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SYNTHESIS AND CHARACTERIZATION OF SILYL - GROUP - CONTAINING FLUORENES

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Cyclization reactions of biphenyl with dichloropropyltrichlorosilane and dichlorobutyltrichlorosilane in the presence of anhydrous aluminum chloride catalyst gave 9 - (2 - trichlorosilylethyl)fluorene and 9 - methyl - 9 - (2 - trichlorosilylethyl) fluorene along with isomeric uncyclized products. All the compounds were structurally identified by GC / MS, ^{1}H and ^{13}C - NMR spectroscopy.

Key words**:** Cyclization of biphenyl, Friedel - Crafts alkylation, Chlorosilyl - ethyl fluorenes.

Introduction

The alkylation of biphenyl was first carried out in the presence of BF_3 catalyst (Romadane 1957, 1959; Romadane *et al* 1957). Based on their work in the 1950s, the products were mixtures of 4 - alkyl - and 4, 4 - dialkylbiphenyl. Although, various fluorenyl - silanes, i.e. dimethylbis (9 - fluorenyl) silane (Patsidis *et al* 1996; Resconi *et al* 1996) and dimethyl (9 - fluorenyl) cyclopentadienylsilane (Silaghi *et al* 1995) are known to be prepared from lithiation reaction of fluorene, the cyclization of biphenyl with alkyl halides containing silyl groups has never been reported.

The present paper describes synthesis of new fluorenyl derivatives containing silicon metal as precursors for blue - light - emitting polyfluorenes. 9 - (2 - trichlorosilylethyl)fluorene and 9 - methyl - 9 - (2 - trichlorosilylethyl)fluorene were synthesized through cyclization reactions of biphenyl with dichloropropyltrichlorosilane and dichlorobutyltrichloro - silane, in the presence of anhydrous aluminum chloride. All these compounds were structurally identified by GC / MS, ^{1}H and ^{13}C - NMR spectroscopy.

Experimental

All reactions were carried out under nitrogen atmosphere. All glassware used was flame - dried or oven - dried before use. Solvents were purified using standard purification procedures (Perrin *et al* 1980). Anhydrous aluminum chloride, trichlorosilane, H_2PtCl_6 (0.1M solution in IPA), triphenylphosphine, $PdCl_2$ and 1,3 - butadiene were purchased from Aldrich Chemical Co. and used without further purification. Biphenyl was purchased from Yakari Pure Chemical Co. while 3 - chloropropyltrichlorosilane and trichlorosilyl - 2 - butene were prepared by the reported procedure (Tsuji *et al* 1974). Dichloropropyltrichlorosilane and dichlorobutyltrichlorosilane were prepared by passing chlorine gas through 3 - chloropropyltrichlorosilane and trichlorosilyl - 2 - butene respectively.

All air - sensitive liquids and dried solvents were transferred by standard syringe or double - tipped - needle technique. Reaction products were analysed by GLC using a capillary column (SE - 30, 30m) or a packed column (10% OV - 101 on 80 - 100 mesh Chromosorb W / AW, 1 / 8 in x1.5 in) on a Varian 3300 gas chromatograph equipped with a flame ionization detector or a thermal conductivity detector. The samples for characterization were purified by preparative GLC using a Varian aerograph series 1400 gas chromatograph with a thermal conductivity detector and a 2m by 1 / 8in. stainless steel column packed with 20% OV - 101 on 80 - 100 mesh chromosorb P / AW. Mass spectra were obtained using a Hewlett - Packard 5890 Series II gas chromatograph equipped with a 5972 mass selective detector.

NMR spectra were recorded on a Varian spectrometer using samples in $CDCl_3$ solution, ^{1}H - NMR spectra at 300 MHz and ^{13}C NMR at 75.4 MHz.

Syntheses. 9 - (2 - Trichlorosilylethyl) fluorene (1). Biphenyl, 80g (519 mmol) and anhydrous aluminum chloride, 4.8g (36 mmol) were charged into a 500c.c. 2 - neck flask attached with a reflux condenser. Biphenyl was allowed to melt under N_2 atmosphere. While it was stirring, dichloropropyl - trichlorosilane, 64g (259.7 mmol) was added very slowly via a syringe. HCl evolution was noticed. The reaction mixture was kept at 130°C for 2 h after that it was worked up by deactiva-ting the $AlCl_3$ with $POCl_3$, 6.6g (43.2 mmol). The reaction mixture was then extracted with dry n - hexane. Low boilers were removed using bulb to bulb distillation, while high boilers were distilled out under vacuum. The product along with the isomers were collected at a b.p. of 130 ~ 134°C / 0.2 torr. Pure 9 - (2 - trichlorosilylethyl)fluorene, 38.28g was obtained through recrystallization from dry Et_2O in 45% yield, based on silane used.

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^1H - NMR. δ 0.93 - 0.99 (m, 2H, CH_2), 2.44 - 2.51 (m, 2H, CH_2), 4.17 - 4.20 (t, 1H, CH), 7.36 - 7.89 (m, 8H, aromatic).
^{13}C - NMR. δ 18.57 (CH_2), 24.71 (CH_2), 47.73 (CH), 120.16, 124.16, 127.36, 127.59, 141.74, 145.41 (aromatic C).
GC / MS (m / e). calcd. for $C_{15}H_{13}SiCl_3$, (M^+) 326, found 326.

9 - Methyl - 9 - (2 - trichlorosilylethyl)fluorene (2a). Eight g (51.88 mmol) biphenyl and 0.33g (2.475 mmol) $AlCl_3$ (anhydrous) were taken into a 50cc, 2 - neck flask connected with a reflux condenser and flushed with N_2. 3.38 Gram (12.97 mmol) of dichlorobutyltrichlorosilane was added via a syringe. The reaction mixture was heated at 100°C for 1 h. After that time the reaction mixture which was purple in colour, was worked up by deactivating the catalyst with $POCl_3$, 0.46g (2.97 mmol). It was extracted with dry n - hexane. Low boilers were removed through bulb to bulb distillation at atmospheric pressure, while high boilers were distilled out at reduced pressure. Yellow oily distillate was obtained at a temperature of 140 ~ 145°C / 0.2 torr which contained a mixture of 3 isomers. The yield of the major product i.e. 9 - methyl - 9 - (2 - trichlorosilylethyl)fluorene was 33% as obtained from GLC analysis. Preparative GC was performed to separate the product which was later on fully characterized by GC / MS, ^1H and ^{13}C - NMR. The other two isomers were characterized as substituted biphenyls as represented by structures (2b) and (2c).

^1H - NMR (2a). δ 0.60 - 0.66 (m, 2H, CH_2), 1.54 (s, 3H, 9 - methyl), 2.24 - 2.30 (m, 2H, CH_2), 7.36 - 7.77 (m, 8H, aromatic).
^{13}C - NMR (2a). δ 19.05 (CH_2), 26.48 (CH_3), 32.56 (CH_2), 51.0 (C_9), 120.13, 122.61, 127.52, 127.64, 141.74, 150.41 (aromatic).
GC / MS (m / e) (2a). Calcd. for $C_{16}H_{15}SiCl_3$ (M^+), 340, found 340.

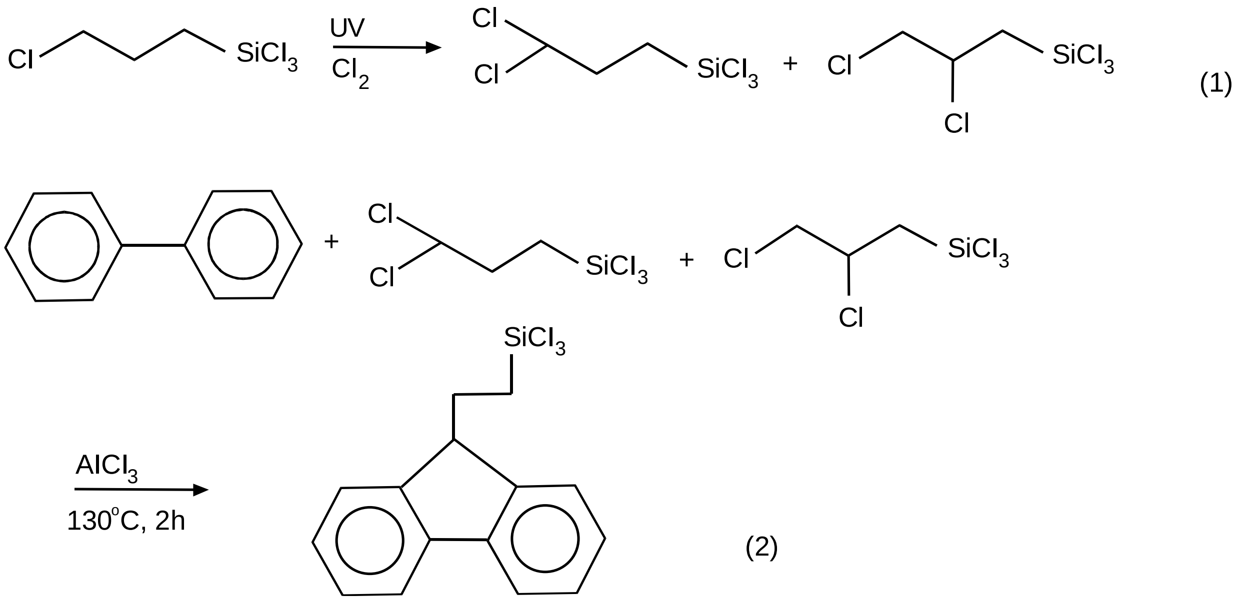
^1H - NMR (2b). δ 1.34 - 1.36 (d t, 5H, CH_3, CH_2), 1.87 - 1.95 (q, 2H, CH_2), 2.78 - 2.85 (h, 1H, CH), 7.27 - 7.62 (m, 9H, aromatic).
^{13}C - NMR (2b). δ 21.03 (CH_3), 21.92 (CH_2), 30.41 (CH_2), 41.33 (CH), 126.78, 126.89, 127.03, 127.16, 139.14, 144.21 (aromatic).
GC / MS (m / e) (2b). Calcd. for $C_{16}H_{17}SiCl_3$ (M^+), 342, found 342.
^1H - NMR (2c). δ 1.33 - 1.35 (d, t, 5H, CH_3, CH_2), 1.85 - 1.94 (q, 2H, CH_2), 2.76 - 2.83 (h, 1H, CH), 7.25 - 7.59 (m, 9H, aromatic).
^{13}C - NMR (2c). δ 21.03 (CH_3), 21.92 (CH_2), 30.41 (CH_2), 41.33 (CH), 126.78, 126.89, 127.03, 127.16, 139.14, 144.21 (aromatic C).
GC / MS (m / e) (2c). Calcd. for $C_{16}H_{17}SiCl_3$ (M^+), 342,found 342.

Results and Discussion

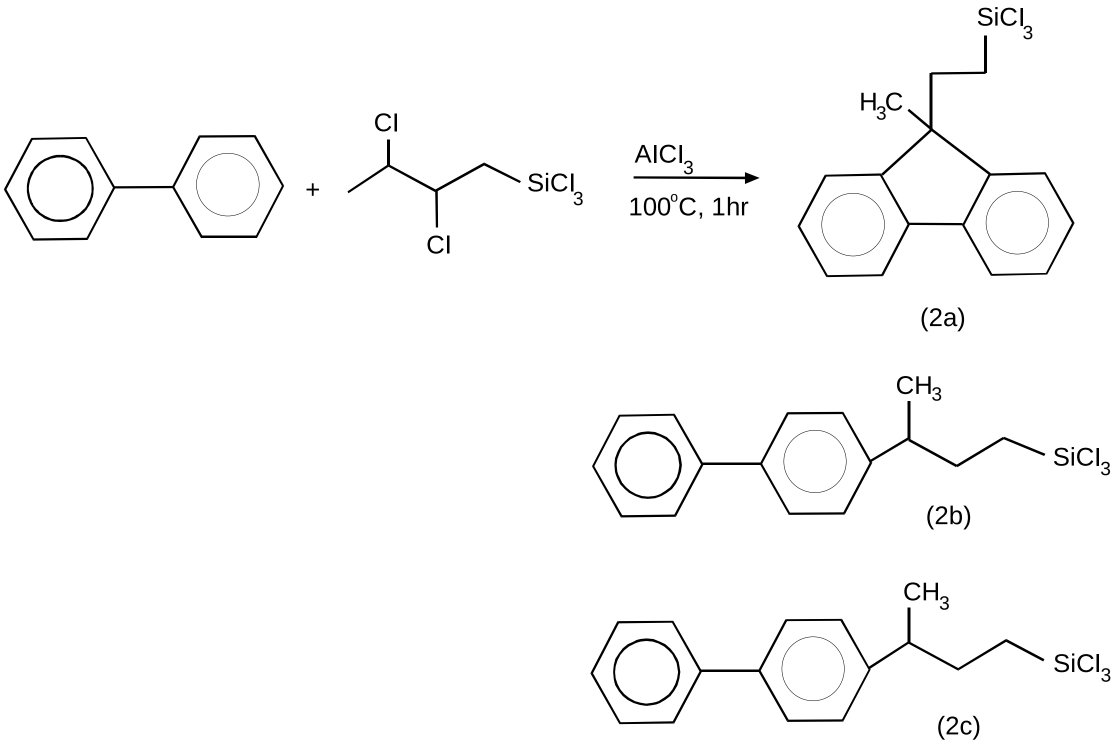
Alkylation reactions. Biphenyl was alkylated with dichloropropyltrichlorosilane in the presence of anhydrous aluminum chloride in order to get 9 - (2 - trichlorosilylethyl)fluorene (1). Dichloropropyltrichlorosilane was obtained by chlorinating 3 - chloropropyltrichlorosilane under UV - irradiation. During the chlorination reaction two isomers of equal ratio i.e. 3, 3 - and 2, 3 - dichloropropyltrichlorosilanes were produced both of which were later on used for the alkylation reaction (rtn. 1 and 2). (1) was obtained in 45% yield, using the molar ratio of 2 : 1 (biphenyl : silane).

The reaction also gave some polymeric material which could not be identified.

Reaction 2 suggests that the γ - C of the dichloropropyltrichlorosilane takes part in the cyclization reaction, forming 9th carbon of the fluorene ring and shifting proton at γ position of 2, 3 - dichloropropyltrichlorosilane to β position after dechlorination.



Scheme 1



......(3)

(2a)

(2b)

(2c)

Scheme 2

Similarly, 9 - methyl - 9 - (2 - trichlorosilylethyl)fluorene (2a) was synthesized from reaction of biphenyl with 2,3 - dichlorobutyltrichlorosilane (rtn. 3). When biphenyl was reacted with 2, 3 - dichlorobutyltrichlorosilane in molar ratio of 4:1 (biphenyl to silane) for 1 h, 9-methyl-9-(2-trichlorosilylethyl)fluorene (2a) was obtained in 33% yield based on silane used. Two uncyclized side products (2b) and (2c) were also produced in lower yields.

Structural elucidation. The ^{1}H - NMR spectrum of (1) shows two multiplets each of relative area 2 and one triplet (rel. Area 1) in aliphatic region. One multiplet at δ 0.93 - 0.99 ppm corres-ponds to the protons at silicon coordinated carbon while the 2nd multiplet at δ 2.44 - 2.51 ppm is attributed to the protons of the 2nd carbon of the ethyl group. The triplet at δ 4.17 - 4.20 ppm is due to the single proton at the 9th carbon of the fluo-rene ring.

In aromatic region, two sets of peaks are originating. The multiplet at 7.36 - 7.89 corresponds to the six protons (1, 2, 3, 6, 7, 8) and peaks at δ 7.82 and 7.84 ppm are due to protons at 4 and 5 position of the fluorene ring.

The ^{13}C - NMR spectrum shows three resolved peaks in aliphatic region while six peaks are observed in aromatic region and is a good coincidence with the ^{1}H - NMR spectrum.

Similarly, structures for 2a, 2b and 2c were deduced from the ^{1}H and ^{13}C - NMR data.

References

Patsidis K, Alt H G, Milius W, Palackal S J 1996 The synthesis, characterization and polymerization behavior of onsa cyclopentadienylfluorenyl complexes; the X-ray structures of the complexes $[(C_{13}H_8)SiR_2(C_5H_4)]ZrCl_2$(R = Me or Ph). *J Organomet Chem* **509**(1) 63 - 71.

Perrin D D, Armarego W L F, Perrin D R 1980 *Purification of laboratory chemicals*. Pergamon Press, New York, USA, pp 1 - 200.

Resconi L, Jones R L, Rheingold A L, Yap G P A 1996 Highmolecular weight atactic polypropylene from metallocene catalysts. 1 - $Me_2Si(\eta - 9 - Flu)_2ZrX_2$(X = Cl, Me). *Organometallics* **15**(3) 998 - 1005.

Romadane I A 1957 Alkylation of naphthalene with normal alcohols in the presence of boron trifluoride under pressure. *Zhur Obshchei Khim* **27** 1833 - 1835.

Romadane I A 1957 Alkylation of naphthalene with iso alcohols in the presence of boron trifluoride. *Zhur Obshchei Khim* **27** 1939 - 1941.

Romadane I A 1959 Alkylation of naphthalene with a molecular compound of ethyl alcohol with boron trifluoride under pressure. *Zhur Obshchei Khim* **29** 102.

Romadane I A, Dokuchaeva V M 1975 Alkylation of naphthalene with secondary and isobutyl alcohols. Latv PSR Zinat Akad Vestis, *Kim Ser* (1) 61 - 65.

Romadane I A, Shuikin N I, Egorov Ya P 1957. Determination of purity of 1and 2 - butylnaphthalenes by ultraviolet spectra. Izvest Akad Nauk SSSR, *Otd Khim Nauk* 648 - 649.

Silaghi D L, Haiduc I, Escudie J, Couret C, Stage J 1995 Investigations in the field of group 14 difluorenyl compounds. *Synth react inorg metorg chem* **25**(4) 575 - 90.

Tsuji J, Hara M, Ohno K 1974 Organic synthesis by means of noble metal complexes. XCII. Palladium catalysed hydrosilation of monoenes and conjugated dienes. *Tetrahedron* **30**(14) 2143 - 2146.