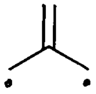
Tetrahedron Letters,Vol.27,No.18,pp 2053-2056,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain ©1986 Pergamon Press Ltd.

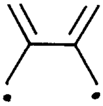
# THE GENERATION AND E.S.R. OBSERVATION OF A DERIVATIVE OF VINYL-TMM (2-METHYLENECYCLOHEPT-3-EN-1,5-DIYL)

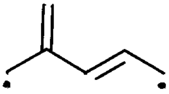
By Richard J. Bushby* and Christine Jarecki
Department of Organic Chemistry, The University, Leeds LS2 9JT

Photolysis of 6,7-diaza-2-methylenebicyclo[3.2.2]nona-3,6-diene in a glassy matrix at 77K gives the triplet biradical, 2-methylenecyclohept-3-en-1,5-diyl, which shows $|D/hc| \simeq 0.019$ and $|E/hc| \simeq 0.006\ cm^{-1}$.

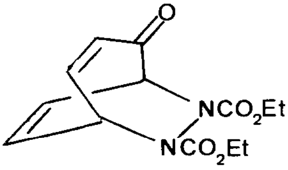
Trimethylene methane, TMM 1, is a 4π non-classical or non-Kekulé isomer of butadiene ($C_4H_6$)[1]. Two 6π non-Kekulé isomers can be written for hexatriene (Tetramethylene ethane, TME 2[2], and vinyl-TMM 3[3]) and seven 8π non-Kekulé isomers of octatetraene[4]. Although TMM and TME have been extensively studied vinyl-TMM and the 8π systems are less well understood. In this paper we report the generation and first direct esr observation of a derivative of vinyl-TMM.


1

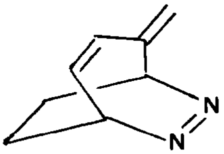

2


3

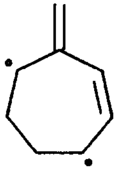
The basis of the synthesis of the biradical precursors was the known cycloaddition reaction between tropone and diethyl azodicarboxylate which gives the bicyclo[3.2.2] compound 4 (63%)[5].



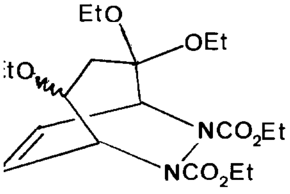
4



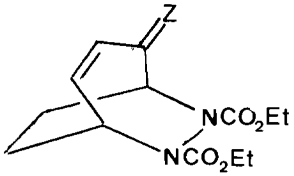
5


6

It was anticipated that this adduct would be readily converted to the diazene 5 which would act as a precursor to the vinyl-TMM biradical 6. In practice the conversion of 4 to 5 was not entirely straightforward. Attempts to find a direct method to selectively reduce the non-conjugated double bond of 4 were not successful. However, the same result could be obtained indirectly and in high yield by treatment of 4 with triethylorthoformate/ethanol/toluene sulphonic acid to give the derivative 7 (91%)[6], catalytic hydrogenation ($H_2$/10% Pd-C/200 psi, 100%), and deprotection ($H^+/H_2O$/dioxan, 69%) to give the enone 8a.

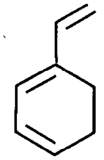


7

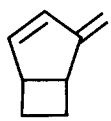


8a Z = O

8b Z = $CH_2$

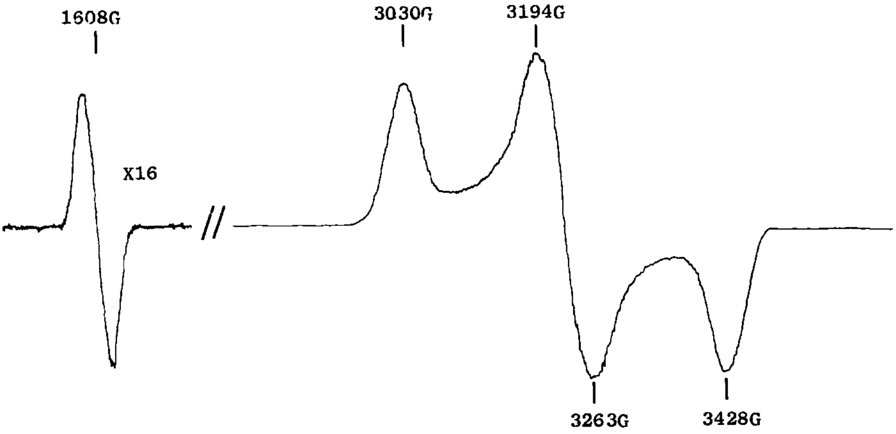


9

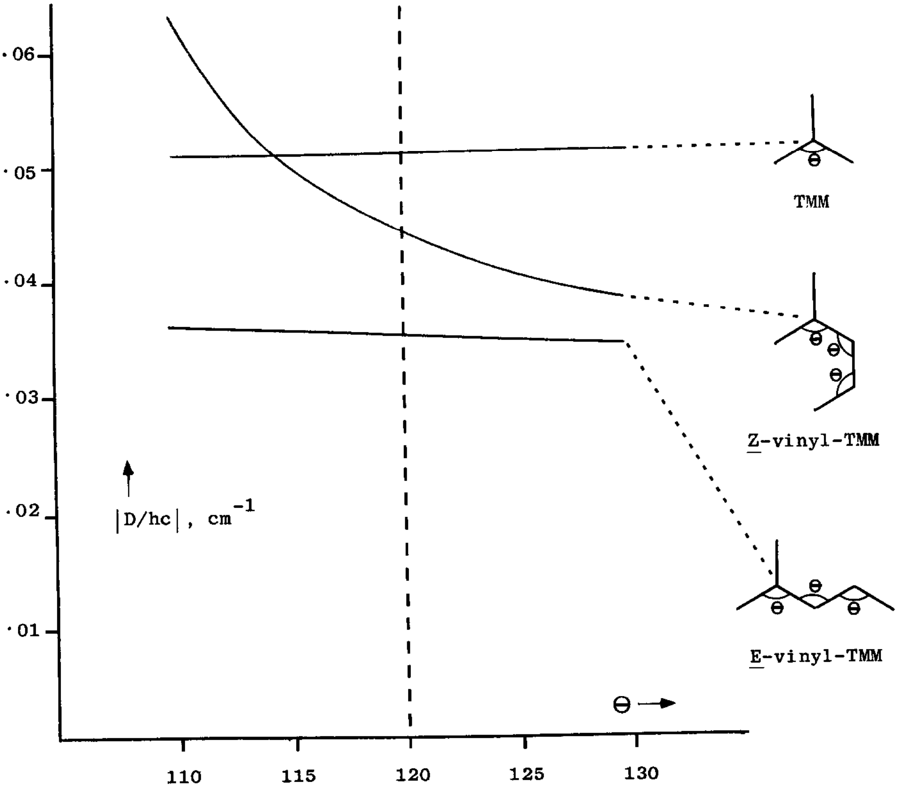


10

Problems were also encountered in converting the enone 8a to the diene 8b. Wittig reactions under a variety of conditions gave at best a 20% yield and a much better route was treatment with methyl lithium (66%) followed by dehydration (toluene sulphonic acid/benzene/4A molecular sieve) (83%). The final steps, hydrolysis ($KOH/H_2O/MeOH$) and oxidation (HgO) proceeded in good overall yield (ca. 80%). The resultant diazene 5 was moderately stable having a half life of about 15 min at 110°C. Among the main $C_8H_{10}$ products from its thermolysis were the expected hydrocarbons 9 and 10[7]. It was virtually insoluble in hydrocarbon and fluorocarbon glasses but when a solution in EPA[8] or methyl-THF/isopropanol[9] glass was irradiated with uv light at liquid nitrogen temperature the triplet esr spectrum shown opposite was obtained. This is characterised by a strong $\Delta m = 2$ transition. The zero field splitting (ZFS) parameters $|D/hc| \simeq 0.019$ and $|E/hc| \simeq 0.006$ $cm^{-1}$ are obtained from the $\Delta m = 1$ region of the spectrum[10]. Values for ZFS parameters can be estimated using the point-charge approximation of McWeeney[11] together with the assumption that the spatial part of the wave function can be constructed from Hückel Molecular Orbitals. The results thus obtained for TMM and vinyl-TMM are shown in the graph[12]. Such calculations are known to overestimate absolute values of $|D/hc|$ by a factor of two but they seem to give fairly reliable relative values[10]. Since these calculated values are based solely on the electron-electron dipolar interaction their magnitude is inversely related to the



Triplet E.S.R. spectrum obtained by u.v. irradiation of diazene 5 in EPA glass [8] at 77K.



Calculated values of |D/hc| for TMM and vinyl-TMM[11,12] mean separation of the electrons. Hence for idealised "120°" geometries they decrease in the order TMM > Z-vinyl-TMM > E-vinyl-TMM. It is also interesting to note that whereas the calculated value for TMM is independent of in-plane angular deformation that for Z-vinyl-TMM is predicted to be highly sensitive to such change. The value $|D/hc|$ obtained experimentally for the biradical 6 is ca. 77% of the experimental value for TMM[13] and it is interesting to note that in our calculations this would correspond to a Z-vinyl-TMM in which the angles $\theta$ had been increased to ca. 125°.

## References and Notes

1. F. Weiss, Quart. Rev., 1970, 24, 278; P. Dowd, Acc. Chem. Res., 1972, 5, 242; J. A. Berson, Acc. Chem. Res., 1978, 11, 446; J. A. Berson in "Diradicals", ed. W. T. Borden, J. Wiley, 1982.
2. P. Dowd, J. Amer. Chem. Soc., 1970, 92, 1066; W. R. Roth, M. Bierman, G. Erker, K. Jelich, W. Gerhartz and H. Görner, Chem. Ber., 1980, 113, 586 and references therein.
3. Vinyl-TMM intermediates have often been proposed for the thermal rearrangements of allylidenecyclopropanes (R. J. Bushby and S. Mann, accompanying paper) and 2-vinyl-1-methylenecyclopropanes (S. Pikulin and J. A. Berson, J. Amer. Chem. Soc., 1985, 107, 8274). They have also been implicated in the thermolysis of 4-allylidene-$\Delta^1$-pyrazolines (K. D. Moeller and R. D. Little, Tet. Lett., 1985, 3417). See also ref. 7 for a reaction involving the biradical 6.
4. A theoretical discussion of an $8\pi$ non-Kekulé polyene may be found in W.T. Borden and E.R. Davidson, J. Amer. Chem. Soc., 1977, 99, 4587, and a metal complex of an $8\pi$ non-Kekulé polyenes is also known; S. Otsuka, A. Nakamura, and K. Tani. J. Chem. Soc. (A), 1971, 154.
5. Y. Kitahara, I. Murata, and T. Nitta, Tet. Lett., 1967, 3003.
6. All new compounds gave satisfactory analytical and spectroscopic data.
7. U. H. Brinker and L. King, J. Amer. Chem. Soc., 1981, 103, 212.
8. 5:5:2, diethyl ether : isopentane : ethanol.
9. 1:1, 2-methyltetrahydrofuran : isopropanol.
10. Examples of triplet spectra for which $|D| \simeq 3|E|$ are not common. One example, 3-methylenephenoxyl, is shown in: M. Rule, A. R. Matlin, D.E. Seeger, E. F. Hilinski, D. A. Dougherty and J. A. Berson, Tet., 1982, 38, 787. This paper contains a useful summary of ZFS parameters obtained for other non-Kekulé polyenes.
11. R. McWeeny, J. Chem. Phys., 1961, 34, 399.
12. The biradicals are assumed to be planar with all C-C bond lengths of 1.427 Å and the p-orbitals represented by point charges 0.68 Å above and below the plane.
13. O. Claesson, A. Lund, T. Gilbro, T. Ichikawa, O. Edlund, and H. Yoshida, J. Chem. Phys., 1980, 72, 1463 and references therein.

We thank Professor P.B. Ayscough and Mr. H.-A. Chia of the Department of Physical Chemistry for help in obtaining the esr spectra.

(Received in UK 28 February 1986)