Cycloaddition of $Bu^n{}_3P \cdot CS_2$: Direct One-pot Conversion of Strained Double Bonds to 2-Alkylidene-1,3-dithiolanes

R. Alan Aitken,* Tracy Massil and Swati V. Raut

School of Chemistry, University of St. Andrews, North Haugh, St. Andrews, Fife, UK KY16 9ST

Reaction of the strained double bond in bicyclo[2.2.1]heptene systems with $Bu^n{}_3P \cdot CS_2$ and an aldehyde provides convenient access to the corresponding 2-alkylidene-1,3-dithiolanes.

Although the red crystalline adducts formed between trialkylphosphines and CS_2 have been known for well over 100 years,[1] their chemistry has been little investigated. Reaction of the tri-*n*-butylphosphine adduct **1** with electron deficient alkynes leads to cycloaddition across the two sulfur atoms to give 2-tri-*n*-butylphosphoranylidene-1,3-dithioles which can be trapped by inter-[2] or intra-molecular[3] protonation or by *in situ* Wittig reaction with an added aldehyde.[4] In the absence of any trap, we have shown that 2:1 adducts with a stabilised ylide structure are formed.[5] Only one report of the interaction of **1** with a double bonded compound has appeared: the reaction with dimethyl maleate in MeOH which produced dimethyl succinate, $Bu^n{}_3PO$, CS_2 and dimethyl ether.[4] On the basis of recent experiments, we believe that this does not involve a cycloaddition but rather conjugate addition of $Bu^n{}_3P$, formed by dissociation of **1**, followed by methanolysis of the resulting stabilised ylide. We now report the first cycloaddition of **1** to alkene double bonds.

While **1** was unreactive towards a wide variety of alkenes including styrene, stilbene, hex-1-ene, cyclohexene and cyclopentene, it reacted rapidly at room temperature with norbornene in diethyl ether to give a pink precipitate. On the basis of analytical and spectroscopic properties,† particularly the observation of ^{13}C NMR signals at δ 240.1 ($^2J_{CP}$ 8 Hz) and 90.9 ($^1J_{CP}$ 39 Hz), this appears to be a 1 : 1 adduct + CS_2 with the novel zwitterionic structure **3**. The *exo* configuration of the dithiolane ring follows from the configuration of the Wittig products described below, but the *exo*/*endo* configuration of the $Bu^n{}_3P^+$ and CS_2^- groups and indeed the state of bonding within this part of the molecule remains uncertain. The thiaphosphetane structure cannot be ruled out. The formation of **3** is readily understood as resulting from initial formation of the expected 1 : 1 adduct **2** which is then stabilised by attack on a second molecule of **1** with displacement of $Bu^n{}_3P$, which was indeed found in the filtrate from the reaction. It is notable that **3** is formed even with a 1 : 1 ratio of norbornene to **1**, the precipitation of **3** obviously providing the driving force for the reaction.

Although **3** is essentially insoluble in diethyl ether, it dissolves readily in CH_2Cl_2 and in this solvent dissociates significantly to regenerate **2**. Thus, addition of benzaldehyde to a solution of **3** in CH_2Cl_2 affords the expected Wittig product **4** in moderate yield. The same product can be obtained by directly reacting norbornene, **1** and PhCHO in CH_2Cl_2, and indeed it is not even necessary to preform **1**: interaction of $Bu^n{}_3P$, CS_2, norbornene and PhCHO in CH_2Cl_2 at room temperature directly affords **4**. The small value of 2 Hz observed for the coupling between C*H*S and the bridgehead CH in **4** indicates the *exo* configuration shown.

The direct transformation of the double bond of norbornene to the 2-alkylidene-1,3-dithiolane of **4** in a one-pot procedure represents a valuable synthetic transformation. The same reaction also occurs for a variety of strained double bond compounds **5**, readily available from the Diels–Alder reaction of cyclopentadiene, to give the products **6** in moderate to good yield (Table 1). In most cases the products could be directly filtered off in pure form after stirring a solution of the reactants in CH_2Cl_2 at room temperature for 24 h. The reaction at only one double bond in dicyclopentadiene **5f** provides further evidence of the selectivity for strained double bonds. Even the two carbon bridged cyclohexa-1,3-diene–maleic anhydride adduct corresponding to **5a** did not react with **1** and the system seems to be very sensitive to the degree of ring strain present. The reaction can also be carried out using MeCHO or Pr^iCHO in place of PhCHO, but ketones do not react under the conditions so far examined.

With norbornadiene, **1** also reacts rapidly in diethyl ether to form a pink precipitate **8**. Elemental analysis of this indicates a gross composition corresponding to the expected **7** + $2CS_2$ but it is insoluble in any common solvent and has an unknown,

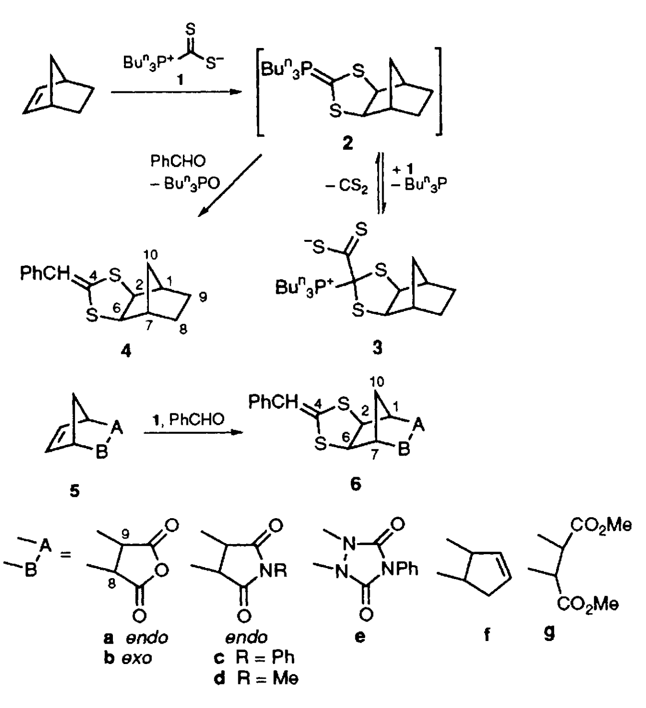
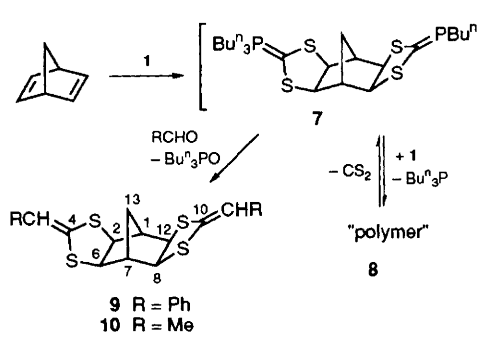


Table 1 Formation of 2-alkylidene-1,3-dithiolanes

Product	Yield (%)	mp/°C	Product	Yield (%)	mp/°C
4	44	77–78	**6e**	91	313–314
6a	80	185–186	**6f**	39	65–67
6b	74	264–265	**6g**	16	105–107
6c	43	157–159	**9**	71	214–216
6d	46	246–247	**10**	70	(oil)



possibly polymeric, structure. If the reaction of **1** with norbornadiene is instead performed in CH_2Cl_2 in the presence of an aldehyde, the expected bis-dithiolanes **9** and **10** are formed in good yield as a mixture of (*E*)- and (*Z*)-isomers.

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Footnote

† All new compounds gave satisfactory microanalytical data.

Selected physical and spectroscopic data for **3**, **4**, **6a** and **9**.

3: Pink powder; mp 106–108 °C; ^{13}C NMR (75 MHz, $CDCl_3$): δ 240.1 (d, $^{2}J_{CP}$ 8 Hz; CS_2^{-}), 90.9 [d, $^{1}J_{CP}$ 39; C(4)], 67.4 [s; C(2), C(6)], 43.4 [s; C(1), C(7)], 32.6 [s; C(10)], 27.3 [s; C(8), C(9)], 25.8 [d, $^{2}J_{CP}$ 8; Bu C(2)], 24.9 [d, $^{3}J_{CP}$ 14; Bu C(3)], 21.1 [d, $^{1}J_{CP}$ 43; Bu C(1)] and 14.0 [s; Bu C(4)]; ^{31}P NMR (32 MHz, $CDCl_3$ H_3PO_4 ext.): δ +41.7; MS (70 eV): *m*/*z* 416 (M^{+}–S, 4%), 372 (M^{+}–CS_2, 2).

4: Colourless crystals; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.4–7.25 (4H, m, Ph), 7.14 (1 H, m, Ph), 6.50 (1 H, s, C*H*Ph), 3.99 and 3.70 [(2H, AB pattern of d, *J* = 8 and 2 Hz, C(2)–H, C(6)–H], 2.32 (2 H, m), 1.95 (1 H, m), 1.6–1.5 (2 H, m) and 1.25–1.1 (3 H, m); ^{13}C NMR: δ 139.7 [C(4)], 137.3 [Ph C(1)], 128.1 [Ph C(3), C(5)], 127.5 [Ph C(2), C(6)], 125.7 [Ph C(4)], 115.1 (*C*HPh), 63.6 and 57.3 [C(2), C(6)], 45.4 and 45.2 [C(1), C(7)], 32.1 [C(10)], 27.8 and 27.5 [C(8), C(9)]; MS (70 eV): *m*/*z* 260 (M^{+}, 10%).

6a: Colourless crystals; ^{1}H NMR: δ 7.4–7.2 (m, 5 H; Ph), 6.62 (s, 1 H; C*H*Ph), 4.20 and 3.93 [2 H, AB pattern of d, *J* = 8 and 2 Hz, C(2)–H, C(6)–H], 3.6–3.5 (2H, m), 3.0–2.9 (2H, m) and 2.38 and 1.67 [2H, AB pattern, *J* = 12 Hz, C(10)–H_2]; ^{13}C NMR: δ 170.8 (CO), 137.5 [C(4)], 137.2 [Ph C(1)], 128.9 [Ph C(3), C(5)], 128.5 [Ph C(2), C(6)], 127.3 [Ph C(4)], 118.9 (*C*HPh), 59.0 and 53.1 [C(2), C(6)], 49.3, 49.1 (2 C) and 48.9 [C(1), C(7), C(8), C(9)] and 37.2 [C(10)]; MS (70 eV): *m*/*z* 330 (M^{+}, 100%).

9: Colourless crystals; ^{1}H NMR: δ 7.4–7.25 (8H, m, Ph), 7.18 (2H, m, Ph), 4.05 and 3.77, 4.03 and 3.74 [2H, AB patterns for (*E*)- and (*Z*)-isomers, *J* = 8 Hz, C(2)–H, C(6)–H, C(8)–H, C(12)–H], 2.52 [2H, m, C(1)–H, C(7)–H] and 1.99 [2H, m C(13)–H_2]; ^{13}C NMR: δ (*E*)-isomer 139.7 [C(4), C(10)], 137.1 [Ph C(1)], 128.3 [Ph C(3), C(5)], 127.9 [Ph C(2), C(6)], 126.4 [Ph C(4)], 117.0 (*C*HPh), 61.4 and 55.2 [C(2), C(6), C(8), C(12)], 53.9 [C(1), C(7)] and 27.0 [C(13)]; δ (*Z*)-isomer 138.2 [C(4), C(10)], 137.1 [Ph C(1)], 128.3 [Ph C(3), C(5)], 127.9 [Ph C(2), C(6)], 126.4 [Ph C(4)], 117.0 (*C*HPh), 61.2 and 55.4 [C(2), C(6), C(8), C(12)], 54.1 and 53.6 [C(1), C(7)] and 27.0 [C(13)]; MS (70 eV): *m*/*z* 424 (M^{+}, 75%).

References

1 A. W. Hofmann, *Liebigs Ann. Chem. Suppl.*, 1861, **1**, 1.

2 M. Sato, N. C. Gonella and M. P. Cava, *J. Org. Chem.*, 1979, **44**, 930.

3 C. Pittman and M. Narita, *J. Chem. Soc., Chem. Commun.*, 1975, 960.

4 H. D. Hartzler, *J. Am. Chem. Soc.*, 1971, **93**, 4961.

5 R. A. Aitken, G. Ferguson and S. V. Raut, *J. Chem. Soc., Chem. Commun.*, 1991, 812; R. A. Aitken, S. V. Raut and G. Ferguson, *Tetrahedron*, 1992, **48**, 8023.