

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-Tetrakis(trimethylsilyl)naphthalene

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

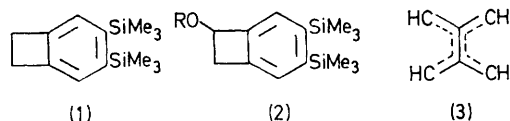
We recently reported on the cobalt-catalysed synthesis of the strained 4,5-bistrimethylsilylbenzocyclobutene (**1**), a useful *o*-xylylene synthon, from co-oligomerization of hexa-1,5-diyne and bistrimethylsilylacetylene (BTMSA).¹ It occurred to us that by introduction of an alkoxy group to the methylene '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-ol³) in neat BTMSA to a refluxing solution of $[\text{CpCo}(\text{CO})_2]$ (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, $\tau(\text{CCl}_4)$ 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.

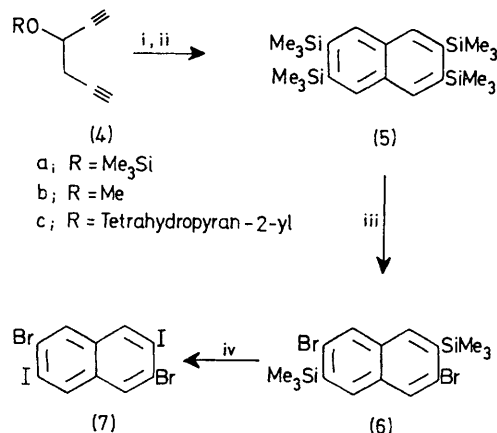
and 334 (3.16) nm; m/e 416 (M^+) and 73 (Me_3Si , 100%). The ethers (4b) and (4c) gave similar results.



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 deshielding⁴ 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 transformations¹ 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 $\text{CF}_3\text{CO}_2\text{H}$ yields naphthalene quantitatively; $\text{CF}_3\text{CO}_2\text{D}$ 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 remark-

able 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



i, Bistrimethylsilylacetylene; ii, $[\text{CpCo}(\text{CO})_2]$; iii, Br_2 , py, CCl_4 ; iv, ICl , CCl_4 . Cp = cyclopentadienyl, py = pyridine.

o-xylylenes from readily available precursors suggests that by appropriate choice of starting acetylenes considerable improvement of currently existing synthetic methods involving benzocyclobutenes² should be possible.

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.)

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