Tetrahedron Letters No. 34, pp 3169 - 3170.
©Pergamon Press Ltd. 1979. Printed in Great Britain.

0040-4039/79/0815-3169$02.00/0

7,10,14-TRI-*t*-BUTYL-3-HYDROXY-1,8-BISDEHYDRO[14]ANNULENE

Yasunobu Onishi, Takeshi Satake, Masahiko Iyoda, and Masazumi Nakagawa*

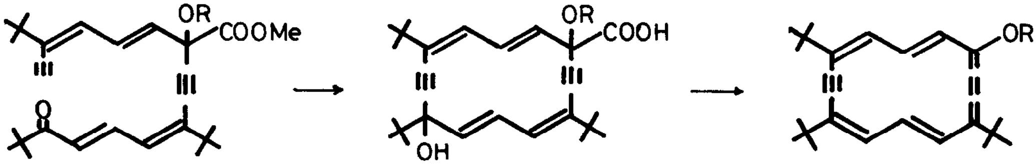
Department of Chemistry, Faculty of Scince, Osaka University, Toyonaka, Osaka 560, Japan

Summary: Tri-*t*-butyl-(β-methoxyethoxy)methoxybisdehydro[14]annulene has been prepared. Cleavage of the ether linkage to give hydroxyannulene was unsuccessful. Treatment of the methoxy analogue with iodotrimethylsilane yielded iodoketone, which gave anion of hydroxyannulene by the reaction with base. Formation of hydroxyannulene could be confirmed by NMR spectroscopy and reconversion of the anion into the methoxyannulene.

In spite of the remarkable development of annulene chemistry, little is known on hydroxyannulene,1) which can be regarded as nonbenzenoid analogue of phenol.

Because we have already prepared 7,10,14-tri-*t*-butyl-3-methoxy-1,8-bisdehydro[14]annulene (V),2) replacement of the methoxyl group by a more easily cleavable group seemed to give a promising precursor for the preparation of hydroxyannulene. Ethynyl hydroxy ester (I)3) was converted into (β-methoxyethoxy)methoxy derivative [II, R=$CH_2OCH_2CH_2OCH_3$=MEM, yellow cryst., mp 27-29°C, 62%]4) by the Corey's method.5) Cyclic glycol monoether (III) obtained from II was treated with ether saturated with hydrogen chloride.2,3) Chromatography of the product afforded IV [red cryst., mp 222-225°C (dec.)]. Attempted cleavage of the ether linkage of IV by means of anhydrous zinc bromide or titanium(IV) chloride5) gave no identifiable product presumably owing to the instability of IV to Lewis acid. The fruitless result forced us to examine the cleavage of the methyl group in the methoxy analogue (V) under mild conditions.

Iodotrimethylsilane has been reported to be an effective agent for cleavage of phenol ether.6) A mixture of V and an excessive iodotrimethylsilane (2.5 mol) in dichloromethane was stirred under nitrogen atmosphere at 0°C for 1 min. A brown liquid obtained on working up the reaction mixture was chromatographed on silica gel and eluted with benzene to give iodoketone [VI, pale yellow cryst., mp 143.2-144.0°C, 25%; Mass(m/e): 490 (M^+), 434 (M^+-56), 363 (M^+-127), 335 (M^+-155); IR(KBr-disk): 2174 w (C≡C), 1646 s (C=O), 1609 s (C=C) cm^{-1}; NMR($CDCl_3$): τ 1.78 (1H, dd, J=16.0, 11.5, H^2), 3.35 (1H, d, J=11.5, H^3), 3.50 (1H, s, H^8), 3.84 (1H, d, J=16.0, H^1), 4.03 (1H, dd, J=9.0, 4.5, H^4), 4.53 (1H, dd, J=8.0, 4.5, H^7), 6.29 (1H, ddd, J=19.0, 9.0, 8.0, H^6), 6.98 (1H, dt, J=19.0, 4.5, H^5), 8.75 s, 8.78 s, 8.80 s (27H, *t*-Bu)].7) The ketone (VI) was found to be unstable and decomposed gradually in a solution.

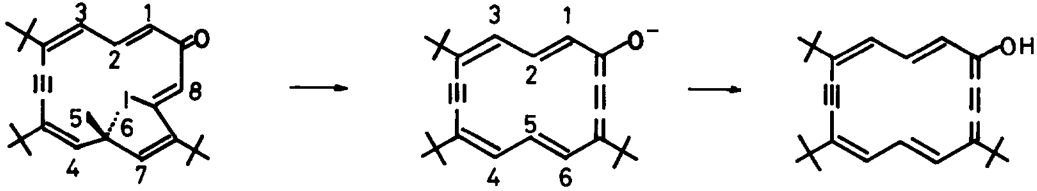


I: R=H, II: R=MEM

III

IV. R=MEM, V: R=Me

Treatment of VI with an excess of diazabicycloundecene (DBU) in THF-d_8 at -50°C gave a deep violet solution. The solution was stood at the same temperature for 22 hrs. under argon atmosphere, and subjected to the measurement of NMR spectrum. A solution of VI in THF was mixed at -65°C with a large excess of DBU in the same solvent. The mixture was allowed to warm to -20°C over a period of 1hr., and diluted with the same cold solvent. Electronic spectrum was measured at -78°C using the solution thus prepared. Absorption intensities were calculated assuming complete conversion. Formation of strongly diatropic anion of tri-*t*-butylhydroxybisdehydro[14]-annulene (VII) is evident from the observed spectroscopic data [NMR(THF-d_8 at -50°C): τ 0.93 (2H, d, H^4, H^6), 1.25 (1H, d, H^3), 1.31 (1H, d, H^1), 8.20 (18H, s, *t*-Bu), 8.26 (9H, s, *t*-Bu), 13.73 (1H, t, H^2), 14.09 (1H, t, H^5); UV(λ_{max}^{THF} nm (ε) at -78°C): 266(14900), 292(15100), 334(35000), 373(66600), 517(17000), 630(17000)]. As quenching of a solution of VII with water in the presence of DBU gave an unidentifiable mixture, deuteriosulphuric acid (1M) was added at -20°C to the solution. Immediate change of colour from deep violet to deep red was observed. Formation of tri-*t*-butylhydroxy[14]annulene (VIII) was revealed by NMR and electronic spectral data [NMR(THF-d_8 at -10°C): τ 0.66 (2H, d, J=13.5), 0.79 (1H, d, J=13.5), 1.01 (1H, d, J=13.5), 6.00 (OH and H_2SO_4), 8.15 (27H, s), 14.55 (2H, t, J=13.5); UV(λ_{max}^{THF} nm (ε) at 0°C): 304 sh(23800), 331(99000), 466 (12000), 529(480), 552(504), 595(3150)]. It has been reported that 2-hydroxy-1,6-methano[10]-annulene gives crystalline keto isomer, although it exsists in an equilibrium mixture of keto and enol isomers in solution in the presence of trace of acid or base. The failure of all attempts to isolate VIII seems to be ascribable to the instability of keto form of VIII. A solution of DBU in THF was added to a solution of VI and dimethyl sulphate in the same solvent at -6°C. After being stirred for 2.25 hrs. at -6°C ∿ 0°C, the mixture was worked up. Chromatographic purification of the product on silica gel yielded the methoxyannulene (V) in a yield of 66%.



VI VII VIII

References and Notes

1) E. Vogel, W. Schröck, and W. A. Böll, *Angew. Chem.*, 78, 2153 (1966).
2) T. Satake, S. Nakatsuji, S. Akiyama, and M. Nakagawa, *Tetrahedron Lett.*, 2153 (1976).
3) T. Satake, S. Nakatsuji, M. Iyoda, S. Akiyama, and M. Nakagawa, *Tetrahedron Lett.*, 1704 (1976).
4) All new crystalline materials gave satisfactory elemental analyses.
5) E. J. Corey, J.-L. Cras, and P. Ulrich, *Tetrahedron Lett.*, 809 (1976).
6) T.-L. Ho and G. A. Olah, *Angew. Chem.*, 88, 847 (1976).
7) The NMR spectral assignments have been made using double resonance and shift reagent methods. The signals of H^1, H^2 and H^3 in VI showed low field shift of 2.36, 1.26 and 0.17 ppm, respectively, on addition of Eu(fod)$_3$. Taking this results into account, the signal at τ 3.50, which showed an appreciable down-field shift (2.26 ppm), was assigned to H^8.

(Received in Japan 1 May 1979)