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(27) A referee has suggested that we will propose a suitable system which according to the HC theory will give inversion. With the substituents which were calculated in Table I, this cannot be achieved. Consideration of other groups which are not included in Table I, e.g., tosylate, involves severe assumptions which make a prediction of a case which should give inversion too speculative.

(28) NOTE ADDED IN PROOF. After the submission of our paper F. Texier, O. Henri-Rousseau and J. Bourgois published a related paper in *Bull. Soc. Chim. Fr., Ser. II*, 86 (1979). The approach of these authors is similar to ours but is totally *qualitative* and therefore does not allow analysis of borderline cases. Furthermore, neglect of the destabilizing 2p(C$^-$)-σ(X) interaction in **2a** may lead to erroneous conclusions, especially in comparing first- and second-row substituents.

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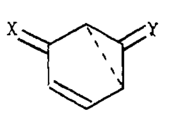
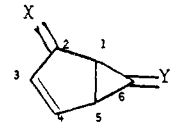
m-Quinomethane: Synthesis of a Covalent–Biradicaloid Pair of Valence Tautomers

Sir:

Two species comprise a covalent–biradicaloid pair when they respectively contain all and one less than all of the complement of bonds permitted by the standard rules of valence. Ring-cleavage reactions frequently implicate such pairs of valence tautomers (e.g., cyclopropane–trimethylene, methylenecyclopropane–trimethylenemethane), and, in general, the isomer of higher covalence is the more stable. However, in the case of the *m*-quinone[1] system symbolized by **1**, where the tautomers **2** and **3** differ by the presence or absence of the C-1–C-5 bond (dashed line), the covalent form **2** will be destabilized by strain, whereas the biradicaloid form **3** will be stabilized by resonance. Thus, the two forms may not differ greatly in energy. Indeed rough bond additivity calculations[2] suggest that, in the case of *m*-quinomethane **1b**, the covalent tautomer **2b** actually is less stable than the biradicaloid one **3b** by ~4 kcal/mol. We report here directed preparations of the valency tautomers, **2b** and **3b**, of *m*-quinomethane, **1b**.[3]



1



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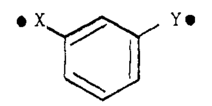
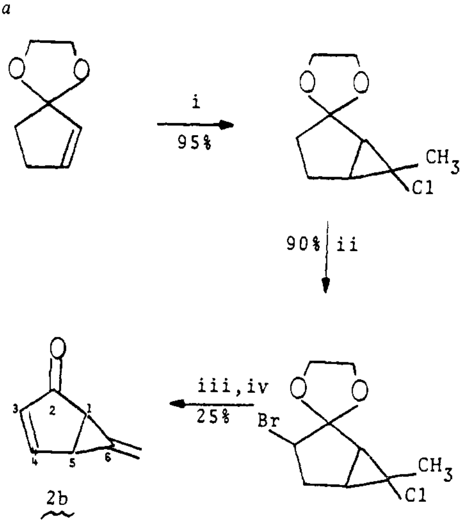


3

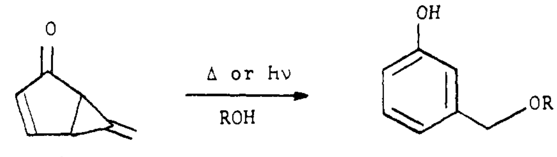
a: X = Y = O
b: X = O, Y = CH_2
c: X = CH_2, Y = O
d: X = Y = CH_2

Scheme I outlines a four-step synthesis of 6-methylenebicyclo[3.1.0]hex-3-ene-2-one (**2b**)[4-6] from cyclopentenone ethylene ketal. Pyrolysis of **2b** (15 m, 150 °C) in ethylene glycol gives the ether **4a**[7,8] in good yield. Similarly, **4a** and its analogue **4b**[4,7,8] are the major products of the photolyses of **2b** (350 nm, 0 °C) in ethylene glycol or methanol solvents, respectively. Photolysis of **2b** in tetrahydrofuran or pyrolysis in *p*-cymene give only insoluble polymeric products. What role, if any, is played by **3b** in these reactions remains to be elucidated.

Scheme I[a]



[a] (i) 2 equiv of BuLi, 2 equiv of CH_3CHCl_2, −30 °C, pentane, following a general procedure of S. Arora and P. Binger, *Synthesis*, 801 (1974); (ii) Br_2, Et_2O, 0 °C, following a general procedure of E. W. Garbisch, *J. Org. Chem.*, **30**, 2109 (1965); (iii) 4 equiv of KO-*t*-Bu, Me_2SO, 60 °C; (iv) Et_2O, 5% H_2SO_4.



2b

4a: R = CH_2CH_2OH
b: R = Me

Irradiation at >310 nm of a degassed, glassy 0.29 M solution of dienone **2b** in 2-methyltetrahydrofuran at 11 K in the cavity of a Varian E-9 electron paramagnetic resonance (EPR) spectrometer (microwave frequency 9.064 GHz) for a few minutes gives rise to a well-defined triplet spectrum which persists for at least an hour. The spectrum, which consists of a group of six lines centered around 3260 G ($\Delta m_s = \pm 1$ transitions) and a weaker line near 1630 G ($\Delta m_s = \pm 2$), can be analyzed[10] in terms of the zero-field splitting (ZFS) parameters, $|D|/hc \simeq 0.027$ cm^{-1}, and $|E|/hc \simeq 0.008$ cm^{-1}, by using an anisotropic g tensor. When a 0.03 M solution of **2b** is irradiated at 77 K, no EPR signal is observed; however, inclusion of 0.25 M benzophenone leads to a triplet spectrum which, although weak, is identifiable as the same as that seen before, superimposed on a doublet impurity peak. A solution 0.3 M in **2b** and 0.25 M in benzophenone, acetophenone, or acetophenone-d_8 irradiated at 10 K gives a strong signal of the same triplet.

The most plausible candidate species for the carrier of the EPR spectrum is a triplet state of the *m*-quinomethane biradical, 3-methylenephenoxyl (**3b**). Two lines of argument, one exclusionary and one circumstantial, support the assignment.

A superficially attractive alternative might be an electronically excited triplet state of the bicyclic enone **2b**, but this is inconsistent with the long lifetime of the signal. Moreover, an enone triplet would be expected[11,12] to show a much larger $|D|/hc$ value (0.2–0.3 cm^{-1}) than that observed.

Although theory[13-15] has been but little tested in this area and hence cannot be conclusive, approximate semiempirical

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calculations of the ZFS parameters using simple Hückel wave functions afford permissive support. For this purpose, we assume that only the dipolar coupling contributes significantly to the ZFS and that spin-orbit effects can be neglected. All the component two-center integrals of the expectation value $\langle D \rangle$ are evaluated by the point-charge approximation of McWeeny,[15] but all three- and four-center integrals are neglected.[13] We calibrate this highly approximate method by calculations of $|D|/hc$ for three known triplet biradicals, trimethylenemethane (TMM), tetramethyleneethane (TME), and 1,8-dimethylenenaphthalene (DMN) as 0.052, 0.049, and 0.040 cm^{-1}, respectively.[16] The corresponding experimental values are 0.024,[17] 0.020,[18] and 0.022[19] cm^{-1}. Clearly, the method tends to overestimate the D values by roughly a factor of 2. Since integral values obtained by the point charge method[15] agree quite well with those obtained[13] by rigorous numerical methods, the evaluation of the integrals probably is not the source of the high D estimates. A more probable origin of the discrepancies is in the use of single configuration wave functions. Other studies[13] have indicated the importance of configuration interaction in the accurate calculation of ZFS parameters.

Values of $|D|/hc$ for **3a**, **3b**, and **3d** calculated by the present approximate method are 0.070, 0.046, and 0.032 cm^{-1}, respectively. Scaling the **3b** value to the above results for TMM, TME, and DMN, we obtain a predicted value of 0.023 cm^{-1}, in good agreement with experiment. The results also suggest that the experimental $|D|/hc$ values for the triplet biradicals (**3a** and **3d**) of *m*-quinone and *m*-quinodimethane should be, respectively, larger and smaller than that of **3b**.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. We are also grateful to the National Science Foundation (CHE-76-00416) and the National Institute of General Medical Sciences (GM-23375) for research support and to the Biotechnology Resources Program of the National Institutes of Health (RR-798) for its support of the Southern New England High-Field NMR Facility.

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(4) Satisfactory combustion analysis and mass spectrometric molecular weight.

(5) ^{1}H NMR (270 MHz, δ units): 7.64 (H_4, 1 H, d × d, $J = 2.199, 5.133$); 5.76 (H_3, 1 H, d, $J = 5.133$); 5.27 (${=}CH_2$, 2 H, s); 3.04 (bridgehead methine, 1 H, m, including $J = 2.199$); 2.76 (bridgehead methine, 1 H, m). ^{13}C NMR (proton splittings by off-resonance decoupling): 27.46 (d); 30.03 (d); 99.62 (t); 128.92 (d); 145.28 (s); 160.20 (d), 204.00 (s). IR (neat film, cm^{-1}): 3100–2800, 1700, 1556.

(6) Purified by gas chromatography at 60 °C on SE-30 or OV-17 columns, injector and detector at 100 °C.

(7) Identified by NMR and mass spectroscopy.

(8) Independently synthesized from *m*-hydroxybenzyl alcohol[9] by successive methanesulfonylation, treatment with the appropriate alkoxide ($HOCH_2CH_2ONa$ or MeONa), and saponification.

(9) Aldrich Chemical Co.

(10) Using the method of P. Kottis and R. Lefebvre, *J. Chem. Phys.*, **41,** 379 (1964), as programmed for a Wang calculator by Professor J. M. McBride, to whom we are indebted.

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(12) C. R. Jones, A. H. Maki, and D. R. Kearns, *J. Chem. Phys.*, **59**, 873 (1973).

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(15) R. McWeeny, *J. Chem. Phys.*, **34,** 399 (1961).

(16) For $|E|/hc$ of TMM, TME, DMN, **3a, 3b,** and **3c,** we obtain 0, 0.0019, 0.0077, 0.0054, 0.0012, and 0.0047 cm^{-1}, respectively. Calculated values for E generally are less reliable than for D[13] and thus are not useful here for structural assignment.

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(18) Since our calculation treats TME as a planar (D_{2h}) structure, we give the experimental value of $|D|/hc$ for 2,3-dimethylenecyclohexa-1,4-diyl (W. R. Roth and G. Erker, *Angew. Chem., Int. Ed. Engl.*, **12**, 503 (1973)), which should be nearly planar. The value for TME itself, which could be twisted out of planarity (see D. A. Dixon, R. Foster, T. A. Halgren, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **100**, 1359 (1978)), is 0.012 cm^{-1} (P. Dowd, *J. Am. Chem. Soc.*, **92,** 1066 (1970)).

(19) R. Pagni, M. N. Burnett, and J. R. Dodd, *J. Am. Chem. Soc.*, **99,** 1972 (1977).

(20) Dox Graduate Fellow, 1978–1979.

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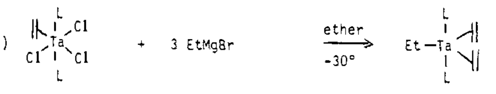
Rapid Selective Dimerization of Ethylene to 1-Butene by a Tantalum Catalyst and a New Mechanism for Ethylene Oligomerization

Sir:

Some time ago we found that $Ta(CH_2CMe_3)_3(CHCMe_3)$,[1] at least 2 mol of PMe_3, and ethylene (40 psi) in pentane at 25 °C produced a homogenous catalyst which rapidly dimerized ethylene selectively to 1-butene. Since such selectivity is rare,[2] we set out to find a plausible explanation. We believe the C_4 chain does not form by "insertion of ethylene into a metal–ethyl bond" but via a metallacyclopentane intermediate.

$Ta(CH_2CMe_3)_3(CHCMe_3)$ reacts with PMe_3 (L) to give $Ta(CHCMe_3)_2L_2(CH_2CMe_3)$.[3] This molecule probably has a trigonal-bipyramidal structure similar to that recently found for $Ta(CHCMe_3)_2L_2(\text{mesityl})$[4] (axial L's and two different neopentylidene ligands which lie in the trigonal plane). It reacts rapidly with ethylene (30 psi) in pentane to give 3 mol of neopentylethylene,[5] one of two "normal" products of neopentylidene cleavage by ethylene,[6,7] and a catalyst which will dimerize ethylene to 1-butene at a rate of ~0.5 turnovers/metal·min at 0 °C; essentially no internal butenes are produced and longer chain products do not appear until 1-butene is virtually the solvent. Removing all volatiles from a typical catalytic reaction at 0 °C leaves a red-brown oil which by ^{13}C NMR (67.89 MHz) contains largely two organometallic compounds in approximately a 70:30 ratio. The same two (in a variable ratio) are seen by ^{13}C NMR in a functioning catalytic reaction in toluene-d_8 at −20 °C. They are extremely soluble in pentane and will not crystallize readily, even at −78 °C.

The reaction between blue $Ta(C_2H_4)L_2Cl_3$[8] and 3 mol of EtMgBr gives what is clearly a close relative of the major organometallic component of the catalytic reaction (**1,** eq 1). The characteristic "virtual" triplet pattern for the PMe_3 ligands in the ^{1}H or ^{13}C NMR spectrum suggests that **1** is also a tri-

(1)


1[9]