

Desulphurisation–Dimerisation of Dithioacetals with $W(CO)_6$

Lam Lung Yeung, Yu Chi Yip, and Tien-Yau Luh*

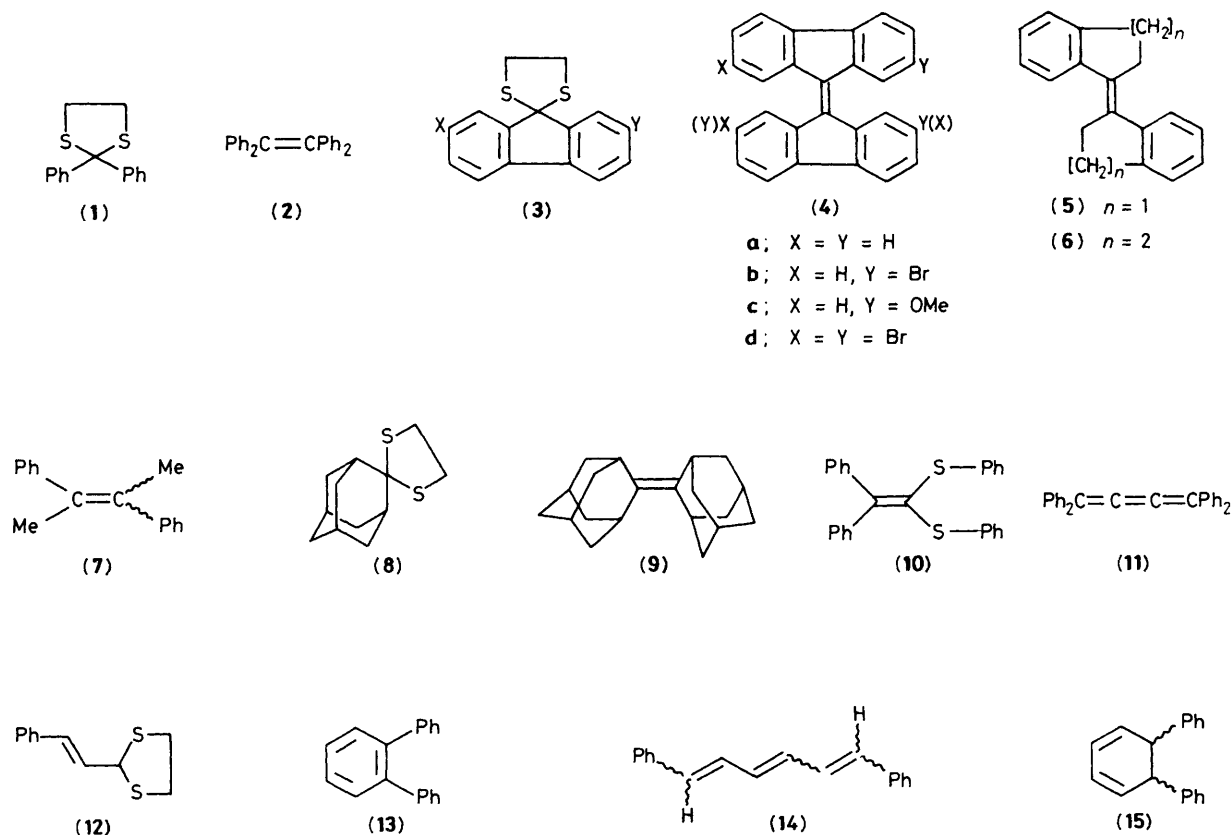
Department of Chemistry, The Chinese University of Hong Kong, Shatin, N.T., Hong Kong

Dithioacetals undergo desulphurisation–dimerisation to give the corresponding dimeric alkenes in good to excellent yields on treatment with $W(CO)_6$.

The dithioacetal functionality is generally used in organic synthesis as a latent carbonyl or methylene group.¹ There are only a few reports of the transformation of dithioacetals into other functions.² It is noted that thiones can react with a carbene precursor such as a diazoalkane to give the corresponding dithioacetals.³ The back reaction considering dithioacetal as the carbene synthon has not been explored. We recently reported that certain reactive carbon–sulphur bonds can be selectively reduced upon treatment with $Mo(CO)_6$ in

tetrahydrofuran (THF).⁴ Dimeric alkenes were sometimes obtained as the by-products from the corresponding dithioacetals. We now describe a useful synthetic procedure for the desulphurisation–dimerisation of dithioacetals. The reaction can also be considered as coupling of two carbonyl equivalents.⁵

In a typical procedure, the organosulphur compounds were mixed with two equivalents of $W(CO)_6$ in chlorobenzene and the mixture was heated under reflux for 24–48 h followed by



chromatographic separation to give the desired products.[†] Thus, the dithioacetal of benzophenone, (1), afforded tetraphenylethene (2) in 97% yield. The dithioacetals derived from fluorenone (3) yielded bifluorenylidenes (4) isolated in excellent yields (a 93%; b 93%; c 88%; d 96%). It is noted that approximately equal amount of *syn* and *anti* isomers were obtained from the reaction of 2-substituted fluorenone derivatives.[‡]

Stilbene was obtained in 45% yield from the reaction with benzaldehyde dithioacetal. In a similar manner, dithioacetals of indanone and tetralone yielded the corresponding dimers

(5) and (6) in 62 and 61% yields, respectively. In all these examples, only (*E*)-isomers were obtained.[§] However, both (*E*)- and (*Z*)-2,3-diphenylbut-2-enes (7)[‡] were isolated in 59% yield in a ratio of 1:1 from the reaction of the dithioacetal of acetophenone with W(CO)₆. It is interesting that the yields of the reaction with monoaryl derivatives were apparently lower than those with diaryl compounds. Presumably, the aryl groups stabilize the reactive intermediate which could be a carbenoid species.⁶

In contrast to molybdenum mediated reactions,³ W(CO)₆ seems to be more reactive for the cleavage of C–S bonds. Thus, the adamantane-2-one dithioacetal (8) gave 2,2'-biadamantylidene (9) in 71% yield while (8) was inactive upon treatment with Mo(CO)₆ under various conditions.³

It is noteworthy that ketene dithioacetal can also smoothly be transformed into cumulene. Hence, the diphenylketene derivative (10) was allowed to react with W(CO)₆ under similar conditions to give tetraphenylbutatriene (11) in 75% yield.

The coupling reaction of an aromatic α,β-unsaturated aldehyde derivative leads to substituted benzenes. The dithioacetal of cinnamaldehyde (12), when treated with W(CO)₆ in chlorobenzene under reflux for 48 h, afforded 1,2-diphenylbenzene (13) in 40% yield. Interestingly, 1,6-diphenylhexatriene (14) was not obtained from this reaction mixture and may presumably undergo thermal cyclization to give the intermediate cyclohexadiene (15) which spontaneously dehydrogenates under the reaction conditions to afford (13).

[†] Selected data: (2): m.p. 222–223 °C;⁷ (4a): m.p. 191–192 °C;⁴ (4b): ¹H n.m.r. δ (CDCl₃) 8.47 [s, 2H, 1-, 1'-H, of *anti* isomer, 18% nuclear Overhauser enhancement (n.o.e.) upon irradiation at δ 8.28], 8.43 [s, 2H, 1-, 1'-H of *syn* isomer, no n.o.e. upon irradiation at δ 8.35], 8.35 (d, *J* 7.5 Hz, 8-, 8'-H of *syn* isomer), 8.28 (d, *J* 7.5 Hz, 8-, 8'-H of *anti* isomer), 7.2–7.7 (m, other aromatic protons for both *syn* and *anti* isomers); *m/z* 484, 486, 488; (4c): ¹H n.m.r. δ (CDCl₃) 8.39 (d, *J* 7.5 Hz, 2H, 8-, 8'-H of *anti* isomer), 8.31 (d, *J* 7.5 Hz, 2H, 8-, 8'-H of *syn* isomer) 8.04 (d, *J* 2 Hz, 2H, 1-, 1'-H of *syn* isomer, no n.o.e. upon irradiation at δ 8.31), 7.97 (d, *J* 2 Hz, 2H, 1-, 1'-H of *anti* isomer, 16% n.o.e. upon irradiation at δ 8.39), 6.8–7.6 (m, other aromatic protons), 3.77 and 3.78 (OMe for both *syn* and *anti* isomer); *m/z* 388, 1451; (4d): m.p. >320 °C (lit.⁸ 429 °C); ¹H n.m.r. δ (CDBr₃) 8.34 (d, *J* 1.5 Hz, 4H), 7.61 (d, *J* 8 Hz, 4H), 7.52 (dd, *J* 8, 1.5 Hz); *m/z* 640, 642, 644, 646, 648; (5): m.p. 142–143 °C;⁹ ¹H n.m.r. δ (CDCl₃) 2.16 (br.s, 8H), 7.20 (4H, m), 7.32 (2H, m), 7.64 (2H, d, *J* 7.5 Hz); *m/z* 232, 116; (6): m.p. 120–123 °C;¹⁰ ¹H n.m.r. δ (CDCl₃) 1.80 (m, 4H), 2.77 (m, 8H), 7.00–7.60 (m, 8H); *m/z* 260, 130; (7): ¹H n.m.r. δ (CDCl₃) 1.90 (s, 3H, *syn* isomer), 2.20 (s, 3H, *anti* isomer);⁷ (9): m.p. 183–184 °C;¹¹ (11): m.p. 234–237 °C;¹¹ (13): m.p. 54–56 °C.¹²

[‡] Attempts to separate the isomers were unsuccessful and the isomeric ratios were determined by n.m.r. spectroscopy.

[§] The stereochemical assignment is based on n.m.r. spectroscopy. For (*Z*)-isomers, the ¹H n.m.r. resonances for 7-, 7'-H in (5) and 8-, 8'-H in (6) should appear at much lower field.

We thank the Croucher Foundation for generous support and United College, The Chinese University of Hong Kong, for partial support.

Received, 19th January 1987; Com. 055

References

- 1 T. W. Greene, 'Protective Groups in Organic Synthesis,' Wiley, New York, 1981, p. 129.
- 2 S. R. Wilson, G. M. Georgiadis, K. N. Khatri, and J. E. Bartmess, *J. Am. Chem. Soc.*, 1980, **102**, 3577.
- 3 A. Schonberg, B. Konig, and E. Einger, *Chem. Ber.*, 1967, **100**, 767; A. Ohno, Y. Ohnishi, M. Fukuyama, and G. Tsuchihashi, *J. Am. Chem. Soc.*, 1968, **90**, 7038.
- 4 T.-Y. Luh and C. S. Wong, *J. Org. Chem.*, 1985, **50**, 5413.
- 5 Y.-H. Lai, *Org. Prep. Proced. Int.*, 1980, **12**, 361; J. E. McMurry, *Acc. Chem. Res.*, 1983, **16**, 405.
- 6 Cf., J. Daub, E. Erhardt, K. H. Jogun, J. Kappler, A. Laumer, R. Pfiz, and J. J. Stezowske, *Chem. Ber.*, 1982, **115**, 1787.
- 7 J. E. McMurry, M. P. Fleming, K. L. Kees, and L. R. Krepski, *J. Org. Chem.*, 1978, **43**, 3255.
- 8 K. Suzuki, M. Minabe, M. Fujimoto, and N. Nohara, *Bull. Chem. Soc., Jpn.*, 1969, **42**, 1609.
- 9 J. Saltiel and J. T. D'Agostino, *J. Am. Chem. Soc.*, 1972, **94**, 6445.
- 10 A. K. Banerjee, M. C. Sulbaran de Carrasco, C. S. V. Frydrych-Houge, and W. B. Motherwell, *J. Chem. Soc., Chem. Commun.*, 1986, 1803.
- 11 K. Brand, *Chem. Ber.*, 1921, **54**, 1987.
- 12 W. E. Bachmann and H. T. Clarke, *J. Am. Chem. Soc.*, 1927, **49**, 2095.