Synthesis and reactivity of pentavalent biphenyl-2,2′-ylenebismuth derivatives

Alexey Yu. Fedorov and Jean-Pierre Finet *

Laboratoire "Chimie, Biologie et Radicaux Libres" UMR 6517 CNRS-Universités d'Aix-Marseille 1 et 3, Faculté des Sciences St Jérôme, case 541, 13397 Marseille Cedex 20, France

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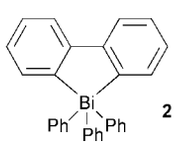
Phenylbiphenyl-2,2′-ylenebismuth diacetate reacted with nucleophiles under basic conditions to give modest to good yields of the *C*-phenylated substrates. Under copper catalysis, it reacted with hydroxy or amino groups to give the products of *O*- or *N*-phenylation. In both sets of reaction conditions, this reagent showed a reduced reactivity compared to the analogous triphenylbismuth diacetate reagent. It showed also a high regioselectivity as only the phenyl derivatives were detected and isolated.

Introduction

The uniqueness of organobismuth compounds as selective reagents in organic chemistry is becoming more widely recognized. A large part of their chemistry involves arylbismuth derivatives, which behave either as oxidizing agents or as arylating reagents towards a number of nucleophilic substrates.[1,2] The chemoselectivity is strongly dependent upon the choice of the bismuth ligands and of the reaction conditions. With triarylbismuth diacetates **1**, selective *C*-, *N*- or *O*-arylation can be

$Ar_3Bi(OAc)_2$ **1**



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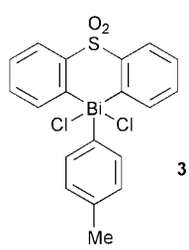

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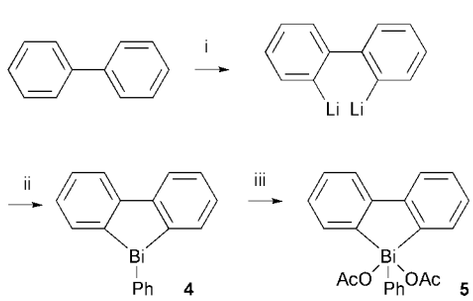
performed under three different sets of reaction conditions:[3] a) *C*- and *O*-arylation *via* a covalent intermediate; b) *O*-arylation under neutral conditions; c) *O*- and *N*-arylation under copper catalysis. However, these reagents require the use of three aryl groups of which only one aryl group is eventually transferred. When the transfer of a highly functionalized aryl group is desired, one possibility of avoiding the loss of two aryl groups would be to use an unsymmetrical triarylbismuth derivative. However, although a limited number of studies have shown the difference in ligand transfer ability in the case of unsymmetrical triarylbismuth derivatives, a selective transfer cannot be realized with such a system.[4,5] An alternative structure to avoid the loss of two ligands would be to use a stabilized form of these two ligands, which would lead to the selective transfer of the third aryl group. One such possibility is to include these two aryl groups in a heterocyclic bismuth substructure. Few structures of this type have been prepared and their reactivity has been barely explored. In 1968, Hellwinkel and Bach synthesised the pentacoordinate biphenyl-2,2′-ylenetriphenyl-λ^5-bismuthane **2**.[6] More recently, Suzuki *et al.* reported the synthesis of various dibenzo[*b*,*e*]bismine compounds which appeared to be moderately stable.[7] The heterocyclic 10,10-dichloro-10-(4′-methylphenyl)-10λ^5-phenothiabismine 5,5-dioxide **3** is a relatively stable substance, which upon treatment with the sodium salt of dibenzoylmethane resulted only in the transfer of the tolyl group, leading to the formation of 1,3-diphenyl-2-tolylpropane-1,3-dione (76%).

As part of our studies on the concept of ligand coupling in heteroaromatic compounds,[8] we decided to investigate the chemistry of pentacoordinate biphenylylbismuth derivatives and in particular the diacetate, as triarylbismuth diacetates can perform the various types of aryl transfer reactions.[3] We now report the synthesis of (biphenyl-2,2′-ylene)phenylbismuth diacetate **5** and its reactions with various types of nucleophilic substrates both under basic conditions and under copper catalysis.

Results and discussion

Biphenyl-2,2′-ylenephenylbismuthane **4** was prepared by a modification of the method of Wittig and Hellwinkel.[9] The TMEDA-adduct of 2,2′-dilithiobiphenyl (TMEDA = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine)[10] was first isolated and then treated with phenylbismuth diiodide to afford the phenylbismuthane **4**. The diacetate **5** was then easily obtained by treatment of **4** with sodium perborate in acetic acid.[11] Under these mild conditions, the diacetate **5** was isolated in a good yield (69%) (Scheme 1).



4 **5**

Scheme 1 *Reagents and conditions*: i, BuLi, TMEDA, 50 °C, 1.5 h; ii, $PhBiI_2$, THF–ether, RT; iii $NaBO_3$, AcOH, RT, 1 h.

The reactions of the cyclic reagent **5** with different nucleophiles under basic conditions were performed in THF using TMG (*N*,*N*,*N*′,*N*′-tetramethylguanidine) as the base (Table 1).

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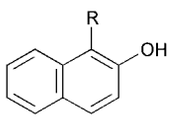
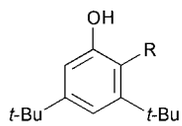
Table 1 Phenylation reactions with **5** under basic conditions[a]

Substrate	Reaction conditions	Products (%)
6	TMG, 24 h, RT	**7** (79); **6** (14); **4** (19)
8	TMG, 48 h, RT	**9** (6); **8** (84); **4** (16)
10	TMG, 17 h, RT	**11** (95); **4** (14)
12	TMG, 24 h, RT	**13** (61); **4** (34)
14	TMG, 18 h, RT and 1 h, 50 °C	**15** (53); **4** (45)
16	TMG, CH_2Cl_2, 1 h, RT and 15 h reflux	No reaction
16	*t*-BuOK, 15 h, 50 °C	**18** (14); **17** (18); **16** (60)
19	TMG, 96 h, RT	No reaction
19	*t*-BuOK, 24 h, RT and 24 h, 50 °C	No reaction

[a] All reactions were performed in THF unless otherwise stated.



6, R = H
7, R = Ph



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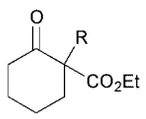
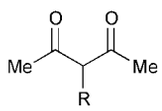
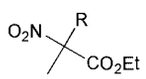


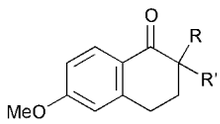
10, R = H
11, R = Ph



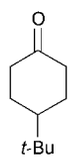
12, R = H
13, R = Ph



14, R = H
15, R = Ph



16, R = R' = H
17, R = Ph, R' = H
18, R = R' = Ph



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With all the substrates (phenols **6** and **8**, β-dicarbonyl compounds **10** and **12**, nitroalkanes **14** and enolized ketones **16**), the reactions appeared to be slower than the similar reactions performed with the corresponding triarylbismuth diacetate derivatives. This reduced reactivity resulted in longer reaction times and/or in lower overall yields. For example, in the case of the phenolic substrates, the very reactive β-naphthol **6** gave a good yield of 1-phenyl-2-naphthol (79%). However, the more sterically hindered 3,5-di-*tert*-butylphenol **8** gave only a very poor yield of the monophenyl derivative **9** (6%). In the case of substrates prone to polyarylation, the behaviour appeared to be substrate-dependent. Indeed, in the case of the 1,3-diketone **12**, the product of monophenylation **13** was obtained in a relatively good yield (61%). In the case of the arylketone **16**, no reaction took place when TMG was used as a base. However, in the presence of the stronger potassium *tert*-butoxide, a reaction occurred but led to a poor yield of the mono- and di-phenylated derivatives, **17** (18%) and **18** (14%) respectively. The cyclohexanone **19** did not lead to any α-arylketone with either TMG or *t*-BuOK as the base. It must be noted that in all cases, the biphenylylbismuth by-product was neither isolated nor detected. The only isolated by-product was the reduction product, the phenylbismuthane **4**.

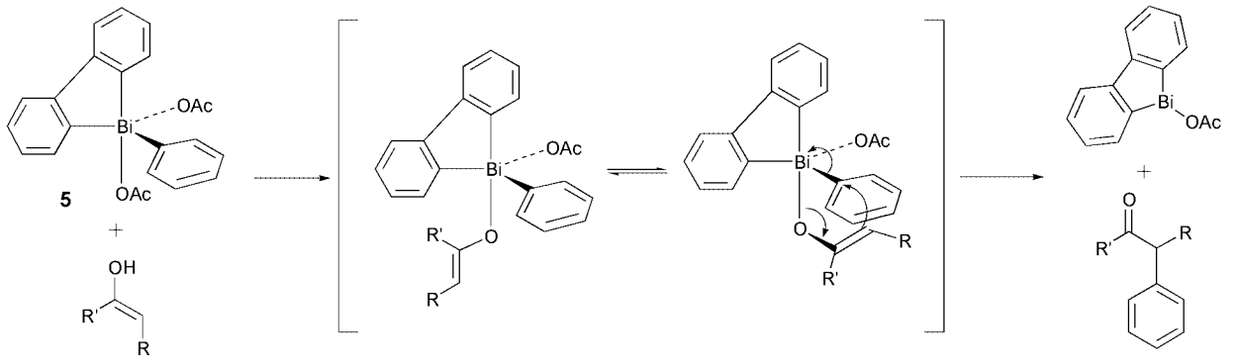
The restricted flexibility induced by the insertion of the bismuth atom into a five membered ring in the biphenyl-2,2′-ylenebismuthane leads to a decrease of the reaction rates similar to the effect of the introduction of an *ortho*-methyl group on the aryl ligand.[12] Moreover, only the ligand coupling product between the substrate and the phenyl substituent has been observed. This is in contrast with the reaction of arylbiphenylylsulfonium[13] or selenonium[14] salts with nucleophiles, which led to mixtures of different ligand coupling products. In this case, tetracoordinate sulfuranes were formed and no significant difference existed between the three aryl–sulfur bonds that could induce selectivity in the ligand coupling process. However, in the case of the trigonal bipyramidal structure of the pentacoordinate bismuth system, the biphenylyl group is blocked in the unfavourable apical plane, as one phenyl of the biphenylyl group forms an equatorial bond to bismuth and the second one lies in the apical position. During the ligand coupling step, the third phenyl group can lie in the equatorial plane, adopting an ideal conformation for the interaction between the two π-systems of the substrate and of the phenyl group (Scheme 2). Thus, this results in the selective coupling of the substrate with the equatorial phenyl ligand.

Table 2 Copper-catalysed phenylation reactions with **5**[a]

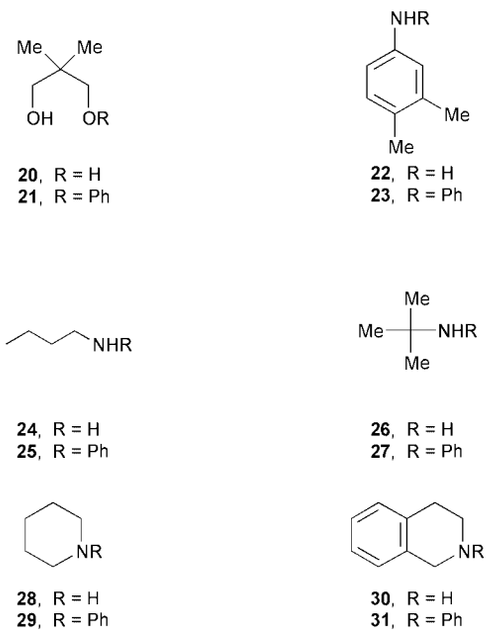
Substrate	Reaction conditions	Product (%)
8	24 h, RT and 24 h, 50 °C	No reaction
20	48 h, 50 °C	**21** (88); **20** (10); **1** (85)
22	14 h, RT	**23** (80); **4** (26)
24	14 h, 50 °C	**25** (64)
26	20 h, 50 °C	**27** (18)
28	3 h, 50 °C	**29** (96)
30	15 h, 50 °C	**31** (78)

[a] All reactions were performed in THF in the presence of copper diacetate (0.1 equiv.).

The reactions of the cyclic reagent **5** with different *O*- and *N*-nucleophiles under copper catalysis conditions were performed in THF using copper(II) diacetate as the catalyst (Table 2). In the case of the *O*-arylation reaction, the cyclic compound **5** was treated with the phenol **8** and the 1,3-diol **20**. The reactivity of **5** appeared again to be significantly reduced by comparison with triphenylbismuth diacetate. Indeed, the copper-catalysed reaction of triphenylbismuth diacetate with the phenol **8** as well as with the 1,3-diol **20** led to high yields of the *O*-phenyl derivatives. By contrast, the cyclic biphenylyl derivative **5** reacted only with the glycol **20** to afford a good yield of the mono-*O*-phenyl derivative **21**. This reduced reactivity was also observed in the case of the *N*-phenylation reaction. In this case, good yields of the *N*-phenylation products were only obtained when the reaction was performed at 50 °C. Even, *tert*-butylamine **26** gave the *N*-phenyl product **27**, however in a rather modest yield (18%). It must be noted that the reaction of **5** with the primary amine **24** afforded only the monophenylated product, when triphenylbismuth diacetate gave a mixture of the mono- and di-phenyl derivatives.



Scheme 2 Mechanism of the ligand coupling step.



In conclusion, insertion of two phenyl groups of triphenylbismuth into a cyclic system allows the selective transfer of only the free phenyl group both in base-catalysed *C*-phenylation and in the copper-catalysed *O*- and *N*-phenylation reactions. The lower reactivity may be of interest as monophenylation of β-dicarbonyl compounds was obtained when a mixture of mono- and di-phenyl products was formed in the reaction with triphenylbismuth derivatives.

Experimental

Melting points were taken on a Büchi capillary apparatus and are uncorrected. NMR spectra were obtained on a Bruker AC200 spectrometer: ^{1}H-NMR at 200.13 MHz and ^{13}C-NMR at 50.32 MHz. Chemical shifts (δ) are reported in ppm for a solution of the compound in $CDCl_3$ with internal Me_4Si and *J* values in hertz. TMEDA refers to *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, TMG refers to *N*,*N*,*N*′,*N*′-tetramethylguanidine and ether refers to diethyl ether. CC refers to column chromatography on silica gel and PLC refers to preparative layer chromatography.

Preparation of phenylbiphenyl-2,2′-ylenebismuth diacetate

Phenylbiphenyl-2,2′-ylenebismuthane (4). A solution of 2,2′-dilithiobiphenyl–TMEDA [10] (4.8 g) in a mixture of anhydrous THF (50 cm^3) and anhydrous ether (70 cm^3) was added to phenylbismuth diiodide (8.1 g). The mixture was stirred for 2.5 hours at room temperature. After addition of water and extraction of the aqueous phase with dichloromethane, the organic phase was dried over $MgSO_4$. Distillation of the solvents under reduced pressure afforded a crude product which was crystallized from dichloromethane–pentane to give **4** (3.7 g, 56%), mp 166 °C, lit.[9] 167–168 °C.

Phenylbiphenyl-2,2′-ylenebismuth diacetate (5). A mixture of sodium perborate monohydrate (0.6 g) and phenylbiphenyl-2,2′-ylenebismuthane (0.9 g) in acetic acid (20 cm^3) was stirred at room temperature for 1 h. The resulting solution was poured into water (40 cm^3) and the mixture was extracted with CH_2Cl_2 (3 × 20 cm^3). The organic extracts were combined, washed with water, dried over $MgSO_4$. The solvent was distilled under reduced pressure to a small volume. A mixture of diethyl ether–pentane (1 : 3) was added and the solution was kept overnight at −15 °C to afford **5** as a colorless powder (0.77 g, 69%), mp 183 °C; δ_H ($CDCl_3$, 200 MHz) 1.80 (6H, s, Me), 7.50–7.75 (7H, m, Ar-H) and 8.10–8.25 (6H, m, Ar-H); δ_C 20.8 (Me), 124.8, 130.8, 131.0, 131.2, 131.3, 131.9, 132.6, 137.5, 155.8 (C-Ar) and 180.2 (Me*C*O) (Found: C, 47.55; H, 3.47. $C_{22}H_{19}BiO_4$ requires: C, 47.49; H, 3.44%).

Arylation reactions with phenylbiphenyl-2,2′-ylenebismuth diacetate in the presence of *N*,*N*,*N*′,*N*′-tetramethylguanidine (TMG)

General procedure. A mixture of the substrate (0.25–0.5 mmol, 1 equiv.) and TMG (1.2 equiv.) in distilled THF (5 cm^3 mmol^{-1} of substrate) was stirred for 10 min at room temperature. Phenylbiphenyl-2,2′-ylenebismuth diacetate (1.2 equiv.) was added and the mixture stirred for the time indicated below. The solvent was distilled off and the residue was purified by chromatography as described below to afford the reaction products identical with authentic samples, unless otherwise stated.

1-Phenyl-2-naphthol (7).[15] 24 h; CC (pentane–ether 7 : 3); colourless plates, mp 84 °C; 79%.

3,5-Di-*tert*-butyl-2-phenylphenol (9).[15] 48 h; CC (pentane–ether 97 : 3) and PLC (pentane–ether 19 : 1); colourless plates, mp 71 °C (pentane); 6%.

Ethyl 1-phenyl-2-oxocyclohexanecarboxylate (11).[16] 17 h; CC (pentane–ether 7 : 3); colourless oil; 95%.

3-Phenylpentane-2,4-dione (13).[16] 24 h; CC (pentane–ether 4 : 1); colourless oil; 61%.

Ethyl 2-phenyl-2-nitropropionate (15).[17] 18 h at room temperature and 1 h at 50 °C; CC (pentane–ether); pale yellow oil; 53%.

Reaction of 6-methoxy-3,4-dihydronaphthalen-1(2*H*)-one with phenylbiphenyl-2,2′-ylenebismuth diacetate. A mixture of 6-methoxy-3,4-dihydronaphthalen-1(2*H*)-one (0.05 g, 1 equiv.),

potassium *tert*-butoxide (0.04 g, 1.2 equiv.) and phenylbiphenyl-2,2′-ylenebismuth diacetate (0.19 g, 1.2 equiv.) in distilled THF (15 cm^3) was stirred for 15 hours at 50 °C. Aqueous work-up followed by column chromatography of the residue (pentane–ether 3:1) afforded 6-methoxy-2,2-diphenyl-3,4-dihydronaphthalen-1(2*H*)-one **18** (0.013 g, 14%), mp 110 °C; δ_H ($CDCl_3$, 200 MHz) 2.75–2.95 (4H, m, H-3 and H-4), 3.80 (3H, s, MeO), 6.56 (1H, d, $J_{H5–H7}$ 2.5, H-5), 7.84 (1H, dd, $J_{H7–H5}$ 2.4, $J_{H7–H8}$ 8.8, H-7), 7.10–7.37 (10H, m, Ar-H) and 8.14 (1H, d, $J_{H8–H7}$ 8.8, H-8); δ_C 26.7 (C-4), 35.1 (C-3), 55.2 (MeO), 59.5 (C-2), 111.9 and 113.3 (C-5 and C-7), 126.5, 126.6, 131.9, 127.9, 128.4, 130.7, 142.2 and 145.6 (C-Ar), 163.3 (C-6) and 197.4 (C-1) (Found: C, 83.79; H, 6.21. $C_{23}H_{20}O_2$ requires: C, 84.12; H, 6.14%). 6-Methoxy-2-phenyl-3,4-dihydronaphthalen-1(2*H*)-one **17** (0.013 g, 18%) obtained as colourless plates, mp 112–113 °C (pentane-ether), lit.[18] 112–114 °C and unreacted starting material **16** (0.03 g, 60%) were also isolated.

Copper-catalysed arylation reactions with phenylbiphenyl-2,2′-ylenebismuth diacetate

General procedure. A mixture of the substrate (1 equiv.), copper diacetate (0.1 equiv.) and phenylbiphenyl-2,2′-ylenebismuth diacetate (1.1 equiv.) in THF (5 cm^3 $mmol^{-1}$ of substrate) was stirred for the time and at the temperature indicated below. The solvent was distilled off and the residue was purified by column chromatography on silica gel (eluant indicated below) to afford the reaction products. When the *N*-phenyl derivative possessed an R_f close to the R_f of the by-product triarylbismuthane, the reaction mixture was treated with a few drops of 35% aqueous HCl. After stirring for 30 min at room temperature, the pH was brought to neutrality by addition of aqueous sodium hydroxide. The solvents were then distilled and the residue was purified by chromatography to afford the phenylation products identical with authentic samples, unless otherwise stated.

3-Phenoxy-2,2-dimethylpropan-1-ol (21).[19] 48 h at 50 °C; (pentane–ether 7:3); colourless oil; 88%.

***N*-(3,4-Dimethylphenyl)-*N*-phenylamine (23).** 14 h at 50 °C; CC (pentane–ether 97:3); plates, mp 55 °C (pentane–ether), lit.[20] 56–57 °C; 80%.

***N*-Butyl-*N*-phenylamine (25).**[21] 14 h at 50 °C; CC (pentane–ether 97:3); yellow oil; 64%.

***N*-(1,1-Dimethylethyl)-*N*-phenylamine (27).**[22] 20 h at 50 °C; CC (pentane–methanol 44:1); colourless oil; 18%.

***N*-Phenylpiperidine (29).**[23] 3 h at 50 °C; CC (pentane-ether 97:3); yellow oil; 96%.

***N*-Phenyl-1,2,3,4-tetrahydroisoquinoline (31).** 15 h at 50 °C; CC (pentane–ether 97:3); mp 45 °C, lit.[24] mp 45–46 °C; 78%.

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References

1 H. Suzuki, T. Ikegami and Y. Matano, *Synthesis*, 1997, 249; J.-P. Finet, *Chem. Rev.*, 1989, **89**, 1487.
2 H. Suzuki and Y. Matano, *Organobismuth compounds: synthesis, properties and uses in organic transformations*, in *Chemistry of Arsenic, Antimony and Bismuth*, ed. N. C. Norman, Blackie Academic & Professional, London, 1998; ch. 6, pp. 283–343.
3 (*a*) J.-P. Finet, *Triphenylbismuth diacetate*, in *Encyclopedia of Reagents for Organic Synthesis*, ed. L. A. Paquette, John Wiley and Sons, New York, 1995; vol. 8, pp. 5344–5345; (*b*) V. A. Dodonov and A. V. Gushchin, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 2043; V. A. Dodonov and A. V. Gushchin, *Russ. Chem. Bull.*, 1993, **42**, 1955.
4 D. H. R. Barton, N. Y. Bhatnagar, J.-P. Finet and W. B. Motherwell, *Tetrahedron*, 1986, **42**, 3111.
5 Y. Matano, T. Miyamatsu and H. Suzuki, *Chem. Lett.*, 1998, 127.
6 D. Hellwinkel and M. Bach, *Liebigs Ann. Chem.*, 1968, **720**, 198.
7 H. Suzuki, T. Murafuji and N. Azuma, *J. Chem. Soc., Perkin Trans. 1*, 1992, 1593.
8 J.-P. Finet, *Ligand Coupling Reactions with Heteroatomic Compounds*, Pergamon Press, Oxford, 1998.
9 G. Wittig and D. Hellwinkel, *Chem. Ber.*, 1964, **97**, 789.
10 W. Neugebauer, A. J. Kos and P. v. R. Schleyer, *J. Organomet. Chem.*, 1982, **228**, 107.
11 S. Combes and J.-P. Finet, *Synth. Commun.*, 1996, **26**, 4569.
12 A. Fedorov, S. Combes and J.-P. Finet, *Tetrahedron*, 1999, **55**, 1341.
13 R. W. LaRochelle and B. M. Trost, *J. Am. Chem. Soc.*, 1971, **93**, 6077; B. M. Trost and H. C. Arndt, *J. Am. Chem. Soc.*, 1973, **95**, 5288.
14 S. Ogawa, S. Sato, T. Erata and N. Furukawa, *Tetrahedron Lett.*, 1991, **32**, 3179; S. Sato and N. Furukawa, *Chem. Lett.*, 1994, 889.
15 D. H. R. Barton, N. Y. Bhatnagar, J.-C. Blazejewski, B. Charpiot, J.-P. Finet, D. J. Lester, W. B. Motherwell, M. T. B. Papoula and S. P. Stanforth, *J. Chem. Soc., Perkin Trans. 1*, 1985, 2657.
16 D. H. R. Barton, J.-C. Blazejewski, B. Charpiot, J.-P. Finet, W. B. Motherwell, M. T. B. Papoula and S. P. Stanforth, *J. Chem. Soc., Perkin Trans. 1*, 1985, 2667.
17 J. J. Lalonde, D. E. Bergbreiter and C.-H. Wong, *J. Org. Chem.*, 1988, **53**, 2323.
18 M. Date, M. Watanabe and S. Furukawa, *Chem. Pharm. Bull.*, 1990, **38**, 902.
19 D. H. R. Barton, J.-P. Finet and C. Pichon, *J. Chem. Soc., Chem. Commun.*, 1986, 65.
20 R. B. Moffett and B. D. Aspergren, *J. Am. Chem. Soc.*, 1960, **82**, 1600.
21 R. A. Brown, S. I. S. Fernando and R. M. G. Roberts, *J. Chem. Soc., Perkin Trans. 1*, 1994, 197.
22 W. J. Hickinbottom, *J. Chem. Soc.*, 1933, 946.
23 G. Verardo, A. G. Giumanini, G. Favret and P. Strazzolini, *Synthesis*, 1991, 447.
24 G. Van Binst, R. Baert, M. Biesemans, C. Mortelmans and R. Salsmans, *Bull. Soc. Chim. Belg.*, 1976, **85**, 1.