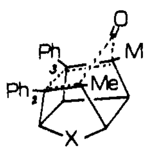

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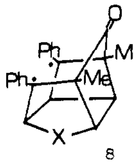

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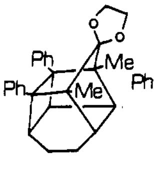

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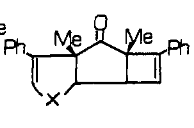

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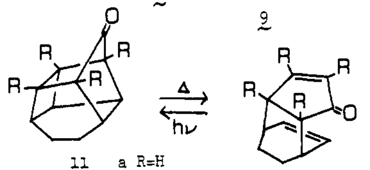


11 a R=H
b R=Cl

12 a R=H
b R=Cl

seem to support that a preferential cleavage of the C_2–C_3 bond of the cyclobutane ring is not essential for the decarbonylation of the cage ketones. It is rather more plausible that efficient overlapping of the developing p orbitals at the C_2–C_3 carbons with those of the ketonic bridge is a major factor. However, the effect of the phenyl groups should not be overlooked. Cage ketones like **11** with no phenyl substituents were synthesized by the irradiation of the corresponding dienones **12**,[15] and their pyrolytic reactions were investigated. Around 450 °C, the ketones **11** underwent a rather simple pyrolysis without decarbonylation reverting to the starting dienones **12** in nearly quantative yields. This reaction is analogous to that of **5**, implying that the phenyl groups participate in the decarbonylation reaction by weakening the C_2–C_3 bond in **1**. It is conceivable that the phenyl groups raise the π-character of the C_2–C_3 bond, resulting in an efficient perturbational interaction in the transition state **7**. Further studies are in progress to investigate the definite nature of the decarbonylation.

References and Notes

(1) Organic Thermal Reactions, 36. Part 35, A. Amano, T. Mukai, T. Nakazawa, and K. Okayama, *Bull. Chem. Soc. Jpn.*, **49**, 1671 (1976).

(2) (a) E. L. Allred and K. J. Voorhees, *J. Am. Chem. Soc.*, **95**, 620 (1973); (b) H. Olsen and J. P. Snyder, *ibid.*, **96**, 7839 (1974); (c) H. Schmidt, A. Schweig, B. M. Trost, H. B. Neubold, and P. H. Scudder, *ibid.*, **96**, 622 (1974); (d) J. A. Berson, S. S. Olin, E. W. Petrillo, Jr., and P. Bickart, *Tetrahedron*, **30**, 1639 (1974); (e) E. L. Allred and J. C. Hinshaw, *Tetrahedron Lett.*, 387 (1972).

(3) (a) B. Halton, M. A. Battiste, R. Rehberg, C. L. Deyrup, and M. E. Brennan, *J. Am. Chem. Soc.*, **89**, 5964 (1967); (b) S. C. Clarke and B. L. Johnson, *Tetrahedron*, **27**, 3555 (1971).

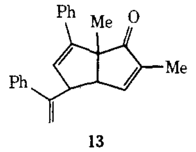
(4) (a) M. Sakai, *Tetrahedron Lett.*, 2297 (1973); (b) G. Kretschmer, I. W. McCay, M. N. Paddon-Row, and R. N. Warrener, *ibid.*, 1339 (1975).

(5) Compound **1c** was obtained by catalytic reduction of **1d**. Compounds, **1a**, mp 127–128 °C, **1b**, mp 134 °C, **1c**, mp 176 °C, and **1e**, mp 123 °C, except for **1d**,[7b] are all new. Satisfactory elemental analyses were obtained for all new compounds reported in this paper.

(6) (a) T. Mukai, Y. Yamashita, H. Sukawa, and T. Tezuka, *Chem. Lett.*, 423 (1975); (b) L. A. Paquette, D. N. Kuhla, J. H. Barrett, and L. M. Leichter, *J. Org. Chem.*, **34**, 2888 (1969).

(7) (a) K. N. Houk, *Tetrahedron Lett.*, 2621 (1970); (b) K. N. Houk and R. B. Woodward, *J. Am. Chem. Soc.*, **92**, 4143 (1970).

(8) The structure of the product is considered to be a five-membered α,β-unsaturated ketone **13** (ν_{CO} 1700 cm^{-1}). Details will be reported elsewhere soon.



13

(9) NMR spectra (in $CDCl_3$, 100 MHz) of **2b**, **2c**, **2d**, and **2e** were similar to each other and chemical shifts of their methyl signals (δ 1.63–1.93) are compatible with that of sp^2-bound methyl groups. One of these signals (Me) splits into doublet-doublet by long-range coupling with H_B and H_C. Especially small values of the coupling constant between H_A, H_B, H_C, and H_D (2.1–4.2 Hz) support the tricyclic structure.

(10) This ketone decomposed at 425 °C to give cyclopentadiene and dihydroindene; R. C. Cookson, J. Hudec, and R. O. Williams, *Tetrahedron Lett.*, 29 (1960).

(11) E. L. Allred and A. L. Johnson, *J. Am. Chem. Soc.*, **93**, 1300 (1971).

(12) C. G. Overberger, M. Valentine, and J. P. Anselme, *J. Am. Chem. Soc.*, **91**, 687 (1969).

(13) (a) J. E. Baldwin, *Can. J. Chem.*, **41**, 2051 (1966); (b) R. MuCulloch, A. R. Rye, and D. Wege, *Tetrahedron Lett.*, 5231 (1969).

(14) (a) D. M. Lemal, E. P. Gosselink, and S. D. McGregor, *J. Am. Chem. Soc.*, **88**, 582 (1966); (b) T. Fukunaga, T. Mukai, Y. Akasaki, and R. Suzuki, *Tetrahedron Lett.*, 2975 (1970).

(15) W. Herz, V. S. Iyer, and M. G. Nair, *J. Org. Chem.*, **40**, 3519 (1975).

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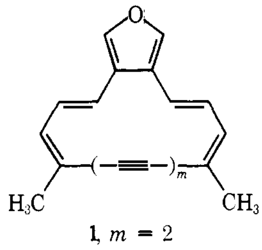
A Reactivity Criterion of Aromaticity and Antiaromaticity in Macrocyclic Annulenes[1]

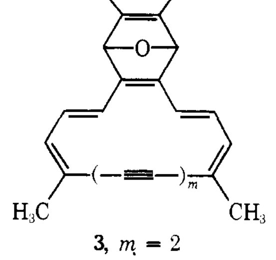
Sir:

The determination of the aromaticity of macrocyclic "Hückel"[2] $(4n + 2)$ π-electron systems and the antiaromaticity of $(4n)$ systems has been mainly based on their magnetic properties, as measured by ^1H NMR spectrometry.[3] By contrast, the classical concept of aromaticity of benzenoid compounds, developed in the last century, was based on reactivity considerations (retention of type, ease of formation). We now report a related reactivity criterion of aromaticity in macrocyclic "Hückel" $[4n + 2]$annulenes, as well as antiaromaticity in macrocyclic $[4n]$annulenes.

The Diels–Alder reaction of dimethyl acetylenedicarboxylate with the dimethylbisdehydro[14]annuleno[*c*]furan (**1**)[4–6] at room temperature to give the adduct **3** (90% yield) has been described previously.[7] Surprisingly, the corresponding reaction with the closely related dimethylmonodehydro[12]annuleno[*c*]furan (**2**)[8] to give **4** could not be effected, even in boiling benzene. We suspected that this lack of reactivity of **2** was due to the potential formation of an antiaromatic $[4n]$annulene derivative, although strain factors might also have played a part. It was therefore decided to synthesize the [16]- and [18]annuleno[*c*]furans (**12**[9a] and **13**[9b]), and to study their Diels–Alder reactions.

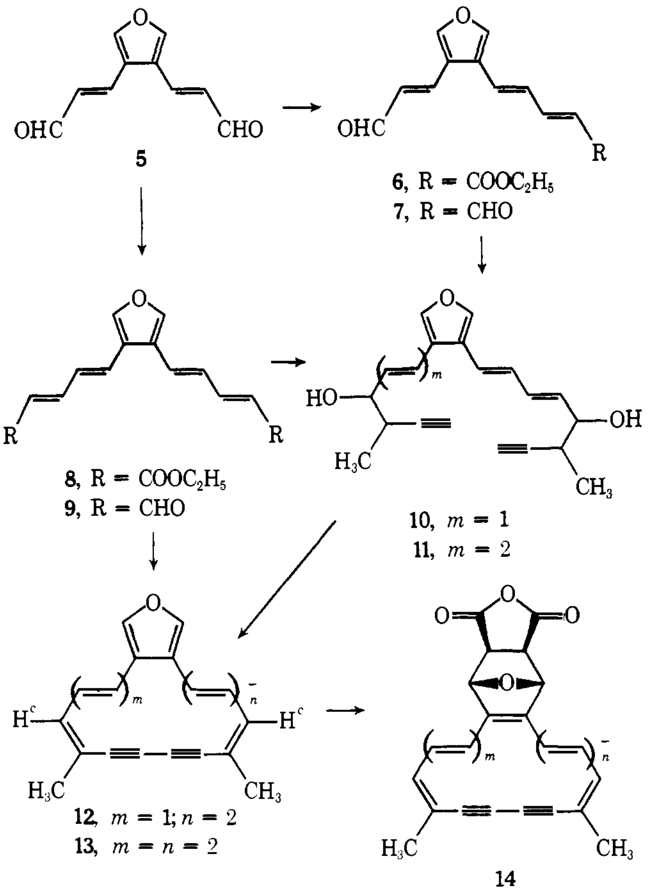


1, $m = 2$
2, $m = 1$



3, $m = 2$
4, $m = 1$

Wittig reaction of the dialdehyde **5**[5,10] with 1 mole equiv of carbethoxymethylenetriphenylphosphorane[11] in CH_2Cl_2 (20°, 20 h) yielded 30% of the monoester **6**[12a] as pale yellow prisms, mp 91–93°.[13] Reduction of **6** with i-Bu_2AlH in benzene (20°, 1 h), followed by oxidation of the resulting diol with MnO_2 in CH_2Cl_2 (20°, 2 h), led to the dialdehyde **7** as pale yellow prisms, mp 114–116°,[13] in 55% yield. Treatment of **7** with an excess of the Mg derivative of 3-bromo-1-butyne[14] in ether–THF (−30 to 0°, 15 min) gave a stereoisomeric mixture of **10**, which on successive coupling with anhydrous $Cu(OAc)_2$ in pyridine–ether (50°, 3.5 h), conversion to the dimesylate with mesyl chloride and $N(C_2H_5)_3$[15] (0°, 1 h), and elimination with 1,5-diazabicyclo[4.3.0]non-5-ene (20°, 4 h), afforded the dimethylbisdehydro[16]annuleno[*c*]furan (**12**)[12b] as orange prisms, mp 137–140°[13] (17% yield based on **7**). The ^1H NMR spectrum of **12** ($CDCl_3$, 100 MHz) had bands, inter alia, at



τ 2.74 (s, furan), 3.6-4.0 (m, H^c), and 8.20 (s, CH_3). The corresponding bands in the "open" analogue **15**[4] are at τ 2.47, 3.62, and 8.02, indicating the 16-membered ring of **12** to be weakly paratropic.

Treatment of triethyl phosphonoacetate (2.3 mole equiv) with NaH (2.3 mole equiv) in THF (0°, 40 min),[16] and then with the dialdehyde **5** (1 mole equiv, 0-20°, 75 min), led to the diester **8**[12a] as yellow prisms, mp 58-61°[13] in 70% yield. Reduction of **8** with i-Bu_2AlH and subsequent oxidation with MnO_2 gave 44% of the dialdehyde **9** as yellow crystals, mp 134-137°.[13] This dialdehyde was then converted in 7% overall yield to the dimethylbisdehydro[18]annuleno[*c*]furan (**13**)[12b] (yellow needles, dec >150°)[13] via the stereoisomeric diols **11**, essentially by the above described method.[17] The ^1H NMR spectrum of **13** ($CDCl_3$, 100 MHz) had bands, inter alia, at τ 2.32 (s, furan), 3.20 (d, $J = 11$ Hz, H^c), and 7.96 (s, CH_3), indicating the 18-membered ring to be weakly diatropic.

Interestingly, the [16]annuleno[*c*]furan (**12**) did not react with an excess of dimethyl acetylenedicarboxylate at room temperature (7 days), whereas the [18]annuleno[*c*]furan (**13**) formed the normal adduct (maroon prisms, dec >180°)[13] in over 90% yield after 2 days. On the other hand, maleic anhydride was found to react with all of the dehydroannuleno[*c*]furans (**1**, **2**, **12**, and **13**) to give exo adducts of type **14**.[18]

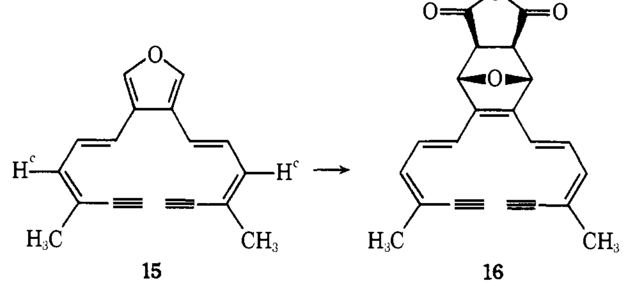


Table I. Bimolecular Rate Constants[a]

Compound	k_B (l. mol^{-1} min^{-1})
Dehydro[12]annuleno[*c*]furan (**2**)	0.01
Dehydro[14]annuleno[*c*]furan (**1**)	2.7
Dehydro[16]annuleno[*c*]furan (**12**)	0.08
Dehydro[18]annuleno[*c*]furan (**13**)	1.7
"Open" model **15**	0.44

[a] Reactions with maleic anhydride in benzene at 23°.

Similarly, reaction of maleic anhydride with the "open" analogue **15**[4] led to the exo adduct **16**.[13]

The bimolecular rate constants (k_B) for the Diels-Alder reactions of maleic anhydride with the dehydroannuleno[*c*]furans **1**, **2**, **12**, and **13**, as well as with the "open" model **15**, are given in Table I.[19,20] The reaction rates of the 14- and 18-membered ring compounds **1** and **13** are clearly faster than those of the model **15**, whereas those of the 12- and 16-membered ring compounds **2** and **12** are slower. It is reasonable to assume that the transition states in these reactions resemble the products to some extent, and that the relative rates reflect the resonance energies of the products. It thus appears that the dehydro[4n + 2]annulenes formed from **1** and **13** are stabilized as compared to the linear polyenyne **16**, whereas the dehydro[4n]annulenes formed from **2** and **12** are destabilized.

Acknowledgment. We thank the Royal Society and the Science Research Council for financial support.

References and Notes

(1) Unsaturated Macrocyclic Compounds. 117. For part 116, see R. R. Jones, J. M. Brown, and F. Sondheimer, *Tetrahedron Lett.*, 4183 (1975).
(2) In "Möbius systems", the requirements for aromaticity and antiaromaticity are reversed (see H. E. Zimmerman, *Acc. Chem. Res.*, **4**, 272 (1971); M. J. S. Dewar, *Angew. Chem.*, **83**, 859 (1971)).
(3) See R. C. Haddon, V. R. Haddon, and L. M. Jackman, *Fortschr. Chem. Forsch.*, **16**, 103 (1971).
(4) P. J. Beeby, R. T. Weavers, and F. Sondheimer, *Angew. Chem.*, **86**, 163 (1974).
(5) T. M. Cresp and F. Sondheimer, *J. Am. Chem. Soc.*, **97**, 4412 (1975).
(6) No particular conformations are implied for the macrocyclic compounds in this publication.
(7) R. T. Weavers and F. Sondheimer, *Angew. Chem.*, **86**, 165 (1974).
(8) R. H. Wightman and F. Sondheimer, *Tetrahedron Lett.*, 4179 (1975).
(9) IUPAC nomenclature: (a) 7,12-dimethyl-8,9,10,11-tetradehydrocyclohexadeca[c]furan; (b) 9,14-dimethyl-10,11,12,13-tetradehydrocyclooctadeca[c]furan.
(10) 3,4-Furandicarboxaldehyde, a precursor of **5**, was prepared most conveniently, in ~40% yield, by the oxidation of 3,4-bis(hydroxymethyl)furan with pyridinium chlorochromate (E. J. Corey and J. W. Suggs, *Tetrahedron Lett.*, 2647 (1975)).
(11) O. Isler, H. Gutmann, M. Montavon, R. Rüegg, G. Ryser, and P. Zeller, *Helv. Chim. Acta*, **40**, 1242 (1957).
(12) Isolated by chromatography on (a) SiO_2 (Woelm, act II); (b) Al_2O_3 (Woelm, act III).
(13) The mass, ^1H NMR and electronic spectra were in accord with the assigned structure.
(14) M. Gaudemar, *Ann. Chim. (Paris)*, **1** (13), 161 (1956); C. Prévost, M. Gaudemar, L. Miginiac, E. Bardone-Gaudemar, and M. Andrac, *Bull. Soc. Chim. Fr.*, 679 (1959).
(15) See R. L. Crossland and K. L. Servis, *J. Org. Chem.*, **35**, 3195 (1970).
(16) See W. S. Wadsworth and W. D. Emmons, *J. Am. Chem. Soc.*, **83**, 1733 (1961); J. Wolinsky and K. L. Erickson, *J. Org. Chem.*, **30**, 2208 (1965).
(17) In this case, the oxidative coupling was carried out with $Cu(OAc)_2 \cdot H_2O$ in DMF (60°, 2.5 h).
(18) The exo stereochemistry follows from the ^1H NMR spectra (see F. A. L. Anet, *Tetrahedron Lett.*, 1219 (1962). In the case of **2**, some endo adduct was also isolated.
(19) Inter alia, see J. Sauer, H. Wiest, and A. Mielert, *Chem. Ber.*, **97**, 3183 (1964); W. C. Herndon, *J. Org. Chem.*, **40**, 3583 (1975).
(20) The bimolecular rate constants were determined from pseudo-first-order reactions. The concentrations of the furans were in the range 0.07-0.7 mmol l.$^{-1}$, and an excess (20-150 mole equiv) of maleic anhydride was used. The reactions were followed by the disappearance of the starting materials, or appearance of products, as determined by the electronic spectra (Unicam SP 1800 ultraviolet spectrophotometer, fitted with a circulating water bath attachment).

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