

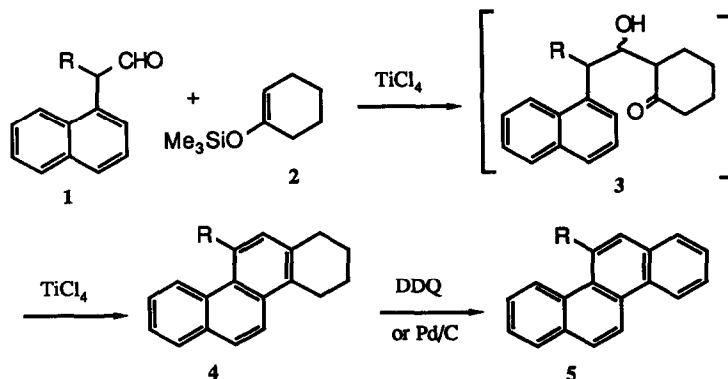
A NEW SYNTHESIS OF POLYCYCLIC AROMATIC HYDROCARBONS VIA TITANIUM(IV)-CATALYZED ALDOL-TYPE CONDENSATION OF SILYL ENOL ETHERS WITH 2-ARYLACETALDEHYDES

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Summary: A novel one-pot synthesis of angular polycyclic hydrocarbon ring systems involving Ti(IV)-catalyzed aldol-type condensation of silyl enol ethers with 2-arylacetaldehydes and cyclization of the adducts is described.

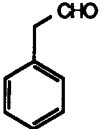
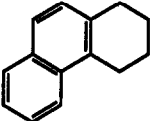
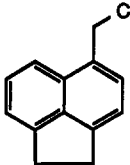
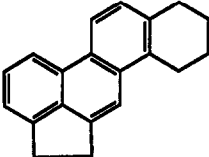
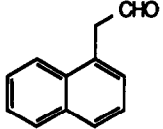
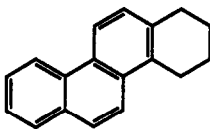
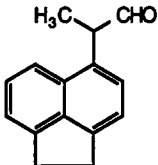
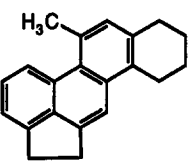
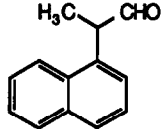
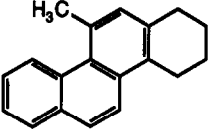
Polycyclic aromatic hydrocarbons (polyarenes) are widely distributed environmental pollutants many of which exhibit carcinogenic activity.¹ However, methods for the synthesis of polyarenes have failed to keep pace with the rapidly expanding research interest in the chemistry and biological properties of molecules of this class. Many of the synthetic methods currently in use have a venerable history, dating back to the 1930s or even earlier.²

We now report a convenient new synthetic approach to angular polyarenes which appears general in its applicability. The method entails reaction of an appropriate 2-arylacetaldehyde derivative, such as 2-(1-naphthyl)propionaldehyde (**1b**), with the silyl enol ether derivative of a cyclic ketone (**2**) by the general procedure of Mukaiyama et al.³ with the difference that a larger ratio of TiCl₄ is employed as catalyst. Under these conditions, the cross aldol-type condensation product formed initially (**3b**) undergoes further reaction entailing cyclization and double dehydration to provide a partially saturated polyarene (**4b**). Dehydrogenation of this hydrocarbon product to a fully aromatic polyarene, e.g. 5-methylchrysene (**5b**), may be readily accomplished either catalytically or with quinone oxidants, such as DDQ.⁴ Some examples of polyarenes synthesized via the reaction of 2-arylacetaldehydes with the trimethylsilyl enol ether of cyclohexanone are presented in Table 1.



a: R = H; b: R = CH₃

Table 1. Polyarenes synthesized via TiCl₄-catalyzed aldol-type condensation and cyclization

Aldehyde	Polyarene product	Yield (%) ^a	Aldehyde	Polyarene product	Yield (%) ^a
		63			54
		65			52
		62			

^aYields are isolated yields of pure products. All new compounds were characterized by mp, high resolution NMR, and mass spectral analysis.

A typical example is represented by the synthesis of chrysenes (**1a**). To a solution of the aldehyde **1a** (1.3 g, 7.6 mmol) and **2** (1.5 g, 9.1 mmol) in 100 ml of CH₂Cl₂ under N₂ was added 22.7 ml of 1M TiCl₄ in CH₂Cl₂ dropwise at -78°C. The resulting dark reddish brown solution was stirred for 2 h at -78°C, then allowed to warm to room temperature and stirred for an additional 48 h. The reaction was quenched by the addition of ice-water, and the product was extracted with ether and worked up conventionally. Purification by chromatography on silica gel furnished 1,2,3,4-tetrahydrochrysenes **4a** (1.13 g, 65%) as a white solid, mp 180-181.5°C. Treatment of **4a** (150 mg) with 2 equiv of DDQ in anhydrous refluxing benzene for 3 h furnished chrysenes (113 mg, 77%), mp 250-252°C (lit.⁵ 253-254°C).

Both the cyclization and the condensation steps appear to be catalyzed by Ti(IV). Thus, with a lower ratio of TiCl₄ (2.0 mmol to 1.5 mmol of **1b**) and milder conditions (2 h at -78°C), the aldol intermediate **3b** could be isolated as the principal product. Compound **3b** on treatment with TiCl₄ at room temperature or polyphosphoric acid at 110°C underwent conversion to 11-methyl-1,2,3,4-tetrahydrochrysenes **4a**.

References

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