Reactions of Carbonyl Compounds with Tervalent Phosphorus Reagents. Part IV.[1] Structure of a Tetracyclone–Dimethyl Phosphonate Adduct revised by *X*-Ray Crystal Analysis

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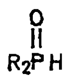
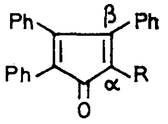
The structure of the αβ-unsaturated ketone product of the thermal reaction of tetracyclone with dimethyl phosphonate has been determined by *X*-ray single-crystal analysis. The unit cell is triclinic with $a = 12{\cdot}088 \pm 0{\cdot}005$, $b = 15{\cdot}817 \pm 0{\cdot}005$, $c = 8{\cdot}914 \pm 0{\cdot}005$ Å, $\alpha = 82{\cdot}6 \pm 0{\cdot}1°$, $\beta = 119{\cdot}0 \pm 0{\cdot}1°$, $\gamma = 120{\cdot}9 \pm 0{\cdot}01°$; $Z = 2$, space group $P\bar{1}$. The structure was solved from diffractometer data by direct methods, and refined by block-diagonal least-squares techniques to *R* 0·083 for 4828 observed reflections. The adduct is now shown to be a γ-ketophosphonate and steric factors are believed to control its formation.

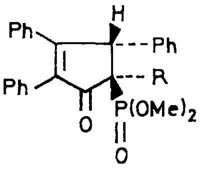
THE reactions between cyclopenta-2,4-dienones and dimethyl phosphonate (1a) are extremely complex,[2-4] and the products formed are largely dependent upon experimental conditions (see Scheme). Among the products two different types of αβ-unsaturated ketone have been described. These are the ketones (3a) and (3b), reported[2] to be formed when 2,3,4,5-tetraphenylcyclopenta-2,4-dienone [tetracyclone (2a)] is treated with (1a) in the presence of morpholine, and the ketone (4a), isolated from a reaction of (2a) when heated under reflux in an excess of dimethyl phosphonate.[3] The structures (3a) and (3b) were assigned[2] by analogy with the adduct (5), from methyl phenylphosphinate and (2a), while that of (4a) was based[3] on analogy with the structure of the adduct (4b), formed by 2-methyl-3,4,5-triphenylcyclopenta-2,4-dienone (2b) and (1a). In view of the apparent contrast in the structures (3) and (4) it was felt that additional evidence should be obtained, and we now report the *X*-ray crystallographic analysis of the ketophosphonate to which structure (4a) has been assigned. Arbusov and his colleagues have independently expressed[4] a similar doubt about the assignment of structure (3a) or (4a) to the αβ-unsaturated ketonic product of these reactions.


$\overset{O}{\overset{\|}{R_2P}}H$

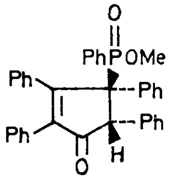
(1) a; R = OMe
b; R = Ph



(2) a; R = Ph
b; R = Me



(4) a; R = Ph
b; R = Me



(5)

EXPERIMENTAL AND RESULTS

Crystal Data.—$C_{31}H_{27}O_4P$, $M = 494{\cdot}5$. Triclinic, $a = 12{\cdot}088 \pm 0{\cdot}005$, $b = 15{\cdot}817 \pm 0{\cdot}005$, $c = 8{\cdot}914 \pm 0{\cdot}004$ Å, $\alpha = 82{\cdot}6 \pm 0{\cdot}05°$, $\beta = 119{\cdot}0 \pm 0{\cdot}05°$, $\gamma = 120{\cdot}9 \pm 0{\cdot}05°$, $U = 1262{\cdot}8$ Å^3, $D_c = 1{\cdot}300$, $Z = 2$, $D_m = 1{\cdot}293$ g cm^3, $F(000) = 520$. No systematic absences, space group $P1$ or $P\bar{1}$; intensity statistics indicated the crystal to be centrosymmetric, the latter therefore adopted. Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å; μ(Cu-K_α) = 13·27 cm^{-1}.

Crystallographic Measurements.—Short prisms were obtained by crystallisation from light petroleum–benzene; (001), (100), and (010) faces were well developed. Intensities were collected on a Wooster four-circle diffractometer from crystals mounted on the *a*, *b*, and *c* axes. No corrections were made for absorption but all the intense reflections were measured with a small crystal, ground to an approximate sphere. 4828 Reflections had intensities large enough to be accepted as observed.

Structure Analysis.—The observed structure factors were analysed by means of a Wilson plot to obtain an approximate absolute scale and an overall isotropic temperature factor (*B* 4·1 Å^2). The F_o values were converted into normalized structure factors (*E*) by means of a computer program supplied by Dr. P. Main. The 408 *E* values >1·77 were used to derive phases. The following reflections were selected to fix the origin and each was given a phase of 0°: $2,\bar{9},5$, $10,\overline{11},\bar{4}$, and $1,\overline{10},4$. Four further reflections: $3,\overline{14},6$, $9,\overline{13},\bar{3}$, $0,4,5$, and $7,\bar{1},0$ were selected as starting phases for the direct phase-determination process, each, in turn, having phases of 0 or 180°. There were 16 sets of phases, including the trivial solution where all phases are 0°. A figure of merit is calculated for each set and the highest value was the trivial solution. The set of phases with the next highest figure of merit gave the

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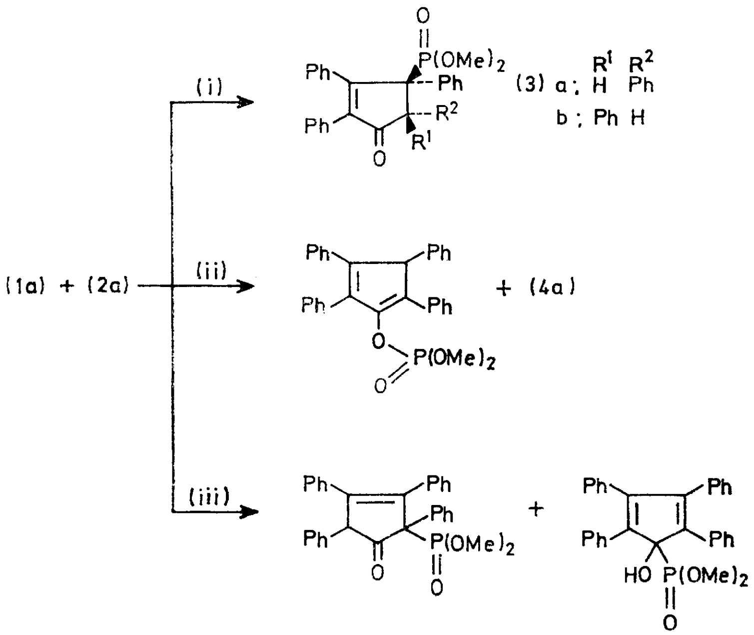
[1] Part III, W. M. Horspool, S. T. McNeilly, J. A. Miller, and I. M. Young, *J.C.S. Perkin I*, 1972, 1113.

[2] M. J. Gallacher and I. D. Jenkins, *J. Chem. Soc.* (*C*), 1971, 210.

[3] J. A. Miller, G. M. Stevenson, and B. C. Williams, *J. Chem. Soc.* (*C*), 1971, 2714.

[4] A. V. Fuzhenkova, A. F. Zinkovskii, and B. A. Arbuzov, *Doklady Akad. Nauk S.S.S.R.*, 1971, **201**, 632 (*Chem. Abs.*, 1972, **76**, 127 092).



SCHEME Reported reactions of tetracyclone with dimethyl phosphonate: (i) Morpholine at 20 °C (ref. 2); (ii) heating under reflux (ref. 3); (iii) $NaHCO_3$ (ref. 3) or Et_3N (ref. 4) at 20 °C

correct solution. An (*E*) Fourier synthesis was computed and 22 of the highest peaks could be identified as forming a reasonable molecule. The highest peak (twice the height of the next highest) was assumed to be the phosphorus atom. Structure factors (F_c) were now calculated for all observed reflections with the co-ordinates obtained for the 22 peaks; *R* was then 0·486. From further F_o syntheses it was possible to identify 36 atoms which had reasonable peak heights and sensible bond lengths and angles. A structure-factor calculation with 2799 reflections and assuming one phosphorus atom and 35 'carbons' with an overall temperature factor *B* of 3·0 gave *R* 0·27. At this point the oxygen atoms were identified and subsequent least-squares refinement (block-diagonal) reduced *R* to 0·15. The positions of the hydrogen atoms were now calculated and included in all calculations of structure factors but they were not themselves refined. The final *R*, after refining non-hydrogen atoms with anisotropic temperature parameters, was 0·083. Final atomic co-ordinates are given in Table 1, and temperature parameters in Table 2. The numbering of the atoms is shown in Figure 1 together with bond lengths and angles. The standard deviation for the P–C bond is 0·010, and for the P–O bonds they are P–O(1) 0·009,

TABLE 1

Fractional co-ordinates, with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
P(1)	0·5343(3)	0·2358(2)	0·2066(4)
O(1)	0·3636(8)	0·1584(6)	0·0937(10)
O(2)	0·5939(8)	0·3202(6)	0·1250(10)
O(3)	0·6067(7)	0·1706(5)	0·2549(9)
O(4)	0·3506(7)	0·0912(6)	0·6251(10)
C(1)	0·3937(10)	0·1508(7)	0·5366(13)
C(2)	0·3411(9)	0·2178(7)	0·4467(13)
C(3)	0·4221(9)	0·2770(7)	0·3705(12)
C(4)	0·5501(9)	0·2629(7)	0·4144(12)
C(5)	0·5128(9)	0·1648(7)	0·5004(13)
C(6)	0·7023(9)	0·3522(7)	0·5346(12)
C(7)	0·8291(10)	0·3692(7)	0·5408(14)
C(8)	0·9670(11)	0·4476(9)	0·6581(15)
C(9)	0·9828(12)	0·5078(9)	0·7683(16)
C(10)	0·8575(12)	0·4932(9)	0·7656(17)
C(11)	0·7181(10)	0·4141)8)	0·6490(14)
C(12)	0·3891(9)	0·3451(7)	0·2514(12)
C(13)	0·2440(10)	0·3085(8)	0·1189(14)
C(14)	0·2048(11)	0·3673(9)	0·0017(16)
C(15)	0·3111(11)	0·4655(8)	0·0155(15)
C(16)	0·4546(11)	0·5036(8)	0·1455(15)
C(17)	0·4961(10)	0·4431(8)	0·2608(15)
C(18)	0·2198(9)	0·2163(7)	0·4509(13)
C(19)	0·0920(10)	0·1263(8)	0·4235(14)
C(20)	−0·0205(11)	0·1245(9)	0·4335(16)
C(21)	−0·0056(12)	0·2130(10)	0·4724(17)
C(22)	0·1211(12)	0·3040(9)	0·4983(18)
C(23)	0·2315(11)	0·3046(8)	0·4852(15)
C(24)	0·6395(10)	0·1615(8)	0·6578(14)
C(25)	0·6989(12)	0·2084(9)	0·8224(16)
C(26)	0·8119(17)	0·1975(13)	0·9674(19)
C(27)	0·8569(15)	0·1397(11)	0·9422(21)
C(28)	0·7996(14)	0·0935(10)	0·7796(21)
C(29)	0·6913(11)	0·1047(8)	0·6360(16)
C(30)	0·5564(13)	0·0874(10)	0·1397(18)
C(31)	0·2781(16)	0·1580(13)	−0·0908(20)
H(1)[C(7)]	0·8197	0·3218	0·4572
H(2)[C(8)]	1·0606	0·4612	0·6577
H(3)[C(9)]	1·0880	0·5636	0·8604
H(4)[C(10)]	0·8672	0·5417	0·8511
H(5)[C(11)]	0·6241	0·4029	0·6481
H(6)[C(13)]	0·1614	0·2321	0·1085
H(7)[C(14)]	0·0892	0·3344	−0·0952
H(8)[C(15)]	0·2799	0·5114	−0·0747
H(9)[C(16)]	0·5403	0·5805	0·1597
H(10)[C(17)]	0·6089	0·4704	0·3543
H(11)[C(19)]	0·0798	0·0578	0·3917
H(12)[C(20)]	−0·1174	0·0555	0·4106
H(13)[C(21)]	−0·0909	0·2107	0·4837
H(14)[C(22)]	0·1336	0·3743	0·5255
H(15)[C(23)]	0·3308	0·3734	0·5091
H(16)[C(20)]	0·6474	0·0681	0·5080
H(17)[C(28)]	0·8441	0·0538	0·7698
H(18)[C(27)]	0·9359	0·1307	1·0511
H(19)[C(26)]	0·8562	0·2310	1·0994
H(20)[C(25)]	0·6563	0·2493	0·1811

TABLE 2

Temperature parameters

(*a*) Anisotropic temperature parameters * (× 105)

Atom	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
P(1)	1332(2)	836(2)	1404(4)	412(1)	461(3)	1396(4)
O(1)	1595(8)	927(8)	991(14)	675(4)	132(12)	1418(12)
O(2)	2037(8)	943(9)	2429(14)	587(4)	806(12)	1856(12)
O(3)	1769(6)	1107(5)	1569(11)	534(3)	−96(9)	2018(11)
O(4)	1430(7)	953(8)	2341(13)	601(4)	1358(12)	2385(12)
C(1)	1074(8)	660(9)	1177(16)	435(4)	504(14)	1448(15)
C(2)	0969(8)	644(8)	1075(15)	418(4)	330(14)	1412(14)
C(3)	0947(8)	564(8)	857(15)	365(4)	300(13)	1267(14)
C(4)	0936(7)	640(7)	990(14)	371(4)	333(13)	1334(13)
C(5)	1002(8)	679(8)	1062(16)	420(4)	510(14)	1425(14)
C(6)	981(8)	612(8)	986(14)	397(4)	421(13)	1348(14)
C(7)	1158(9)	760(9)	1206(17)	495(5)	437(15)	1630(16)
C(8)	1292(11)	919(11)	1565(20)	645(6)	768(19)	1981(19)
C(9)	1500(11)	934(12)	1278(23)	636(6)	545(20)	2091(21)
C(10)	1614(12)	1048(11)	1447(22)	645(6)	148(20)	2080(21)
C(11)	1195(9)	797(10)	1203(17)	538(5)	212(16)	1676(17)
C(12)	967(8)	649(8)	1072(15)	379(4)	364(13)	1414(14)
C(13)	1216(9)	766(10)	1240(18)	515(5)	685(16)	1746(17)
C(14)	1330(10)	976(11)	1321(21)	649(6)	860(19)	2011(19)
C(15)	1406(10)	1038(10)	1530(20)	568(5)	810(18)	2075(19)
C(16)	1370(10)	904(10)	1543(19)	494(5)	710(17)	2015(18)
C(17)	1259(10)	775(10)	1189(19)	474(5)	725(16)	1884(18)
C(18)	0980(8)	612(8)	1055(15)	432(4)	388(14)	1389(14)
C(19)	1196(9)	788(9)	1360(18)	531(5)	624(16)	1895(17)
C(20)	1302(10)	870(11)	1680(20)	666(6)	767(19)	2156(19)
C(21)	1468(11)	1172(13)	2039(22)	852(7)	708(22)	2415(22)
C(22)	1616(11)	1286(12)	2126(23)	733(7)	357(21)	2601(23)
C(23)	1254(9)	847(10)	1566(18)	567(5)	250(17)	1961(18)
C(24)	1148(9)	710(10)	1227(18)	478(5)	746(16)	1627(16)
C(25)	1696(12)	885(13)	1606(23)	694(7)	922(20)	1937(19)
C(26)	2180(19)	752(24)	2181(31)	1020(11)	1439(28)	2424(24)
C(27)	1657(15)	1149(17)	1671(33)	986(9)	1794(27)	3310(29)
C(28)	1641(14)	1484(14)	2313(31)	876(7)	1619(26)	3342(29)
C(29)	1307(10)	975(10)	1555(20)	617(5)	895(18)	2219(20)
C(30)	1855(12)	1492(12)	2107(25)	722(6)	−227(21)	2657(25)
C(31)	2338(17)	1601(19)	2096(30)	1200(11)	332(30)	2347(27)

(*b*) Isotropic temperature parameters

	$B/Å^2$		$B/Å^2$
H(1)[C(7)]	3·776	H(11)[C(19)]	4·048
H(2)[C(8)]	4·777	H(12)[C(20)]	4·345
H(3)[C(9)]	5·087	H(13)[C(21)]	5·257
H(4)[C(10)]	4·720	H(14)[C(22)]	5·346
H(5)[C(11)]	3·636	H(15)[C(23)]	4·239
H(6)[C(13)]	3·612	H(16)[C(29)]	4·984
H(7)[C(14)]	5·122	H(17)[C(28)]	6·700
H(8)[C(15)]	5·158	H(18)[C(27)]	7·470
H(9)[C(16)]	4·431	H(19)[C(26)]	7·467
H(10)[C(17)]	4·357	H(20)[C(25)]	5·291

* In the form: $\exp\{-(h^2b_{11} + k^2b_{22} + l^2b_{33} + hlb_{13} + hkb_{12} + klb_{23})\}$.

TABLE 3

Equations of mean planes in the form: $lX + mY + nZ = d$ where X, Y, and Z are co-ordinates in Å relative to the orthogonal axes.† The deviations of the atoms from the plane (Å) are given in square brackets. Atoms marked * are not included in the derivation of the plane. [Planes (*A*), (*B*), (*C*), and (*D*) refer to the aromatic rings]

Atoms	l	m	n	d
Plane (*A*) [C(6) −0·004, C(7) 0·001, C(8) −0·001, C(9) 0·003, C(10) −0·006, (C11) 0·006, C(4)* 0·082]	−0·289	−0·675	0·679	0·133
Plane (*B*) [C(12) 0·012, C(13) 0·003, C(14) −0·008, C(15) −0·002, C(16) 0·017, C(17) −0·022, C(3)* 0·012]	−0·552	0·571	0·607	1·439
Plane (*C*) [C(18) 0·010, C(19) −0·001, C(20) −0·007, C(21) 0·007, C(22) 0·003, C(23) −0·011, C(2)* 0·068]	−0·048	−0·206	0·977	2·835
Plane (*D*) [C(24) −0·007, C(25) −0·004, C(26) 0·011, C(27) −0·009, C(28) −0·002, C(29) 0·010, C(5)* −0·109]	0·883	0·452	−0·129	2·386
Plane (*E*) [C(1) 0·058, C(2) 0·000, C(3) −0·057, C(4) 0·084, C(5) −0·084, P(1)* −1·360, O(1)* −2·556, O(2)* −1·226, O(3)* −1·544, O(4)* 0·179, C(6)* 1·412, C(12)* −0·287, C(18)* 0·038, C(24)* 0·818, C(30)* −2·819, C(31)* −3·656]	0·249	0·448	0·859	4·174

Angles (deg.) between planes: (*E*)–(*A*) 77·9; (*E*)–(*C*) 42·7; (*E*)–(*B*) 50·2; (*E*)–(*D*) 71·8.

† *Z* is perpendicular to (001), *Y* is parallel to *b*, and *x* is perpendicular to *Y* and *Z*.

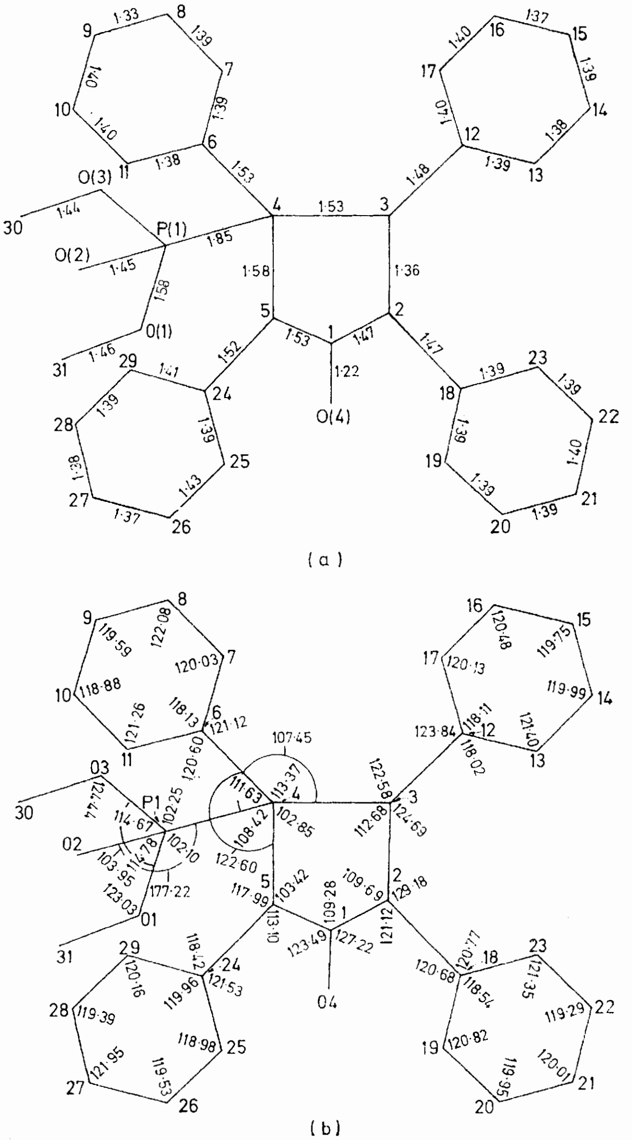


FIGURE 1 Bond lengths and angles, together with atom numbering system used in the analysis

P–O(2) 0·010, and P–O(3) 0·009 Å. Other bonds have standard deviations in the range 0·014—0·024 Å. Figure 2 shows a view of the molecule projected on the plane *bc**.

The only intermolecular distances $<3{\cdot}5$ Å are: C(8) $\cdots$ C′(8) 3·31, C(15) $\cdots$ O′(2) 3·27, C(16) $\cdots$ C′(16) 3·30, and C(30) $\cdots$ C′(30) 3·21 Å (primed atoms are in the molecule at $\bar{x},\bar{y},\bar{z}$).

Observed and calculated structure factors are listed in Supplementary Publications No. SUP 20946 (8 pp.).*

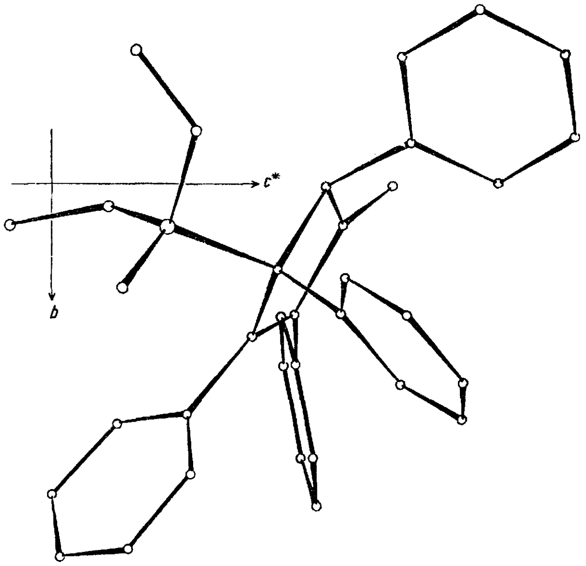


FIGURE 2 A view of the molecule projected on the bc^* plane

DISCUSSION

The mean planes of the benzene rings are given in Table 3; there are no deviations outside experimental error. The central five-membered ring is also planar.

The *X*-ray analysis reveals that the ketophosphonate, originally assigned structure (4a) is not a β-ketophosphonate, but is the γ-ketophosphonate (3a). The *cis*-fusion of the methine hydrogen and the phosphorus atoms in (3a), already indicated [3] by the value of the vicinal coupling constant [*J*(PCCH) 14·0 Hz], is confirmed. We have found the γ-ketophosphonate (3a) to be a high-melting solid (m.p. 217—218 °C),† but the phosphonate assigned structure (3a) was isolated as an oil.[2] This difference, together with the differences in ^{1}H n.m.r. spectra, which have been discussed elsewhere,[3] indicates that a more detailed examination of the adducts formed in the presence of morpholine might be of interest.

The present result is significant with regard to a general rationalisation of the reactions between cyclopentadienones and reagents containing the $>$P(O)H group. It has been suggested [3] that steric factors may be important in controlling product formation, and the fact that dimethyl phosphonate (1a) is now known to react with tetracyclone (2a) at the β-carbon of the ketonic ring, but with (2b) at the α-position, is consistent with this suggestion. Furthermore, the related reactions of the bulkier [with respect to (1a)] reagent diphenylphosphine oxide (1b) result in attack at the α-position with either (2a) or (2b). Previous results [2] gave grounds for suggesting [3] that electronic factors were not likely to be decisive in directing addition to either the β- or α-positions of tetracyclone (2a), and the contrast between the reactions of diphenylphosphine oxide (1b) and dimethyl phosphonate (1a) with tetracyclone (2a) would appear to confirm the dominance of steric effects.

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1972, Index issue.

† A similar m.p. has been reported by M. P. Serridge (Ph.D. Thesis, University of Leicester, 1968; we thank Dr. T. L. Gilchrist for this information) and by the authors in ref. 4.