Pergamon

Tetrahedron, Vol. 52, No. 27, pp. 9101-9110, 1996

0040-4020/96 $15.00 + 0.00

PII: S0040-4020(96)00461-9

Carbopalladation-Sulphonylation of Allene : A Versatile Preparation of 2-Vinyl or 2-Aryl Allyl Sulphones

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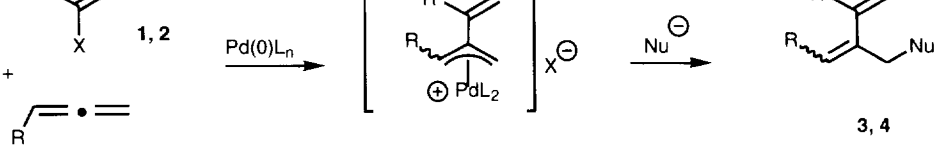
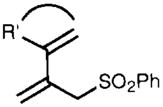
Abstract : The allene carbopalladation process can be realized with various vinylic or aromatic derivatives, in the presence of sodium benzenesulphinate, and allows the preparation of the entitled sulphones. Copyright © 1996 Elsevier Science Ltd

Since its first description in 1984,[1,2] the catalytic carbopalladation process of allenic compounds has received a great deal of interest from our group[3-7] and others[8-14], especially for the preparation of cyclic[4, 8-14] or polycyclic[13] compounds. Very recently, an enantioselective version of that reaction has even been reported.[11c] In the carbopalladation process, small amounts of a palladium zerovalent complex catalyze the reaction between a vinylic **1** or an aromatic derivative **2** (iodide, bromide or enol triflate) and an allenic compound, allowing the *in situ* formation of a π-allylic palladium complex, bearing an unsaturated moiety at the central carbon atom. The nucleophilic attack of this complex leads to dienic compounds **3** (or to substituted styrenes **4**) .



In the course of these studies, various nucleophiles have been used : malonate type compounds[1], amines[2], alcohols[8] and carboxylic acids[11a] and the products **3** and **4** are regio and stereoselectively formed in satisfactory yields. On the contrary we tried in our laboratory to substitute such π-allylic complexes by classical reducing reagents, like ammonium formate[15] or boron hydrides,[16] but the expected dienes were only obtained with low yields.[17]

Sodium arenesulphinates have been widely used as nucleophiles in π-allylic palladium complexes chemistry.[18] They allow the formation with good yields of allylic sulphones which can be used as precursor of organometallics or easily reduced to the corresponding alkenes by treatment with sodium amalgam.[19] Consequently, we became interested by the realization of the carbopalladation of 1,2-propadiene using different unsaturated halides in the presence of sodium benzenesulphinate in order to have an easy access to sulphones **5** and **6**, the synthetic interest of which as dienes and/or allylic sulphones being evident. It is noteworthy that such compounds **5** and **6** have been previously prepared by different ways[20,21], but our approach appears more direct and versatile. To our knowledge, the use of sodium benzenesulphinate with allenes has only been reported in one case of 1,2-propadiene dimerisation under a carbon dioxide atmosphere producing compound **5a**.[22]



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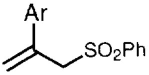
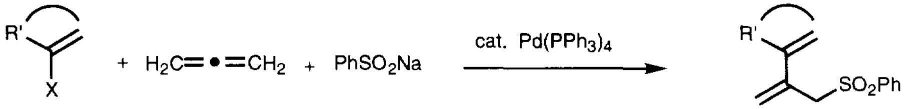


6

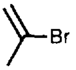
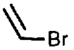
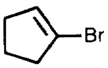
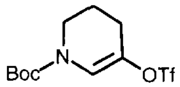
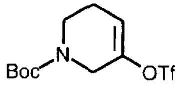
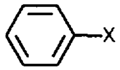
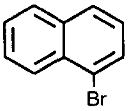
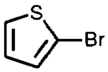
In this paper, we will describe our results about the preparation of butadienyl and styryl sulphones via the carbopalladation of 1,2-propadiene in the presence of sodium benzenesulphinate (Table).

When this reaction was carried out overnight at room temperature using 2-bromopropene **1a** or vinyl bromide **1b** in the presence of an excess of $PhSO_2Na$ and 5 mol % of $Pd(PPh_3)_4$, dienic sulphones **5a** and **5b** were obtained respectively with acceptable yields (entries 1 and 2). DMSO or DMF could be used as solvent without any influence. It was interesting that the procees could occur at this temperature because of an easy polymerization of **5b** upon simple concentration at 40-50°C. With 1-bromocyclopentene **1c**, the expected compound **5c** was only obtained in 10% yield at room temperature. By simple heating the reaction mixture at 75°C overnight, yield increased to 70% without degradation of the final product (entries 3 and 4).

The same reaction could also be realized with triflates **1d** and **1e** giving respectively **5d** and **5e** with good yields even at room temperature (entries 5, 6). In these reactions, two molar equivalents of lithium chloride were added, according to our previous described results.[3b,f] Thus, this carbopalladation-sulphonylation process under mild conditions is also possible when using enol triflates and this methodology can even be employed with N-Boc protected amines.



1, 2 **5, 6**

Entry			Solvent	Temperature	Product	Yield *
1		**1a**	DMF	R.T.	**5a**	69 %
2		**1b**	DMSO	R.T.	**5b**	54 %
3		**1c**	DMSO	R.T.	**5c**	15 %
4			DMSO	75 °C		70 %
5		**1d**	DMSO **	R.T.	**5d**	76 %
6		**1e**	DMSO **	R.T.	**5e**	72 %
7	 X = Br	**2a**	DMF	R.T.	**6a**	no reaction
8	X = I	**2a'**	DMSO	R.T.		no reaction
9	X = Br	**2a**	DMSO	65 °C		66 %
10		**2b**	DMSO	75 °C	**6b**	79 %
11		**2c**	DMSO	75 °C	**6c**	69 %
12		**2d**	DMSO	65 °C	**6d**	59 %

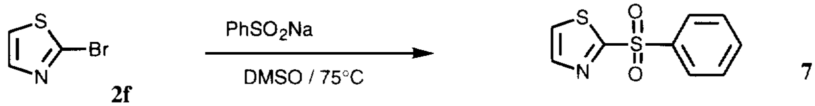
* Yields refer to isolated purified material and are unoptimised.

** Two molar equivalents of LiCl were added.[3b,f]

Table.

In a second time, we have studied this allene carbopalladation-sulphonylation reaction starting from aromatic halides **2**. No reaction proceeded at room temperature, as it was observed with phenyl bromide **2a** or iodide **2a'** (entries 7 and 8) ; starting materials were then almost completely recovered. But when the reaction was run in DMSO at 75°C with phenylbromide **2a**, 4-methylphenylbromide **2b**, 1-naphtylbromide **2c** or 2-bromothiophene **2d**, the expected sulphones **6a-d** were respectively obtained with good yields (entries 9-12).

Lastly, 2-bromo-1,3-thiazole **2f** did not react in the expected way. In this reaction, we only obtained the aromatic nucleophilic substitution product **7** in 18% yield. This sulphone was characterized by ^1H and ^{13}C NMR as well as by Mass Spectrometry. Such a nucleophilic sustitution of aromatic halide, even without addition of a palladium complex, has already been described fifty years ago.[23]



In conclusion, we have developed a new and simple method for the synthesis of 2-vinyl or 2-aryl allylic sulphones **5** and **6** which are, as every allylic sulphones, interesting building block in organic synthesis,[24] particularly in transition metal-mediated substitution[25] and Julia-Kociensky olefination.[26] They can also be easily alkylated,[24] oxidized to form aldehydes,[27] or reduced to form alkenes.[19]

So, the use of sodium benzenesuphinate as nucleophile in the carbopalladation-functionalization of allene opens new potentialities for this already well developed methodology[7].

EXPERIMENTAL SECTION

General remarks. All reactions were conducted in oven-dried glassware under nitrogen. Tetrahydrofuran was distilled under nitrogen from sodium-benzophenone ketyl. Dimethyl sulfoxide, dimethylformamide and diisopropylamine were distilled from calcium hydride. Analytical TLC analyses were performed on Merck precoated Kieselgel 60-F_{254} (aluminum-backed sheets) with visualisation by UV light and/or anisaldehyde dip. Flash chromatography using Merck silica gel 60 (230-400 mesh) refers to the procedure of W.C. Still et al.[28] Capillary GLC analyses were performed on a Varian 3300 gas-chromatograph (column DB5, 25m) equipped with a flame ionization detector. IR spectra were recorded on a Perkin-Elmer 298 spectrophotometer. ^1H NMR spectra were measured at 200MHz on a Bruker AC 200 spectrometer. Data, reported using the residual solvent proton resonance of $CDCl_3$ (δ_H = 7.25) as the internal reference, are as follows in the order : chemical shift (δ in ppm relative to TMS), multiplicity (s, d, t, q, m, br for singulet, doublet, triplet, quartet, multiplet, broad), coupling constants (J, in Hz), number of protons. ^{13}C NMR were measured at 50MHz on the same instrument, using $CDCl_3$ solvent peak at $\delta_C = 77.0$ as the reference. Mass Spectra (m/z, relative intensity) were obtained (electron impact mode, at 70 eV) with a Nermag R10-10S quadrupole mass spectrometer coupled with a Delsi-DI 700 gas chromatograph fitted with a OV1 capillary column (25m x 0.32 mm i.d). Melting points were determined on a Büchi 530 apparatus and are reported uncorrected. Microanalyses were performed by the "Service Central d'Analyse" of CNRS in Vernaison.

Materials. Allene was purchased from Union Carbide.[29] Vinyl and aromatic halides **1,2** were commercial products. 1-Bromocyclopentene[30] **1c** was prepared according to the literature procedure. Triflates **1d,e** were obtained from N-Boc-3-piperidone[31] and commercial N-phenyltriflimide[32] according to a recently published work.[33,34]

Triflates[34] 1d and 1e :

A solution of LDA (14.3 mmol) was prepared from diisopropylamine (14.3 mmol) and n-BuLi (2.5M solution in hexane, 5.7 ml, 14.3 mmol) in THF (25ml). This solution was cooled at -78°C and N-Boc-3-piperidone[31] (2g, 10 mmol) in THF (5 ml) was added with a syringe. After 15 min, N-phenyltriflimide (4.3g, 12 mmol) in THF (10 ml) was added. The reaction mixture was then warmed up very slowly to 20°C, and stirred at room temperature overnight. After evaporation of the solvent under vacuum, the residue was dissolved in CH_2Cl_2 (60 ml). The solution was then filtered on neutral alumina (Grade I) and evaporated. Flash chromatography (Petroleum Ether/ AcOEt : 80/20) of the crude oil on 100g silica gel gave 2.21g (67%) of the two regiomer triflates **1d** and **1e** (**1d**/**1e** = 70/30) which were obtained pure after a second flash chromatography on 200 g silica gel, the major regiomer **1d** being slightly more polar.

1-t-Butyloxycarbonyl-1,2,3,4-tetrahydro-5-trifluoromethanesulfonyloxypyridine 1d.

obtained as a mixture of two rotamers, as seen from some signals which are splitted in ^1H and ^{13}C NMR.
TLC (SiO_2, 80/20 : Petroleum Ether/Et_2O) : Rf = 0.48. ^1H NMR (200 MHz, $CDCl_3$) δ : 7.24 and 7.07 (2s, 1H); 3.45-3.65 (m, 2H); 2.44 (t, J = 6.3 Hz, 2H); 1.93 (m, 2H); 1.50 (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$) δ : 152.66 and 152.29 (1C) ; 135.14 and 134.23 (1C); 122.93 and 122.58 (1C) ; 119.47 (q, J = 319 Hz, $\underline{C}F_3$) ; 82.96 ; 42.57 and 41.42 (1C) ; 29.02 ; 26.16 ; 24.78.

1-t-Butyloxycarbonyl-1,2,3,6-tetrahydro-5-trifluoromethanesulfonyloxypyridine 1e.

TLC (SiO_2, 80/20 : Petroleum Ether/Et_2O) : Rf = 0.50. ^1H NMR (200 MHz, $CDCl_3$) δ : 5.93 (m, 1H); 4.05 (m, 2H); 3.50 (t, J = 5.7 Hz, 2H); 2.30 (m, 2H); 1.48 (s, 9H).

Typical procedure for the preparation of allylic sulphones :

preparation of **3-Methyl-2-(phenylsulphonyl)methyl-1,3-butadiene 5a.**[22]

In a 75 cm^3 stainles steel autoclave, fitted with a rubber septum, a mixture of 58 mg (0.05 mmol) of $Pd(PPh_3)_4$ and 0.246 g (1.50 mmol) of sodium benzenesulphinate, previously stirred under nitrogen for 15 min, was covered with 4 ml of DMF. 0.1 ml (1.73 mmol) of liquid allene[29] was added, followed by 0.071 ml

(0.80 mmol) of 2-bromopropene. The autoclave was rapidly closed and the mixture was stirred at room temperature for 24h. After dilution with 10 ml of ether and 10 ml of water, the aqueous solution was extracted with ether (2x10 ml). The combined organic layers were washed with brine (10 ml), dried ($MgSO_4$) and concentrated under reduced pressure. Purification by flash chromatography (Petroleum ether / Et_2O : 75/25) yielded 0.123 g (69 %) of pure colorless liquid **5a**.

IR (film, cm^{-1}) : 3090; 3060; 3000; 2980; 2925; 1595; 1445; 1310; 1150; 1085. ^1H NMR (200 MHz, $CDCl_3$) δ : 7.85 (dd, J = 8.2Hz and 1.5Hz, 2H); 7.60-7.42 (m, 3H); 5.38 (s, 1H); 5.08 (s, 1H); 5.01 (s, 1H); 4.98 (s, 1H); 4.08 (s, 2H); 1.84 (s, 3H) in good agreement with the already described spectrum[22]. ^{13}C NMR (50 MHz, $CDCl_3$) δ : 140.63; 138.55; 135.94; 133.66; 128.90 (2C); 128.65 (2C); 121.27; 115.14; 60.30; 20.85.

2-[(Phenylsulphonyl)methyl]-1,3-butadiene 5b.[20a]

Purified by flash chromatography (Petroleum ether / Et_2O : 75/25). Yield : 54 %

IR (film, cm^{-1}) : 3090; 3060; 3000; 2980; 2925; 1595; 1445; 1305; 1155; 1085. ^1H NMR (200 MHz, $CDCl_3$) δ : 7.87 (d, J = 7 Hz, 2H); 7.60 - 7.35 (m, 3H); 6.28 (dd, J = 17.5 Hz and 11 Hz, 1H); 5.33 (s, 1H); 5.18 (d, J = 17.5 Hz, 1H); 5.07 (s, 1H); 5.06 (d, J = 11 Hz, 1H); 4.00 (s, 2H) in good agreement with the already described spectrum[20a]. ^{13}C NMR (50 MHz, $CDCl_3$) δ : 138.33; 136.20; 134.28; 133.75; 128.96 (2C); 128.71 (2C); 124.08; 115.76; 58,65.

1-(3'-Phenylsulphonyl-1'-propen-2'-yl)cyclopentene 5c.

Yellow solid obtained after flash chromatography (Petroleum ether / Et_2O / CH_2Cl_2 : 48/48/4). Yield : 70 % . Mp = 103-104°C. GLC (DB5, 30m, 240°C): t_R = 394 s. IR (KBr, cm^{-1}): 3060; 2975; 2945; 2910; 2830; 1625; 1590; 1585; 1445; 1290; 1165; 1130; 1085; 910; 895; 790; 755; 685. ^1H NMR (200 MHz, $CDCl_3$) δ : 7.86 (m, 2H); 7.65 - 7.46 (m, 3H); 5.61 (s, 1H); 5.18 (s, 1H); 5.05 (s, 1H) 4.06 (s, 2H); 2.45 - 2.20 (m, 4H); 1.80 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ : 141.56; 138.62; 133.58; 132.28; 130.05; 128.79 (2C); 128.75 (2C); 120.01; 61.17; 33.39; 32.57; 22.99. MS (m/z, %): 248 (45, $M^{+\cdot}$); 184 (25); 169 (12); 143 (21); 107 (86); 106 (63); 105 (21); 92 (11); 91 (100); 79 (60); 78 (30); 77 (53); 67 (13); 66 (14); 65 (15); 53 (14); 51 (29); 41 (24); 39 (26). Anal. found: C, 67.65 ; H, 6.33. Calcd. for $C_{14}H_{16}O_2S$: C, 67.73 ; H, 6.50%.

1-t-Butoxycarbonyl-5-(3'-phenylsulphonyl-1'-propen-2'-yl)-1,2,3,4-tetrahydropyridine 5d.

Two molar equivalents of LiCl are added to the $Pd(PPh_3)_4$ and $PhSO_2Na$ solid initial mixture.

Purified by flash chromatography (Petroleum ether / Et_2O : 50/50). Yield : 76 %.

IR (film, cm^{-1}): 3100; 3060; 2980; 2925; 1700; 1645; 1395; 1105; 1155. ^1H NMR (200 MHz, $CDCl_3$) δ : 7.86 (d, J = 7.4 Hz, 2H); 7.70 - 7.40 (m, 3H); 6.95 and 6.92 (2s, 1H); 5.16 (s, 1H); 4.99 and 4.92 (2s, 1H); 4.04 (s, 2H); 3.55 - 3.28 (m, 2H); 2.07 (t, J = 6.2 Hz, 2H); 1.85 - 1.65 (m, 2H); 1.54 and 1.50 (2s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$) δ : 152.45 and 152.04 (1C); 138.85; 134.63; 133.58; 128.83 (4C); 125.57 and 124.91(1C); 116.50 and 116,11 (1C); 114.69 and 114.30 (1C); 81.34; 60.65 and 60.02 (1C); 41.85 and 40.88 (1C); 28.27 (3C); 22.61; 21.06.

1-t-Butoxycarbonyl-5-[3'-phenylsulphonyl-1'-propen-2'-yl]-1,2,3,6-tetrahydropyridine 5e.
Two molar equivalents of LiCl are added to the $Pd(PPh_3)_4$ and $PhSO_2Na$ solid initial mixture.
Purified by flash chromatography (Petroleum ether / Et_2O : 50/50). Yield : 72 %
IR (film, cm^{-1}): 3100; 3060; 2980; 2925; 1690 (br); 1650; 1420; 1320; 1245; 1150. ^1H NMR (200 MHz, $CDCl_3$) δ : 7.84 (m, 2H); 7.68 - 7.40 (m, 3H); 5.89 (m, 1H); 5.25 (s, 1H); 5.02 (s, 1H); 4.05 (s, 2H); 3.94 (s, 2H); 3.33 (t, J = 5.7Hz, 2H); 2.18 - 2.00 (m, 2H); 1.48 (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$) δ : 154.62; 138.54; 133.70; 133.65; 131.77; 128.95 (2C); 128.66 (2C); 125.42; 118.63; 79.72; 60.34; 43.52; 39.90; 28.41 (3C); 25.33.

2-Phenyl-3-phenylsulphonyl-1-propene 6a.[21a]
Purified by flash chromatography (Et_2O) and recristallization from isopropyl ether/hexane. Yield : 66 %.
TLC (SiO_2, CH_2Cl_2) : Rf = 0.5 . Mp = 102°C (lit.[21a] : 106°C). GLC (DB5, 30m, 240°C) : t_R = 464 s. ^1H NMR (200 MHz, $CDCl_3$) δ : 7.78 (m, 2H); 7.53-7.15 (m, 8H); 5.59 (s, 1H); 5.23 (s, 1H); 4.27 (s, 2H). MS (m/z (%) : 258 (6, $M^{+\cdot}$); 194 (47); 179 (12); 117 (100); 116 (32); 115 (86); 91 (31); 77 (26); 51 (22); 39 (11).

2-(4'-Methylphenyl)-3-phenylsulphonyl-1-propene 6b.[21b]
Purified by flash chromatography (Petroleum ether / Et_2O / CH_2Cl_2 : 48/48/4). Yield : 79 %.
TLC (SiO_2, CH_2Cl_2) : Rf = 0.53. Mp = 100°C (lit.[21b] : 92°C). GLC (DB5, 30m, 240°C) : t_R = 570 s.
^1H NMR (200 MHz, $CDCl_3$) δ : 7.77 (m, 2H); 7.62 - 7.30 (M, 4H); 7.17 (d, J = 8.1 Hz, 2H); 7.04 (d, J = 8.1 Hz, 2H); 5.54 (s, 1H); 5.12 (s, 1H); 4.24 (s, 2H); 2.29 (s, 3H). MS (m/z (%) : 272 (15, $M^{+\cdot}$); 208 (42); 193 (10); 132 (12); 131 (100); 129 (18); 128 (11); 117 (12); 116 (41); 115 (34); 91 (33); 77 (19); 51 (12) .

2-(1'-Naphtyl)-3-phenylsulphonyl-1-propene 6c.
Purified by flash chromatography (Petroleum ether/Et_2O/CH_2Cl_2 : 45/45/10) and recristallization from isopropyl ether to an orange solid. Yield : 69% . Mp = 104-105°C. TLC (SiO_2, CH_2Cl_2) : Rf = 0.59.
IR (film, cm^{-1}): 3060; 2920; 1630; 1490; 1510; 1480; 1450; 1400; 1305 (br); 1260; 1240; 1200; 1150 (br); 1085; 1025; 1005; 995; 825; 895. ^1H NMR (200 MHz, $CDCl_3$) δ : 7.95 - 7.10 (m, 12H); 5.76 (s, 1H); 5.55 (s, 1H); 4.39 (s, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ : 138.72; 137.93; 135.65; 133.55; 133.36; 130.36; 128.70 (2C); 128.49; 128.18; 128.13 (2C); 126.21; 125.92; 125.76; 125.39; 125.05; 124.81; 63.44.
Anal. found: C, 73.95 ; H, 5.19. Calcd. for $C_{19}H_{16}O_2S$: C, 74.01 ; H, 5.23%.

2-(3'-Phenylsulphonyl-1'-propen-2'-yl)thiophene 6d.
Violet solid purified by flash chromatography (Petroleum ether / Et_2O / CH_2Cl_2 : 47/47/6). Yield : 59 %.
Mp = 68-70°C. TLC (SiO_2, CH_2Cl_2) : Rf = 0.7. GLC (DB5, 30m, 240°C) : t_R = 476 s. IR (film, cm^{-1}): 3100; 3070; 2985; 2930; 1975; 1905; 1815; 1615; 1525; 1480; 1445; 1305 (br); 1235; 1150 (br). ^1H NMR (200 MHz, $CDCl_3$) δ : 7.85 (m, 2H); 7.66 - 7.36 (m, 3H); 7.12 (dd, J = 1.2 Hz and 5.0Hz, 1H); 6.88 (m, 2H); 5.62 (s, 1H); 5.03 (s, 1H); 4.22 (s, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ : 142.52; 138.06; 133.76;

130.02; 129.90 (2C); 128.70 (2C); 127.54; 125.32; 125.26; 119.63; 62.26. MS (m/z, %) : 264 (17, $M^{+\cdot}$); 200 (47); 124 (10); 123 (100); 116 (10); 109 (16); 97 (15); 79 (29); 77 (37); 51 (20); 45 (45); 39 (16). Anal. found: C, 58.89 ; H, 4.50. Calcd. for $C_{13}H_{12}O_2S_2$: C, 59.09 ; H, 4.58%.

2-Phenylsulphonyl-1,3-thiazole 7.[35]
Purified by flash chromatography (Petroleum ether/Et_2O/CH_2Cl_2 : 47/47/6). Yield : 18 %. TLC (SiO_2, CH_2Cl_2) : Rf = 0.34. Mp = 85°C (litt.[35] : 85 - 87.5°C). GLC (DB5, 30m, 120 - 240°C / 10°C/min) : t_R = 765 s. IR (KBr, cm^{-1}): 3120; 3070; 2960; 2920; 2850; 1820; 1785; 1730; 1650; 1585; 1470; 1450; 1230 (br); 1170; 1150; 1090; 910. ^1H NMR (200 MHz, $CDCl_3$) δ : 8.13 (d, J = 1.5 Hz, 1H); 8.09 (d, J = 1.5 Hz, 1H); 7.97 (d, J = 3.0Hz, 1H); 7.70 - 7.53 (M, 4H). ^{13}C NMR (50 MHz, $CDCl_3$) δ : 167.12; 145.37; 138.84; 134.38; 129.48 (2C); 128.67 (2C); 125.98. MS (m/z, %) : 225 (3, $M^{+\cdot}$); 163 (5); 162 (11); 132 (12); 161 (100); 117 (9); 77 (57); 58 (28); 57 (5); 51 (26); 50 (6).

Acknowledgment : N.V. wishes to thank "Ministère de l'Enseignement Supérieur et de la Recherche" for a fellowship.

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(*Received in Belgium* 22 *March* 1996; *accepted* 14 *May* 1996)