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1,2-CYCLOPROPA-4,5-CYCLOBUTABENZENE. A NOVEL STRAINED BENZENE DERIVATIVE

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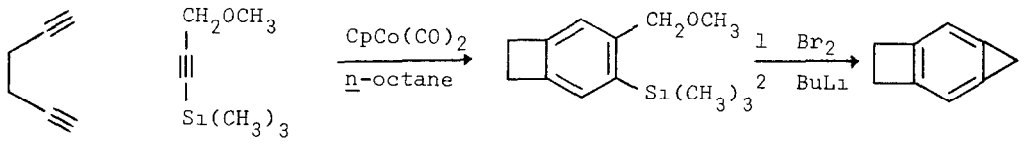
A recent report[1] concerned with the synthesis of 1,2-cyclopropopa-4,5-cyclobutabenzene (4) (30-40% yield) via the Billups-route[2] to benzocyclopropenes prompts us to report our own efforts to obtain this fascinating hydrocarbon via the Radlick-route[3]. The required precursor 3 was synthesized as shown in the scheme, the crucial step involving the cobalt catalyzed cooligomerization[4] of trimethylsilylpropargylether 2 and 1,5-hexadiyne (1).

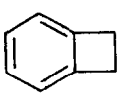


1 2 3 4

Ether 2 was prepared from propargylmethylether[5] by treatment with n-butyl-lithium followed by trimethylsilylchloride in ether [90%, b.p. 144-145°, NMR (CCl_4) τ 6.00 (s, 2H), 6.70 (s, 3H), 9.83 (s, 9H)][6]. Reaction of 1 with 2 in the presence of catalytic amounts of η^5-cyclopentadienyl cobalt dicarbonyl using high dilution conditions[4] gave the benzocyclobutene 3 as a colorless oil [55%, b.p. (microstill) 60° (oil bath temperature)/0.01T,

m/e 220 (M^+, 3%), 205 (60%), 175 (100%), NMR (CCl_4) τ 2.88 (b.s., 1H), 3.02 (b.s., 1H), 5.58 (b.s., 2H), 6.72 (s, 3H), 6.83 (s, 4H), 9.72 (s, 9H)][6]. Electrophilic displacement of the silyl-group with bromine (Br_2/CCl_4/RT) resulted in 4-methoxymethyl-5-bromobenzocyclobutene purified by column chromatography (silica) and microdistillation (60°/0.01 T) as a colorless oil [65%, m/e 228, 226 (M^+, 1·1, 29%), 147 (100%); NMR (CCl_4) τ 2.87 (b.s., 2H), 5.60 (b.s., 2H), 6.60 (s, 3H), 6.85 (b.s., 4H)][6]. This bromide was then treated with a slight excess of n-butyl-lithium in THF at -70° (deep red coloration), followed by reflux (30 mins). Vacuum transfer of the volatiles and p.g.l.c. (10' x 3/8", UCW 98 20% Chrom W-AW, dmsc glass) gave cyclopropacyclobutabenzene 4 as a light yellow oil of pungent odor [∿ 5%[7], m/e 116 (M^+, 62%), 115 (100%), NMR (d_8-THF) τ 3.05 (s, 2H) 6.83 (b.s., 6H), UV (ether) λ max 285, 288, 295]. One of the side products in the formation of 4 is 2-methoxymethylbenzocyclobutene [m/e 148, NMR (CCl_4) τ 3.03 (m, 3H), 5.66 (s, 2H), 6.73 (s, 3H), 6.84 (s, 4H)][6], possibly derived from 4 by reaction with lithium methoxide.

It is interesting to note that while the electronic spectrum of 4 clearly exhibits strain related bathochromic shifts when compared to benzocyclobutene (5)[8], 1,2.4,5-dicyclobutabenzene (6)[9] and cyclopentaindacene 7[10], the NMR spectrum reveals fairly "normal" chemical shifts. This is in



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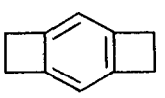

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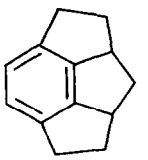

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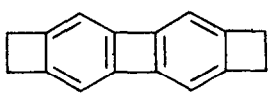

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contrast to 2,3.6,7-dicyclobutabiphenylene (8)[11] the aromatic protons of which absorb at relatively high field [$\tau(CCl_4)$ 3.85], possibly due to the antiaromatic character of the central four-ring[12].

Finally, it appears that the approach to benzocyclopropenes developed by Billups[2] is a more viable route to other annelated derivatives.

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References and Notes

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6 All new isolated compounds gave satisfactory analytical and/or spectral data

7 Compound 4 could not be obtained completely pure due to apparent decomposition on exposure to g c. conditions. Its physical and chemical properties agree well with the reported data[1].

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