 73 only are observed and double resonance establishes that their sole precursor

---

(1) Bouma, W. J.; MacLeod, J. K.; Radom, L. *J. Am. Chem. Soc.* **1980**, *102*, 2246–52.

(2) (a) Van de Sande, C. C.; McLafferty, F. W. *J. Am. Chem. Soc.* **1975**, *97*, 4617–20. (b) For other relevant papers, see ref 1.

(3) Bouma, W. J.; MacLeod, J. K.; Radom, L. *J. Chem. Soc., Chem. Commun.* **1978**, 724–5. *J. Am. Chem. Soc.* **1979**, *101*, 5540–5. *Adv. Mass Spectrom.*, in press.

(4) Jensen, F. R.; Neese, R. A. *J. Org. Chem.* **1972**, *37*, 3037–8.

(5) For general experimental conditions, see ref 1.

(6) If H/D scrambling in **2a** and **2b** were to occur, an even larger number of product ions would be observed for the reaction with acetonitrile, namely, *m/z* 69, 70, and 71 from **2a** and *m/z* 71, 72, and 73 from **2b**.

0002-7863/80/1502-7927$01.00/0

ions are m/z 60 and 62, respectively. Thus, pathway A must be the only one operative. *We can therefore state unequivocally that those $C_3H_6O^{+\cdot}$ ions from 1,4-dioxane which show a $C_2H_4^{+\cdot}$ transfer must have the acyclic structure* **1**[7,8] *and have a lifetime of at least 1 ms.* Our results thus provide experimental substantiation of the ab initio prediction[1] of a stable C···C ring-opened isomer of the trimethylene oxide cation radical.

---

(7) The possibility that ion **1** could undergo a 1,2-hydrogen shift to give another low-energy species $CH_3CHO^{+\cdot}CH_2$,[1] which could then be the ion which transfers $C_2H_4^{+\cdot}$, can be ruled out. The above $C_3H_6O^{+\cdot}$ isomer, generated from fragmentation of the molecular ions of either 4-methyl-1,3-dioxolane[1] or 4,5-dimethyl-1,3-dioxolane, shows reactions with both acetonitrile and pyridine[9] which are different from those of the $C_3H_6O^{+\cdot}$ ion from 1,4-dioxane.

(8) We consider that the transfer of $C_2H_4^{+\cdot}$ from the molecular ion of trimethylene oxide to acetonitrile is also likely to occur via the C···C ring-opened ion **1**.

(9) Baumann, B. C.; MacLeod, J. K., unpublished results.

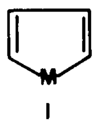
Bruno C. Baumann, John K. MacLeod,* Leo Radom
Research School of Chemistry
Australian National University
Canberra, ACT 2600, Australia

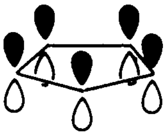
Received June 28, 1980

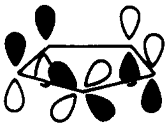
Cyclic 4π Stabilization. Combined Möbius–Hückel Aromaticity in Doubly Lithium Bridged $R_4C_4Li_2$ Systems[1]

Sir:

How can cyclic 4π electron topologies, usually associated with "antiaromaticity", be stablized? We propose a simple solution to this problem: two energetically favorable molecular orbitals, one Hückel and one Möbius in character,[2] are utilized. Consider the generalized metallocycle, I, in which M contributes no π electrons but offers vacant orbitals of p (II) and d (III) symmetry. The four π electrons of the butadiene moiety can now be delocalized effectively in two MO's, II (Hückel type, no phase inversions) and III (Möbius type, one phase inversion; the nodal plane passing through M does not count).[2] Since different basis sets of atomic orbitals are utilized in II and III, combined Hückel–Möbius character results.

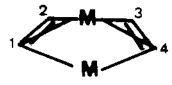

I


II

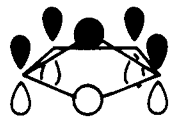

III

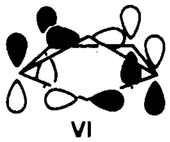
Although many metallacycles are known[3,4] and the possibility of d-orbital involvement (III) has been considered in detail,[3,5] we are not aware of any 4π systems (I) which demonstrate the special stabilization associated with "aromaticity".[6] Perhaps the C–M σ bonds in I are too long to permit effective overlap in orbitals like III. There is a way around this diffculty.

Instead of completing the ring by means of a coplanar atom (M in I), this can be achieved by two atoms or groups, M in IV, placed roughly between C_1 and C_4 but above and below the carbon plane. This would confer greater geometrical flexibility with regard to the C_1–C_4 separation. In Hückel MO V, s orbitals of M are utilized; in Möbius MO VI, the involvement of M p orbitals is required.

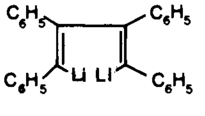


IV(C_{2v})

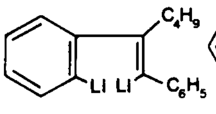

V


VI

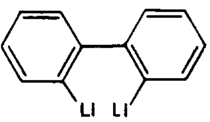
We think it is likely that systems like IV are already known experimentally, although their nature has not been recognized. Diphenylacetylene dimerizes with metallic lithium to give a dilithiated species,[7] traditionally written in the all-cis form, VII, perhaps because of its utility in preparing various heterocycles (I).[4] Diphenylacetylene reacts with n-butyllithium anomalously. The reaction does not stop with a simple triple bond addition; specific metalation of a single "pseudoacidic" ortho phenyl hydrogen occurs as well to give VIII.[8] VII, VIII, and o,o'-dilithiobiphenyl (IX)[4c] can be regarded as derivatives of IV-Li possibly favoring double lithium bridging.



VII



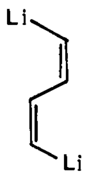
VIII



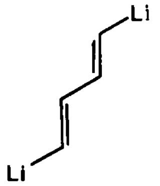
IX

We have investigated this problem by means of molecular orbital calculations. Numerous trial structures for $C_4H_4Li_2$ were examined by utilizing the semiempirical MNDO method.[9] The most energetically competitive structures (including IV and X–XIII) were recalculated, by use of the minimal STO-3G basis set and full-geometry optimization within the symmetries selected.[10] Single point split valence basis 4-31G//STO-3G calculations followed; the lowest energy structural forms (IV-Li and XIII-Li) were then optimized with the 4-31G basis (4-31G//4-31G).[10] Table I summarizes the energies and provides some geometrical information; the supplementary material can be consulted for the full geometries.

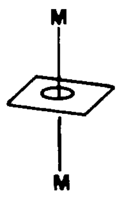
X(C_{2v})



XI(C_{2h})



XII(C_{2h})



XIII(D_{4h})

In addition to the structures shown (IV and X–XIII), lower symmetry alternatives were also considered. These include C_s and

---

(1) Presented at the Annual Chemical Congress, The Chemical Society, Durham, England, April 1980 (See: *Chem. Brit.* **1980**, *16*, 385) and at the Royal Society of Chemistry International Symposium, "Metall-Organics in Organic Synthesis", Swansea, Wales, July 1980.

(2) Heilbronner, E. *Tetrahedron Lett.* **1964**, 1923. Zimmerman, H. *Acc. Chem. Res.* **1971**, *4*, 272.

(3) For leading references see: Thorn, D. L.; Hoffmann, R. *Nouv. J. Chim.* **1979**, *3*, 39.

(4) (a) Leavitt, F. C.; Manuel, T. A.; Johnson, F.; Matternas, L. U.; Lehman, D. S. *J. Am. Chem. Soc.* **1960**, *82*, 5099. Braye, E. H.; Hübel, W.; Caplier, I. *Ibid.* **1961**, *83*, 4406. (b) Eisch, J. J.; Galle, J. E. *J. Organomet. Chem.* **1975**, *96*, C23. Eisch et al. describe VII as a "crystalline yellow-dietherate". (c) Wakefield, B. J. "The Chemistry of Organolithium Compounds"; Pergamon Press: Oxford, 1974.

(5) Craig, D. P. *J. Chem. Soc.* **1959**, 997. Böhm, M. C.; Gleiter, R. *J. Chem. Soc., Perkin Trans. 2*, **1979**, 443.

(6) Bushby, R. J.; Patterson, A. S. *J. Organomet. Chem.* **1977**, *132*, 163. Bushby et al. have called attention to the 4π Möbius character of the bridged structure of allyllithium. Also see: Reetz, M. T. *Tetrahedron* **1973**, *29*, 2189.

(7) Schlenk, W.; Bergmann, E. *Liebigs Ann. Chem.* **1928**, *463*, 71. Smith, L. I.; Hoehn, H. J. *Am. Chem. Soc.* **1941**, *63*, 1184.

(8) (a) Mulvaney, J. E.; Garlund, Z. G.; Garlund, S. L.; Newton, D. J. *J. Am. Chem. Soc.* **1966**, *88*, 476. (b) Mulvaney, J. E.; Groen, S.; Carr, L. J.; Garlund, Z. G.; Garlund, S. L. *Ibid.*, **1969**, *91*, 388. (c) Mulvaney, J. E.; Newton, D. J. *J. Org. Chem.* **1969**, *34*, 1936. Also see: Curtin, D. Y.; Quirk, R. P. *Tetrahedron* **1968**, *24*, 5791. Bridging lithium species may explain results reported by: Hoberg, H.; Gotor, V. *J. Organomet. Chem.* **1978**, *148*, 1.

(9) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.*, **1977**, *99*, 4899, 4907. The parameterization for lithium (Thiel, W.; Clark, T., unpublished) is still in the development stage.

(10) The Gaussian 76 program with the standard basis sets was used: Binkley, J. S.; Whiteside, R. A.; Hariharan, P. C.; Seeger, R.; Pople, J. A.; Hehre, W. J.; Newton, M. D. *QCPE* **1979**, *11*, 368.

0002-7863/80/1502-7928$01.00/0