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A SIMPLE TWO-STEP PARA-DIACETYLATION OF BENZENE AND P-XYLENE

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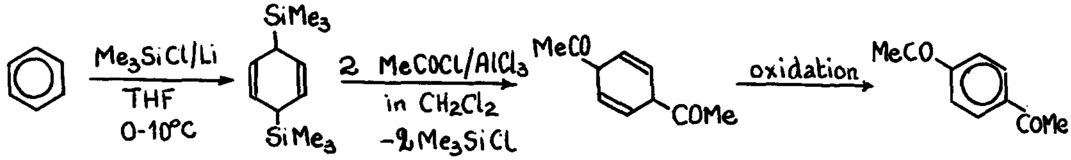
SUMMARY : Aromatic hydrocarbons (benzene, p-xylene) are conveniently p-diacetylated by the regiospecific reductive p-disilylation/diacetylation process, followed by oxidative aromatization. The reaction uses trimethylchlorosilane which is recovered during the course of reaction. It gives diacetyl cyclohexadiene intermediates, novel species which prove relatively stable in an inert atmosphere.

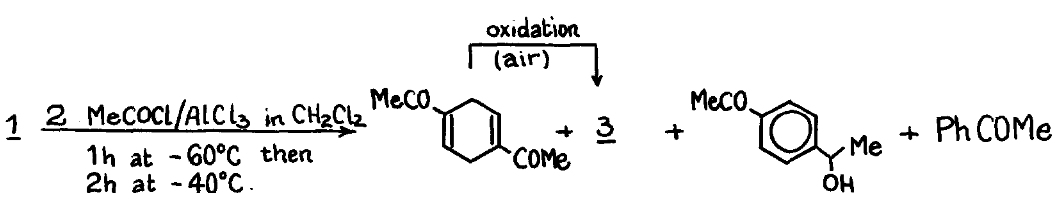
It is well known that direct diacylation of the benzene ring is not practical under the Friedel and Crafts conditions even when one starts from bis (trimethylsilyl)-benzene[1]. On the other hand, the acetylation of allylsilanes[2] generally proceeds in high yields[3] under very mild conditions.

Since the reductive direct disilylation of benzene affords almost quantitatively the bis(allylsilane) 1[4], we followed the organosilicon route in the synthesis of p.-diacetylbenzene 3. The scheme proposed was the following[5] :



1 : 85-100%[4] 2 3

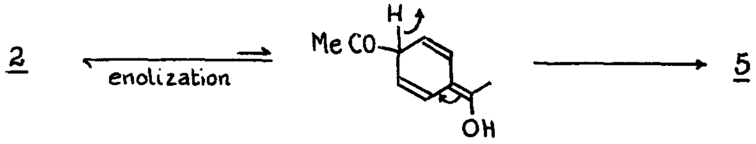
When the reaction medium was left in the presence of air after acetylation, benzene was regiospecifically converted into 3 in about 70 % yield from 1 besides small amounts of 6 and 5 :



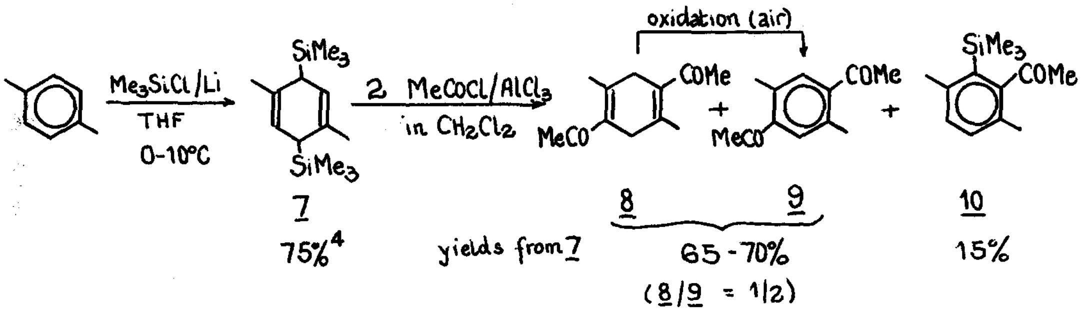
4 5 6

70% global yield from 1 ~20% 10%

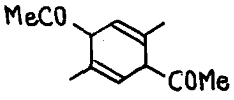
Substance 2 was not identified under our reaction conditions. However, the new substance 4, resulting from the isomerization of 2 (conjugation) is relatively stable and was unambiguously identified by NMR spectroscopy. The presence of 6 was due to the desilylation from HCl (present in the $AcCl/AlCl_3$ complex or formed during the course of the reaction), whereas 5 could be formed as follows :



p.-Xylene underwent a similar regiospecific reaction but no keto-alcohol was detected :

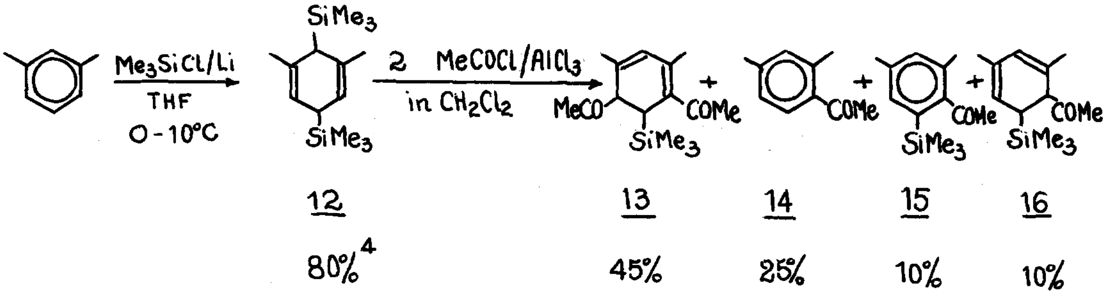


8 was slowly converted into 9 in the presence of air. 10 was not isolated in a pure state, and thus was not identified with absolute certainty. Substance 11 was in one case isolated as the only reaction product after work up but in subsequent attempts we could not isolate again this intermediate ; 11 was identified by NMR spectroscopy, 8 and 11 were previously unknown.

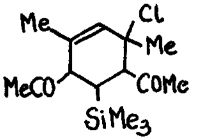


11

Likewise the behaviour of m-xylene was investigated but competitive mono- and diacetylation were observed :



Because of steric considerations and since aromatization can be accompanied by desilylation[6], monoacetylation must give 16 as the precursor of 15 and 14. Acetylation of 16, as observed by us for other 1-silyl 1,3-dienes, should occur at the 1,4-positions giving 17, and then 13 after dehydrochlorination.



17

13, 15 and 16 are new compounds ; 15 was not isolated in a pure state.

In all cases Me_3SiCl was recovered during the course of acetylation.

EXPERIMENTAL SECTION - The silylated precursors 1, 7 and 12 were prepared as previously described[2]. All the reagents including $AlCl_3$ were degassed before use.

Diacetylation of 2. 2 (4.5 g, 0.02 mol.) in CH_2Cl_2 (20 ml) was slowly added to the complex $AcCl/AlCl_3$ prepared from AcCl (3.2 g, 0.04 mol.), $AlCl_3$ (5.4 g, 0.04 mol) in CH_2Cl_2 (60 ml) at - 60°, in an inert atmosphere. After 1 h at this temperature the reaction mixture is left 2 h at - 40° then poured (without warming) onto ice-cold water being 10 % NH_4Cl. After extraction with ether, drying over Na_2SO_4, and removal of ether under vacuum (25 mmHg), 2.8 g of an orange crystalline mass remained. The products were separated on a silicagel column with different eluents : CH_2Cl_2 for 6 and CH_2Cl_2/Et_2O c.a. 1/1 (vol.) for 3, 4 and 5.

Diacetylation of 7. Under the same conditions, from 7 (5 g. 0.02 mol), we obtained 3.3 g of crude product which was further treated as in the above case. In one attempt from 7 (6.2 g, 0.027 mol), $AlCl_3$ (7.3 g, 0.054 mol) and AcCl (4.3 g., 0.054 mol.), we obtained 5 g of crude product which slowly crystallized. Crystals were filtered off and identified as the practically pure 11.

Diacetylation of 12. Under the same conditions from 2 (5 g. 0.02 mol.), we obtained 4.1 g of an orange liquid. 15 and 16 were separated on a silica column with pentane as eluent. 14 is obtained (with a very small amount of an impurity) with CH_2Cl_2 and 13 with CH_2Cl_2/Et_2O c.a. 1/1 (vol.) as eluent.

Physico-chemical properties of the formed products

° The well-known aromatic ketones 3, 6, 9 and 14 as well as the keto-alcohol 5 were identified by comparing their physicochemical properties with those of authentic samples. The other aromatic products 10 and 15 have NMR and IR data in complete accordance with the proposed structures.

° Cyclohexadienic intermediates 4, 8, 11 and 13 gave satisfactory C, H analytical data. They were identified by proton NMR spectroscopy[7] (δppm, CCl_4 as solvent, $CHCl_3$ at 7.27 ppm as internal reference ; s : singlet, d : doublet, m : multiplet).

4 : 2.30, s, 6H, 2 Me-CO- ; 3.1, m, 4H, 2-CH_2- ; 6.9, m, 2H, 2 C=CH-.

8 : 1.90, m, 6H, 2Me-C=C- ; 2.20, s, 6H, 2 Me-CO- ; 2.95, m, 4H, 2-CH_2-C=C-.

11 : 1.55, m, 6H, 2Me-C=C- ; 1.95, s, 6H, 2 Me-CO- ; 3.45, m, 2H, 2 CH-CO- ; 5.40, m, 2H, 2 C=CH-.

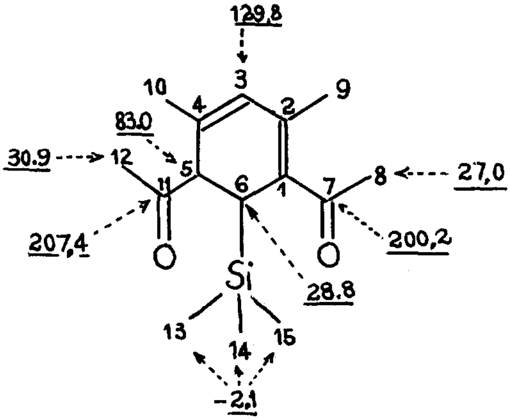
13 : - 0.20, s, 9H (-$SiMe_3$) ; 1.70, m, (3H) (Me-C=C-) ; 1.80, m, 3H, (Me-C=C-) ; 1.90, s, 3H, Me-COC , 2.15, s, 3H, Me-CO-C=C- ; 2.60, m, 1H and 2.70, m, 1H, CH-Si and

CH-CO- non attributed ; 5.60, m, 1H, C=CH-.

16 was identified in the mixture 16-15 (ethylenic protons) and conversion into 15.

Moreover 4, 8 exhibit in IR spectroscopy ν (conjugated C=O) ∿ 1680 cm^{-1} whereas 11 has ν (non conjugated C=O) at 1700 cm^{-1} and 13 has two absorption bands at 1680 cm^{-1} (conjugated carbonyl) and 1710 cm^{-1} (non conjugated carbonyl).

The structure of 13 was confirmed by NMR, ^{13}C spectroscopy δppm, $CDCl_3$ as solvent, TMS (0 ppm) as internal standard.



Non assigned : 136.9 ; 135.2 ; 131.5 ; C_1, C_2, C_4.
23.2 ; 20.2 : C_9, C_{10}.

References and Footnotes

1 - K. Dey, C. Eaborn and D.R.M. Walton, Organometallics in Chem.Synth. 1, 151(1970). C. Eaborn, J.Organometal.Chem., 100, 43(1975) and references herein.

2 - M. Laguerre, J. Dunoguès, R. Calas and N. Duffaut, J.Organometal.Chem. 112, 49(1976). Since this report yields were optimized (M. Laguerre, Ph.D. Thesis, Bordeaux (France), p. 9(1979).

3 - R. Calas and J. Dunoguès, J.Organometal.Chem. 27 , C 21(1971).

4 - R. Calas, J. Dunoguès, J-P. Pillot, C. Biran, F. Pisciotti and B. Arréguy. J.Organometal Chem. 85, 149(1975) ; J-P. Pillot, J. Dunoguès and R. Calas, Tetrahedron Letters 1871 (1976) ; J-P. Pillot, G. Déléris, J. Dunoguès and R. Calas, J.Org.Chem. 44 , 3397(1979). For good reviews see E.W. Colvin, Chem.Rev. 15(1978) and T.H.Chan and I. Fleming, Synthesis 761(1979).

5 - Communication of preliminary results at the 5th Intern.Symp. on Organosilicon Chem. Karlsruhe (West Germany) August 14-18 (1978) Abstr. p. 220.

6 - G. Félix, M. Laguerre, J. Dunoguès and R. Calas, Angew.Chem.Intern.Ed., in press.

7 - ^1H and ^{13}C NMR spectra are available on request.

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