# Nickel-catalysed Decarbonylation of Thioesters

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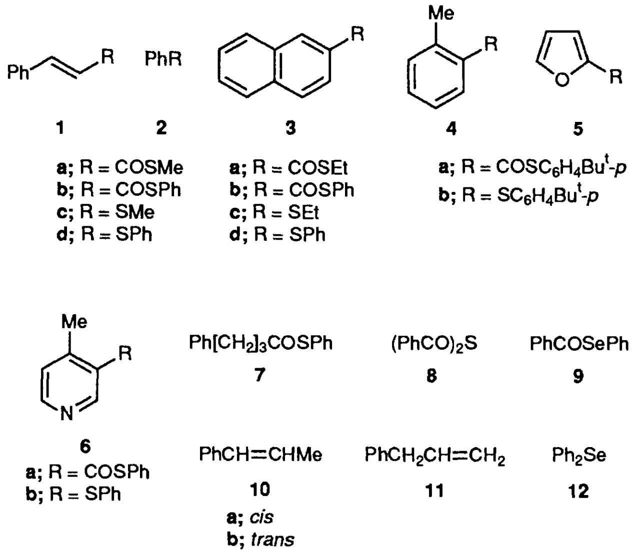
A new method of synthesis of vinyl aryl sulphides and diaryl sulphides from α,β-unsaturated and aroyl thioesters by low-valent nickel-mediated decarbonylation is presented.

In continuation of an extended study of the behaviour of vinyl and aryl sulphides towards low-valent nickel species[1] an investigation of the reactions of various thioesters (ArCH=CHCOSR, ArCOSR) under the influence of the latter transition metal has been undertaken. An earlier study of aliphatic and alicyclic α-pyridyl thiocarboxylates had shown that their exposure to zinc and nickel dichloride in dimethylformamide (DMF) leads to loss of the carbonylthiopyridine unit and the formation of alkenes.[2] Since this observation implied ready insertion of nickel into the carbonyl–sulphur bond system and decarbonylation of carboxylic acid derivatives, it suggested that standard thioesters might be vulnerable to decarbonylation without loss of other groups and thus be transformable into sulphides in a reaction scheme of use in organochemical synthesis. The data in Table 1 illustrate that this hope now has been realized.

**Table 1** Decarbonylation of thioesters and related compounds[a]

| Starting compound | Reaction temp./°C | Reaction time/h | Product | Product yield (%) |
|---|---|---|---|---|
| **1a** | 23 | 3 | **1c**[j] | 79 |
| **1b** | 23 | 1 | **1d**[k] | 79 |
| **2a**[b] | 23 | 0.8 | **2c** | 63 |
| **2b**[c] | 80 | 6 | **2d** | 79 |
| **3a**[d,e] | 23 | 20 | **3c**[l] | 73 |
| **3b**[c] | 50 | 18 | **3d**[m] | 71 |
| **4a** | 50 | 20 | **4b** | 55[o] |
| **5a** | 10 | 0.5 | **5b** | 49 |
| **6a** | 23 | 48 | **6b** | 86[o] |
| **7**[f] | 23 | 1.5 | 1.5 : 1.5 : 1 **10a**[n]–**10b**[n]–**11** | 61 |
| **8**[g,h] | 50 | 20 | 3 : 1 **2b–2d** | 42 |
| **9**[i] | 50 | 48 | **12** | 76 |

[a] With $NiCl_2 \cdot 6H_2O$ (2 equiv.), activated Zn dust (2 equiv.) and $Ph_3P$ (8 equiv.) in DMF (ref. 3). [b] Ref. 4. [c] Ref. 5. [d] Ref. 6. [e] Starting material recovered in a reaction without $NiCl_2 \cdot 6H_2O$. [f] Starting material recovered, when $Ph_3P$ was replaced by $Ph_2P[CH_2]_3PPh_2$. [g] Ref. 7. [h] The use of 4 equiv. of the nickel species produces a 2 : 1 mixture (95% yield) of biphenyl and benzophenone, a result not observed in the decarbonylation of **2b** under these conditions. [i] Ref. 8. [j] Ref. 9. [k] Ref. 10. [l] Ref. 11. [m] Ref. 12. [n] Ref. 13. [o] Based on consumed starting thioester.



The decarbonylations of thioesters were carried out in DMF solution at relatively mild temperature with the use of an excess of low-valent, triphenylphosphine-ligated nickel species (zinc and nickel dichloride) and furnished products in medium to good yields. Thus, thioesters of cinnamic (**1a**,**1b**), benzoic (**2a**,**2b**) and β-naphthoic (**3a**,**3b**) acids were converted into β-thiostyrenes (**1c**,**1d**) and diaryl sulphides (**2c**,**2d**,**3c**,**3d**), respectively. The transformation of a thioester of *o*-toluic acid (**4a**) into a diaryl sulphide (**4b**) shows that steric hindrance plays only a minimal role in the reaction. The success of decarbonylation of a furoic acid derivative (**5a** → **5b**) indicates strong preference of oxidative addition of the nickel species at the carbonyl–sulphur site over insertion into the furan carbon–oxygen bond centre.[1] Finally, the possible ligation of the nickel nucleus by pyridines had no ill effect on the reaction, as revealed by the decarbonylation of the γ-methylnicotinic acid derivative (**6a** → **6b**).

All the above decarbonylations were executed on thioesters whose carbonyl carbon is attached to an $sp^2$-hybridized carbon site. Had this not been the case, *i.e.* had thioesters of saturated acids been employed, alkene products (instead of sulphides) would have been expected.[2,14] Thus, the conversion of the γ-phenylbutyric acid derivative **7** into the propenylbenzenes **10** and allylbenzene **11** was expected and represents a limitation to the method of sulphide synthesis. When the nickel-induced reaction was performed on a thioanhydride **8**, the loss of both one and two equivalents of carbon monoxide was observed, thioester **2b** and sulphide **2d** being produced.[15] Finally, an aroyl selenide **9** behaved like its sulphur analogue **2b**, decarbonylation leading to diphenyl selenide **12**.

Whereas the mechanism of the carbonyl extrusion process remains unproven (and no nickel-bearing intermediate has been isolated), it most likely involves oxidative addition of $(Ph_3P)_2Ni^0$ to the thioesters, rearrangement of the resultant $ArCONiSR(Ph_3P)_2$ complex (or its alkenic equivalent) into the complex $ArNiCO(SR)(Ph_3P)$ (and $Ph_3P$), and reductive elimination of a phosphine-ligated nickel carbonyl species with the liberation of aryl (or alkenyl) thioether products.

In summary, an experimentally simple procedure for the conversion of α,β-unsaturated or aromatic acids into deacylated sulphides (*via* thioesters) is in hand.[16,17]

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## References

1 E. Wenkert, T. W. Ferreira and E. L. Michelotti, *J. Chem. Soc., Chem. Commun.*, 1979, 637; E. Wenkert and T. W. Ferreira, *J. Chem. Soc., Chem. Commun.*, 1982, 840; M. Tiecco, L. Testaferri, M. Tingoli, D. Chianelli and E. Wenkert, *Tetrahedron Lett.*, 1982, 4529; M. Tiecco, L. Testaferri, M. Tingoli and E. Wenkert, *Tetrahedron*, 1983, **39**, 2289; E. Wenkert, M. H. Leftin and E. L. Michelotti, *J. Chem. Soc., Chem. Commun.*, 1984, 617; E. Wenkert, J. M. Hanna, Jr., M. H. Leftin, E. L. Michelotti, K. T. Potts and D. Usifer, *J. Org. Chem.*, 1985, **50**, 1125; M. Tiecco, M. Tingoli and E. Wenkert, *J. Org. Chem.*, 1985, **50**, 3825; E. Wenkert, M. E. Shepard and A. T. McPhail, *J. Chem. Soc., Chem. Commun.*, 1986, 1390; E. Wenkert and A. Han, *Heterocycles*, 1990, **30**(2), 929.

2 T. Goto, M. Onaka and T. Mukaiyama, *Chem. Lett.*, 1980, 709.

3 M. Tiecco, L. Testaferri, M. Tingoli, D. Chianelli and M. Montanucci, *Synthesis*, 1984, 736; M. Tiecco, M. Tingoli, L. Testaferri, D. Chianelli and E. Wenkert, *Tetrahedron*, 1986, **42**, 1475.

4 I. B. Douglass and C. E. Osborne, *J. Am. Chem. Soc.*, 1953, **75**, 4582.

5 K. Miyaki and S. Yamagishi, *J. Pharm. Soc. Jpn.*, 1956, **76**, 436.

6 H. Hauptmann, B. Wladislaw, L. L. Nazzario and W. F. Walter, *Liebigs Ann. Chem.*, 1952, **576**, 45.

7 M. Mikolajczyk, P. Kielbasiñski and H. M. Schiebel, *J. Chem. Soc., Perkin Trans. 1*, 1976, 564.

8 T. G. Back, S. Collins and R. G. Kerr, *J. Org. Chem.*, 1981, **46**, 1564.

9 W. E. Truce, J. A. Simms and M. M. Boudakian, *J. Am. Chem. Soc.*, 1956, **78**, 695.

10 L. I. Smith and H. R. Davis, Jr., *J. Org. Chem.*, 1950, **15**, 824.

11 J. Jacques, *Bull. Soc. Chim. Fr.*, 1955, 231.

12 A. H. Weinstein and R. M. Pierson, *J. Org. Chem.*, 1958, **23**, 554.

13 M. J. S. Dewar and R. C. Fahey, *J. Am. Chem. Soc.*, 1963, **85**, 3645.

14 *Cf.* K. Ohno and J. Tsuji, *J. Am. Chem. Soc.*, 1968, **90**, 99; J. Blum, S. Kraus and Y. Pickholtz, *J. Organomet. Chem.*, 1971, **33**, 227.

15 *Cf.* B. M. Trost and F. Chen, *Tetrahedron Lett.*, 1971, 2603.

16 For a related study involving $Pd^0$- and $Rh^I$-mediated chemistry see K. Osakada, T. Yamamoto and A. Yamamoto, *Tetrahedron Lett.*, 1987, 6321.

17 In view of the ease of nickel-induced sulphur extrusion (E. Wenkert and M. E. Shepard, unpublished observations; M. E. Shepard, Ph.D. dissertation, University of California-San Diego, 1985) caution must be exercised not to cause overreaction of the thioester.