Hexa-1,5-diyn-3-ol Ethers as Tetramethynyl Synthons in Cobalt-catalysed Acetylene Co-oligomerisations; a One-step Synthesis of 2,3,6,7-Tetrakistrimethylsilylnaphthalene

By Raymond L. Funk and K. Peter C. Vollhardt*

(*Department of Chemistry, University of California, Berkeley, California* 94720)

Summary Reaction of hexa-1,5-diyn-3-ol ether derivatives with bistrimethylsilylacetylene in the presence of catalytic amounts of [CpCo(CO)$_2$] (Cp = cyclopentadienyl) gives 2,3,6,7-tetrakistrimethylsilylnaphthalene.

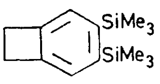
We recently reported on the cobalt-catalysed synthesis of the strained 4,5-bistrimethylsilylbenzocyclobutene (**1**), a useful *o*-xylylene synthon, from co-oligomerization of hexa-1,5-diyne and bistrimethylsilylacetylene (BTMSA).[1] It occurred to us that by introduction of an alkoxy group to the methylene 'back bone' of the starting diyne one might gain access to further more highly functionalized benzocyclobutenes, *e.g.* (**2**), of great potential in organic synthesis.[2] Specifically, if after use of the benzocyclobutene as an *o*-xylylene synthon the alkoxy group were to be removed (as the alcohol) in subsequent transformations the starting diyne-ether would have essentially provided the synthetic equivalent of a tetramethynylethylene unit [*e.g.* (**3**)]. We report the first successful application of such a scheme.

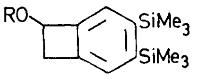
Addition of ether (**4a**) (readily available from hexa-1,5-diyn-3-ol[3]) in neat BTMSA to a refluxing solution of [CpCo(CO)$_2$] (5 mol %) in BTMSA under anaerobic and dry conditions over a period of several days followed by chromatography on silica gave the unusual, strained naphthalene derivative (**5**) in one step (30%) as colourless crystals,† m.p. 232—233 °C, $\tau(CCl_4)$ 2·04 (s, 4H) and 9·54 (s, 36H); λ_{max} (95% EtOH) 244 (log ϵ 5·15), 256sh (4·14), 273 (4·84), 284sh (3·75), 292sh (3·54), 311sh (2·79), 320 (2·91), 326 (2·92),

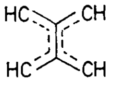
---

† All new compounds gave satisfactory analytical and spectral data.

and 334 (3·16) nm; *m/e* 416 (M^+) and 73 (Me$_3$Si, 100%). The ethers (**4b**) and (**4c**) gave similar results.

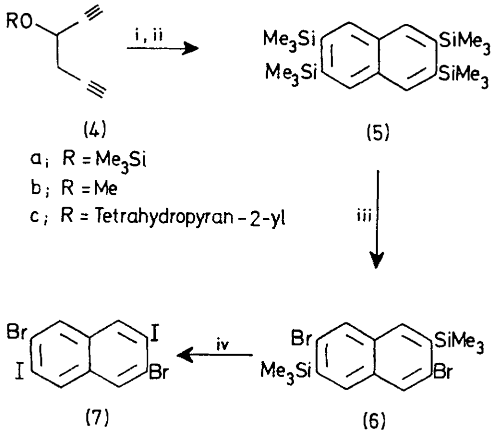

(1)


(2)


(3)

The direct formation of (**5**) from (**4**) most likely proceeds *via* an intermediate of the type (**2**) followed by opening of the 4-membered ring, subsequent trapping of the *o*-xylylene by BTMSA, and loss of alcohol either during the reaction or on chromatographic purification. The spectral characteristics of (**5**) reflect the marked effect of substitution by four bulky trimethylsilyl groups: steric deshielding[4] of the proton magnetic resonances and bathochromic shifts and increased extinction coefficients of the electronic absorptions.[5]

The versatility of the *o*-bistrimethylsilyl-aromatic unit in organic transformations[1] as applied to (**5**) serves to provide chemical proof for its structure as well as to demonstrate its usefulness as a precursor to other substituted naphthalenes. For example, treatment with an excess of CF$_3$CO$_2$H yields naphthalene quantitatively; CF$_3$CO$_2$D cleanly results in 2,3,6,7-tetradeuterionaphthalene. Bromination (2 equiv.) can be accurately followed by n.m.r. spectroscopy and proceeds cleanly *via* the mono-bromo-derivative exclusively to the 2,6-dibromo-isomer (**6**) in 89% yield, m.p. 213—215 °C; τ (CCl$_4$) 2·07 (s br, 2H), 2·30 (s br, 2H), and 9·50 (s, 18H); *m/e* 432, 430, and 428 (1:2:1, M^+). Protodesilylation of (**6**) gives 2,6-dibromonaphthalene.[6] Treatment of (**6**) with iodine monochloride (2 equiv.) converts it into the dibromodi-iodo-compound (**7**) in 88% yield, m.p. >210 °C (decomp.) τ(CS$_2$) 1·83 (s, 2H) and 2·10 (s, 2H); *m/e* 540, 538, and 536 (1:2:1, M^+). The remarkable selectivity in electrophilic substitutions of (**5**), the result of a combination of steric and electronic effects, indicates that by proper choice and application of electrophiles a large variety of complex substituted naphthalenes might become available. In addition, the ready *in situ* generation of *o*-xylylenes from readily available precursors suggests that by appropriate choice of starting acetylenes considerable improvement of currently existing synthetic methods involving benzocyclobutenes[2] should be possible.



i, Bistrimethylsilylacetylene; ii, [CpCo(CO)$_2$]; iii, Br$_2$, py, CCl$_4$; iv, ICl, CCl$_4$. Cp = cyclopentadienyl, py = pyridine.

We thank the California Division of the American Cancer Society, the National Institute of Health, the National Science Foundation, and the A.P. Sloan Foundation for financial support.

(*Received, 6th July* 1976; *Com.* 762.)

---

[1] W. G. L. Aalbersberg, A. J. Barkovich, R. L. Funk, R. L. Hillard III, and K. P. C. Vollhardt, *J. Amer. Chem. Soc.*, 1975, **97**, 5600; R. L. Hillard III and K. P. C. Vollhardt, *Angew. Chem.*, 1975, **87**, 744; *Angew. Chem. Internat. Edn.*, 1975, **14**, 712.

[2] W. Oppolzer, *J. Amer. Chem. Soc.*, 1971, **93**, 3833; W. Oppolzer and K. Keller, *ibid.*, p. 3836; W. Oppolzer, *Tetrahedron Letters*, 1974, 1001; T. Kametani, Y. Kato, T. Honda, and K. Fukumoto, *Heterocycles*, 1976, **4**, 241; T. Kametani, H. Nemoto, H. Ishikawa, K. Shiroyama, and K. Fukumoto, *J. Amer. Chem. Soc.*, 1976, **98**, 3378; P. G. Sammes, *Tetrahedron*, 1976, **32**, 405.

[3] F. Sondheimer, Y. Amiel, and Y. Gaoni, *J. Amer. Chem. Soc.*, 1962, **84**, 270.

[4] W. Adcock, B. D. Gupta, T. C. Khor, D. Doddrell, and W. Kitching, *J. Org. Chem.*, 1976, **41**, 751.

[5] D. Seyferth, D. R. Blank, and A. B. Evnin, *J. Amer. Chem. Soc.*, 1967, **89**, 4793.

[6] J. Paviot and J. Hoarau, *J. Chim. Phys.*, 1967, **64**, 1415.