Angewandte Chemie International Edition

DOI: 10.1002/anie.201206101

Heteroradialenes

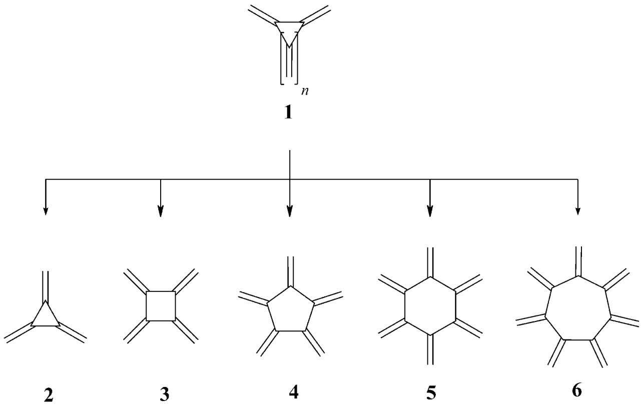
Phospharadialenes—A New Kid in Town

*Henning Hopf**

heteroradialenes · materials chemistry · oxocarbons · phospharadialenes · squaraines

Renewed interest in radialene chemistry has led to theoretical and spectroscopic studies of cyclic polycarbonyl compounds such as cyclobutanetetraone and its homologues as well as the preparation of the first [3]phospharadialene derivative. The radialenes and their countless derivatives with their unusual π-electronic properties promise interesting applications in material science.

Radialenes (**1**, Scheme 1) are hydrocarbons consisting exclusively of semicyclic double bonds;[1] in addition to the linear oligoenes, the annulenes, the fulvenes, and the dendralenes[2] they form the fifth class of unsaturated compounds that can be generated from ethylene units. Whereas the parent systems [3]- (**2**), [4]- (**3**), and [6]radialene (**5**) have all been described in the chemical literature,[1] [5]radialene (**4**) is currently unknown, although several derivatives of this pentaene, for example the decamethyl derivative, have been reported.[3] None of the higher vinylogues of this series, beginning with [7]radialene (**6**), have so far been described, although some calculations on these hydrocarbons have appeared.

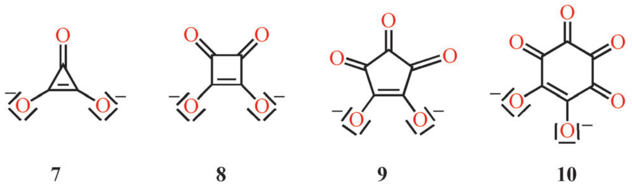


Scheme 1. The [*n*]radialenes.

Heteroradialenes, the topic of this Highlight, are formally obtained by replacing one or more of the terminal $=CH_2$ groups of a radialene hydrocarbon by one or more isovalent heteroatoms or heteroatom-containing fragments. These substitutes could be oxygen or sulfur, for example, or an imine function. While the name "oxocarbon" bears a clear relationship to the radialene hydrocarbon from which it is derived, the derivatives in which one or more of the carbonyl oxygen atoms are replaced by other atoms or groups have been given the rather vague name of "pseudo-oxocarbons". When the C=O groups are replaced by nitrogen-containing groups many authors speak of "squaraines" rather than azacarbons. The introduction of phosphorus-containing groups leads to phospha[*n*]radialenes (see below).

The replacement of the methylene groups in radialene **2** by heteroatoms results in a rapid increase in structural variety, since the two heterorganic substituents may not only be identical or not but can also occur in neighboring or non-neighboring positions. Furthermore, whenever there are two or more heteroorganic substituents of, for example, the imine ($CH_2 \rightarrow NR$) or the phospha type discussed below ($CH_2 \rightarrow PR$), the problem of diastereoisomerism arises, since the substituents R can point towards to or away from each other.

The oxa derivatives of the radialenes were defined by West and Powell as cyclic multicarbonyl compounds in which "all or nearly all of the carbon atoms are bonded to carbonyl or enolic oxygens or their hydrated or deprotonated equivalents".[5] When talking about oxocarbons, therefore, it is usually not the neutral $(CO)_n$ compounds one is referring to but their corresponding ions. Among these, the most thoroughly studied are the oxocarbon ions deltate (**7**), squarate (**8**), croconate (**9**), and rhodizonate (**10**, Scheme 2). The synthesis and chemistry of these charged compounds, some of which were prepared in the very early days of organic chemistry, have been reviewed several times in the past, and also more recently.[5]



Scheme 2. The classical oxocarbon ions.

Although the "classical (preparative) phase" of oxocarbon chemistry came to an end about 20 years ago, there are recent indications of a renewed interest in these heterocyclic

---

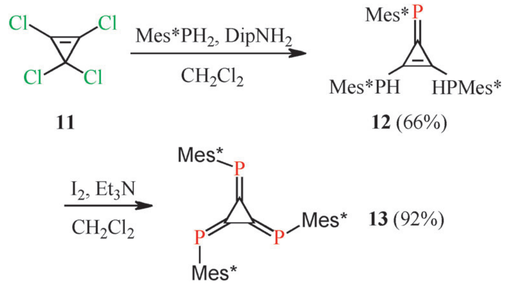
[*] Prof. Dr. H. Hopf
Institut für Organische Chemie
Technische Universität Braunschweig
Hagenring 30, 38106 Braunschweig (Germany)
E-mail: h.hopf@tu-bs.de

compounds, especially from a theoretical viewpoint, the possibility of detecting the neutral "radialones" and their congeners by spectroscopic methods, and the practical applications of these π systems.

According to theoretical calculations, the neutral oxocarbons $[\mathrm{CO}]_n$ are thermodynamically unstable against decomposition into carbon monoxide. After some early calculations by Gleiter et al. in 1995,[6] theoretical studies on cyclobutanetetraone has been revisited recently by the research groups of Jiao, Gleiter, Borden, who applied more-advanced computational methods (B3LYP, (12/12)CASSCF).[7,8] These new calculations suggest that the tetraketone should possess a triplet ground state, rather than the intuitively expected singlet ground state.[6] Whether it could be prepared under conditions where it might be stable towards ring opening and/or decarbonylation remains an open question, though. In another recent study, Borden and co-workers corroborated the computational evidence that the neutral molecule possesses a $^3\mathrm{B}_{2u}$ ground state and suggested experiments to confirm their computational results.[9] These experiments have in the meantime been carried out by Wang and co-workers, who performed low-temperate negative-ion photoelectron spectroscopic analysis of the squarate ion $\mathrm{C}_4\mathrm{O}_4^{-}$.[10] The energetic scheme for the neutral oxocarbon could be derived from their results, thereby demonstrating that the predictions of the research groups of Gleiter and Borden concerning the electronic nature of cyclobutanetetraone were qualitatively correct. In a 2012 publication on the molecular orbitals of the oxocarbons $(\mathrm{CO})_n$, the research groups of Hoffmann, Borden, Gleiter, and co-workers extended these theoretical calculations all the way to $(\mathrm{CO})_6$, which is predicted to have a singlet ground state. The difference between the electronic nature of the ground states of $(\mathrm{CO})_4$ and $(\mathrm{CO})_6$ is thought to originate from interactions between 2p atomic orbitals on non-nearest-neighbor carbon atoms. These interactions are much weaker in $(\mathrm{CO})_6$ than in $(\mathrm{CO})_4$ because of the much larger distances between the respective carbon atoms in the former oxocarbon.[11]

As already mentioned, the oxocarbons and their derivatives are often charged compounds related to **7**–**10** (Scheme 2). The preparation of an uncharged representative is hence of considerable importance, especially if the derivatives concerned contain multiple bonds which are themselves unstable, such as P=C bonds. As has been widely reported,[12] one way to reduce the reactivity of this unit is by way of kinetic stabilization by using very bulky substituents. This is the case in the very recently described 4,5,6-triphospha[3]radialene **13** prepared by Miyake, Sasamori, and Tokitoh;[13] the stability of this radialene derivative is augmented by the cross-conjugation of the [3]radialene core.

As shown in Scheme 3, perchlorocyclopropene (**11**), which is often used as a substrate in radialene chemistry,[1,4] also served here as the starting material. Treatment of **11** with the bulky (2,4,6-tri-*tert*-butylphenyl)phosphine (Mes*PH$_2$) in the presence of 2,6-diisopropylaniline (DipNH$_2$) in dichloromethane at room temperature under argon for 5 h led to a diasteromeric mixture of 4-phosphatriafulvenes **12** as a stable orange solid in good yield (66 %). Oxidation of this substitution product with iodine in dichloromethane furnished the phospha[3]radialene **13** in excellent yield as a deep-purple solid which can be handled under ambient conditions in air without decomposition.

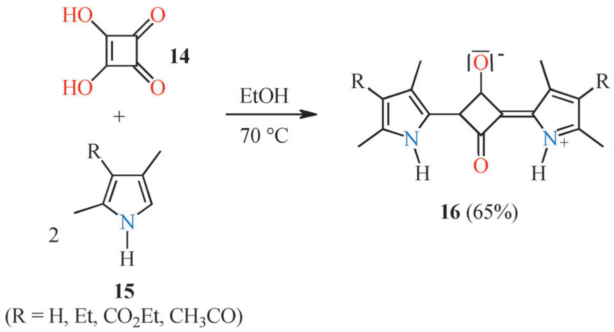


Scheme 3. Preparation of the first triphospha[3]radialene.

The structure shown in Scheme 3 with the paddle-wheel arrangement of the substituents follows from X-ray structural data. The UV spectrum of **13** shows a strong absorption at $\lambda_{\max} = 526$ nm, far red-shifted compared to that of [3]radialene (**2**; $\lambda_{\max} = 289$ nm). It was concluded from electrochemical measurements that the phosphorus-containing cross-conjugated skeleton makes **13** an excellent electron acceptor, thus hinting at a possible application of it, and related compounds, as a component for the construction of molecular electronic devices (see below).

Among the oxocarbons and their derivatives, no class of compounds has been studied as intensively as the squaraines. This is true both from the preparative viewpoint and for the practical applications of these compounds, as demonstrated by several excellent reviews.[14,15] The most important synthetic method to prepare squaraines is basically still derived from the original approach by Treibs and Jacob in 1965,[16] that is, the reaction of squaric acid (**14**) with two equivalents of an activated arene, a π-electron-rich heteroorganic compound such as the pyrrole **15**, or an anhydro base. As in the original case, the 1,3-regioisomer **16** is normally the favored condensation product (Scheme 4), but the 1,2-isomer can also be formed.

Since the number of electron-rich components to choose from is huge, the number of synthesized squaraines is also very large.[15] The last few years have witnessed the preparation of many novel types of squaraines, including squaraine-based rotaxanes[17] and polysquaraines, which are of interest



Scheme 4. The preparation of squaraines according to Treibs and Jacob.

in connection with the preparation of low-band-gap semiconductor polymers.[18,19]

The practical use of these π systems, which can be compared electronically to the cyanine dyes, rests largely on their photophysical behavior. Squaraines normally display sharp and intense low-energy absorption maxima, frequently associated with a strong fluorescence in solution.[14] The countless practical applications for which squaraines have been investigated include for photoconductivity,[20] data storage,[21] light-emitting field-effect transistors,[22] solar cells,[23] fluorescence patterning,[24] and photosensitizers for photodynamic therapy.[25]

Among the more recent applications of the squaraines in "molecular electronics", an example from the solar cell area is noteworthy.[26] It is a constant challenge in the development of organic photovoltaic (OPV) cells to find donors that improve the OPV efficiency by extending the cell photoresponse into the visible and near-IR region. Squaraines, with their large absorption coefficients, provide these donors. As has now been demonstrated,[27] blending different squaraine donors results in a distinct increase in the quantum efficiency within this spectral region (300–900 nm). As a consequence of the enormous structural variety available for the squaraines (see Scheme 4) this approach promises to provide many new "tailor-made" OPV cells.

Received: July 30, 2012

---

[1] Two comprehensive reviews on radialenes have appeared: a) H. Hopf, G. Maas, *Angew. Chem.* **1992**, *104*, 953–977; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 931–954; b) G. Maas, H. Hopf, *The Chemistry of Functional Groups* (Eds.: S. Patai, Z. Rappoport), *The Chemistry of Dienes and Polyenes, Vol. I & II* (Ed.: Z. Rappoport), Wiley, Chichester, **1997**, chap. 21, pp. 927–977; cf. M. Gholami, R. R. Tykwinski, *Chem. Rev.* **2006**, *106*, 4997–5027.

[2] For the most recent review on [*n*]dendralenes, see H. Hopf, M. S. Sherburn, *Angew. Chem.* **2012**, *124*, 2346–2389; *Angew. Chem. Int. Ed.* **2012**, *51*, 2298–2338.

[3] M. Iyoda, H. Otani, M. Oda, Y. Kai, Y. Baba, N. Kasai, *J. Am. Chem. Soc.* **1986**, *108*, 5371–5372; cf. M. Iyoda, A. Mizusuna, H. Kurata, M. Oda, *J. Chem. Soc. Chem. Commun.* **1986**, 1794–1796.

[4] *Oxocarbons* (Ed.: R. West), Academic Press, New York, **1980**.

[5] V. E. de Oliveira, R. Diniz, L. F. C. de Oliveira, *Quim. Nova* **2009**, *32*, 1917–1925.

[6] R. Gleiter, I. Hyla-Kryspin, K.-H. Pfeifer, *J. Org. Chem.* **1995**, *60*, 5878–5883.

[7] H. Jiao, G. Frapper, J.-F. Halet, J.-Y. Saillard, *J. Phys. Chem. A* **2001**, *105*, 5945–5947.

[8] X. Zhou, D. A. Hrovat, R. Gleiter, W. T. Borden, *Mol. Phys.* **2009**, *107*, 863–870.

[9] X. Zhou, D. A. Hrovat, W. T. Borden, *J. Phys. Chem. A* **2010**, *114*, 1304–1308.

[10] J.-C. Guo, G.-L. Hou, S.-D. Li, X.-B. Wang, *J. Phys. Chem. Lett.* **2012**, *3*, 304–308.

[11] X. Bao, X. Zhou, C. F. Lovitt, A. Venkatraman, D. A. Hrovat, R. Gleiter, R. Hoffmann, W. T. Borden, *J. Am. Chem. Soc.* **2012**, *134*, 10259–10270.

[12] T. Baumgartner, R. Réau, *Chem. Rev.* **2006**, *106*, 4681–4727, and references therein.

[13] H. Miyake, T. Sasamori, N. Tokitoh, *Angew. Chem.* **2012**, *124*, 3514–3517; *Angew. Chem. Int. Ed.* **2012**, *51*, 3458–3461.

[14] A. Ajayaghosh, *Acc. Chem. Res.* **2005**, *38*, 449–459; cf. S. Sreejith, P. Carol, P. Chithra, A. Ajayaghosh, *J. Mater. Chem.* **2008**, *18*, 264–274.

[15] L. Beverina, P. Salice, *Eur. J. Org. Chem.* **2010**, 1207–1225.

[16] A. Treibs, K. Jacob, *Angew. Chem.* **1965**, *77*, 680–681; *Angew. Chem. Int. Ed. Engl.* **1965**, *4*, 694–695.

[17] E. Arunkumar, C. C. Forbes, B. C. Noll, B. D. Smith, *J. Am. Chem. Soc.* **2005**, *127*, 3288–3289.

[18] J. Eldo, A. Ajayaghosh, *Chem. Mater.* **2002**, *14*, 410–418.

[19] G. Brocks, A. Tol, *J. Phys. Chem.* **1996**, *100*, 1838–1846.

[20] K. Law, F. Bailey, *J. Org. Chem.* **1992**, *57*, 3278–3286.

[21] M. Emmelius, G. Pawlowski, H. W. Vollmann, *Angew. Chem.* **1989**, *101*, 1475–1502; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1445–1471.

[22] E. C. P. Smits, S. Setayesh, T. D. Anthopoulos, M. Buechel, W. Nijssen, R. Coehoorn, P. W. M. Blom, B. de Boer, D. M. de Leuw, *Adv. Mater.* **2007**, *19*, 734–739.

[23] J.-H. Yum, P. Walter, S. Huber, D. Rentsch, T. Geiger, F. Nuesch, F. De Angelis, M. Grätzel, M. K. Nazeeruddin, *J. Am. Chem. Soc.* **2007**, *129*, 10320–10321.

[24] L.-H. Liu, K. Nakatani, R. Pansu, J.-J. Vachon, P. Tauc, E. Ishow, *Adv. Mater.* **2007**, *19*, 433–436.

[25] A. Avellaneda, C. A. Hollis, X. He, C. J. Sumby, *Beilstein J. Org. Chem.* **2012**, *8*, 71–80.

[26] P. F. Santos, L. V. Reis, P. Almeida, J. P. Serrano, A. S. Oliveira, L. F. Vieira Ferreira, *J. Photochem. Photobiol. A* **2004**, *163*, 267–269.

[27] X. Xiao, G. Wei, S. Wang, J. D. Zimmerman, C. K. Renschaw, M. E. Thompson, S. R. Forrest, *Adv. Mater.* **2012**, *24*, 1956–1960.