# Letters to the Editor

## Unusual rearrangement upon dehydration of *cis*-4,7-diallyl-4,7-dihydroxy-4,7-dihydro[2.2]paracyclophane

*N. V. Vorontsova, V. I. Rozenberg,* E. V. Vorontsov, D. Yu. Antonov, and Yu. N. Bubnov*

*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: lera@ineos.ac.ru*

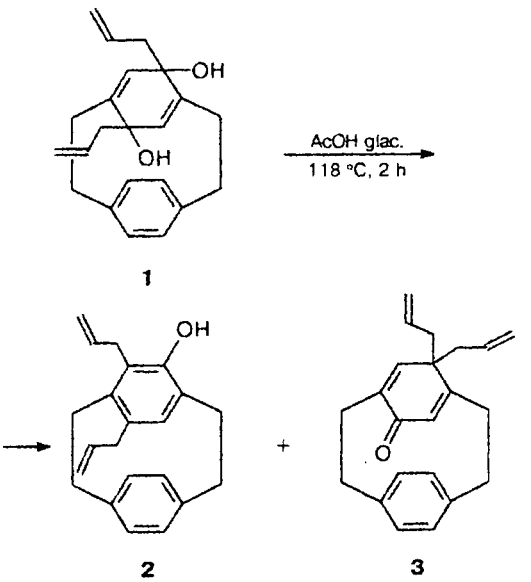
It is known that 1,4-diallyl-1,4-dihydroxy-,[1] 1,4-dihydroxy-1,4-diphenyl-,[2] and 4-alkyl-1,4-dihydroxy-1-phenylcyclohexa-2,5-dienes[3] are dehydrated by acids (and sometimes on heating) and undergo rearrangements to form the corresponding disubstituted phenols. We have found that the dehydration of *cis*-4,7-diallyl-4,7-dihydroxy-4,7-dihydro[2.2]paracyclophane (**1**) in an acidic medium affords,[4] along with the expected phenol, *viz.*, 5,7-diallyl-4-hydroxy[2.2]paracyclophane (**2**), (22%), its structural isomer, 7,7-diallyl-4,7-dihydro-[2.2]paracyclophan-4-one (**3**) as the main product (yield 45%), which is, as far as we know, the first *para*-semiquinoid[5] representative in the [2.2]paracyclophane series (Scheme 1).

The rearrangements found for **1** can be used for the development of a method for the synthesis of new polysubstituted phenols of [2.2]paracyclophane and open the chemistry of semiquinoids in the [2.2]paracyclophane series.

Phenol **2** is a colorless oil unstable in air. Its structure was established by mass spectrometry, $^1$H NMR spectroscopy using the NOESY technique, and IR spectroscopy. Semiquinoid compound **3** is a light-yellow crystalline substance. Its structure was established by $^1$H NMR spectroscopy using the NOESY and COSY techniques, $^{13}$C NMR, UV, and IR spectroscopy, and mass spectrometry.

**5,7-Diallyl-4-hydroxy[2.2]paracyclophane (2).** MS (EI, 70 eV), $m/z$ ($I_{rel}$ (%)): 304 [M]$^+$ (12); 263 [M − All]$^+$ (1.9); 205

**Scheme 1**

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[M − 2 All + H]$^+$ (17.2); 172 [M − 104 − CO]$^+$ (13.5); 159 [M − 104 − All]$^+$ (21); 104 [M − 199 − H]$^+$ (54.1); 199 (100). IR (KBr), ν/cm$^{-1}$: 3570 (OH). Found: *m/z* 304.4298. 304.4247 [M]$^+$. $C_{22}H_{24}O$. Calculated: 304.4247. $^1$H NMR (400.13 MHz, $CDCl_3$), δ: 2.50—3.50 (m, 12 H, *bridg.*-C<u>H</u>$_2$—C<u>H</u>$_2$—, two —C<u>H</u>$_2$—CH=); 4.56 (s, 1 H, O<u>H</u>); 4.98—5.17 (m, 4 H, two C<u>H</u>$_2$=CH); 5.86 (m, 2 H, two —C<u>H</u>=CH$_2$); 6.14 (s, 1 H, H-8); 6.38, 6.60, 6.70, 6.85 (d, H-12, H-13, H-15, H-16, $^3J$ = 7.8 Hz).

**7,7-Diallyl-4,7-dihydro[2.2]paracyclophan-4-one (3).** M.p. 58.5—59.0 °C. Found (%): C, 86.80; H, 7.95. $C_{22}H_{24}O$. Calculated (%): C, 86.85; H, 8.10. MS (EI, 70 eV), *m/z* ($I_{rel}$ (%)): 304 [M]$^+$ (19.0); 263 [M − All]$^+$ (26.5); 200 [M − 104]$^+$ (2.2); 199 [M − 104 − H]$^+$ (1.7); 172 [M − 104 − CO]$^+$ (9.7); 159 [M − 104 − All]$^+$ (32.7); 131 [M − 104 − CO − All]$^+$ (26.8); 104 (100). UV (EtOH), $\lambda_{max}$/nm (ε): 231 (900), 345 (223). IR, ν/cm$^{-1}$: 1630, 1650 (C=O). $^1$H NMR (400.13 MHz, $CDCl_3$), δ: 2.11—2.33 (m, 2 H, —C<u>H</u>$_2$—CH=); 2.88—3.10 (m, 2 H, —C<u>H</u>$_2$—CH=); 4.81 (dd, 1 H, *cis*-CH<u>H</u>=CH—, $^3J$ = 10.4 Hz); 4.87 (dd, 1 H, *trans*-C<u>H</u>H=CH—, $^3J$ = 17.1 Hz); 5.01 (dd, 1 H, *trans*-C<u>H</u>H=CH—, $^3J$ = 17.1 Hz); 5.07 (dd, 1 H, *cis*-CH<u>H</u>=CH—, $^3J$ = 10.4 Hz); 5.12 (s, 1 H, H-5); 5.27 (s, 1 H, H-8); 5.31 (m, 1 H, —CH$_2$—C<u>H</u>=); 5.77 (m, 1 H, —CH$_2$—C<u>H</u>=); 6.76, 6.85, 7.05, 7.11 (d, H-12, H-13, H-15, H-16, $^3J$ = 7.8 Hz).

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