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ON THE SILYLATION OF DIARYLCARBINOLS

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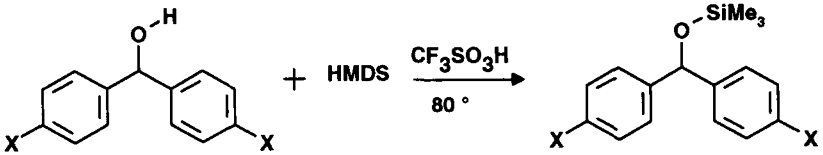
Abstract : Because of their dismutation into benzophenones and diphenylmethanes, it is necessary to use chlorotrimethylsilane and not triflic acid as a catalyst for the silylation of diarylcarbinol with hexamethyldisilazane.

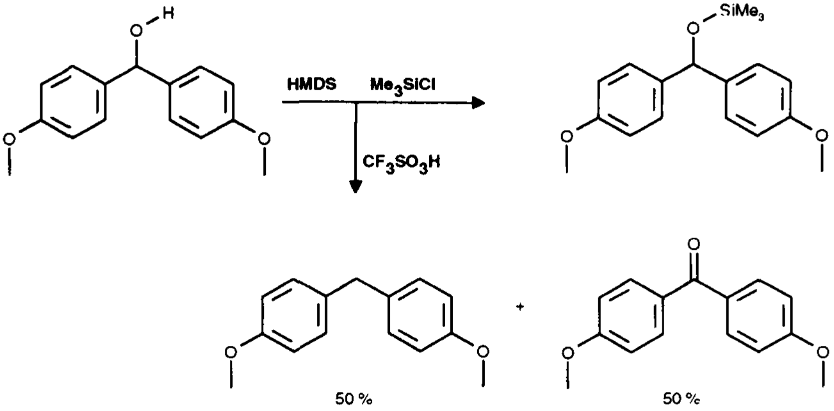
While working on the reactivity of silylated arylcarbinols, we tried to use hexamethyldisilazane for the silylation of diarylcarbinols **1a** and its 4,4'-dichloro derivative **1b**. No reaction occurred at reflux temperature, but a 100% nmr yield in silylated alcohols **2a,b** was obtained when triflic acid was used as a catalyst



1a X = H
1b X = Cl

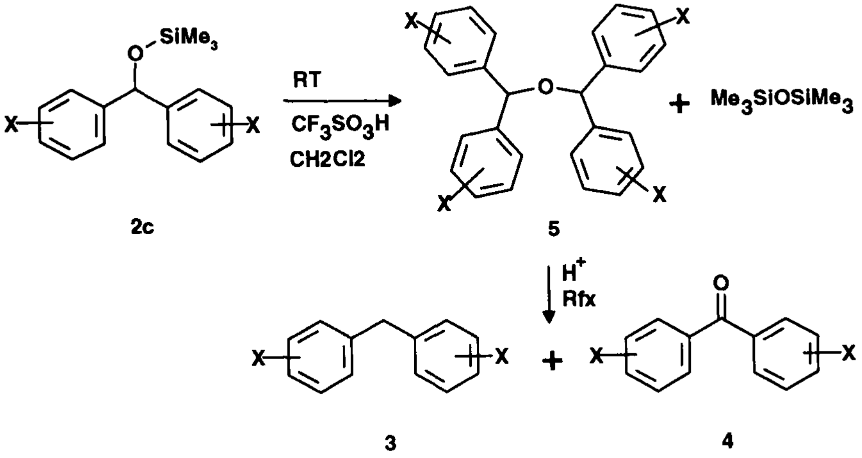
2a 100 %
2b 100 %

However, 4,4'-dimethoxydiphenylcarbinol (**1c**) does not gives the silylated alcool **2c** under these conditions, and we obtained only a 50/50 % isolated yield in 4,4'-dianisylmethane (**3c**) and 4,4'-dimethoxydiphenylmethane (**4c**).

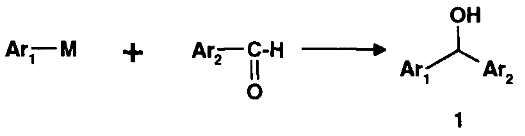


Searching in the literature showed that such a dismutation of diarylcarbinols was already known : this reaction, which occurred in strongly acidic media[1] and has also been observed while heating phenyl pyridazinyl carbinols[2] , proceeds *via* a hydride transfer mecanism[3] from a bis-diphenylmethyl ether intermediate[1c]. We checked that, by treatment of silyl ethers **2** at room temperature with a small amount of triflic acid, bis diarylmethyl ethers **5** were quantitatively obtained, and that heating the reaction medium at 60° leads to the dismutation.

We found that when chlorotrimethylsilane was used as the catalyst instead of triflic acid for the silylation of diarylcarbinols with hexamethyldisilazane, a near quantitative yield in silylated ether **2** was always obtained. A list of the diarylcarbinols which were silylated by using this method is given in the Table ; almost all these silyl ethers dismute when treated by a slight amount of triflic acid. Non



commercial diarylcarbinols utilized in this study were obtained according to the literature[6] or from a Grignard reaction between aromatic aldehydes and organomagnesium or organolithium compounds.



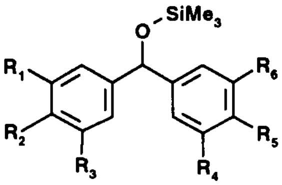
EXPERIMENTAL

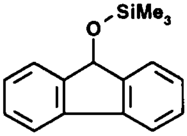
Melting points are uncorrected, IR spectra were recorded on a Perkin-Elmer 1600 spectrometer, and the nmr spectra on a Hitachi Perkin-Elmer R-600, at 60 MHz, using tetramethylsilane as an internal reference. Elemental analyses were performed by the 'Service Central de microanalyses' of CNRS, in Vernaison, France, and were not made for the water sensitive silylated alcools **2**.

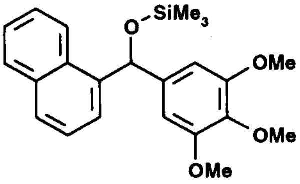
Bis-3,4-methylenedioxybenzhydrol.

A solution of n-butyllithium (1.85 N) in hexanes (180 ml, 333 mmole) was added to a cooled (-78°) solution of 5- bromodioxole[4] (67 g, 333 mmole) in anhydrous tetrahydrofuran. The mixture was stirred for one hour, then a solution of piperonal (50 g,

TABLE







R_1	R_2	R_3	R_4	R_5	R_6
H	H	H	H	H	H
H	OMe	H	H	OMe	H
H	H	H	OMe	OMe	H
H	OMe	H	O-CH$_2$-O		H
H	O-CH$_2$-O		O-CH$_2$-O		H
OMe	OMe	OMe	H	H	H
OMe	OMe	OMe	H	OMe	H
OMe	OMe	OMe	O-CH$_2$-O		H
OMe	OMe	OMe	OMe	OMe	OMe
H	Cl	H	H	Cl	H

333 mmole) in tetrahydrofuran (200 ml) was added (-78°). After warming at room temperature, water (10 ml) was added and the organic solvents were evaporated ; methylene dichloride and water (10 ml) were added, and the organic solution was washed with water. After drying and evaporation of the methylene dichloride solution, a 94% yield of the benzhydrol was obtained, mp 90-1° (ethyl acetate) ; ir (KBr) ν cm^{-1} : 3310, 3125,

1500, 1485, 1440, 1135 ; ^{1}H nmr (CDCl$_3$) δ ppm : 2.50 (s, 1 H, deuterium oxide exchangeable), 5.58 (s, 1 H), 5.87 (s, 4H), 6.69-6.81 (m, 6 H).

Anal. calcd. for $C_{15}H_{12}O_5$: C, 66.17 ; H, 4.44 ; O, 29.38 . Found : C, 66.07 ; H, 5.58 ; O, 29.41.

3,4,5-Trimethoxy-3,4-methylenedioxybenzhydrol.

A few drops of dibromoethane were added to a hot (55°) suspension of magnesium (6.5 g, 267 mmole) in tetrahydrofuran (140 ml). After the begining of the reaction, a solution of 5-bromo-1,3-benzodioxole[4] (50 g, 249 mmole) in tetrahydrofuran (150 ml) was added (30mn) while keeping the temperature at 55°. After stirring for 2 hours at the same temperature, a solution of 3,4,5-trimethoxybenzaldehyde (48.8 g, 249 mmole) in tetrahydrofuran (150 ml) was added (30 mn), then the mixture was heated (60°) for 1 hour. The solvent was evaporated, then a solution of ammonium chloride (70 g) in water (300 ml) was added. After extraction with methylene dichloride, drying and evaporation, the alcohol was obtained in 71% yield ; mp 111-2° (ethyl acetate) ; ir (KBr) ν cm^{-1} : 3330, 3230, 1595, 1500, 1485, 1465, 1435, 1125 ; ^{1}H nmr (CDCl$_3$) δ ppm : 2.90 (s, 1 H, deuterium oxide exchangeable), 3.80 (s, 9 H), 5.61 (s, 1 H), 5.90 (s, 2 H), 6.56 (s, 2 H), 6.72-6.82 (m, 3 H).

Anal. calcd. for $C_{17}H_{18}O_6$: C, 64.14 ; H, 5.70 ; O, 30.16. Found, C, 63.95 ; H, 5.68 ; O , 30.12.

3,4,5,3',4',5'-Hexamethoxybenzhydrol.

Sodium borohydride (3.5 g, 0.993 mole) was slowly added to a solution of 3,4,5,3',4',5'-hexamethylbenzophenone (15 g, 0.545 mole) in ethanol (150 ml) ; the mixture was stirred at 0° for 15 mn then the solution was refluxed for 1 hours. After cooling, acetic acid (42 ml was added, and the solvent was evaporated ; water (100 ml) was added and the product was extracted with methylene dichloride ; the organic phase was washed with a sodium carbonate solution then dried. After evaporation, the alcohol was cristallized in a ethyl acetate/heptane mixture, giving a 62 % yield of the benzhydrol, mp = 127-9 °C, ir (KBr) ν cm^{-1} : 3450, 1595, 1510, 1460, 1130, 1120 ; ^{1}H nmr (CDCl$_3$) δ ppm : 3.78 (s, 18 H), 5.61 (s, 1 H), 6.57 (s, 4 H).

3,4,5,3',4',5'-Hexamethoxybenzhydryl trimethylsilyl ether

Chlorotrimethylsilane (3 drops) was added (syringe) to a mixture of hexamethyldisilazane (10 ml, 44.5 mmole) and 3,4,5,3',4',5'-hexamethoxy- benzhydrol (5 g, 13.8 mmole).The mixture was refluxed for 40 mn, the hexa-methyldisilazane excess was evaporated (sublimation of ammonium chloride), giving a quantitative yield of the silyl ether as a non colored liquid ; ^{1}H nmr ($CDCl_3$) δ ppm : 0.13 (s, 9 H), 3.80 (s, 18 H), 5.60 (s, 1 H), 6.55 (s, 4 H).

Benzhydryl trimethylsilyl ether (2a).

Triflic acid (0.05 ml) was added (syringe) to a mixture of hexamethyldisilazane (100 ml, 474 mmole) and benzhydrol (92.2 g, 500 mmole). The mixture was heated (80°) for 30 mn, the hexamethyldisilazane excess was evaporated then the silyl ether was distilled, giving a 96% yield in pure compound ; bp 85-7° (0.2 mmHg) ; ^{1}H nmr ($CDCl_3$) δ ppm : 0.06 (s, 9 H), 5.77 (s, 1 H), 7.28 (s, 10 H).

With 6 drops of chlorotrimethylsilane as a catalyst, the yield was 98% (1 h, 80°).

Bis benzhydryl ether (5a).

Triflic acid (0.05 ml, 0.56 mmole) was slowly added (syringe) to stirred silyl ether (**2a**) (15 g, 58 mmole) cooled at 0°. The solid compound obtained after 1 mn was dissolved in methylene dichloride, then washed with water, giving a 98 % yield in pure ether **5a** identical to the known compound[5].

Trimethylsilylether of 1-naphthyl 3,4,5-trimethoxyphenyl carbinol.

Chlorotrimethylsilane (3 drops) was added (syringe) to a mixture of hexamethyl- disilazane (100 ml) and 1-naphthyl 3,4,5-trimethoxyphenyl carbinol (40 g, 147 mmole). The mixture was heated at reflux for 40 mn, the hexamethyldisilazane excess was evaporated (sublimation of ammonium chloride), giving a quantitative yield in the silyl ether as a yellow oil ; ^{1}H nmr ($CDCl_3$) δ ppm : 0.09 (s, 9 H), 3.72 (s, 6 H), 3.79 (s, 3 H) 6.36 (s, 1 H), 6.80 (s, 2 H), 7-8.2 (m, 7 H).

Dismutation of 4,4'-dimethoxybenzhydryl trimethylsilyl ether (2c).

Triflic acid (0.05 ml, 0.56 mmole) was added (sirynge) at room temperature, to a stirred solution of ether **2c** (13.2 g, 42 mmole) in chloroform (20 ml). After 2 hours, a quantitative yield in bis-benzhydryl ether **5c** was obtained, ^{1}H nmr ($CDCl_3$) δ ppm : 3.68 (s, 12 H), 5.19 (s, 2 H), 6.71(d, J=8.4 Hz, 1 H), 7.16 (d, J=8.4 Hz, 1H) [7].

The above solution was heated at 60° for 15 mn, then methylene dichloride (50 ml) and water (50 ml) were added. After washing, the organic phase was dried then evaporated. The obtained solid was filtered then washed with heptane, giving a 44 % yield in 4,4'-dimethoxybenzophenone identical to the commercial compound. The heptane solution was evaporated, giving a 42 % yield in dianisylmethane, identical to the known compound[1b].

Dismutation of bis-4,4'-dichlorobenzhydryl ether (5b).

A solution of ether **5b** (2.3 g, 10 mmole) and triflic acid (0.05 ml, 0.57 mmole) in chloroform (5 ml) was heated at 60° for 5 hours. Methylene dichloride (10 ml) and water (10 ml) were added. After washing, the organic phase was dried then evaporated. The solid obtained was filtered, then washed with diisopropyl ether, giving a 32 % yield in 4,4'-dichlorobenzophenone identical to the commercial compound. Evaporation of the washing residue gives a 38 % yield in 4,4'-dichlorodiphenylmethane identical to the commercial compound.

REFERENCES

[1] a) Kny-Jones F.G. and Ward AM., *J. Chem. Soc.*, 535, (1930).
b) Balfe M.P., Kenyon J. and Thain E.M., *J. Chem. Soc.*, 790, (1952).
c) Burton H. and Cheeseman G.W.H., *J. Chem. Soc.*, 986, (1953).

[2] Heinisch G., *Bull. Soc. Chim. Belg.*, **101**, 579 (1992).
Heinisch G. and Waglechner R., *J. Heterocyclic Chem.*, **21**, 1727 (1984).
Heinisch G., Luszczak E. and Pailer M., *Monatsh. Chem.*, **105**, 763 (1974).

[3] Bartlett P.D. and McCollum J.D., *J. Am. Chem. Soc.*, **78**, 1441 (1956).

[4] Feuglas E., *Bull. Chem. Soc. France*, **8**, 1892 (1964).

[5] Knoevenagel E., *Ber.*, **36**, 2827 (1903).

[6] Cushman M., Nagarathnan D., Gopal D., He H.M., Lin, C.M. and Hamel E., *J.Med. Chem.*, **35**, 2293 (1992).

[7] Henneuse C., Gillard K., Noiset O., Marchand-Brynaert J., *Bull. Soc. Chim. France*, **132**, 333 (1995)

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