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Corannulene Synthesis Via the Pyrolysis of Silyl Vinyl Ethers

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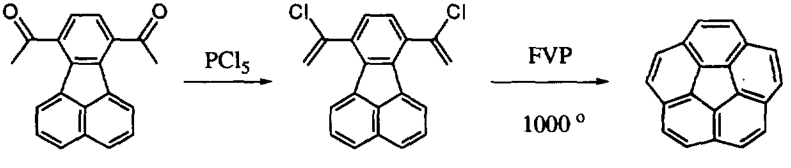
Abstract: *The bis(trimethylsilyl enol ether) derived from 7,10-diacetylfluoranthene undergoes pyrolysis to afford corannulene. This is important in cases where the usual precursor, the bis(chlorovinyl) derivative, is not accessible from the diketone.* Copyright © 1996 Elsevier Science Ltd

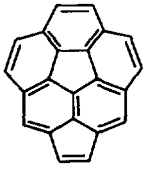
The simplest curved-surface hydrocarbon possessing a carbon framework that can be identified on the buckminsterfullerene (C_{60}) surface is corannulene (1). Given the considerable attention afforded to C_{60} and the related carbon cages,[1] the synthesis and properties of these bowl-like hydrocarbons has attracted quite a bit of attention. Although corannulene has been known for some time,[2] it remained relatively inaccessible until the report of a new synthesis by Scott, et al.[3] (eq 1).



(1)

1

We have used variations of this method for the synthesis of a number of bowl-shaped hydrocarbons that we have referred to as "buckybowls" due to their relationship with buckminsterfullerene or "buckyball." Such examples are the cyclopentacorannulene **2**,[4] and the semibuckminsterfullerenes **3**[5] and **4**.[6] We also used this



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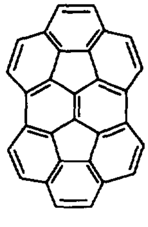

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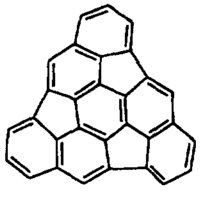
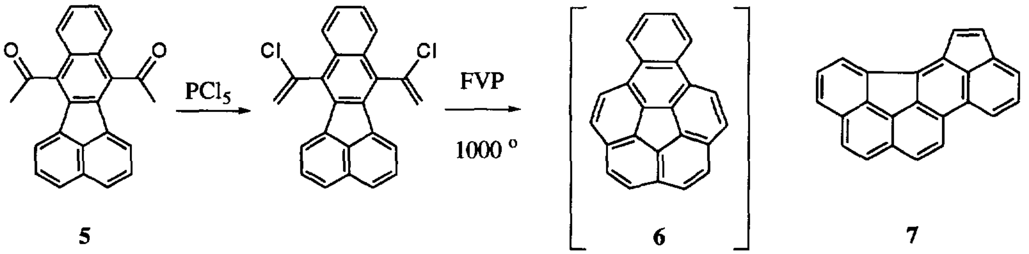


4

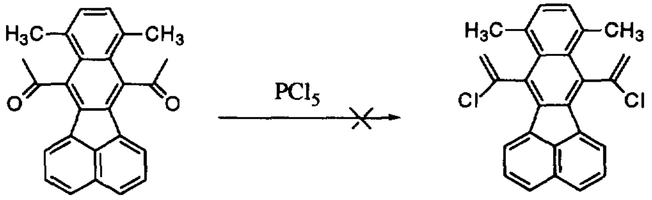
route with the benzofluoranthene **5** in an attempt to synthesize benzocorannulene (**6**).[7] However, the only product was the planar hydrocarbon **7** where the two ring closures had occurred in different directions: one to the upper benzene ring, and the second to the lower napthalene ring.



5 **6** **7**

(not formed) (only product formed)

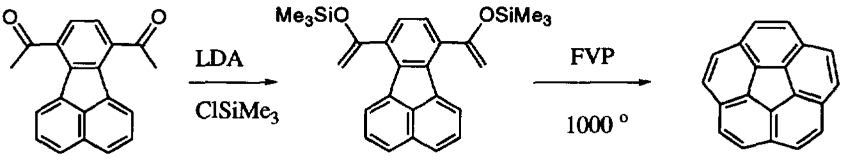
Herein we report our attempts to force corannulene formation with the use of methyl groups—if they were to survive the pyrolysis—to block ring closure to the benzo group. We initially planned to pyrolyze the bis(chlorovinyl) derivative **9**, but reaction of the diketone **8** with PCl_5 failed completely. Hence another route



8 **9**

was required and, since the diketones are very convenient intermediates, we explored conversion of the ketone to some other functionality that would undergo pyrolysis in a fashion similar to the vinyl chlorides. This requires a somewhat labile group since the likely mechanism involves loss of the group with rearrangement to afford a vinyl carbene, or, alternatively, cycloaddition whereupon the group in question is lost during (or after) aromatization of the newly formed six-membered ring.[3a]

We now report that vinyl silyl ethers can also serve as precursors to corannulenes by pyrolysis (eq 2). 7,10-Diacetyl-fluoranthene reacts with LDA to produce the dienolate which can then be captured with chlorotrimethylsilane. Pyrolysis of the bis ether at 1000 °C affords corannulene in around 8% isolated yield



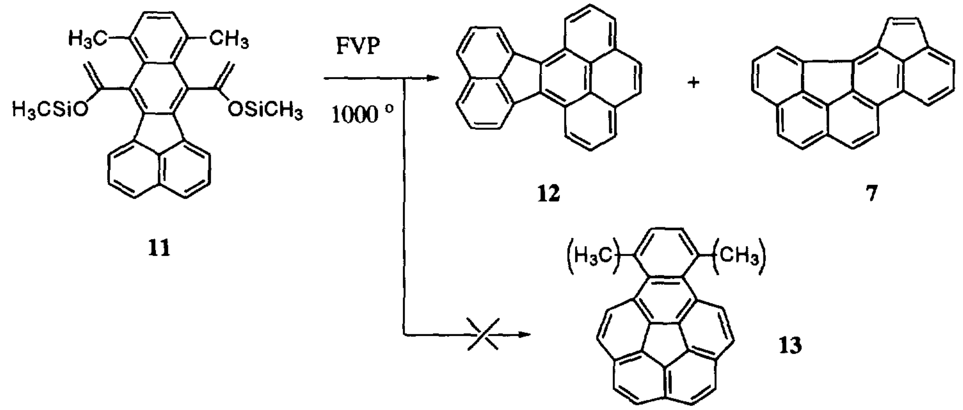
(2)

10 **1**

which is only slightly lower yield in our hands than from the bis chlorovinyl derivative.

In a typical procedure, LDA (1.5 M in THF, 2.29 mL, 3.43 mmol) was added dropwise to a solution of 7,10-diacetylfluoranthene (300.0 mg, 1.14 mmol) in 20 mL THF at -78 °C. After stirring for 20 min, trimethylsilyl chloride (0.73 mL, 5.72 mmol) was slowly dropped in, and after 30 min, the solution was warmed to room temperature for another 3h. Saturated Na_2CO_3 (20 mL) was added followed by extraction with CH_2Cl_2 (3 x 30 mL). The combined extracts were dried ($MgSO_4$), filtered and evaporated. The residue was recrystallized from ethanol to give **10** (181 mg, 42 %) as a light yellow crystal.[8] The pyrolysis of **10** was carried out in three runs of 245 mg to afford 43 mg of pyrolyzate. Purification by column chromatography on silica gel (240-400 mesh; 30% benzene in hexane) impregnated with 2% 2,4,7-trinitro-9-fluorenone[9] afforded pure **1** (11.6 mg, 8%).

The failure of the reaction of **8** with PCl_5 is presumed to be due to the steric congestion that hinders reaction at the carbonyl carbon. The strategy with silyl ether formation is that neither deprotonation nor silylation take place at the carbonyl carbon, and this reduces the steric problems. In fact, diketone **8** reacts smoothly with LDA, and subsequent reaction with chlorotrimethylsilane affords **11**. However, pyrolysis did not lead to the benzocorannulene **13**, but rather afforded **7** together with the previously unknown pyrene derivative **12**. The procedures are exactly as above. Diketone **8** (235 mg, 0.70 mmol) gave **11** (257 mg, 76%) as a light yellow crystal.[10] Pyrolysis of **11** (100 mg, 0.197 mmol) gave 18.5 mg crude pyrolyzate; purification by column chromatography (silica gel/cyclohexane) gave **7**[11] (4.6 mg, 8%) and **12**[12] (10.2 mg, 16%).



In conclusion, the pyrolysis of vinyl silyl ethers is shown as an alternative to chlorovinyl derivatives for corannulene synthesis. This is especially important for cases where the chlorovinyl ethers are not accessible due to steric congestion of the substrate ketones. Moreover, it is also shown that nonplanar products (e.g., **7** and **12**) will predominate over curved-surface products (**13**) when the latter alternative paths are possible.

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8. Mp 59-61 °C. ^{1}H NMR, δ 8.39 (d, J=7.1Hz, 2H), 7.84 (d, J=8.1Hz, 2H), 7.61 (t, J=7.8Hz, 2H), 7.29 (s, 2H), 4.80 (s, 2H), 4.76 (s, 2H), 0.12 (s, 18H). ^{13}C NMR, δ 156.75, 136.65, 135.56, 135.24, 132.75, 129.63, 127.91, 127.58, 126.76, 124.52, 96.17, 0.18. (Satisfactory C,H analysis).
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10. Mp 146-48 °C. ^{1}H NMR (2 rotational isomers; we have encountered this for a number of congested 7,10-disubstituted fluoranthenes), δ 8.52 (d, J=7.2 Hz), 8.47 (d, J=7.3 Hz), 7.83 (d, J=8.2Hz, 2H), 7.60 (t, J=7.4Hz, 2H), 7.20 (s, 2H), [4.88 (s), 4.85 (s), 4.61 (s), 4.51 (s), 4 vinyl singlets], [3.04 (s), 3.03 (s), tot. 6H], [0.30 (s) + 0.23 (s), tot. 18H]. ^{13}C NMR, δ 155.55, 135.63, 134.74, 134.38, 132.62, 129.94, 129.74, 129.57, 127.28, 126.04, 123.24, 123.10, 96.04, 95.48, 24.12, 0.37, 0.30. HRMS calcd for $C_{32}H_{36}Si_2O_2$: 509.2332(M+1), 508.2254(M); found 509.2286(M+1), 508.2281(M).
11. Spectral data identical with an authentic sample of **7**.[7]
12. Orange solid, mp 226-228 °C. ^{1}H NMR δ 9.19 (d, J=7.6Hz, 2H), 8.73 (d, J= 7.1Hz, 2H), 8.25 (d, J=7.5Hz, 2H), 8.16 (t, J=7.8Hz, 2H), 8.13 (s, 2H), 7.95 (d, J=8.2Hz, 2H), 7.78 (t, J=7.2Hz, 2H); ^{13}C NMR δ 138.01, 134.79, 134.27, 131.87, 129.34, 128.89, 127.98, 127.72, 127.65, 126.24, 125.24, 125.04, 123.19, 122.02. HRMS calcd for $C_{26}H_{14}$: 327.1174(M+1), 326.1096(M); found 327.1174 (M+1), 326.1103 (M).

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