GENERAL SYNTHESIS OF 2,3-SUBSTITUTED 5-MEMBERED HETEROCYCLIC QUINONES

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Abstract - 4,7-Dimethoxybenzo[*b*]furan, -thiophene, -selenophene and 4,7-dimethoxyindole have been prepared by a two-step procedure involving a cyclization-dehydration of the acetals (**1**). The oxidative demethylation of 4,7-dimethoxybenzo[*b*]thiophene, -selenophene and 4,7-dimethoxyindole afforded the corresponding quinones whereas 4,7-dimethoxybenzo[*b*]furan gave 5,5'-bisbenzo[*b*]-furan-1,4-dionyl (**4b**).

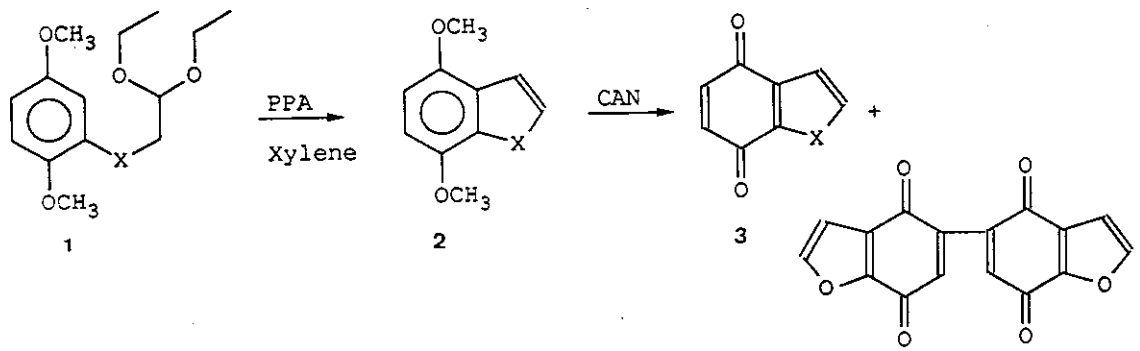
INTRODUCTION

Due to their significance in biological systems and wide occurrence in natural products,[1-2] fused heterocyclic quinonoid systems have become attractive targets in organic synthesis. Examples of their biological activity can be found in electron transport chains, protein carboxylation and lipidic oxidation protection.[3] Quinones are also present as active pharmacophores in antineoplastic drugs[4-6] (they form the second largest class of antitumor agents approved for clinical use in the USA), antibiotic[7-8] and antimalaric[9-13] agents. The prime characteristic of the quinone moiety is its ability to undergo reversible oxidation-reduction[14] and to form semiquinone and oxygen radicals (the superoxide anion is not particularly toxic to cells, but the hydroxyl radical is thought to be responsible for the majority of oxygen radical toxicity).[15] Indeed, in vivo, quinones can be activated by enzymatic reduction to a semiquinone radical (one electron reduction) which autoxidizes forming the superoxide anion radical by reacting with molecular oxygen.[16] However, hydroquinones and quinones may act as oxygen radical scavengers and play a role of protection against oxidative stress. This biochemical

importance has spurred continual efforts towards new or improved methods for the synthesis of the heterocyclic quinonoid nucleus.[8,17]

In the course of our studies[5-6,18] on antitumoral/antiinflammatory agents, it was necessary to prepare simple heterocyclic quinones. Thus, we sought to develop a general method for the preparation of 2,3-unsubstituted benzo[*b*]furan, -thiophene, -selenophene-4,7-diones and indole-4,7-dione. Our strategy for the synthesis of the heterocyclic quinones begins with the cyclization of acetals (**1**), followed by the oxidative demethylation of the 4,7-dimethoxy derivatives (**2**) (Scheme 1).

The acid-catalyzed cyclodehydration of acetals was previously employed for the preparation of benzo[*b*]furans,[19-20] benzo[*b*]thiophenes,[20-21] indoles[22] and benzo[*b*]selenophenes[23] using polyphosphoric acid (PPA) in aromatic solvents,[19,21] trifluoroacetic anhydride in trifluoroacetic acid[22] or phosphorus pentoxide in phosphoric acid.[20,23] However, no general procedures have been reported in the literature. The oxidative demethylation was classically carried out using ceric ammonium nitrate (CAN).[24-25]



1 2 3 4b

1a X= NH **2a** X= NH **3a** X= NH

1b X= O **2b** X= O **3c** X= S

1c X= S **2c** X= S **3d** X= Se

1d X= Se **2d** X= Se

1e X= $NCOCF_3$ **2e** X= $NCO_2C_2H_5$

Scheme 1

RESULTS AND DISCUSSION

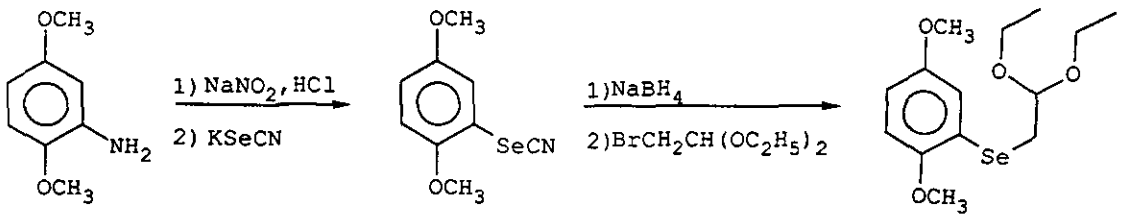
Acetals (**1a-c**) (Scheme 1) were prepared by alkylation of commercial 2,5-dimethoxyaniline (Aldrich-Chemie), 2,5-dimethoxyphenol[26] and 2,5-dimethoxythiophenol[27] with bromoacetaldehyde diethyl acetal in dimethylformamide using sodium hydrogen carbonate[28] as base (**1a**) or in dimethyl sulfoxide using potassium hydroxide[19] (**1b**) or potassium carbonate[29] as base (**1c**). For the synthesis of the selenium derivative (**1d**), we prepared 2,5-dimethoxy-1-selenocyanatobenzene (**5**) (Scheme 2) by the reaction of potassium selenocyanate (commercial or prepared from potassium cyanide and selenium) with 2,5-dimethoxyphenyldiazonium chloride. 2,5-Dimethoxy-1-selenocyanatobenzene was treated with sodium borohydride to afford the selenide anion which was treated with bromoacetaldehyde diethyl acetal to give **1d**. Results are reported in Table I.

Cyclization of the acetals (**1b-d**) with PPA in xylene afforded 4,7-dimethoxybenzo[*b*]furan, thiophene and selenophene (**2b-d**) in good yields (Table I). The *N*-unsubstituted indole (**2a**) was obtained by cyclization in xylene containing PPA following initial trifluoroacetylation of the amino group. The stirring was particularly significant in this reaction. In fact, it was found that vigourous stirring decreased the yield of the product and increased the formation of polymer. Soft magnetic stirring afforded the best yields and good purity.

Table I: Preparation of the acetals (**1**), cyclization and oxidative demethylation of **2**

Compound	Yield (%)	Compound	Yield (%)	Compound	Yield (%)
1a	71	**2a**	63	**3a**	74
1b	80	**2b**	80	**3b**	0[a]
1c	77	**2c**	70	**3c**	70
1d	80	**2d**	61	**3d**	49
1e	98	**2e**	78	--	--

[a]: Oxidative demethylation of **2b** afforded **4b** in 90% yield.



5 **1d**

Scheme 2

The oxidative demethylation of sulfur and selenium derivatives (**2c-d**) afforded heterocyclic quinones (**3c-d**) in moderate yields, whereas the oxygen derivative (**2b**) gave the dimer (**4b**) in 90% yield (Scheme 1)(Table I) even with shortened reaction time. The formation of diquinone was previously reported in the oxidation of 1,4-dimethoxybenzene and 1,4-dimethoxytoluene with ceric sulfate[30] or argentic oxide,[31] however with ceric ammonium nitrate, the oxidative demethylation was selective.[24] Although efficient electrochemical[32] and chemical[33] synthesis of bi-1,4-naphthoquinonyl derivatives has been reported, it is the first case, at our knowledge, of selective oxidative dimerization using ceric ammonium nitrate. 1-Ethoxycarbonyl-4,7-dimethoxyindole (**2e**), prepared by treatment of **2a** with sodium hydride and ethyl chloroformate,[7] with ceric ammonium nitrate in aqueous acetonitrile afforded a mixture of *N*-unsubstituted and substituted quinones which was immediately treated with aqueous acetic acid to yield **3a**.

EXPERIMENTAL

Tlc analyses were performed on 3 10cm plastic sheets precoated with silica gel $60F_{254}$ (Merck), 0.2 mm (solvent system: ethyl acetate/ hexane 2:3). Melting points are uncorrected. ^{1}H-Nmr spectra were recorded on a WP60 and AM400WB BRUKER spectrometers in an appropriate deuterated solvent with TMS as internal reference. The mass spectra were taken with a RIBERMAG spectrometer (60eV). The microanalyses were performed by CNRS laboratories (Vernaison).

2-(2,5-Dimethoxyanilino)acetaldehyde diethyl acetal (**1a**)

A solution of 3.08 g (20 mmol) of 2,5-dimethoxyaniline, 3.1 ml (20 mmol) of bromoacetaldehyde diethyl acetal and 1.7 g (20 mmol) of $NaHCO_3$ in 25 ml of DMF was boiled under reflux for 96 h. After rotary evaporation of the bulk of the solvent, the product was dissolved in 100 ml of ether and the resulting solution was washed with water (3 × 50 ml) and dried over anhydrous Na_2SO_4. Rotary evaporation of the solvent and vacuum distillation of the residue gave **1a** (3.82 g, 71%); bp 141-142°C(1 mm Hg); ^{1}H-nmr ($CDCl_3$) : δ 1.20(6H, t, ^{3}J=7 Hz, 2 × CH_3), 3.62(4H, m, 2 × OCH_2), 3.74(3H, s, OCH_3), 3.80(3H, s, OCH_3), 3.88(2H, d, ^{3}J=5 Hz, NCH_2), 4.70(1H, t, ^{3}J=5 Hz, CH), 6.10-6.74(4H, m, 3H arom. + NH); Anal. Calcd for $C_{14}H_{23}NO_4$: C 62.43; H 8.61; N 5.20. Found: C 62.80; H 8.58; N 5.34.

2-(2,5-Dimethoxyphenyloxy)acetaldehyde diethyl acetal (**1b**)

A solution of 3.08 g (20 mmol) of 2,5-dimethoxyphenol, 3.1 ml (20 mmol) of bromoacetaldehyde diethyl acetal and 1.29 g (20 mmol) of KOH in 10ml of DMSO was refluxed for 6 h. The mixture was treated as **1a**. Yield: 4.32 g, 80%; bp 143-145°C(3 mm Hg); ^{1}H-nmr ($CDCl_3$): δ 1.24(6H, t, ^{3}J=7 Hz, 2 × CH_3), 3.72(4H, m, 2 × OCH_2), 3.76(3H, s, OCH_3), 3.82(3H, s, OCH_3), 4.05(2H, d, ^{3}J=5 Hz, OCH_2), 4.89(1H, t, ^{3}J=5 Hz, CH), 6.41(1H, dd, ^{3}J=8.6 Hz, ^{4}J=2.7 Hz, H4), 6.57 (1H, d, ^{4}J=2.7 Hz, H2), 6.81(1H, d, ^{3}J=8.6 Hz, H5); Anal. Calcd for $C_{14}H_{22}O_5$: C 62.20; H 8.20. Found: C 62.00; H 8.21.

2-(2,5-Dimethoxyphenylthio)acetaldehyde diethyl acetal (**1c**)

To a solution of 3.38 g (20 mmol) of 2,5-dimethoxythiophenol, 5.45 g (40 mmol) of K_2CO_3 and 135 mg (0.8 mmol) of KI in 50ml of DMSO was added dropwise 3.1 ml (20 mmol) of bromoacetaldehyde diethyl acetal. The solution was stirred for 2 h at room temperature. The mixture was filtered and poured into 120 ml of water. The solution was extracted with ether (3 × 50 ml). The ethereal solution was washed with 10% NaOH (2 × 50 ml) and brine (2 × 50 ml). Rotary evaporation of the solvent and vacuum distillation of the residue gave 1c (4.40 g, 77%); bp 150-151°C(1 mm Hg); ^{1}H-nmr ($CDCl_3$): δ 1.19(6H, t, ^{3}J=7.1 Hz,

2 × CH_3), 3.10(2H, d, ^3J=5 Hz, SCH_2), 3.51(4H, m, 2 × OCH_2), 3.76(3H, s, OCH_3), 3.84(3H, s, OCH_3), 4.68(1H, t, ^3J=5 Hz, CH), 6.81(2H, m, H4 H5), 7.08(1H, d, ^4J=3 Hz, H2); Anal. Calcd for $C_{14}H_{22}O_4S$: C 58.71; H 7.74; S 11.20. Found: C 59.02; H 7.81; S 11.35.

2,5-Dimethoxy-1-selenocyanatobenzene (5)

7.9 g (0.1 mol) of selenium was added to a solution of 9 g (0.14 mol) of KCN in 25 ml of water at room temperature. The solution was filtered and stored at 0°C (Solution A).

A solution of 7.5 g (0.1 mol) of $NaNO_2$ in 15 ml of water was added dropwise to a solution of 15.3 g (0.1 mol) of 2,5-dimethoxyaniline in 25ml of conc. HCl and 25ml of H_2O at 0°C. Sodium acetate was added until pH=4.5 (Solution B).

The solution A was added dropwise to the solution B at 0°C. After nitrogen evolution ceased (1 h), the precipitate was filtered and dried to give 5 (17.0 g, 72%); mp 55-56°C; ^{1}H-nmr ($CDCl_3$): δ 3.81(3H, s, OCH_3), 3.85(3H, s, OCH_3), 6.85(2H, m, H. arom.), 7.22(1H, m, H. arom.); Anal. Calcd for $C_9H_9NO_2Se$: C 44.64; H 3.75; N 5.78; Se 32.61. Found: C 44.56; H 3.76; N 6.03; Se 32.75.

2-(2,5-Dimethoxyphenylseleno)acetaldehyde diethyl acetal (1d)

To a solution of 2.42 g (10 mmol) of 5 in 100ml of ethanol under nitrogen was slowly added 435 mg (12 mmol) of $NaBH_4$. The solution was stirred at room temperature for 1.5 h and 1.55 ml (10 mmol) of bromoacetaldehyde diethyl acetal was added dropwise. The solution was stirred for 2 h. After rotary evaporation of the bulk of the solvent, the product was dissolved in 100 ml of CH_2Cl_2 and the resulting solution was washed with water (3 50 ml) dried over anhydrous Na_2SO_4. Rotary evaporation of the solvent and vacuum distillation of the residue gave 1d (1.94 g, 80%); bp 151-152°C(1 mm Hg); ^{1}H-nmr ($CDCl_3$): δ 1.21(6H, t, ^3J=7.2 Hz, 2 × CH_3), 3.10(2H, d, ^3J=5.1 Hz, $SeCH_2$), 3.60(4H, m, 2 × OCH_2), 3.78(3H, s, OCH_3), 3.84(3H, s, OCH_3), 4.77(1H, t, ^3J=5.1 Hz, CH), 6.78(2H, m, 2H arom.), 7.03(1H, m, 1H arom.); Anal. Calcd for $C_{14}H_{22}O_4Se$: C 50.45; H 6.65; Se 23.69. Found: C 50.81; H 6.71; Se 23.78.

N-(Trifluoroacetyl)-2-(2,5-dimethoxyanilino)acetaldehyde diethyl acetal (1e)

Compound (**1e**) was prepared by known procedure[22] in 98% yield; bp 138-140°C(1 mm Hg); ^{1}H-nmr ($CDCl_3$): δ 1.10(6H, t, ^{3}J=7 Hz, 2 × CH_3), 3.10-3.60(6H, m, 2 × OCH_2 + NCH_2), 3.74(3H, s, OCH_3), 3.83(3H, s, OCH_3), 4.78(1H, t, ^{3}J=5.2 Hz, CH), 6.70-7.00(3H, m, H2H4H5); Anal. Calcd for $C_{16}H_{22}F_3NO_5$: C 52.60; H 6.07; N 3.83. Found: C 52.97; H 6.08; N 3.90.

General procedure for heterocyclization

A solution of 10 mmol of acetal (**1b-e**) in 60 ml of degassed xylene and 3 ml of PPA was magnetically stirred under reflux for 1 h. The organic layer was separated. Rotary evaporation of the solvent gave pure compound (**2**).

2a (Yield 63%): mp 131-132°C; ^{1}H-nmr ($CDCl_3$): δ 3.80(3H, s, OCH_3), 3.89(3H, s, OCH_3), 6.53-6.90(3H, m, H3H5H6), 8.02(1H, d, ^{3}J=2.5 Hz, H2), 8.59(1H, s, NH); Anal. Calcd for $C_{10}H_{11}NO_2$: C 67.78; H 6.26; N 7.90. Found: C 70.04; H 6.22; N 8.01.

2b (Yield 80%): mp 43-45°C; ^{1}H-nmr ($CDCl_3$): δ 3.90(3H, s, OCH_3), 3.97(3H, s, OCH_3), 6.52(1H, d, ^{3}J=9 Hz, H6), 6.74(1H, d, ^{3}J=9 Hz, H5), 6.87p(1H, d, ^{3}J=2.2 Hz, H3), 7.47(1H, d, ^{3}J=2.2 Hz, H2); Anal. Calcd for $C_{10}H_{10}O_3$: C 67.41; H 5.66. Found: C 67.57; H 5.67.

2c (Yield 70%): mp 86-88°C; ^{1}H-nmr ($CDCl_3$): δ 3.92(3H, s, OCH_3), 3.96(3H, s, OCH_3), 6.68(2H, s, H5H6), 7.28(1H, d, ^{3}J=4.9 Hz, H3), 7.67(1H, d, ^{3}J=4.9 Hz, H2); Anal. Calcd for $C_{10}H_{10}O_2S$: C 61.83; H 5.19; S 16.51. Found: C 61.97; H 5.21; S 16.87.

2d (Yield 61%): mp 105-107°C; ^{1}H-nmr ($CDCl_3$): δ 3.92(3H, s, OCH_3), 3.96(3H, s, OCH_3), 6.68(2H, s, H5H6), 7.28(1H, d, ^{3}J=4.9 Hz, H3), 7.67(1H, d, ^{3}J=4.9 Hz, H2); Anal. Calcd for $C_{10}H_{10}O_2Se$: C 49.81; H 4.18; Se 32.74. Found: C 50.03; H 4.17; Se 32.94.

1-Ethoxycarbonyl-4,7-dimethoxyindole (**2e**)

Compound (**2e**) was prepared by known procedure[7] in 78% yield.

2e : mp 110-112°C; ^{1}H-nmr ($CDCl_3$): δ 1.40(3H, t, ^{3}J=7 Hz, CH_3) 3.81(3H, s, OCH_3), 3.93(3H, s, OCH_3), 4.42(2H, q, CH_2), 6.51(1H, d, ^{3}J=3.6 Hz, H3), 6.81(1H, d, ^{3}J=8.5 Hz, H6), 6.90(1H, d, ^{3}J=8.5 Hz, H5), 7.39(1H, d, ^{3}J=3.6 Hz, H2); Anal. Calcd for $C_{13}H_{15}NO_4$: C 62.64; H 6.07; N 5.62. Found: C 62.76; H 6.10; N 5.78.

Oxidative demethylation of **2b-e**

To a solution of compound **(2b-e)** (1 mmol) in 2.5 ml of acetonitrile was added a solution of 1.65 g(3 mmol) of ceric ammonium nitrate in 2.5 ml of water. After stirring for 1.5 h at room temperature, the reaction mixture was extracted with chloroform. The chloroform layer was dried over Na_2SO_4 and concentrated on a rotary evaporator. The crude product was purified by crystallization or flash chromatography.

3a (Yield 74%): mp 177-178°C(lit. 180°C[34]); ^{1}H-nmr ($CDCl_3$): δ 6.53(1H, d, ^{3}J=2.6 Hz, H3), 6.61(1H, d, ^{3}J=10.3 Hz, H6), 6.65(1H, d, ^{3}J=10.3 Hz, H5), 7.25(1H, d, ^{3}J=2.6 Hz, H2), 12.70(1H, bs, NH); ms: m/z 147(M^+, 46%), 119(M^+-CO, 18%), 93(100%), 91(24%).

3c (Yield 70%): mp 129-130°C(lit. 130-131°C[35]); ^{1}H-nmr ($CDCl_3$): δ 6.84(1H, d, ^{3}J=10.2 Hz, H6), 6.85(1H, d, ^{3}J=10.2 Hz, H5), 7.55(1H, d, ^{3}J=5 Hz, H3), 7.71(1H, d, ^{3}J=5 Hz, H2); ms: m/z 164(M^+, 75%), 136(M^+-CO, 27%), 110(100%), 108(43%).

3d (Yield 49%): mp 83-86°C; ^{1}H-nmr ($CDCl_3$): δ 6.75(1H, d, ^{3}J=10 Hz, H6), 6.95(1H, d, ^{3}J=10 Hz, H5), 7.83(1H, d, ^{3}J=5.6 Hz, H3), 8.42(1H, d, ^{3}J=5.6 Hz, H2); ms: m/z 212(M^+, 100%, ^{80}Se), 184(M^+-CO, 29%, ^{80}Se), 158(30%), 156(34%); Anal. Calcd for $C_8H_4O_2Se$: C 45.52; H 1.91; Se 37.41. Found: C 45.76; H 1.87; Se 37.68.

4b (Yield 90%): mp 250°C; ^{1}H-nmr ($CDCl_3$): δ 6.94(2H, d, $^3J_{2,3}$=5.5 Hz, H3), 7.11(2H, dd, $J_{2,6}$=1.9 Hz, $^3J_{2,3}$=5.5 Hz, H2), 8.30(2H, d, $J_{2,6}$=1.9 Hz, H6); ^{13}C-nmr ($CDCl_3$): 111.9(d, C3), 112.3(s, C7a), 140.4(s, C3a), 140.6(d, C2), 154.0(s, C5), 154.2(d, C6), 185.7(s, C4C7); ms: m/z 294(M^+, 100%), 238(M^+-2CO, 14%), 210(M^+-3CO, 42%), 182(M^+-4CO, 16%), 154(M^+-5CO, 14%), 126(M^+-6CO, 16%); Anal. Calcd for $C_{16}H_6O_6$: C 65.32; H 2.06. Found: C 65.46; H 1.98.

REFERENCES

1. R. H. Thomson "Naturally Occurring Quinones III"; Chapman and Hall Ltd: London, 1987.

2. M. Alvarez, M. Salas, and J. A. Joule, *Heterocycles*, 1991, 32, 759.

3. H. Nohl, W. Jordan, and R. J. Youngman, *Adv. Free Rad. Biol. Med.*, 1986, 2, 211.

4. G. Powis, *Free Rad. Biol. Med.*, 1989, 6, 63.

5. N. Cotelle, S. Moreau, P. Cotelle, J. P. Catteau, J. L. Bernier, and J. P. Hénichart, *Chem. Res. Toxicol.*, 1991, 4, 300.

6. N.Cotelle, S.Moreau, J.P.Catteau, J.L.Bernier, and J.P.Hénichart, *Free Rad. Biol. Med.*, 1991, 11, 63.

7. Y. Kitahara, S. Nakahara, R. Numata, and A. Kubo, *Chem. Pharm. Bull.*, 1985, 33, 2122.

8. A. Kubo, Y. Kitahara, S. Nakahara, and R. Numata, *Chem. Pharm. Bull.*, 1983, 31, 341.

9. A. J. Lin, R. S .Pardini, B. J. Lillis, and A. C. Sartorelli, *J. Med. Chem.*, 1974, 17, 668.

10. T. H. Porter, F. S. Skelton, and K. Folkers, *J. Med. Chem.*, 1972, 15, 34.

11. T. H. Porter, A. Von Klaudy, and K. Folkers, *J. Med. Chem.*, 1973, 16, 1310.

12. M. D. Friedman, P. L. Stotter, T. H. Porter, and K. Folkers, *J. Med. Chem.*, 1973, 16, 1314.

13. Y. C. Martin, T. M. Bustard, and K. Riley-Lynn, *J. Med. Chem.*, 1973, 16, 1089.

14. A. Brunmark and E. Cadenas, *Free Rad. Biol. Med.*, 1989, 7, 435.

15. H. Sies, *Angew. Chem. Int. Ed. Engl.*, 1986, 25, 1058.

16. K. Kappus, *Biochem. Pharmacol.*, 1986, 35, 1.

17. P. E. Brown, R. A. Lewis, and M. A. Waring, *J. Chem. Soc. Perkin Trans. 1*, 1990, 2979.

18. S. Capelle, B. Planckaert, P. Cotelle, and J. P. Catteau, *J. Chim. Phys.*, 1992, 89, 561.

19. P. Barker, P. Finke, and K. Thompson, *Synth. Commun.*, 1989, 19, 257.

20. P. Spagnolo, M. Tiecco, A. Tundo, and G. Martelli, *J. Chem. Soc. Perkin Trans. 1*, 1972, 556.

21. P. A. Plé and L. J. Marnett, *J. Heterocyclic Chem.*, 1988, 25, 1271.

22. J. E. Nordlander, D. B. Catalane, K. D. Kotian, R. M. Stevens, and J. E. Haky, *J. Org. Chem.*, 1981, 46, 778.

23. R. B. Mitra, K. Rabindran, and B. D. Tilak, *Curr. Sci. Ind.*, 1954, 23, 263.

24. P. Jacob, P. S. Callery, A. T. Shulgin, and N. Castagnoli, *J. Org. Chem.*, 1976, 41, 3627.

25. L. Syper, K. Kloc, J. Mlochowski, and Z. Szulc, *Synthesis*, 1979, 521.

26. L. Testaferri, M. Tiecco, M. Tingoli, D. Chianelli, and M. Montanucci, *Synthesis*, 1983, 751.

27. P. Jacob, G. Anderson, C. K. Meshul, A. T. Shulgin, and N. Castagnoli, *J. Med. Chem.*, 1977, **20**, 1235.

28. A. Blackhall, and R. H. Thomson, *J. Chem. Soc.*, 1954, 3916.

29. T. Hirota, Y. Tashima, K. Sasaki, T. Namba, and S. Hayakawa, *Heterocycles*, 1987, **26**, 2717.

30. Y. H. C. Giza, K. A. Kun, and H. G. Cassidy, *J. Org. Chem.*, 1962, **27**, 679.

31. D. V. Rao, H. Ulrich, and A. A. R. Sayigh, *J. Org. Chem.*, 1975, **40**, 2549.

32. J. H. P. Schutte, J. A. K. Du Plessis, G. Lachmann, A. M. Viljoen, and H. D. Nelson, *J. Chem. Soc. Chem. Commun.*, 1989, 1290.

33. S. L. Vorobeva, and I. V. Magedov, *J. Chem. Research*, 1992, 70.

34. F. Seemann, E. Wiskott, P. Nicklaus, and F. Troxler, *Helv. Chim. Acta*, 1971, **54**, 2411.

35. L. F. Fieser and R. G. Kennely, *J. Am. Chem. Soc.*, 1935, **57**, 1611.

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