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Investigations of the Tetrachlorosilane-Ethanol Induced Self Condensations of Ketones.[1]

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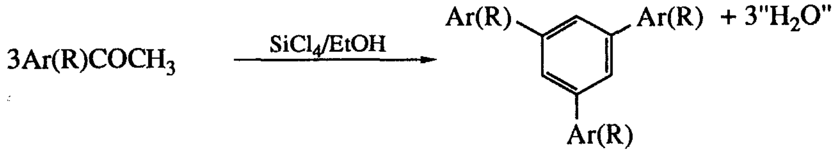
Abstract. *Silicon tetrachloride-ethanol induced self condensation of ketones to yield tri- or hexasubstituted benzenes, can be diverted in a variety of ways, dependent on the steric hindrance of the ketone. A number of examples of cyclic ketone condensations are given, and the surprising result from condensation of propiophenone as compared with acetophenone is presented.*

We recently disclosed the facile general process shown in equation 1.[2] This process must proceed by two aldol condensations followed by a cyclisation. The exact timing of the losses of "water" (presumably silyloxy species in fact) is unknown.



(1)

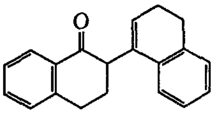
(1) (2)

The overall rate of condensation varies greatly with substitution on the aromatic ring of (1). Thus the reaction of 4-bromoacetophenone is much slower than acetophenone. In a competition experiment at room temperature over 6h, a 2:1 mixture of acetophenone and 4-bromoacetophenone gave only (**2**, Ar=Ph) in 76% yield (based on acetophenone) with no evidence for either (2 Ar = 4-BrC$_6$H$_4$) or the mixed product.

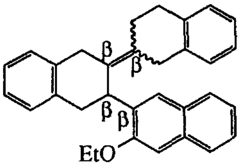
We have also used the reaction to make the corresponding hexasubstituted (triannulated) benzenoids from cyclopentanone and cyclohexanone[2]. In order to explore the scope of the reaction we examined the products from α- and β-tetralones and indan-1- and indan-2-ones, which may be regarded as substituted cyclohexanones and cyclopentanones.

#All new compounds have been characterised by elemental analysis, ^{1}H, ^{13}C nmr and mass spectra.

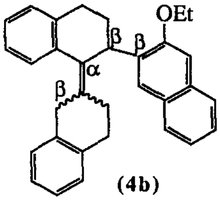
α-Tetralone gave (3) (73%) m.p. 135.5°C[3] produced by a ***single*** aldol type condensation. β-Tetralone gave a single compound of type (4) (63%) m.p. 107°C as the major product, by two aldol condensations but no cyclisation. Instead, enol ether formation and prototropic shifts occur. From the various available possibilities, we have been able to assign the structure as either (4a) and (4b). Indan-1-one gave 22% of the hexa-substituted product (5) m.p. 369°C[4], but the major product (69%) was the simple aldol product (6), m.p. 148°C[4]. Indan-2-one however gave (5) in 75% yield.



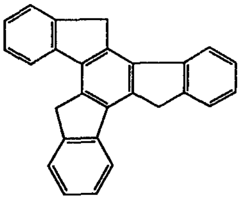
(3)



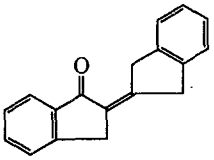
(4a)



(4b)



(5)



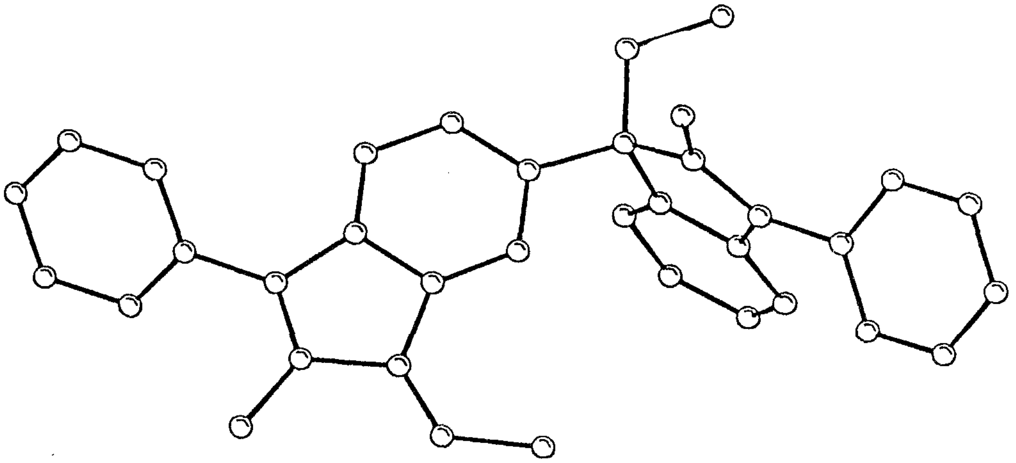
(6)

These experiments show that formation of aromatic compounds as in equation 1 can be inhibited either by slowing the rate of the second aldol condensation (α-tetralone, indan-1-one) or by slowing the cyclisation to give the newly formed benzene ring (β-tetralone).

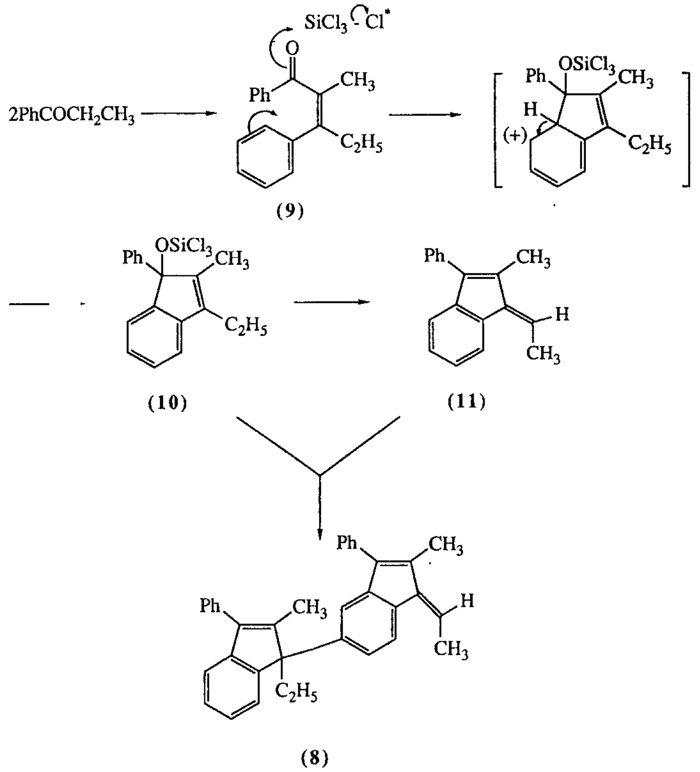
We therefore felt it worthwhile to systematically investigate compounds $PhCOCH_2X$ (7), and started by comparing acetophenone (7, X = H) with propiophenone (7, X = CH_3). In our hands, acetophenone led rapidly to (2, Ar = Ph) ***only***. Propiophenone did not yield any of the corresponding product (1,3,5-triphenyl-2,4,6-trimethylbenzene) but instead, on reaction with two equivalents of $SiCl_4$/EtOH at 23°C for 48h gave a crystalline material (8), m.p. 170°C in 43% yield. Surprisingly, the compound had a molecular weight corresponding to $C_{36}H_{32}$, and is the product of ***three*** aldol condensations of four molecules of propiophenone. The only major peak in the e.i. mass spectrum, other than the molecular ion, is due to the loss of an ethyl group.

Even at 600 MHz, ^1H nmr failed to unravel the complex aromatic region of (8), but it delineated the presence of $CH_3CH{=}CR^1R^2$, and two $CH_3CR^1{=}CR^2R^3$ groupings as well as an $C_2H_5CR_3$ group. The presence of these groups was confirmed by ^{13}C nmr, which additionally showed the presence of an aliphatic quarternary carbon with a signal at δ 62.4. An X-ray investigation of the product gave its structure as (8).

The crystals are orothorhombic, space group Pbca with cell dimensions a = 8.998(1), b = 26.333(2), c = 22.664(3)A and Z = 8 of $C_{36}H_{33}$, Mr = 465.66. Cell dimensions and intensity data were obtained using a FAST area detector diffractometer and Mo-K_α radiation (λ=0.71069A) as previously described[5]. A total of 19660 reflections were measured which gave 4187 unique but only 1947 observed ($F_o > 2\sigma(F_o)$) data. This low proportion reflects the very small size and poor crystallinity of the specimen used. Nevertheless, the structure was routinely solved by direct methods and refined by least squares. The two phenyl rings were treated as regular hexagons. Non-hydrogen atoms were refined anisotropically and all hydrogens were included in idealised positions. The final R value was 0.076 for 378 parameters. A diagram of the molecule is given in the Figure. Full details of the crystallography, including atomic coordinates, thermal parameters, bond lengths and angles have been deposited as supplementary data.



Our postulate for the formation of (**8**) is shown in the Scheme. Compound (**9**), formed by a single aldol condensation is sufficiently hindered sterically that it does not readily undergo a further such condensation. Instead, aromatic attack on the silicon activated ketone group occurs to give (**10**) which, in turn, yields (**11**). Condensation of (**10**) and (**11**) yields the final product (**8**).



* $SiCl_4$ is used for convenience, though clearly species $Cl_xSi(OEt)_{4-x}$ will actually be involved.

Scheme

Thus a simple change from (7, X = H) to (7, X = CH_3) leads to a profound change in the nature of the product. We shall report further on the tetrachlorosilane induced self condensations of $ArCOCH_2X$, in which X ≠ H or CH_3.

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