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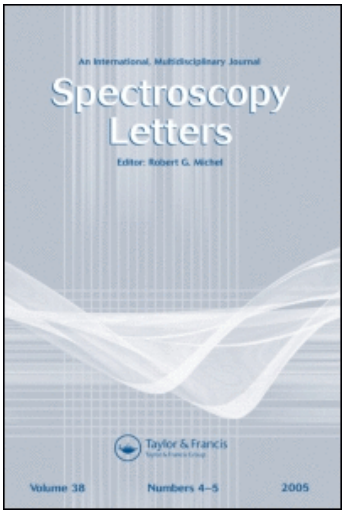

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^{1}H and ^{13}C Nmr Determination of Polysubstituted Diphenylmethane Dimers Mechanism of Their Formation by Reduction of Polymethoxylated Benzophenones

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SPECTROSCOPY LETTERS, 33(5), 755–775 (2000)

^{1}H AND ^{13}C NMR DETERMINATION OF POLYSUBSTITUTED DIPHENYLMETHANE DIMERS MECHANISM OF THEIR FORMATION BY REDUCTION OF POLYMETHOXYLATED BENZOPHENONES

Key Words : 11-Chloro-2,5,15,18-tetramethoxy-17-(24-chlorobenzyl)triphenyl methane; 11-bromo -2,5,15,18-tetramethoxy-17-(24-bromobenzyl)triphenyl methane; diphenylmethane; benzophenone; benzhydrol; benzofluorene; reduction; sodium borohydride; trifluoroacetic acid ; ^{1}H and ^{13}C NMR; 2D NMR.

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ABSTRACT

Reduction of substituted benzophenones **1** with sodium borohydride and trifluoro-acetic acid yields diphenylmethanes **3** as well as dimers **5** and **6**. The complete structure of these substituted diphenylmethane dimers **5** may be accurately determined by ^{1}H, ^{13}C, 2D NMR analysis, and a mechanism for their formation is suggested.

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INTRODUCTION

Conversion of aryl ketones to the corresponding hydrocarbons is a frequently encountered reaction in organic synthesis. Among the relatively few direct one-step methods available [1, 2] for this transformation, the ionic hydrogenation using sodium borohydride in the presence of Brönsted acid [3] is very interesting. Indeed, this convenient method not only gives the corresponding hydrocarbons, but it also uses sodium borohydride, whose price is low compared with silanes. During the course of a program requiring the use of this reaction to obtain substituted diaryl methanes **3**, we questioned the structure of the by-products and the possible formation of benzofluorene **4** [4, 5], which could be obtained by cyclization of the intermediate cation **2** [2, 4], (FIG. 1).

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Analysis of the NMR spectra of the aromatic by-products showed that they do not possess the structure of the benzofluorene **4** (FIG. 1). In order to elucidate the nature and the scale of formation of these compounds, several experiments of reduction of benzophenones **1** with sodium borohydride and trifluoroacetic acid [6], were performed (FIG. 2). The results are summarized in Table 1.

We report here physical characteristics of compounds **3, 5, 6** and the complete assignments for all chemical shifts of protons and carbons, where we have been permitted to know the structure of these compounds.

EXPERIMENTAL

IR spectra were recorded in the solid state (KBr pellets) on a Brücker IFS 48

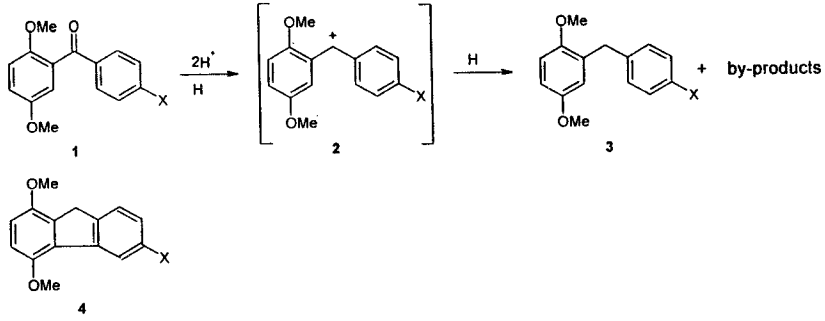

FIG. 1. Reaction Scheme

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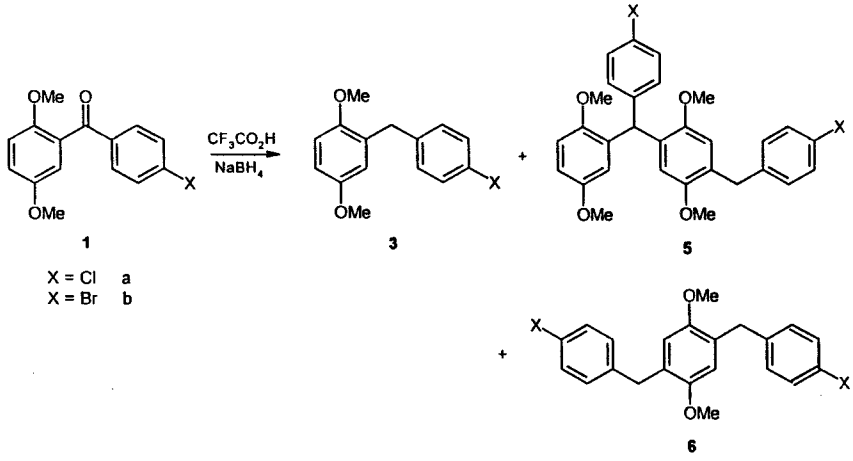

FIG. 2. Reduction of Activated Benzophenones to the Substituted Diphenylmethanes with Sodium Borohydride and Trifluoroacetic Acid.

TABLE 1

Reduction of Substituted 2,5-dimethoxybenzophenones with $NaBH_4$ / CF_3CO_2H

Entry	X	Time (h)	**3** (%)[a]	**5** (%)[a]	**6** (%)[a]
1	**Cl**	12	61	39	0
2	**Cl**	18	46[b]	48[b]	0
3	**Cl**	44	40	34	10[b]
4	**Br**	12	63	37	0
5	**Br**	18	42[b]	52[b]	0

[a] Yields were determined by ^1H and ^{13}C NMR. [b] Isolated yield.

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spectrometer. The structure of all products were determined by ^1H and ^{13}C NMR spectroscopy in $CDCl_3$ on a Brücker AC 300 spectrometer operating, respectively, at 300.133 MHz and 75.469 MHz, using a 5 mm dual ^1H / ^{13}C probehead at 25°C (Service RMN - Université Lille I, France). Chemical shifts are expressed downfield from TMS (0 ppm). The complete assignments of ^1H and ^{13}C NMR signals of **6a** and **6b** were performed on a Brücker AC 300. Homonuclear chemical shift correlation, 2D experiments [7], and heteronuclear shift correlated NMR spectra [8] were obtained by using the pulse sequence described in the Brücker program NOESY.AU, COLOC.AU and XHCORR.AU. Others spectral data are listed in Table 2. Mass spectra were recorded on a Nermag R10-10H. Melting points were determined with a Metler

TABLE 2

Spectra data NMR techniques used for compounds **5a** and **5b**

Program	Number of scans	Number of increments	Spectral width F_2 (^{13}C)	F_1 (^1H)
NOESY.AU	8	128	--------	2551
XHCORR.AU	8	128	11650	2551
COLOC.AU	8	128	11650	2551

FP1 and are uncorrected. Elemental analyses were performed by the "Service Central de Microanalyses" of CNRS, in Vernaison, France.

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Synthesis of the 2,5-dimethoxy-1-(4'-chlorobenzyl)benzene 3a and 11-chloro-2,5,15,18-tetramethoxy-17-(24-chlorobenzyl)triphenyl methane 5a.

Sodium borohydride pellets (7.0 g, 185 mmol) were slowly added to a stirred solution of 2,5-dimethoxy-1-(4'-chlorobenzoyl)benzene [9] (5 g, 18.5 mmol) and trifuoroacetic acid (100 mL, 130 mmole) in dichloromethane (50 mL). The mixture was stirred at room temperature for 18 hours. A solution of 1N NaOH (100 mL) was added and the organic layer was extracted with dichloromethane (2×20 mL) and dried over $CaCl_2$. The solvent was evaporated under *vacuum* yielding a solid. Purification by column chromatography on silica gel (250 g), eluting with petroleum ether/diethyl ether (8:2) gave the compound **3a** (2.18 g, 46%) and **5a** (2.68 g, 48%) as white solids. When the reaction mixture is stirred at room temperature for 44 hours (Table 2, entry 3), the compound **6a** is isolated with a 10% yield as a white solid.

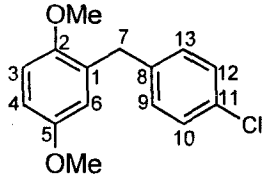

FIG. 3. Chemical Structure of Compound **3a**

Compound **3a** displayed the following $\nu_{max.}$ (KBr) : 2998, 2947, 2831 (C-H), 1590, 1495, 1459 (C=C), 1219, 1045 (C-O), 711 (C-Cl) cm^{-1} ; mp 42°C ; Anal. Calcd. for $C_{15}H_{15}ClO_2$: C 68.57, H 5.75, O 12.18. Found : C 68.60, H 5.71, O 12.20.

^1H NMR : δ_H(300 MHz, $CDCl_3$) 3.74 (3H, s, 2-OMe), 3.76 (3H, s, 5-OMe), 3.91 (2H, s, H7), 6.66 (1H, d, J36=3.0, H6), 6.73 (1H, dd, J34=8.8, J64=3.0, H4), 6.80 (1H, d, J43=8.8, H3), 7.14 (2H, d, J109=J1213=8.5, H9 and H13), 7.20 (2H, d, J910=J1312 =8.5, H10 and H12) ; ^{13}C NMR : δ_c(75 MHz, $CDCl_3$) 35.7 (C7), 55.6 (5-OMe), 56.0 (2-OMe), 111.4 (C3 and C4), 116.8 (C6), 128.3 (C10 and C12), 130.2 (C9 and C13), 130.3 (C1), 131.6 (C11), 139.1 (C8), 151.6 (C2), 153.5 (C5).

Compound **5a** displayed the following $\nu_{max.}$ (KBr) : 3003, 2944, 2831 (C-H), 1588, 1498 (C=C), 1214-1045 (C-O), 728 (C-Cl) cm^{-1} ; m/z 526 (for ^{37}Cl, ^{35}Cl, MH^+, 9.3%), 525 (for ^{37}Cl, ^{35}Cl, M^+, 22.8%), 524 (for ^{35}Cl, MH^+, 65.9%), 523 (for ^{35}Cl, M^+, 29.0%), 522 (for ^{35}Cl, M^+, 100%) ; mp 90°C ; Anal. Calcd. for $C_{30}H_{28}Cl_2O_4$: C 68.84, H 5.39, O 12.23. Found : C 68.69, H 5.41, O 12.40.

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TABLE 3

^{1}H NMR chemical shifts of aromatics protons with the identical coupling constant

6.99 ppm	2H	d	J = 8.3 Hz
7.14 ppm	2H	d	J = 8.3 Hz
7.20 ppm	2H	d	J = 8.3 Hz
7.23 ppm	2H	d	J = 8.3 Hz

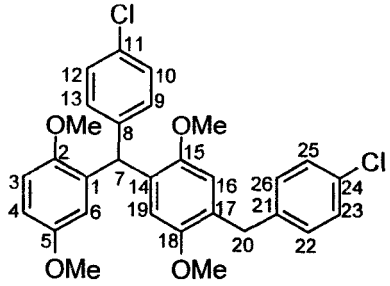

FIG. 4. Chemical Structure of Compound **5a**

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The ^{1}H and ^{13}C NMR data for **5a** are listed in Tables 4 and 5. By comparison with 2-methyl-1,4-dimethoxybenzene [8, 9], we can assign the chemical shifts of five protons and two carbons : δ_H(300 MHz, $CDCl_3$) 3.89 (2H, s, H20), 6.08 (1H, s, H7), 6.42 (1H, d, J46=3.0, H6), 6.73 (1H, dd, J34=8.8, J64=3.0, H4), 6.80 (1H, d, J43=3.0, H3) ; δ_c(75 MHz, $CDCl_3$) 35.4 (C20), 43.0 (C7).

Compound **6a** displayed the following $\nu_{max.}$ (KBr) : 2983, 2933, 2831 (C-H), 1590, 1400, 1468 (C=C), 1219-1038 (C-O), 733 (C-Cl) cm^{-1} ; m/z 390 (for ^{37}Cl,

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TABLE 4

^{1}H NMR spectral data (p.p.m. from $SiMe_4$ in $CDCl_3$ as solvent at 300 MHz) for compound **5a**

18-OMe	15-OMe	2-OMe	5-OMe	H(20)	H(7)	H(19)	H(6)	H(16)	H(4)	H(3)	H(9) H(13)	H(22) H(26)	H(10) H(12)	H(23) H(25)
3.54	3.57	3.63	3.67	3.89	6.07	6.35	6.42	6.59	6.73	6.80	6.99	7.14	7.20	7.23
3H	3H	3H	3H	1H	1H	1H	1H	1H	1H	1H	2H	2H	2H	2H
(s)	(s)	(s)	(s)	(s)	(s)	(s)	(d)	(s)	(dd)	(d)	(d)	(d)	(d)	(d)
							J=3.0		J=8.8 J=3.0	J=8.8	J=8.3	J=8.3	J=8.3	J=8.3

TABLE 5

^{13}C NMR spectral data (p.p.m. from $SiMe_4$ in $CDCl_3$ as solvent at 75 MHz) for compound **5a**

C(20)	C(7)	5-OMe	18-OMe	2-OMe	15-OMe	C(4)	C(3)	C(19)	C(16)	C(6)	C(17)	C(10) C(12)	C(23) C(25)	C(22) C(26)	C(9) C(13)
35.4	43.0	55.6	56.1	56.5	56.6	110.8	111.9	113.8	114.6	117.2	127.8	128.1	128.3	130.3	130.5

(continued)

C(14)	C(24) C(11)	C(1)	C(21)	C(8)	C(15)	C(18)	C(5)	C(2)
130.8	131.6	133.5	139.6	142.3	151.1	151.2	151.7	153.3

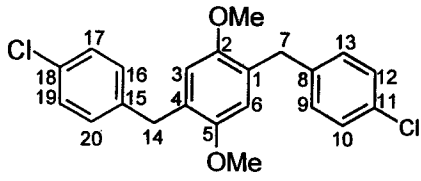

FIG. 5. Chemical Structure of Compound **6a**

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^{35}Cl, MH^+, 11.2%), 389 (for ^{37}Cl, ^{35}Cl, M^+, 15.3%), 388 (for ^{35}Cl, MH^+, 66.4%), 387 (for ^{35}Cl, M^+, 24.1%), 386 (for ^{35}Cl, M^+, 100%) ; mp 140°C ; Anal. Calcd. for $C_{22}H_{20}Cl_2O_2$: C 68.23, H 5.20, O 8.26. Found : C 68.44, H 5.29, O 8.42.

^1H NMR : δ_H(300 MHz, $CDCl_3$) 3.70 (6H, s, 2-OMe, 5-OMe), 3.90 (4H, s, H7 and H14), 6.55 (2H, s, H3 and H6), 7.19 (4H, d, J=8.3, H10, H12, H17 and H19), 7.21 (4H, d, J=8.3, H9, H13, H16, H20); ^{13}C NMR : δ_c(75 MHz, $CDCl_3$) 35.4 (C7 and C14), 56.1 (2-OMe, 5-OMe), 113.5 (C3 and C6), 127.8 (C1 and C4), 128.4 (C10, C12, C17 and C19), 130.1 (C9, C13, C16 and C20), 131.6 (C11 and C18), 139.5 (C8 and C15), 151.2 (C2 and C5).

Synthesis of the 2,5-dimethoxy-1-(4'bromobenzyl)benzene 3b and 11-bromo-2,5,15,18-tetramethoxy-17-(24-bromobenzyl)triphenyl methane 5b

Sodium borohydride (6.0 g, 160 mmol) was slowly added to a stirred solution of 2,5-dimethoxy-1-(4'-bromobenzoyl)benzene [8] (5 g, 15.5 mmol) and trifluoroacetic acid (85 mL, 110 mmole) in dichloromethane (50 mL). The mixture was stirred at room temperature for 18 hours. Work-up was done as for

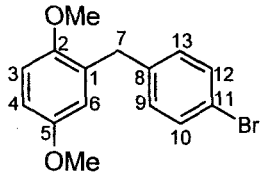

FIG. 6. Chemical Structure of Compound **3b**

2,5-dimethoxy-1-(4'-bromobenzyl)benzene **3a**. Purification by column chromatography on silica gel (250 g), eluting with petroleum ether/diethyl ether (8:2) gave the compound **3b** (2.0 g, 42%) and **5b** (1.4 g, 52%) as a white solid.

Compound **3b** displayed the following $\nu_{max.}$ (KBr) : 2983, 2933, 2831 (C-H), 1590, 1500, 1466 (C=C), 1219-1038 (C-O), 733 (C Br) cm^{-1} ; mp 49°C ; Anal. Calcd. for $C_{15}H_{15}BrO_2$: C 58.65, H 4.92, O 10.42. Found : C 58.57, H 4.93, O 10.45.

^1H NMR : δ_H(300 MHz, $CDCl_3$) 3.75 (3H, s, 2-OMe), 3.77 (3H, s, 5-OMe), 3.91 (2H, s, H7), 6.68 (1H, d, J36=2.9, H6), 6.76 (1H, dd, J34=8.8, J64=2.9, H4), 6.82 (1H, d, J43=8.8, H3), 7.11 (2H, d, J109=J1213=8.3, H9 and H13), 7.20 (2H, d, J910=J1312 =8.3, H10 and H12) ; ^{13}C NMR : δ_c(75 MHz, $CDCl_3$) 35.7 (C7), 55.7 (5-OMe), 56.0 (2-OMe), 111.4 (C3 and C4), 116.9 (C6), 119.7 (C11), 130.2 (C1), 130.7 (C9 and C13), 131.3 (C10 and C12), 139.9 (C8), 151.6 (C2), 153.5 (C5).

Compound **5b** displayed the following $\nu_{max.}$ (KBr) : 2996, 2943, 2829 (C-H), 1588, 1499 (C=C), 1214-1045 (C-O), 719 (C-Br) cm^{-1}; m/z 615 (for ^{81}Br, ^{79}Br,

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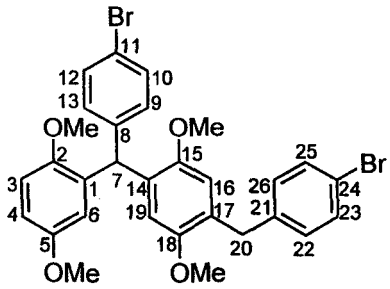

FIG. 7. Chemical Structure of Compound **5b**

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MH^+, 15.5%) 614 (for ^{81}Br, ^{79}Br, M^+, 51.6%) 613 (for ^{79}Br, MH^+, 41.0%) 612 (for ^{79}Br, M^+, 100%) ; mp 84°C ; Anal. Calcd. for $C_{30}H_{28}Br_2O_4$: C 58.84, H 4.61, O 10.45. Found : C 58.54, H 4.76, O 10.26.

The ^1H and ^{13}C NMR data for **5b** are listed in Tables 6 and 7. By comparison with 2-methyl-1,4-dimethoxybenzene [8, 9], we can assign the chemical shifts of five protons and two carbons : ^1H NMR: δ_H(300 MHz, $CDCl_3$) 3.87 (2H, s, H20), 6.01 (1H, s, H7), 6.41 (1H, d, J46=3.0, H6), 6.72 (1H, dd, J34=8.8, J64=3.0, H4), 6.79 (1H, d, J43=3.0, H3) ; ^{13}C NMR: δ_c(75 MHz, $CDCl_3$) 35.4 (C20), 43.1 (C7).

RESULTS AND DISCUSSION

After purification of the crude mixture to eliminate the compound **3a** (X = Cl), we supposed that a possible structure for the by-proctucts was that of benzofluorene **4a** [4, 5] or of substituted triarylmethane **7a** [9] (FIG. 8).

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TABLE 6

^{1}H NMR spectral data (p.p.m. from $SiMe_4$ in $CDCl_3$ as solvent at 300 MHz) for compound **5b**

18-OMe	15-OMe	2-OMe	5-OMe	H(20)	H(7)	H(19)	H(6)	H(16)	H(4)	H(3)	H(9) H(13)	H(22) H(26)	H(23) H(25)	H(10) H(12)
3.53	3.57	3.63	3.67	3.87	6.01	6.31	6.41	6.59	6.72	6.79	6.93	7.09	7.34	7.37
3H	3H	3H	3H	1H	1H	1H	1H	1H	1H	1H	2H	2H	2H	2H
(s)	(s)	(s)	(s)	(s)	(s)	(s)	(d)	(s)	(dd)	(d)	(d)	(d)	(d)	(d)
							J=3.0		J=8.8 J=3.0	J=8.8	J=8.3	J=8.8	J=8.8	J=8.3

TABLE 7

^{13}C NMR spectral data (p.p.m. from $SiMe_4$ in $CDCl_3$ as solvent at 75 MHz) for compound **5b**

C(20)	C(7)	5-OMe	18-OMe	2-OMe	15-OMe	C(6)	C(4)	C(19)	C(16)	C(3)	C(11)	C(24)	C(1) C(14)	C(9) C(13)	C(10) C(12)
35.4	43.1	55.5	56.1	56.4	56.6	110.7	111.9	113.5	114.0	117.1	119.6	119.7	127.7	130.6	130.9

(continued)

C(22) C(26)	C(23) C(25)	C(17)	C(21)	C(8)	C(15)	C(18)	C(5)	C(2)
131.0	133.3	133.4	140.1	142.8	151.1	151.2	151.6	153.3

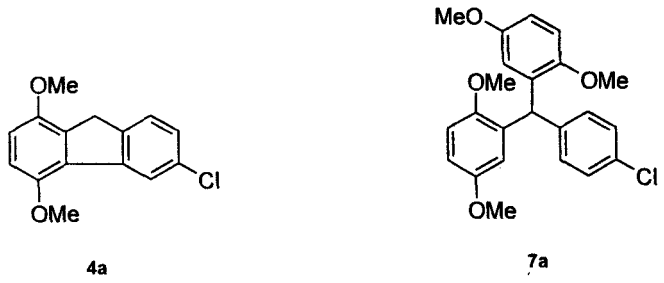

FIG. 8. Structure of the Substituted Benzofluorene **4a** and Triarylmethane **7a**

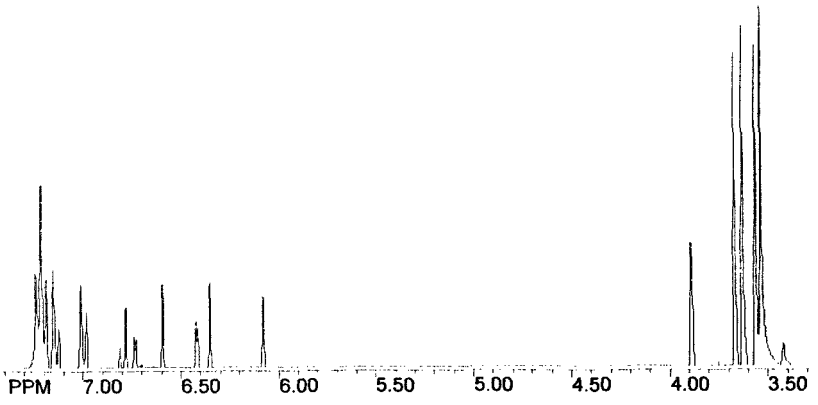

FIG. 9. ^{1}H NMR spectrum of the by-products **4a** and **7a** (X = Cl) obtained during the reduction of the 2,5-dimethoxy-1-(4'-chlorobenzoyl)benzene **1a**

However, we questioned the apparent contradictions between the structure of these by-products and the ^{1}H NMR spectrum (FIG. 9).

1) Analysis of the ^{1}H NMR spectral width δ = 3.5-3.7 ppm corresponding to the methoxy groups, shows that, if there are two by-products, the mixture was composed by **4a** and **7a** with a 2/1 molar ratio (FIG. 10).

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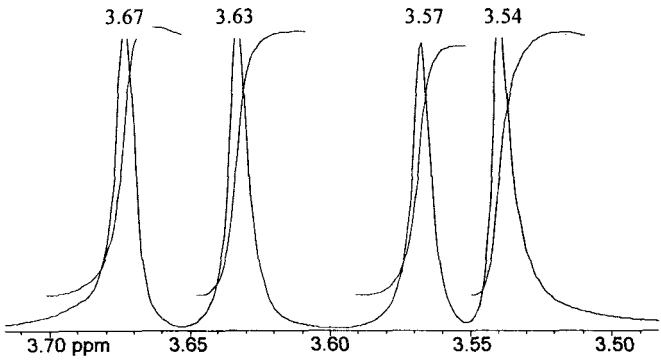

FIG. 10. ^{1}H NMR spectrum of methoxy groups of by-products isolated after reduction of 2,5-dimethoxy-1-(4'-chlorobenzoyl)benzene **1** (X = Cl)

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2) The number of aliphatic hydrogens corresponding to the singlets δ_H = 3.89 and δ_H = 6.07 ppm shows that the mixture would be formed from **4a** and **7a** on a 50/50 ratio (FIG. 11).

3) The same result is obtained by analysis of the ^{1}H NMR spectral width δ = 6.3-6.9 and δ = 6.9-7.3 corresponding to the aromatic protons of the 2,5-dimethoxyphenyl and *p*-chlorophenyl groups, respectively (FIG. 12).

In this paper, we attempted to elucidate the precedent points and to assign all protons and carbons chemical shifts by correlating results obtained with various NMR techniques.

In a first approach, we were interested by the aliphatic protons (FIG. 11). Because these hydrogens are correlated with two aromatic protons at 7.14 ppm (FIG. 13); the first by-product, obtained in the reduction of benzophenone **1**

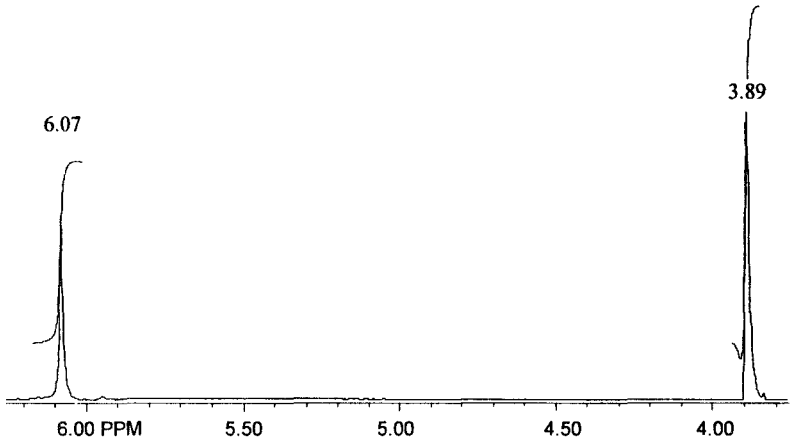

FIG. 11. Aliphatic hydrogens of by-product isolated after reduction of **1a**

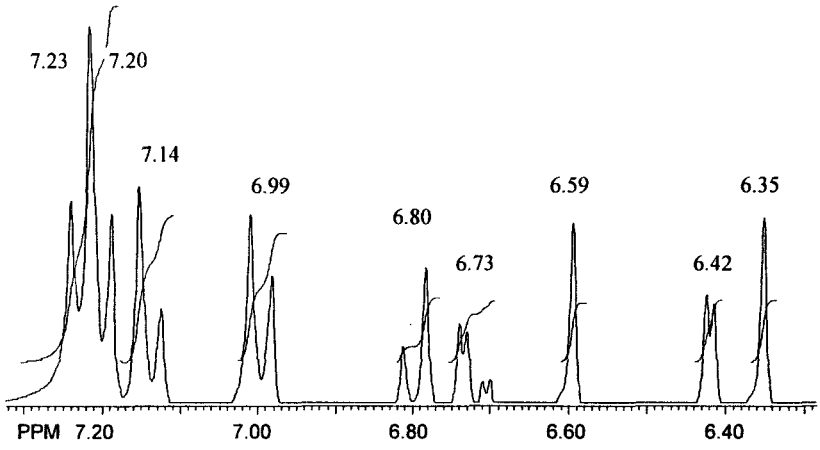

FIG. 12. Aromatic hydrogens of by-product isolated after reduction of **1a**

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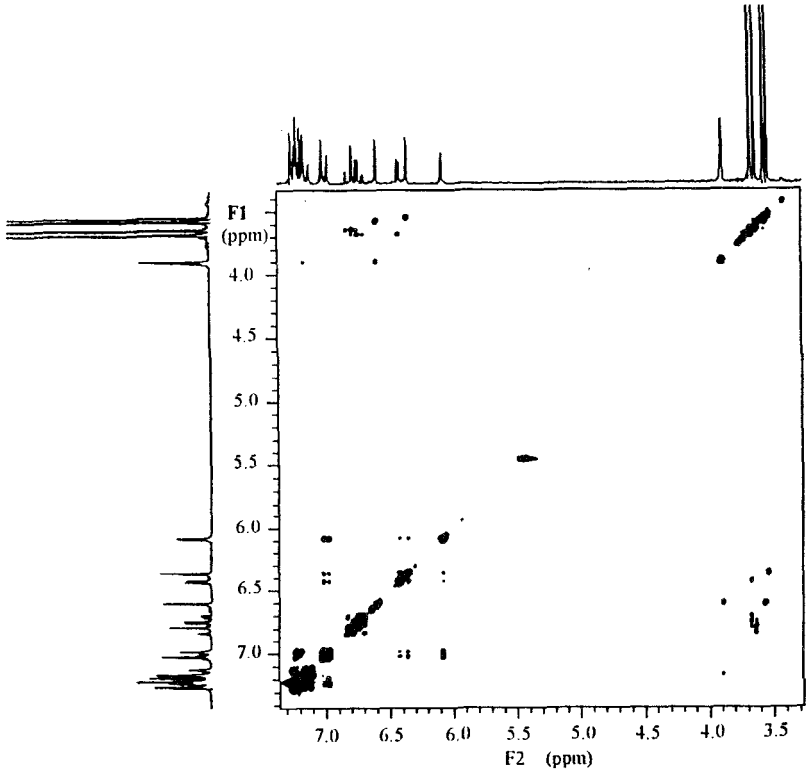

FIG. 13. NOESY spectrum of diphenylmethane dimer 5a

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with sodium borohydride and trifluoroacetic acid can not possess the structure of the benzofluorene **4** (FIG. 1). Thus , we supposed that only one by-product was formed during the studied reduction.

The correlation with the analytical analyses and the mass spectra data allowed us to eliminate compound **7** as a by-product of the reaction and to consider the structure of the unknown compound as a dimer of **3a**.

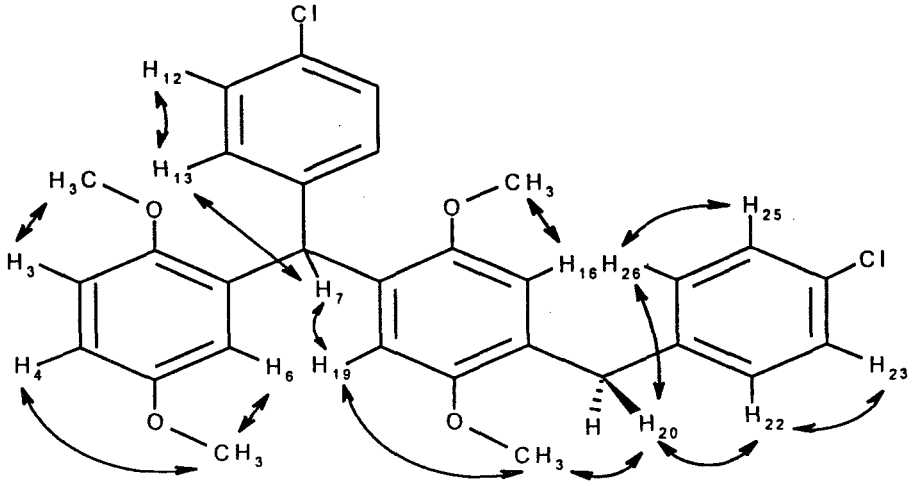

FIG. 14. NOESY Correlation observed for the diphenylmethane dimers **5a**

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For the dimer **5a**, the 2-OMe and 8-OMe were, respectively, obtained from the NOESY correlation of the methoxy group with the known protons H6 (6.42 ppm), H4 (6.73 ppm) and H3 (6.80 ppm). The chemical shift of H20 is known from the studies of similar products such as **3a** and **3b**. The correlation of this hydrogen with H16 and 18-OMe allowed us to attribute their chemical shift (H16 : 6.59 ppm ; 18-OME : 3.54 ppm) and the assignment of 15-OMe (3.57 ppm) and H19 (6.35 ppm) (FIG. 14).

The complete analysis of the NOESY spectra (FIG. 13) indicates that the dimer is constituted by four groups of two aromatic protons with the same coupling constant (Table 3) which can be arranged in two groups by using the irradiation technique.

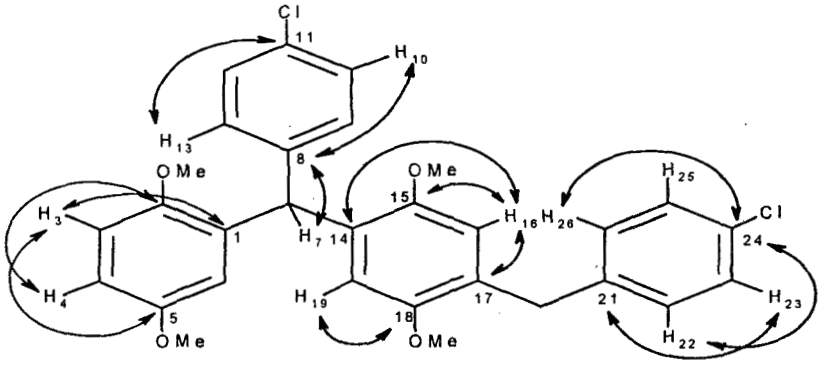

FIG. 15. HETCOR Correlation observed for the diphenylmethane dimers 5a

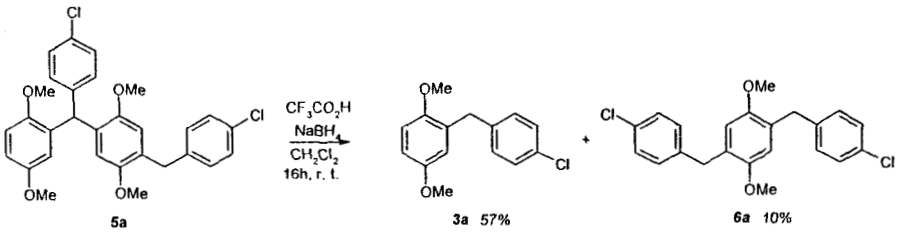

FIG. 16. Cleavage of the diphenylmethane dimer **5a** with $CF_3CO_2H/NaBH_4$

When an irradiation was realized at 6.99 ppm, the doublet at 7.20 ppm changed to singlet without modification of the 7.14 ppm and 7.23 ppm doublets and irradiation of the 7.23 ppm doublet changed only the doublet at 7.14 ppm to singlet.

The C3, C4, C6, C9, C12, C13, C16, C19, C22, C23, C25 and C26 positions were then obtained from the COLOC correlation between these carbons and the

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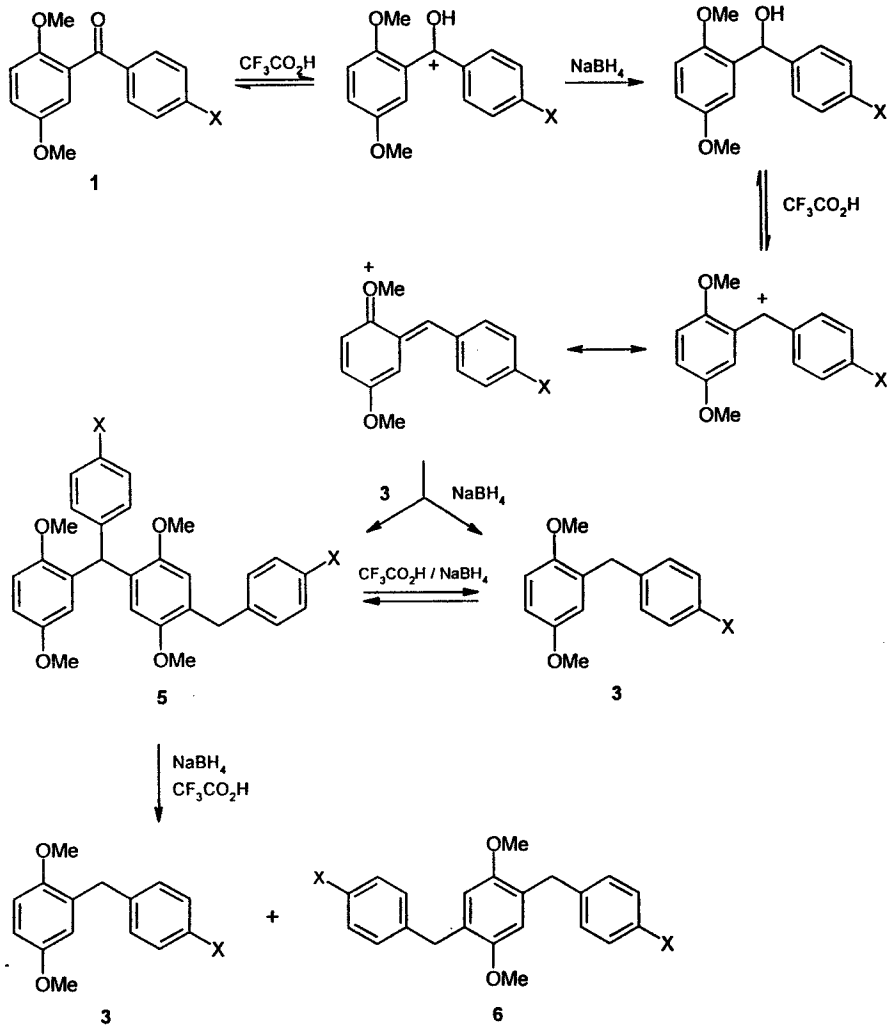

FIG. 17. Mechanism of the reduction of activated benzophenones **1**

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corresponding hydrogen. The C1, C2, C5 C8, C11, C14, C15, C17, C18, C21 and C24 positions were performed by analysis of the XHCORR spectra (FIG 15).

The same results were obtained from the NMR studies of the compound **5b**.

CONCLUSION

Different NMR techniques were used to identify and assign protons and carbons chemical shifts for compounds **5a** and **5b** which were obtained, for the first time, during the reduction of 2,5-dimethoxy-1-(4'-chlorobenzoyl)benzene and 2,5-dimethoxy-1-(4'-bromobenzoyl)benzene, respectively. Because the reaction of these dimers with sodium borohydride and trifluoroacetic acid gave diarylmethane (FIG. 16), we have been able to suggest a mechanism for reduction of activated benzophenones **1** in these conditions (FIG. 17).

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REFERENCES

[1] a) D. N. Kursanov, Z. N. Parnes ans N. M. Loim, *Synthesis*, (1974) 633. b) H. L. Bradlow and C. A. Vanderwerf, *J. Am. Chem. Soc.*, 69 (1947) 1254. c) D. Todd, *Org. React.*, 4 (1948) 378. d) D. N. Kursanov, Z. N. Parnes G. I. Bassova, N. M. Loim and V. I. Pdanovich, *Tetrahedron*, 23 (1967) 2235. e) D. N. Kursanov, N. M. Loim, V. A. Boranova, L. V. Moiseeva, L. P. Zakulev and Z. N. Parnes, *Synthesis*, (1973) 420. f) J. L. Fry, M. Orfanopoulos, M. G. Adlington, W. R. Dittman and Jr. S. B. Silverman, *J. Org. Chem.*, 43, (1978) 374. g) G. A. Olah, M. Arvanaghi and L. Ohannessian, *Synthesis*, (1986) 770. h) A. Srikrishna, J. A. Sattigeri, R. Viswajanani and C. V. Yelamaggad, *Synlett*, (1985) 93. i) V. G. S. Box and P. C. Meleties, *Tetrahedron Lett.*, 39 (1998) 7059.

[2] H. Mayr and B. Dogan, *Tetrahedron Lett.*, 38 (1997) 1013.

[3] G. W. Gribble, W. J. Kelly and S. E. Emery, *Synthesis,* (1978) 763.

[4] A. Legrand, B Rigo, J. P. Hénichart B. Norberg, F. Camus, F. Durant and D. Couturier, *J. Heterocyclic. Chem.,* in Press (2000).

[5] C. Waterlot, A. Legrand, B Rigo and D. Couturier, *Spectroscopy Lett.,* in Press (2000).

[6] C. W. Smith, S. J. Ambler and D. J. Steggles, *Tetrahedron Lett.*, 34 (1993) 7447.

[7] A. Bax, R. Freeman and G. A. Morris, *J. Magn. Reson.*, 42 (1981) 169.

[8] J. A. Wilde and P. H. Bolton, *J. Magn. Reson.*, 59 (1984) 343.

[9] C. Waterlot, Thesis dissertation, Lille, France, No. 2513 (1999).

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