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B E L O N G I N G T O T H E P A P E R

Microwave-Assisted Copper-Catalyzed Preparation of Diaryl Chalcogenides

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General Experimental Details

All NMR experiments were carried out on a 400 MHz spectrometer (400 MHz for ¹H and 100 MHz for ¹³C) in CDCl₃. NMR chemical shifts are reported in ppm referenced to the solvent peak of CDCl₃ (7.26 ppm for ¹H and 77.16 ppm for ¹³C, respectively). ES mass spectra reported are for M⁺ ions of ⁸⁰Se and ¹³⁰Te. Microwave reactions were carried out in a Biotage Initiator 60 EXP focused microwave reactor equipped with an IR sensor for continuous monitoring of the reaction temperature. Melting points are uncorrected. 6-Bromo-2,2,4-trimethyl-1,2-dihydroquinoline (**8b**),¹ di-1-naphthyl ditelluride,² -diselenide,² -disulfide,² di-*n*-octyl ditelluride,³ -diselenide⁴ and -disulfide⁵ were prepared according to a literature procedure. Spectroscopic data for known compounds [diphenyl telluride,⁶ diphenyl selenide,⁷ diphenyl sulphide,⁸ 4-methylphenyl phenyl telluride (**1a**),⁹ 4-methylphenyl phenyl selenide (**1b**),¹⁰ 4-methylphenyl phenyl sulfide (**1c**),⁸ 1-naphthyl phenyl telluride (**2a**),¹¹ 1-naphthyl phenyl selenide (**2b**),¹⁰ 1-naphthyl phenyl sulfide (**2c**),⁸ 4-hydroxyphenyl phenyl telluride (**3a**),¹² 4-hydroxyphenyl phenyl selenide (**3b**),⁷ 4-hydroxyphenyl phenyl sulfide (**3c**),⁸ 4-(dimethylamino)phenyl phenyl telluride (**4a**),¹³ 4-(dimethylamino)phenyl phenyl selenide (**4b**),¹⁴ 4-(dimethylamino)phenyl phenyl sulfide (**4c**),¹⁵ phenyl 3-pyridyl selenide (**5b**),^{10,16} phenyl 3-pyridyl sulfide (**5c**),¹⁰ 4-bromophenyl phenyl selenide (**6**)¹⁰] were in good agreement with the reported data.

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Experimental and spectral data for compounds 5a, 7a, and 7b

Phenyl 3-Pyridyl Telluride (5a): Purification was carried out by flash chromatography using pentane and ethyl acetate (85:15) as eluent. ^1H NMR δ 8.86 (dd, J = 1.0, 2.0, 1H), 8.50 (dd, J = 1.6, 4.8, 1H), 7.95 (dm, J = 1.8, 1H), 7.68 (m, 2H), 7.12-7.26 (several peaks, 4H). ^{13}C NMR δ 157.2, 148.8, 145.0, 138.6, 129.8, 128.5, 124.8, 113.5, 112.6. Anal. Calcd. for $\text{C}_{11}\text{H}_9\text{NTe}$: C, 46.72; H, 3.21, Found: C, 46.72; H, 3.20.

4-Hydroxyphenyl *n*-Octyl Selenide (7a). Purification was carried out by using flash chromatography on silica, eluting with ethyl acetate and pentane (1:19) to give the title compound **7a** as a white solid: mp 55 – 57 °C. ^1H NMR δ 7.42 (d, J = 8.6, 2H), 6.74 (d, J = 8.6, 2H), 4.79 (s, 1H), 2.81 (t, J = 7.6, 2H), 1.63 (m, 2H), 1.36-1.25 (several peaks, 10H), 0.87 (t, J = 6.6, 3H). ^{13}C NMR δ 14.2, 22.8, 29.2, 29.3, 29.3, 29.9, 30.3, 31.9, 116.2, 120.6, 135.8, 115.2. Anal. Calcd. for $\text{C}_{14}\text{H}_{22}\text{OSe}$: C, 58.96; H, 7.78. Found: C, 58.97; H, 7.81.

4-Hydroxyphenyl *n*-Octyl Sulfide (7b). Purification was carried out by using flash chromatography on silica, eluting with ethyl acetate and pentane (1:19) to give the title compound **7b** as a white solid, mp 72 – 74 °C. ^1H NMR δ 7.28 (d, J = 8.7, 2H), 6.78 (d, J = 8.7, 2H), 5.30 (b s, 1H), 2.82 (t, J = 7.4, 2H), 1.61 (m, 2H), 1.39-1.26 (several peaks, 10H), 0.88 (t, J = 6.9, 3H). ^{13}C NMR δ 14.2, 22.8, 29.2, 29.3, 29.3, 29.9, 30.3, 31.9, 116.3, 120.6, 135.8, 155.2. Anal. Calcd. for $\text{C}_{14}\text{H}_{22}\text{OS}$: C, 70.54; H, 9.30. Found: C, 70.39; H, 9.11.

^1H NMR spectrum of **5a**

¹³C NMR spectrum of **5a**

¹H NMR spectrum of **7a**

¹³C NMR spectrum of **7a**

¹H NMR spectrum of **7b**

¹³C NMR spectrum of **7b**

¹H NMR spectrum of **8c**

¹³C NMR spectrum of **8c**

¹H NMR spectrum of **8d**

¹³C NMR spectrum of **8d**

13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃
Temp. 25.0 C / 298.1 K
File: phSequene_13C

PULSE SEQUENCE: s2pul
Relax. delay 3.000 sec
Pulse 125.8 degrees
Acq. time 1.815 sec
Width 18761.7 Hz
11936 repetitions
OBSERVE C13, 75.44 MHz
DECOUPLE H1, 300.03 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 16.0 hours

TH observe

```
Archive directory: /home/vnmr1/vnmrsys/data
Sample directory:
```

Pulse Sequence: s2pul

Solvent: CDCl₃

Temp. 25.0 C / 298.1 K

File: Phsquine3_1H

PULSE SEQUENCE: s2pul

Pulse 43.2 degrees

Acq. time 3.700 sec

Width 4800.8 Hz

16 repetitions

OBSERVE H1, 300.03 MHZ

DATA PROCESSING

Line broadening 0.2 Hz

FT size 65536

Total time 1 minute

¹³C NMR spectrum of **8e**

¹H NMR spectrum of **10b**

PULSE SEQUENCE: s2pul
Pulse 35.0 degrees
Acq. time 3.744 sec
Width 6000.6 Hz
32 repetitions
OBSERVE H1, 399.98 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 2 minutes

¹³C NMR spectrum of **10b**

¹H NMR spectrum of **10c**

^{13}C NMR spectrum of **10c**

¹H NMR spectrum of **10d**

¹³C NMR spectrum of **10d**

13C OBSERVE

Pulse Sequence: s2pul

Solvent: CDCl₃
Temp. 25.0 C / 298.1 K
File: PyOHSpH_13C

PULSE SEQUENCE: s2pul
Relax. delay 3.000 sec
Pulse 125.8 degrees
Acq. time 1.815 sec
Width 18761.7 Hz
10880 repetitions
OBSERVE C13, 75.44 MHz
DECOUPLE H1, 300.03 MHz
Power 37 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 14.6 hours