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THE CYCLOADDITION REACTION OF 3,4-DIMETHYL-1-THIO-1-PHENYLPHOSPHOLE WITH TROPONE

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Abstract—3,4-Dimethyl-1-thio-1-phenylphosphole reacts, under elevated temperatures, with tropone to give two [4+2] isomeric adducts: *Endo-syn*-5,6-dimethyl-3-thio-3-phenyl-3-phosphatricyclo $[5.3.2.0^{2,6}]$dodec-4,8,11-trien-10-one (1) and *Endo-anti*-5,6-dimethyl-3-thio-3-phenyl-3-phosphatricyclo$[5.3.2.0^{2,6}]$dodec-4,9,11-trien-8-one (2). In addition to the *endo-exo,syn-anti* relationship the phosphorus configuration in 1, 2 and some derivatives was also elucidated by means of NMR-shift reagents and ${}^{2}J_{PH}$ coupling constants.

Various [4+2] and [6+4] cycloaddition reactions of tropones have recently been extensively studied. Thus cyclopentadiene,[1] for example, and some of its derivatives[2] form mainly [6+4] adducts with tropone at room temperature, whereas at elevated temperatures the [4+2][2,3] adducts predominate.

Being interested in the behaviour of phospholes in cycloaddition reactions, the addition of 3,4-dimethyl-1-thio-1-phenylphosphole[4] to tropone[5] was investigated. A solution of equimolar quantities of phosphole and tropone in methyl propylketone heated for 4–6 days at 100° under nitrogen gave two major products (1 and 2). (No reaction occurred under milder conditions, i.e. 25°–60° for several days.)

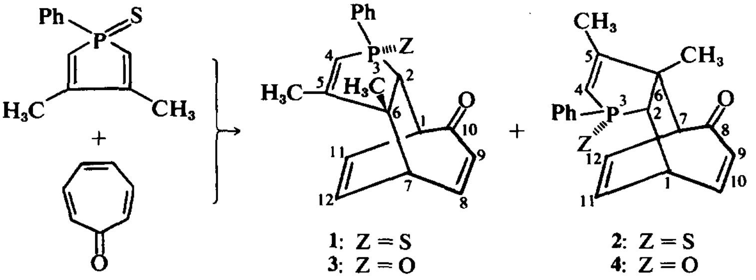
Compounds 1 (m.p. 162°–163°) and 2 (m.p. 195°–196°) were separated on a neutral alumina column and were shown to be the 1:1 adducts of the phosphole and tropone by elemental analysis and mass spectra ($M^{\oplus}$ *m/e* 326). The IR spectra (ν_{max}^{KBr} 1650, 1600 and 1655, 1600 (C=C—C=O) for 1 and 2 respectively) indicated an $\alpha\beta$-unsaturated CO group thereby cancelling out the possibility of a [6+4] cycloaddition reaction.

Six possible structures can be put forward for each one of the possible [4+2] adducts according either to the *exo-endo* configuration, the *syn-anti* relationship between the P-atom and the C=O group, and the two possible P-configurations. The decision as to which possible isomer was obtained, was provided by NMR data (Table 1a, b; Fig 1) recorded on 100 and 60 MHz instruments. The signal assignments in the NMR spectra of 1 and 2 were based on the chemical shifts but mainly on the proton-proton coupling constants deduced from a double irradiation experiment (on the 100 MHz instrument, see Table 1a, b), and on the phosphorus-proton coupling constants obtained by a heterospin decoupling experiment (on the 60 MHz instrument).

These NMR data proved unequivocally that compounds 1 and 2 are indeed the products of a $[4+2]\pi$ cycloaddition reaction in which the tropone was the diene and the phosphole the dienophile.

The difference between the two isomers (1 and 2) originates from the phospholenic moiety; in one isomer, the P-atom is *syn* in respect to the CO group, whereas in the other it is in the *anti* configuration.

The *endo* geometry suggested for the phospholenic moiety in both 1 and 2 is based on the following three facts: (a) The very small H(1), H(2), vicinal coupling constants (0 and 1·5 Hz for 1 and 2 respectively). (b) The ${}^{3}J_{PH(1)}$ values (14 and 9 Hz for 1 and 2 respectively) fit the expected



1: Z = S
3: Z = O

2: Z = S
4: Z = O

Table 1a. Chemical Shifts for Compounds 1–4 (δ ppm)

Compound	C_6-$\underline{CH}_3$	C_5-$\underline{CH}_3$	H_2	H_7	H_1	H_4	H_9	H_{11}	H_{12}	H_8	H_{10}	Ph H_α	Ph $H_{\beta,\gamma}$
1	1·33	2·00	2·43	3·50	4·33	5·81	5·84	6·18	6·41	7·01	—	7·76	7·41
	s	dd	d	ddd	ddm	dd	dd	ddd	ddd	dd		dm	m
3	1·37	2·03	2·37	3·50	4·12	5·95	5·85	6·30	6·45	7·02	—	7·66	7·48
	s	dd	d	ddd	ddm	dd	dd	ddd	ddd	dd		dm	m
2	1·36	2·02	2·63	3·66	3·98	5·81	5·79	6·68	6·04	—	7·15	7·83	7·45
	s	dd	dd	dd	dm	dd	dd	ddd	ddd		dd	dm	m
4	1·39	2·04	2·50	3·69	3·81	5·93	5·80	6·72	6·06	–	7·15	7·66	7·50
	s	dd	dd	dd	dm	dd	dd	ddd	ddd		dd	dm	m

Table 1b. Coupling Constants for Compounds 1–4 (Hz)

Compound	$^4J_{PH}$*	$^3J_{PH_1}$	$^2J_{PH_2}$	$^2J_{PH_4}$	$^2J_{PH_\alpha}$**	$H_{3,4}$	$H_{1,2}$	$H_{8,9}$	$H_{7,9}$***	$H_{7,8}$	$H_{7,12}$	$H_{7,11}$***	$H_{11,12}$	$H_{1,12}$***	$H_{1,11}$	$H_{1,10}$	$H_{1,9}$***	$H_{9,10}$
1	1·5	14·0	6·0	26·0	14·0	1·5	0·0	11·0	2·0	9·0	7·0	1·5	8·0	1·5	7·0	—	—	—
3	1·5	8·0	6·0	22·0	12·0	1·5	0·0	11·0	2·0	9·0	7·0	2·0	8·0	1·5	7·0	—	—	—
2	1·5	9·0	5·0	26·0	13·0	1·5	1·5	—	—	—	7·0	1·0	8·0	1·0	8·0	9·0	2·0	11·0
4	1·0	8·0	5·0	22·0	7·0	1·5	1·5	—	—	—	7·0	1·5	8·0	1·5	8·0	9·0	2·0	11·0

* $J_{PC_4C_5\text{-}\underline{CH}_3}$.
** J between the phosphorus nucleus and the α-protons of the Ph-P.
*** Allylic coupling constant.

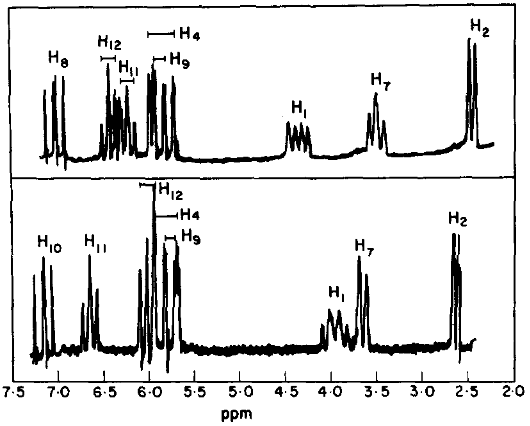


Fig 1. Partial NMR spectrum of compounds 1 and 2.

values for this configuration, assuming a Karplus-like relationship[6] between the P—C—C—H(1) dihedric angle and $^3J_{PH(1)}$. (c) The compatibility of the $\Delta\delta$ values obtained by complexation with Eu(fod)$_3$ to d (distance) correlations with the *endo* geometry, as opposed to the *exo* one (Table 2). The $\Delta\delta$ to d correlation, was based on the assumption that the complexation occurs on the carbonyl site.[8]

The *endo-exo* and *syn-anti* relationship having been assigned, the question of the P-configuration had to be settled.

Oxidation of 1 and 2, by 30% H_2O_2 in chloroform–acetone solution yielded the phosphine oxides 3 and 4 respectively. Compounds 3 (m.p. 177–178°) and 4 (m.p. 193–194°) (mass spectra M$^{\oplus}$ *m/e* 310) showed strong P=O absorptions, (ν_{max}^{KBr} 1190, 1170 for 3 and 1190, 1165 cm^{-1} for 4) as expected. The NMR spectra were very similar to those of 1 and 2 apart from the chemical shifts of the H(1), H(2) protons, these being directly influenced by the P=S groups' anisotropy.* (Table 1a). This similarity indicates that the configuration of the P atom in both 3 and 4 remains unchanged, as would be expected during such an oxidation process.[9]

Reduction of 3 with trichlorosilane ($HSiCl_3$) in dry benzene yielded the corresponding phosphine 5, (mass spectra M$^{\oplus}$ *m/e* 294; disappearance of the absorptions at 1190, 1170 cm^{-1}). In the NMR spectra (Experimental) the expected changes caused by the alteration of P(IV) to P(III)[10] could be well observed.

Of significance was the low $^2J_{PH(2)}$ value,[11,12] from which we concluded that the P-configuration is such that the P-phenyl group in V is *cis* to the C—H(2) bond.

It was found[11] that $^2J_{PH(2)}$ is only slightly changed when either a Me or a Ph group is attached to the P atom. Thus it does not seem likely that an additional double bond (C(4)C(5)) in 5 should invert the observed *J* values. Furthermore, the fact that $^2J_{PH(2)}$ in 1, 2, and 5 are in the same order of magnitude (6; 6 and 3 Hz respectively, as compared to a value of *ca* 25 Hz expected for a $\underline{Ph}$—P—C—$\underline{H}$(2) *trans* relationship,[11] indicates that a conclusion can be drawn for the P—C—H angle even from the oxide or sulphide *J*-values.

The configuration of the P-atom in both 1 and 3 should be the same as in 5 because reduction of P=O with $HSiCl_3$[13] and oxidation[9] of P=S to P=O with H_2O_2 both proceed with retention of configuration.

Table 2

Compound	Proton	d_{endo} (Å)^a	d_{exo} (Å)^a	$\Delta\delta$ (ppm)^b (M.R.)^c
1	C_5-$\underline{CH}_3$	6·9	5·6	0·5 (0·78)
1	C_6-$\underline{CH}_3$	4·6	5·7	0·85 (0·78)
1	H_4	6·8	4·7	0·72 (0·78)
1	H_2	3·2	4·2	2·55 (0·78)
2	C_5-$\underline{CH}_3$	5·1	3·4	1·18 (0·84)
2	C_6-$\underline{CH}_3$	3·3	4·6	3·65 (0·84)
2	H_4	6·7	4·5	0·93 (0·84)
2	H_2	4·5	5·3	2·15 (0·84)

^{a}d = The distance between the carbonyl oxygen atom and the proton.
$^b\Delta\delta = \delta$ complexed $-$ δ uncomplexed.
^{c}M.R. = [Eu(fod)$_3$]/[Substrate].

Table 3

Compound	Proton	d_{anti} (Å)^a	d_{syn} (Å)^b	$\Delta\delta$ (ppm)^c (M.R.)^d
3	H_2	3·2	2·6	0·77 (0·15)
3	H_1	2·3	3·4	1·40 (0·15)
3	H_4	3·0	3·0	0·28 (0·15)
3	H_{11}	2·7	4·8	0·60 (0·15)
4	H_2	3·2	2·6	0·88 (0·16)
4	H_1	2·4	3·4	1·45 (0·16)
4	H_4	3·0	3·0	0·25 (0·16)
4	H_{11}	3·0	5·0	1·45 (0·16)

^{a}d *anti* = The distance between the phosphoryl O atom and the proton (The P=O possessing the *anti* configuration to the C—H(2) bond).
^{b}d *syn* = The distance between the phosphoryl O atom and the proton (The P=O possessing the *syn* configuration to the C—H(2) bond).
$^c\Delta\delta = \delta$ complexed $-$ δ uncomplexed.
^{d}M.R. = [Eu(fod)$_3$]/[Substrate].

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*The anisotropic effect of P=S as opposed to P=O could be nicely observed in the comparison of 8-oxo-8-phenyl-8-phosphabicyclo[3.2.1]octan-3-one with the 8-thio analogue which showed that in the case of the P=S a slightly stronger paramagnetic effect was present. Alteration of the P configuration on the other hand completely changed the whole spectra.

On the basis of the above conclusions and the similarity between the $^2J_{PCH(2)}$ value in **1** and **3** as well as in **2** and **4**, the P-configuration in the latter pair should be the same as in the former.

The correlation between $\Delta\delta$ and d for complexes of **3** and **4** with Eu(fod)$_3$ has been examined, as has been previously shown by us,[14] in phosphabicyclic compounds bearing both P=O and C=O groups, complexation takes place on the P=O group, as was also found in this case. From the $\Delta\delta/d$ correlation shown partially in Table 3, it seems that the Eu atom of the Eu(fod)$_3$ is not colinear with the P=O bond, nevertheless the $\Delta\delta$ values for particular pairs of protons which can be compared (Table 3) seems to be in accordance with the suggested P-configuration.

EXPERIMENTAL

M.ps were taken on a Unimelt Thomas and Hoover's Capillary m.p. apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer Infracord model 337 spectrophotometer. NMR spectra were taken on a Varian HA-100 and Jeol JMN-C-60 HL spectrometers, for 5–10% soln in CDCl$_3$, containing TMS as an internal standard. Mass spectra were taken on an Hitachi Perkin-Elmer RMU-6 instrument, the samples being introduced directly into the ion source through a vacuum-lock, electron energy 70 eV.

3,4-Dimethyl-1-thio-1-phenylphosphole was prepared according to Mathey *et al.*[4] Tropone was prepared from cyclohepta-1,3,5-triene by the method of Radlick.[5]

5,6-*Dimethyl*-3-*thio*-3-*phenyl*-3-*phosphatricyclo*[5.3.2.0^{2,6}]*dodec*-4,8,11-*trien*-10-*one and* 5,6-*dimethyl*-3-*thio*-3-*phenyl*-3-*phosphatricyclo*[5.3.2.0^{2,6}]*dodec*-4,9,11-*trien*-8-*one*, (**1** *and* **2**). A soln of 3,4-dimethyl-1-thio-1-phenylphosphole (2g) and tropone (0·97 g) in methyl propylketone (15 ml), was refluxed for 4 days under N$_2$. After evaporating the solvent under reduced pressure, the obtained dark, viscose oil was chromatographed on a neutral alumina column (Woelm, grade 2). Elution with benzene-petrol ether (1 : 1) yielded pure **1** (1·0 g) and **2** (600 mg). Compound **1** was recrystallised from EtOA (white needles), m.p. 162–163°; ν_{max}^{KBr} 3030, 2950, 1650, 1630, 1600, 1470, 1430, 1380, 1270, 1160, 1100, 905, 870, 850, 830, 805, 760, 740, 725, 710, 690, 655, 505 cm^{-1}. (Found: C, 69·91; H, 5·46; P, 9·30; S, 10·06. C$_{19}$H$_{19}$OPS requires: C, 69·92; H, 5·87; P, 9·49; S, 9·82%).

Compound **2** (white cubic crystals) was recrystallised from EtOAc-ether, m.p. 195–196°; ν_{max}^{KBr} 3025, 2930, 2880, 1655, 1625, 1600, 1475, 1430, 1380, 1315, 1290, 1270, 1170, 1140, 1090, 1025, 930, 910, 850, 780, 750, 725, 710, 695, 660, 600, 575, 505 cm^{-1}. (Found: C, 69·98; H, 5·61; P, 9·34; S, 10·04. C$_{19}$H$_{19}$OPS requires: C, 69·92; H, 5·87; P, 9·49; S, 9·82%).

5,6-*Dimethyl*-3-*oxo*-3-*phenyl*-3-*phosphatricyclo*[5.3.2.0^{2,6}]*dodec*-4,8,11-*trien*-10-*one*, (**3**). To a soln of **1** (0·75 g) in CHCl$_3$ (2 ml), a 30% H$_2$O$_2$ soln (1 ml) was added, followed by addition of acetone until the soln became homogenous. The mixture was stirred at room temp for 4 days (until completion of the reaction according to TLC), then chloroform (150 cc) was added and the soln was washed with 5% FeSO$_4$ aq until a negative KI test. After evaporation of the dried soln (Na$_2$SO$_4$), the product (0·64 g) was recrystallised from EtOAc-ether (white plates), m.p. 177–178°; ν_{max}^{KBr} 3040, 2960, 2925, 1660, 1630, 1600, 1590, 1435, 1380, 1250, 1190, 1170, 1105, 900, 870, 845, 830, 810, 760, 740, 720, 700, 690, 680 cm^{-1}. (Found: M$^+$ 310; C$_{19}$H$_{19}$O$_2$P requires: MW 310).

5,6-*Dimethyl*-3-*oxo*-3-*phenyl*-3-*phosphatricyclo*[5.3.2.0^{2,6}]*dodec*-4,9,11-*trien*-8-*one*, (**4**). Compound **2** (80 mg) was oxidized by 30% H$_2$O$_2$, under the same conditions described for the oxidation of **1** to **3**, yielding a crystalyne product (70 mg), m.p. 193–194° (EtOAc-ether), ν_{max}^{KBr}3060, 2960, 2920, 1660, 1635, 1610, 1590, 1440, 1380, 1250, 1190, 1165, 1140, 1090, 1030, 930, 900, 870, 850, 840, 745, 720, 710, 700, 690, 640 cm^{-1}. (Found: M$^+$ 310; C$_{19}$H$_{19}$O$_2$P requires: MW 310).

5,6-*Dimethyl*-3-*phenyl*-3-*phosphatricyclo*[5.3.2.0^{2,6}]*dodec*-4,8,11-*trien*-10-*one*, (**5**). To a stirred soln of **3** (68 mg) in dry benzene (10 ml) an excess of HSiCl$_3$ (1·5 ml) was added in one portion. The mixture was stirred under N$_2$ at room temp for 1/2 hr and then refluxed for 2 hr. After cooling, N$_2$-purged water (5 ml) were added, causing the precipitation of a white solid. The mixture was filtered under N$_2$, yielding a turbide benzenic soln. The white solid was washed twice with 10 ml portions benzene. The combined benzenic soln was washed with small portions of 5% NaHCO$_3$aq, then water, dried (Na$_2$SO$_4$) and evaporated yielding white, viscose oily product (45 mg); ν_{max}^{neat} 3020, 2960, 2920, 2860, 1660, 1635, 1600, 1535, 1385, 1260, 1100, 1085, 1020, 905, 810, 750, 740, 730, 670 cm^{-1}. (Found: M$^+$ 294; C$_{19}$H$_{19}$OP requires: MW 294); δ 1·10s (C$_6$-CH$_3$); 1·85 dd ($^4J_{PH}$ = 1·5 Hz; $^4J_{\underline{H_4}C_5\text{-}\underline{CH_3}}$ = 1·5 Hz; C$_5$-$\underline{CH}_3$); 2·23 d ($^3J_{PH}$ = 3 Hz; H$_2$); 3·35 dd* ($J_{H_{7,8}}$ = 9·0 Hz; $J_{H_{7,12}}$ = 7·0 Hz; H$_7$); 3·90 m (H$_1$); 5·38 dd ($^2J_{PH}$ = 21 Hz; H$_4$); 5·78 dd* ($J_{H_{8,9}}$ = 11·0 Hz; H$_9$); 6·13 dd* ($J_{H_{11,12}}$ = 8·0 Hz; $J_{H_1H_{11}}$ = 7·0 Hz; H$_{11}$); 6·35 dd* (H$_{12}$); 6·93 dd ($J_{H_{7,8}}$ = 7·0 Hz; H$_8$); 7·28 m (Ph, 5H) ppm.

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*Broadened by allylic coupling.