Letters to the Editor

Stereoselective nucleophilic addition of butyllithium and triallylborane to [2.2]paracyclophane-4,7-quinone

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

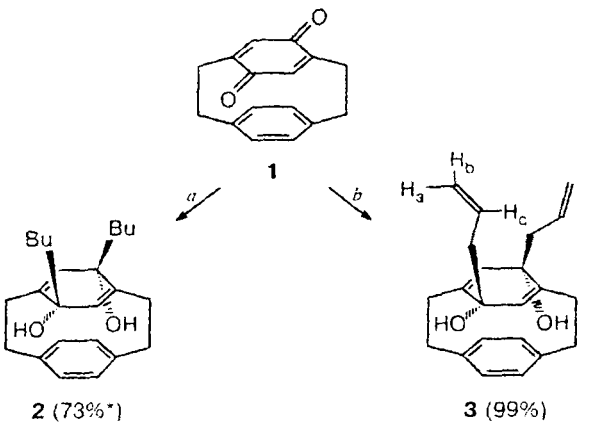
As part of continuing studies of stereoselective processes in the [2.2]paracyclophane series,[1,2] we carried out experiments on the nucleophilic addition of organometallic reagents to racemic [2.2]paracyclophane-4,7-quinone (**1**)[3].

It is known that the reactions of organomagnesium compounds with *para*-quinones proceed both as 1,2- and 1,4-addition,[4,5] whereas the reactions of organolithium derivatives[4] and triallylborane[6,7] afford only 1,2-addition products. Actually, the reaction of quinone **1** with EtMgI yielded a complex mixture of different hydroxy derivatives, whereas the reaction of compound **1** with BuLi proceeded regio- and stereoselectively to form, according to the ^{1}H NMR data, *cis*-4,7-dibutyl-4,7-dihydroxy-4,7-dihydro[2.2]paracyclophane (**2**) in 51% yield, and 30% of the initial quinone **1** was recovered.

The reaction of quinone **1** with All_3B also proceeded stereoselectively to give (after alkaline hydrolysis) *cis*-4,7-diallyl-4,7-dihydroxy-4,7-dihydro[2.2]paracyclophane (**3**) in quantitative yield (Scheme 1).

It should be noted that the reactions of quinone **1** both with BuLi and All_3B afforded diols only as one of the *cis* isomers of two possible *cis* and one *trans* isomer. The ^{1}H NOESY spectra of compounds **2** and **3**, in which the signals for the OH groups correlate with the signals for the protons of the unsubstituted [2.2]paracyclophane ring, are unambiguously indicative of the *endo* orientation of the hydroxy groups. Actually, the attack of the nucleophile on the carbonyl groups of quinone **1** from the side which is not shielded by the second [2.2]paracyclophane ring is the most favorable direction, which agrees with the literature data on the addition of

Scheme 1



* With respect to the consumed quinone **1**.

Reagents and conditions: *a*. BuLi/PhMe, 20 °C, 10 h; *b*. All_3B/CH_2Cl_2, from −78 to 20 °C, 1 h, then MeOH and NaOH.

Translated from *Izvestiya Akademii Nauk, Seriya Khimicheskaya*, No. 3, pp. 568—569, March, 2000.

organomagnesium and organolithium reagents to 5-formyl-4-hydroxy[2.2]paracyclophane.[1] As a result, the hydroxy groups in these diols are in the *endo* orientations.

Compounds **2** and **3** were obtained as white crystalline compounds. Both compounds were characterized by mass spectrometry, ^{1}H NMR spectroscopy, and elemental analysis.

***cis*-4,7-Dibutyl-4,7-dihydroxy-4,7-dihydro[2.2]paracyclophane (2).** M.p. 119.5—120 °C. Found (%): C, 81.56; H, 9.74. $C_{24}H_{34}O_2$. Calculated (%): C, 81.31; H, 9.67. MS (EI, 70 eV), *m/z* (I_{rel} (%)): 354 [M]$^+$ (0.80); 336 [M – H_2O]$^+$ (7.31); 297 [M – Bu]$^+$ (13.61); 104 (100). ^{1}H NMR (400.13 MHz, $CDCl_3$), δ: 0.83 (t, 6 H, 2 C$\underline{H}_3$, ^3J = 7.2 Hz); 1.05—1.50 (m, 12 H, 2 $(CH_2)_3$); 1.90 (s, 2 H, 2 OH); 2.12—2.55 (m, 2 H, bridging C$\underline{H}_2$); 2.65—3.15 (m, 6 H, bridging C$\underline{H}_2$); 4.89 (s, 2 H, H(5), H(8)); 6.96 and 7.05 (both dd, 2 H each, H(12), H(13), H(15), H(16), ^3J = 7.8 Hz, ^4J = 1.8 Hz).

***cis*-4,7-Diallyl-4,7-dihydroxy-4,7-dihydro[2.2]paracyclophane (3).** M.p. 101—101.5 °C. Found (%): C, 81.83; H, 8.00. $C_{22}H_{26}O_2$. Calculated (%) C, 81.95; H 8.13. MS (EI, 70 eV), *m/z* (I_{rel} (%)): 304 [M – H_2O]$^+$ (1.30); 281 [M – All]$^+$ (38.34); 263 [M – H_2O – All]$^+$ (3.70); 240 [M – 2 All]$^+$ (14.21), 104 (100). ^{1}H NMR (400.13 MHz, $CDCl_3$), δ: 2.20 (s, 2 H, 2 OH); 1.95—2.05, 2.15—2.30, 2.62—2.73, and 2.83—3.05 (all m, 12 H, two bridging –C$\underline{H}_2$–C$\underline{H}_2$, two –C$\underline{H}_2$–CH=); 4.90 (s, 2 H, H(5), H(8)); 5.03 (d, 2 H, two H_a, ^3J = 24.1 Hz); 5.10 (d, 2 H, two H_b, ^3J = 9.7 Hz); 5.76 (m, 2 H, two H_c); 6.92 and 7.06 (both d, 2 H each, H(12), H(13), H(15), H(16), ^3J = 7.8 Hz).

This work was financially supported by the Russian Foundation for Basic Research (Project Nos. 97-03-32972a and 96-15-97289) and by the Scientific Training Center of Chemistry of Organometallic Compounds (Grant 234, the Federal Target Program "Integration").

References

1. E. V. Sergeeva, V. I. Rozenberg, E. V. Vorontsov, T. I. Danilova, Z. A. Starikova, A. I. Yanovsky, and Yu. N. Belokon', *Tetrahedron Asymmetry*, 1996, **7**, 3445.
2. N. V. Vorontsova, V. I. Rozenberg, O. L. Tok, and Yu. N. Bubnov, *Izv. Akad. Nauk, Ser. Khim.*, 1997, **12**, 2271 [*Russ. Chem. Bull.*, 1997, **46**, 2271 (Engl. Transl.)].
3. D. J. Cram and A. C. Day, *J. Org. Chem.*, 1966, **31**, 1227.
4. H. M. Crowford, *J. Am. Chem. Soc.*, 1939, **61**, 3310.
5. L. J. Smith and H. H. Hoehn, *J. Am. Chem. Soc.*, 1939, **61**, 2619.
6. B. M. Mikhailov, G. S. Ter-Sarkisyan, and N. A. Nikolaeva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1968, 541 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1968, **17**, 547 (Engl. Transl.)].
7. G. S. Ter-Sarkisyan, N. A. Nikolaeva, V. G. Kiselev, and B. M. Mikhailov, *Zh. Org. Khim.*, 1971, **41**, 152 [*J. Org. Chem. USSR*, 1971, **41** (Engl. Transl.)].

Received July 27, 1999;
in revised form December 6, 1999

Synthesis of 4,6-dinitro-2-trihalogenomethyl-2,3-dihydrobenzo[*b*]furans

V. V. Rozhkov,* A. M. Kuvshinov, and S. A. Shevelev

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 117913 Moscow, Russian Federation.
Fax: +7 (095) 135 5328. E-mail: vrozhkov@chat.ru

A method for the synthesis of previously unknown 4,6-dinitro-2-trihalogenomethyl-2,3-dihydrobenzo[*b*]furans has been elaborated. The method is based on condensation of 2,4,6-trinitrotoluene with fluoral or chloral in the presence of K_2CO_3 with subsequent intramolecular cyclization of the resulting 2-picryl-1-(trihalogenomethyl)ethanols.

Key words: 2,4,6-trinitrotoluene, fluoral, chloral, condensation, intramolecular cyclization, 4,6-dinitro-2-trihalogenomethyl-2,3-dihydrobenzo[*b*]furans.

We found that alcohols obtained by the condensation of 2,4,6-trinitrotoluene (TNT) with fluoral or chloral, *viz.*, 2-picryl-1-(trifluoromethyl)ethanol (**1a**) and 2-picryl-1-(trichloromethyl)ethanol (**1b**), undergo, by the action of bases, intramolecular cyclization (with substitution of the *ortho*-nitro group), which leads to 4,6-dinitro-2-trifluoromethyl-2,3-dihydrobenzo[*b*]furan (**2a**) and 4,6-dinitro-2-trichloromethyl-2,3-dihydrobenzo[*b*]furan (**2b**) (Scheme 1).

The reaction goes smoothly with specified aldehydes or their hydrates; it may serve as a convenient method for preparation of these previously unknown compounds

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 3, pp. 569—570, March, 2000.

1066-5285/00/4903-0573 $25.00