# New version of redox-troponization — oxidative expansion of a *para*-semiquinoid ring in the reaction of 4-methyl-4-bromomethyl-2,5-cyclohexadien-1-one with tetrakis(triphenylphosphine)palladium

***V. A. Nikanorov,* G. V. Gavrilova, A. V. Yur'ev, V. I. Rozenberg, and O. A. Reutov***

*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
*28 ul. Vavilova, 117813 Moscow, Russian Federation.*
*Fax: +7 (095) 135 5085. E-mail: vanik@ineos.ac.ru*

4-Methyl-4-bromomethyl-2,5-cyclohexadien-1-one reacts with $Pd(PPh_3)_4$ in benzene to give 4-methyl-2,4,6-cycloheptatrien-1-one. The reaction occurs as intramolecular carbometallation of the enone fragment of the starting dienone followed by rearrangement—dehydrometallation or involves a sequence of steps, *viz.*, homolytic abstraction of the halogen atom, cyclization, recyclization, and dehydrogenation.

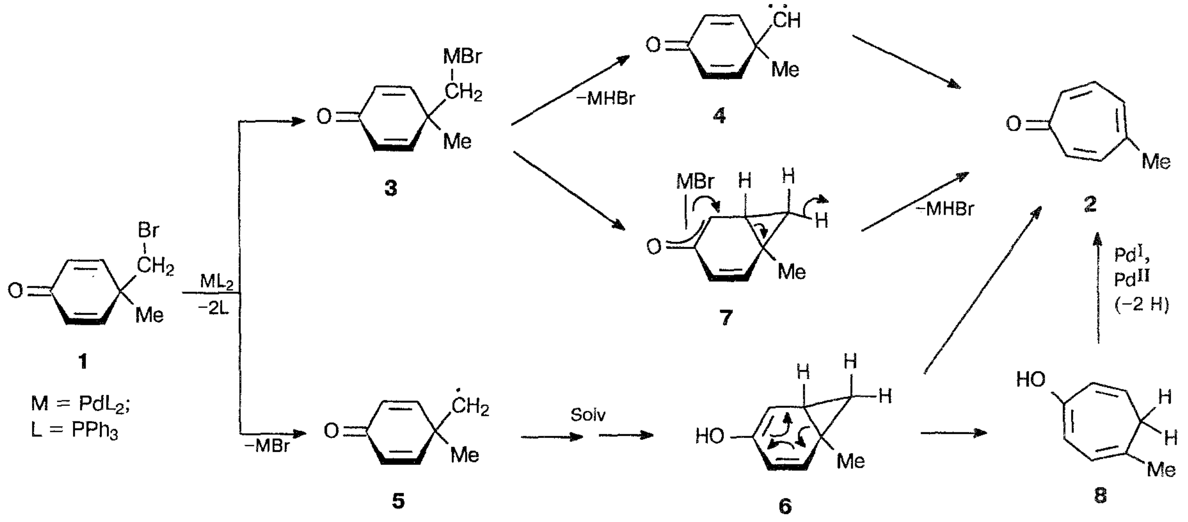
**Key words**: carbocyclic systems, ring expansion; cyclohexadienones; nonbenzenoid aromatic systems of the tropone series; organometallic activation of a C—Hal bond; Pd derivatives in organic synthesis.

Previously we discovered redox-troponization of *gem*-di- and -trihalomethyl substituted *ortho*- and *para*-semiquinoid systems (2,4- or 2,5-cyclohexadien-1-ones) through the action of Zn or triphenylphosphine complexes of zero-valent platinum group metals to give seven-membered nonbenzenoid aromatic compounds of the tropone series.[1] The expansion of the ring during this reaction is in agreement with carbene α-decomposition of α-halogen-containing σ-organometallic intermediates (—CX(Hal)—MHal → $MHal_2$ + $—C(X)^{+-}$ or —(X)C:, where X = H, Hal; Hal = Cl, Br; M = Ni, Pd, Pt, or Zn).[2,3]

In the present work we suggest the use of *gem*-monohalomethyl substituted *para*-semiquinoid systems as starting compounds for the organometallic synthesis of nonbenzenoid aromatic derivatives (Scheme 1).

We found that a representative of this class of compounds, 4-methyl-4-bromomethyl-2,5-cyclohexadien-1-one (**1**) recently described by us[4] can react with $Pd(PPh_3)_4$ to give 4-methyl-2,4,6-cycloheptatrien-1-one (**2**), *i.e.*, the same product as we obtained previously by treating the analogous $CHBr_2$-substituted dienone with the same reagent, $Pd(PPh_3)_4$, according to our standard redox-troponization procedure.[5] The reaction found (see

**Scheme 1**



Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 1836—1837, September, 1995.

Scheme 1) may be considered to be principally a new version of redox-troponization. In fact, carbenoid $\alpha$-decomposition of the possible $\sigma$-organometallic intermediate **3** with elimination of hydride bromide $PdHBr(PPh_3)_2$ yielding carbene **4** (in the singlet or triplet state) now seems substantially less probable than fragmentation of dibromide $PdBr_2(PPh_3)_2$ in the previously studied systems based on *gem*-$CHBr_2$ substituted dienone.[5] However, the assumed homolytic abstraction of the halogen atom by the metal *via* intermediates **5** and **6** does not yet account for the formation of product **2**, since an authentic reaction of this type discovered by Barbier *et al.*,[6] who treated 2,6-di-*tert*-butyl-4-methyl-4-bromomethyl-2,5-cyclohexadien-1-one with the $Bu_3Sn^{\bullet}/Bu_3SnH$ system, gave the 4,5-dihydro derivative of the corresponding tropone, rather than the tropone itself. In view of the foregoing, the most likely pathway of the reaction found by us is either intramolecular carbometallation of the enone fragment of molecule **3** after insertion of $Pd^0$ into the C—Br bond (*cf.* known intermolecular addition of organopalladium compounds to multiple bonds[7]) followed by rearrangement accompanied by dehydrometallation of intermediate **7**, or valence isomerization of the possible dihydro derivative (**6** → **8**), which follows the pattern of norcaradiene-tropilidene rearrangements,[8] and subsequent dehydrogenation of **6** or **8** to tropone **2** through the action of $Pd^I$ or $Pd^{II}$ derivatives present in the system (*cf.* other reactions of oxidation of organic compounds by palladium salts or complexes[9,10]).

## Experimental

**Reaction of 4-methyl-4-dibromomethyl-2,5-cyclohexadien-1-one (1) with tetrakis(triphenylphosphine)palladium.** A solution of dienone **1** (0.04 g, 0.2 mmol) and $Pd(PPh_3)_4$ (0.23 g, 0.2 mmol) in 20 mL of anhydrous $C_6H_6$ in an argon atmosphere was agitated using a vibratory stirrer for ~24 h. The solvent was evaporated, and the residue was chromatographed on a column packed with Chemapol 40/100 μ silica gel ($l$ = 10 cm, $d$ = 2.5 cm) using $Et_2O$ as the eluent and finally was purified on Silpearl UV-254 plates (with $Et_2O$ ($R_f$ 0.47) and then a 1:1 THF—hexane mixture as eluents). Product **2** was isolated as a pale yellow oil, yield 3.5 mg (15 %). The $^1H$ NMR spectrum and mass spectrum of the compound obtained correspond to the published data.[5,11]

This work was carried out with financial support from the Russian Foundation for Basic Research (Project No. 95-03-09784) and the International Science Foundation (Grants MHW 000 and MHW 300).

## References

1. V. A. Nikanorov, G. V. Gavrilova, S. V. Sergeev, V. I. Rozenberg, and O. A. Reutov, *Metalloorg. Khim.*, 1989, **2**, 102 [*Organomet. Chem. USSR*, 1989, **2**, 51 (Engl. Transl.)].
2. G. V. Gavrilova, V. A. Nikanorov, V. I. Bakhmutov, A. A. Gavrilov, V. I. Rozenberg, and O. A. Reutov, *Metalloorg. Khim.*, 1990, **3**, 299 [*Organomet. Chem. USSR*, 1990, **3**, 139 (Engl. Transl.)].
3. G. V. Gavrilova, A. A. Aleshkin, V. A. Nikanorov, D. P. Krut'ko, V. I. Rozenberg, and O. A. Reutov, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 519 [*Russ. Chem. Bull*, 1995, **44**, 502 (Engl. Transl.)].
4. G. V. Gavrilova, V. A. Nikanorov, A. V. Yur'ev, V. I. Rozenberg, and O. A. Reutov, *Metalloorg. Khim.*, 1990, **3**, 333 [*Organomet. Chem. USSR*, 1990, **3**, 157 (Engl. Transl.)].
5. V. A. Nikanorov, G. V. Gavrilova, V I. Rozenberg, and O. A. Reutov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 2345 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1987, **36**, 2174 (Engl. Transl.)].
6. M. Barbier, D. H. Barton, M. Devys, and R. S. Topgi, *Tetrahedron,* 1987, **43**, 5031.
7. S. Cacchi, F. La Torre, and D. Misiti, *Tetrahedron Lett.*, 1979, 4591.
8. F. A. L. Anet, *J. Am. Chem. Soc.*, 1964, **86**, 438.
9. I. I. Moiseev, *π-Kompleksy v zhidkofaznom okislenii olefinov* [*π-Complexes in the Liquid-Phase Oxidation of Olefins*], Nauka, Moscow, 1970 (in Russian).
10. P. M. Henry, *Palladium Catalyzed Oxidation of Hydrocarbons*, D. Reidel, Dordrecht, 1980.
11. V. I. Bakhmutov, M. V. Galakhov, V. A. Nikanorov, G. V. Gavrilova, V. I. Rozenberg, and O. A. Reutov, *Dokl. Akad. Nauk SSSR*, 1987, **295**, 1376 [*Dokl. Chem.*, 1987, **295** (Engl. Transl.)].

*Received February 6, 1995*