TRIPYRIDYLCYCLOPROPENE DERIVATIVES AND THEIR CONVERSION TO HEXAPYRIDYLBENZENE

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Abstract. 1,2,3-tris(4-pyridyl)cyclopropene carrying a 3-benzenesulfonyl group has been synthesized, and other cyclopropenes carrying pyridine and pyridinium rings. Some of these can be converted to hexa(4-pyridyl)benzene and its pyridinium analog.

Cyclopropenyl anions are very unstable [1], but should be accessible with strongly electronattracting substituents. We have reported that 1,2,3-tricyanocyclopropene is too reactive to handle, or to generate the corresponding anion [2]. Thus we have turned to pyridine substituents [3]. As hoped, tripyridylcyclopropenes are easily prepared and reasonably stable. N-Alkylation produces the strongly electron-attracting pyridinium ring. We now wish to describe the syntheses of these compounds, and their conversion to the previously unknown hexa(4pyridyl)benzene. Studies on the corresponding cyclopropenyl anion will be reported elsewhere.

The dipyridylvinylsulfone **2** [4] was prepared from pyridine-4-carboxaldehyde and 4-pyridylmethylsulfone **1** [4], and treated with 4-pyridyldichloromethane (**3**) [4] and NaH in dimethylacetamide. The cyclopropene sulfone **4** was formed in 72% isolated yield, mp 203-205° d. and characterized by IR (1830 cm⁻¹, cyclopropene), H-NMR, C-NMR (12 peaks, 1 at 56.4 ppm), UV (275 nm, 1.1×10^4 , 309 nm, 1.9×10^4), MS (FAB 412, 270; EI 270 for M - SO₂Ph) and Anal: Found (Calc) C, 70.25 (70.06); H, 4.11 (4.16); N, 10 28 (10.21); S, 7.91 (7.79). The reaction involves nucleophilic addition of the anion of **3**, followed by cyclization and HCl elimination. If the sulfone **2** is treated instead with **1** and NaH, 1,2,3-tris(4-pyridyl)cyclopropyl phenyl sulfone is formed in 37% yield, mp 243-244.5° d (MS, Anal, H-NMR). This is converted with KOtBu to cyclopropene **5** in 66% yield by elimination of benzenesulfinic acid. Compound **5** had mp 127.5°-129°, and showed IR 1833 cm⁻¹ (cyclopropene), UV (309 nm, 2.3×10^4 , 330 nm, 1.9×10^4), H-NMR δ 3 3 (s, 1H), 7.1 (d, 2H), 7.5 (d, 4H), 8.45 (d, 2H) and 8.75 (d, 4H). C-NMR (8 peaks, 1 at 23.8 ppm). MS-CI 272 (M + 1), Anal: Found (Calc) C, 79.34 (79.68); H, 4.88 (4.83); N, 15.37 (15.49).



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N^r 7 Reaction of 4 with sodium methoxide affords 6 [4] in 70% yield. Strikingly, treatment of the sulfone 4 with sodium naphthalide in THF at -78° afforded hexa(4-pyridyl)benzene 7 in 80% isolated yield. It had mp >360°, a simple AB quartet in the H-NMR at δ 8.2 and 6.75, C-NMR (4 peaks at 149.5, 148.7, 139.2, 127.7 ppm), and MS (FAB) of 541 (M + 1); Anal: Found (Calc) C, 79.68 (79.98); H, 4 55 (4.47); N, 15.43 (15.54). This reaction probably involves generation of the cyclopropenyl radical, its dimerization to a bis-cyclopropene, and the electron-promoted rearrangement of this species to the benzene derivative, as we have observed earlier with triphenylcyclopropene derivatives [5-7].

In the N-methylpyridinium series we have also examined the sulfone **8** (SbF6⁻ and triflate)₃ [4], and the chloride **9** (SbF6⁻)₃ [4]. Both compounds are converted by sodium naphthalide to the hexapyridiniumbenzene salts **10** [4], again probably through dimerization of the corresponding radical. However, this is not the only pathway from cyclopropenes to benzenes Treatment of the tripyridiniumcyclopropene (Ph₄B⁻)₃ **11** [4] with lithium tetramethylpiperidide under some conditions can also afford the benzene **10**. In this case we believe that the cyclopropenyl anion **12** adds to the cyclopropene **11** [cf. 6] to produce a cyclopropenylallyl system; this cyclizes to a dihydrobenzene anion that then oxidizes to afford the benzene. As support of thus, addition of the **1**,2,3-tri(4-pyridyl)allyl anion to the cyclopropene sulfone **4** yields the cyclopropenylallyl derivative **13** [4], which can be methylated to afford **14** [4]. Both compounds are converted to the corresponding benzenes **7** and **10** under mildly basic conditions.

We have converted both 6 and 8 to the remarkable cyclopropenyl cation 15 [4], while 11 can be used to generate the anion 12. Furthermore, the hexapyridiniumbenzene derivative 10 has been reduced with two electrons to a benzene dianion derivative that shows a triplet ESR spectrum. The physical studies on these species will be described elsewhere





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