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

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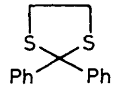
Dithioacetals undergo desulphurisation–dimerisation to give the corresponding dimeric alkenes in good to excellent yields on treatment with $W(CO)_6$.

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]

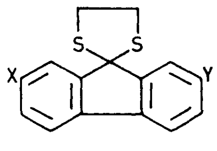
In a typical procedure, the organosulphur compounds were mixed with two equivalents of $W(CO)_6$ in chlorobenzene and the mixture was heated under reflux for 24—48 h followed by



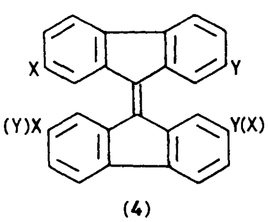
(1)

$Ph_2C{=}CPh_2$

(2)

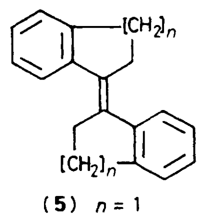


(3)

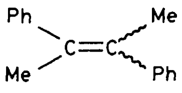


(4)

a; X = Y = H
b; X = H, Y = Br
c; X = H, Y = OMe
d; X = Y = Br



(5) $n = 1$
(6) $n = 2$



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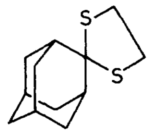

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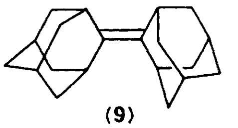

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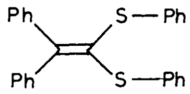
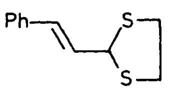


(10)

$Ph_2C{=}C{=}C{=}CPh_2$

(11)



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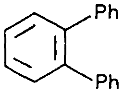

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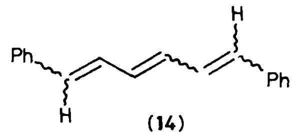

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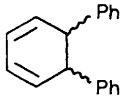

(15)

chromatographic separation to give the desired products.† Thus, the dithioacetal of benzophenone, (**1**), afforded tetraphenylethene (**2**) in 97% yield. The dithioacetals derived from fluoreneone (**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 adamantan-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**).

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† *Selected data:* (**2**): m.p. 222—223 °C;[7] (**4a**): m.p. 191—192 °C;[4] (**4b**): ^{1}H n.m.r. δ ($CDCl_3$) 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**): ^{1}H n.m.r. δ ($CDCl_3$) 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); ^{1}H n.m.r. δ ($CDBr_3$) 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] ^{1}H n.m.r. δ ($CDCl_3$) 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] ^{1}H n.m.r. δ($CDCl_3$) 1.80 (m, 4H), 2.77 (m, 8H), 7.00—7.60 (m, 8H); *m/z* 260, 130; (**7**): ^{1}H n.m.r. δ($CDCl_3$) 1.90 (s, 3H, *syn* isomer), 2.20 (s, 3H, *anti* isomer);[7] (**9**): m.p. 183—184 °C[7]; (**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 ^{1}H 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

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