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New routes for synthesis of branched functionalized benzenoid compounds by using tetrachlorosilane-ethanol reagent

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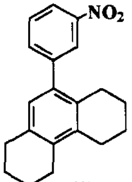
Abstract: *The successive reactions of some cyclic ketones with aryl methyl ketones mediated by tetrachlorosilane-ethanol, provide an attractive and convenient route to branched functionalized benzenoid compounds. Selective unsymmetrical branched triarylbenzenes have synthesized by inducing the reaction of ketones with dypnones in quantitative yields.* © 1997, Elsevier Science Ltd. All rights reserved.

Branched functionalised benzenoid compounds are versatile organic intermediates[1-3] for the synthesis of buckminsterfullerenes (C_{60}), pharmaceuticals, sensitizers for photographic processes as well as for preparation of conjugated star polyaromatics.

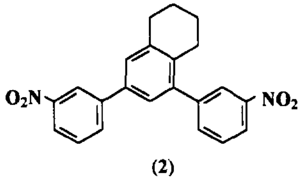
In our previous reports, it was shown that tetrachlorosilane induced self condensation of ketones to yield tri- or hexa-substituted benzenes[4-6]. We introduce here a facile procedure to induce mixed condensation of aryl methyl ketones and cyclic ketones with the aid of tetrachlorosilane - ethanol system. From a synthetic point of view, it would of course be more useful to be able to effect a mixed aldol condensation to yield unsymmetrical triarylbenzene derivatives. It has been reported that the condensation of two different ketones to produce ketols or α,β-unsaturated ketones, has seldom been applied to two different acyclic ketones and limited utility for mixed condensation[7]. So, we have examined the reactions of cyclic ketones e.g. cyclohexanone, α-tetralone, with nitro- or methoxyacetophenone.

The best results in mixed condensation products were obtained with using five equivalents of tetrachlorosilane and two equivalents of different ketones (results were given in table 1). The reaction has value in that it is applicable to derivatives of aryl methyl ketones and aryl or alkyl cyclic ketones using extremely mild conditions. On reaction of cyclohexanone with 3'-nitroacetophenone, compounds (1), (2) and (3) were obtained; products (4), (5) and (6) which are nearly the same in both yields and the condensation manner were produced from the reaction with 4'-nitroacetophenone. Compounds (2) or (5) produced in yields 56, 62% by two fold aldol condensation of one mole of cyclohexanone with two moles of 3'- or 4'-nitroacetophenone followed by a cyclization. The lower yields of self condensation of 3'- or 4'-nitroacetophenone (compounds 3 or 6) are attributable to competing reactions.

On the other hand the reactivity of aryl methyl ketones toward aldol condensation are more than that of alicyclic ketone using TCS-EtOH. In entry 3 three products(7, 8, 9) were obtained from the reaction of α-tetralone with 3'-nitroacetophenone. But the reaction with 4'-nitroacetophenone (entry 4) gave only compound (10) which results from condensation of two moles of α-tetralone and one mole of 4'-nitroacetophenone. In contrast, the reaction of α-tetralone with 4’-methoxyacetophenone gave compounds (11) and (12) in yields 64% and 22% respectively. Compound (11) is formed from condensation of two moles of 4’-methoxyacetophenone with one mole of α-tetralone, but compound (12) is formed from two fold aldol condensation followed by a cyclization for three moles of 4’-methoxyacetophenone.



(1)



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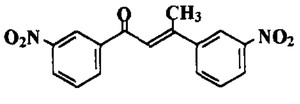
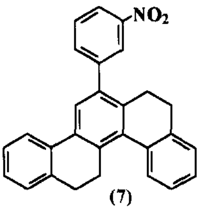


(3)

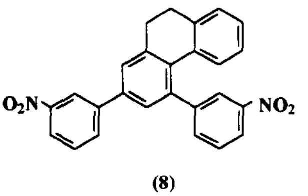
Table 1. Reaction of cyclic ketones with aryl methyl ketones in the presence of tetrachlorosilane-ethanol.

Entry no.	Substrate 1	Substrate 2	time (h)	Product[a]	Yield (%)
1.	Cyclohexanone	3’-Nitroacetophenone	15	1,2,3,4,5,6,7,8-octahydro-9-(3’-nitrophenyl) phenanthrene **(1)** + 1,3-Bis(3’-nitrophenyl) 5,6,7,8-tetrahydronaphthalene **(2)** + 1,3-Bis(3’-nitrophenyl)-2-buten-1-one **(3)**	28 56 9
2.	Cyclohexanone	4’-Nitroacetophenone	13	1,2,3,4,5,6,7,8-Octahydro-9-(4’-nitrophenyl)-phenanthrene **(4)** + 1,3-Bis(4’-nitrophenyl) 5,6,7,8-tetrahydronaphthalene **(5)** + 1,3-Bis(4’-nitrophenyl)-2-buten-1-one **(6)**	21 62 11
3.	α-Tetralone	3’-Nitroacetophenone	17	6-(3’-nitrophenyl)-7,8,11,12-tetrahydrobenzo*[d]*chrysene **(7)** + 1,3-Bis(3’ nitrophenyl)-9,10-dihydrophenanthrene **(8)** + 1,3,5-Tris(3’-nitrophenyl)-benzene **(9)**	44 41 9
4.	α-Tetralone	4’-Nitroacetophenone	18	6-(4’-nitrophenyl)-7,8,11,12-tetrahydrobenzo-*[d]*chrysene **(10)**	71
5.	α-Tetralone	4’-Methoxy-acetophenone	14	1,3-Bis(4’-methoxyphenyl)-9,10-dihydro-phenanthrene **(11)**[8] + 1,3,5-tri(4’-methoxyphenyl)benzene **(12)**	64 22

a) All products were fully characterized by both spectral and elemental analysis after purification.



(7)



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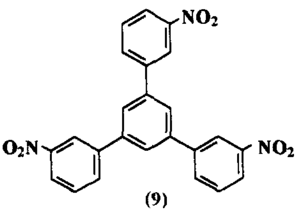


(9)

This may reflect that the relative reactivity of TCS towards the ketone affected by electron availability of the substituents. The reaction is believed to proceed via reaction of silyl enol ethers of ketones. Moreover the results in table 1 provide convincing evidence that, the silyl enol ethers of acetophenone derivatives are more stable than that of cyclohexanone due to the conjugation with the benzene ring.

In spite of the wide applicability of mixed triarylbenzenes, a literature survey reveals that few reagents have been used and their preparations are tedious. The literature methods[9-12] are inconvenient and unsuitable for synthesis of all but only the simplest compounds and often result in low yields.

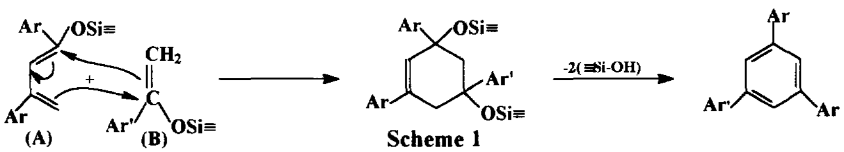
As part of our interest in developing new methods for the selective and efficient synthesis of unsymmetrical triarylbenzene, we have treated aryl methyl ketones with β-methylchalcones in the presence of two equivalents of tetrachlorosilane (TCS) and excess of absolute ethanol at room temperature to afford diphenylarylbenzene or diarylphenylbenzene derivatives in quantitative yields.

. We noticed that, electron withdrawing substituents inhibit the second aldol condensation and a cyclization, two equivalents of TCS-EtOH induced self-condensation of 4`-nitroacetophenone and afforded only the corresponding β-methylchalcone (6) by a single aldol type condensation and no triarylbenzene derivative. Instead of that, the reactions in entries 6 to 12 carried out to give unsymmetry triarylbenzenes even whether the ketone (entries 9,10) or β-methylchalcones (entries 11,12) possesses electron withdrawing groups such as -NO_2, $COOC_2H_5$. The results in the table 2 show that substituents in the ketone generally appear to effect equilibrium yields of triarylbenzene. The reaction conditions were found to be compatible with ethers, halogens and nitro group (table 2).

Table 2. Reaction of 1,3-diaryl-2-buten-1-ones (13) or 1,3-Bis(3`-nitro phenyl)-2-buten-1-one (14) or 1,3-Bis(4`Carbethoxyphenyl)-2-buten-1-one (15) with aryl methyl ketones.

Entry no.	Ketone	dypnone	Time (h)	Product [a]	Yield (%)
6.	4`-Chloroacetophenone	**(13)**	17	1-(4`-chlorophenyl)-3,5-diphenylbenzene **(16)**	74
7.	4`-Bromoacetophenone	**(13)**	14	1-(4`-Bromophenyl)-3,5-diphenylbenzene **(17)**	79
8.	4`-Methoxyacetophenone	**(13)**	13	1-(4`-Methoxyphenyl)-3,5-diphenylbenzene **(18)**	82
9.	4`-Nitroacetophenone	**(13)**	18	1-(4`-Nitrophenyl)-3,5-diphenylbenzene **(19)**	85
10.	3`-Nitroacetophenone	**(13)**	15	1-(3`-Nitrophenyl)-3,5-diphenylbenzene **(20)**	88
11.	Acetophenone	**(14)**	18	1,3-Bis(3`-nitrophenyl)-5-phenylbenzene **(21)**	71
12.	Acetophenone	**(15)**	16	1,3-Bis(4`-Carbethoxyphenyl)-5-phenylbenzene **(22)**	68

a)Products were purified by column chromatography and characterized byspecral and elemental analysis.



Scheme 1

The reaction pathway leading to highly branched, functionalized triarylbenzenes is proposed in Scheme1 which involves the formation of (A) and (B) as key intermediates[13] and their subsequent cyclization by direct 1,4-attack of dienophile (B) onto the diene (A) in presence of HCl, followed by rearomatisation via elimination of two silanol species (≡Si-OH).

In a typical procedure for the reaction in table 2 : to a mixture of acetophenone (5 mmol) and 1,3-Bis (4'-carbethoxyphenyl)-2-buten-1-one (15) (5 mmol) in absolute ethanol (25 ml), tetrachlorosilane (1.2 ml, 10 mmol) was added by syringe. The mixture was stirred with exclusion of moisture at ambient temperature (25°), then poured into water (50 ml) and extracted with chloroform (2x50 ml). The extracts were dried over anhydrous $MgSO_4$, and the solvent removed by distillation, The product (22) was purified using petroleum ether (60-80°C)-ethyl acetate as eluent m.p. = 107-9°C.

Unlike many other reagents available[14], tetrachlorosilane-ethanol can be used for synthesis of kinetic enolates. The generation of thermodynamically equilibrated mixture of enol-silyl ethers from unsymmetrical ketones proceeds at mild conditions. As can be seen from the above described results, these reactions provide convenient and more efficient methods to prepare highly branched involve different functional groups, new synthetic pathways have been elaborated.

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8. IR(KBr plate) ν = 2980-2940(CH-), 2830(CH_3), 1600-1580(C=C), 1510, 1250, 1180, 830, 770 cm^{-1}; ^1H-NMR ($CDCl_3$) δ = 7.93(s, 1H, ArH), 7.87-7.84(d, 1H, ArH), 7.62-7.59(d, 2H, ArH), 7.43-7.34(m, 4H, ArH), 7.26-7.24(m, 2H, ArH), 7.01-6.97(d, 4H, ArH), 3.87(s, 6H, $2CH_3$), 2.8-2.78(m, 4H, $2CH_2$); M.S.(m/z, %) = 392(M^+, 100), 393(M^++1, 25.6), 361(1.2), 330(0.6), 253(3.4) ; $C_{28}H_{24}O_2$ (392) , Calc. C 85.71, H 6.12% , Found C 85.3, H 6.43% .
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