A Study of the Reaction between the Dichloromethylphosphine–Aluminium Chloride Complex and Terpenes. Part 2.† Reaction of the PCl_2Me–$AlCl_3$ Complex and Camphene, and an *X*-Ray Crystallographic Study of the Products

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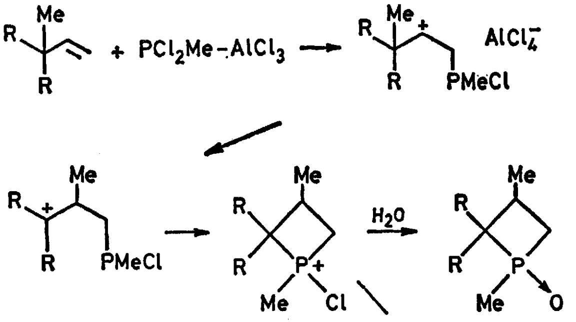
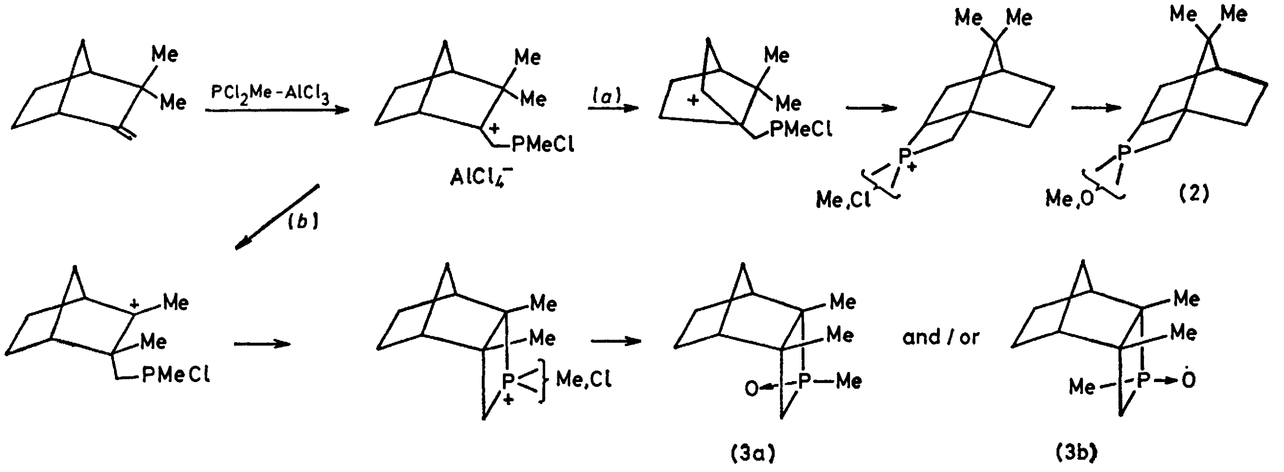
The reaction between the PCl_2Me–$AlCl_3$ complex and camphene yields, after hydrolysis, a phosphetan oxide (3a) and a chlorophosphine oxide (4a), whose structures were established by spectrometric analysis and single-crystal *X*-ray diffraction studies. The mechanism of their formation is discussed.

THE reaction between a branched olefin and the PCl_2Me–$AlCl_3$ complex usually yields, after hydrolysis, a substituted phosphetan oxide *via* a methyl 1,2-shift (Scheme 1).[1] The reasons for this behaviour are (*i*) the higher stability of the tertiary carbenium ion; (*ii*) the formation of the four-membered phosphetan ring rather than the highly strained and very unstable three-membered phosphiran ring.[2]



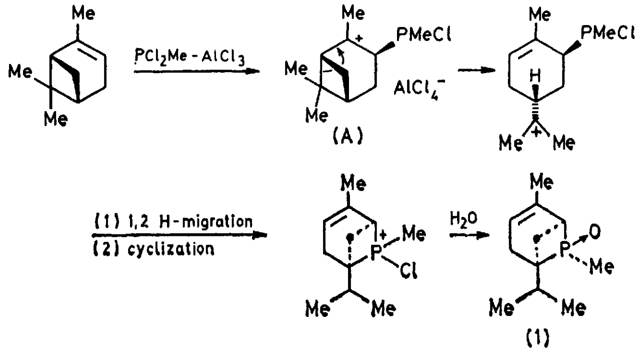
SCHEME 1

With α-pinene, we showed recently[3] that the major product (1) arises from the primary adduct A by double-bond formation with opening of the cyclobutane ring, rather than its enlargement by a 1,2-carbon migration (Scheme 2).



SCHEME 3

In the camphene molecule, such a stabilization cannot occur and we anticipated the formation of compounds with a phosphetan ring arising either by the camphane–bornane skeleton rearrangement [path (*a*)] or the Nametkin methyl 1,2-shift [path (*b*)] (Scheme 3).



SCHEME 2

RESULTS AND DISCUSSION

The experience showed that path (*b*) prevails, since we were able to isolate the compound (3a). But in addition, and rather unexpectedly, a second component of the reaction mixture was characterized as the chloro-

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† Part 1 is ref. 3.

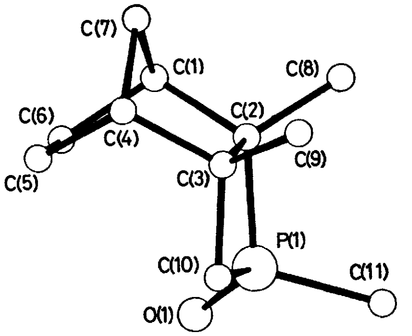
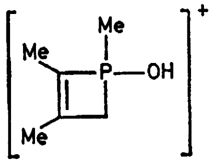


FIGURE 1 Perspective view of compound (3a)

phosphine oxide (4a). Its mechanism of formation will be discussed below.

Addition of camphene to a pre-formed solution of the $PCl_2Me-AlCl_3$ complex in CH_2Cl_2 at 10 °C gave, after 15 h at room temperature and then quenching by ice-cold water, two main compounds [(3a) and (4a)] which could be separated by chromatography on Florisil after distillation.

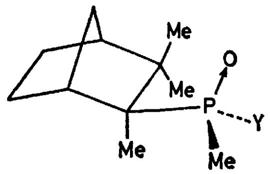
Compound (3a) (30% yield), m.p. 67—69 °C, has spectral characteristics which clearly suggest the structure shown rather than the alternative (2). The three methyl signals are doublets in the ^1H n.m.r. spectrum with J of 12, 19, and 2 Hz, falling into the known range for J_{HCP}, J_{HCCP}, and J_{HCCCP}, respectively;[1,4] in structure (2) only one methyl would have been coupled to phosphorus. Furthermore there is no methine adjacent to phosphorus. In the mass spectrum the base peak is at *m/e* 131 which can be attributed to the fragment B.



(B)

Confirmation of structure (3a) was given by *X*-ray analysis. The crystal structure contains two crystallographically independent but chemically identical units. The molecule is shown in Figure 1. The phosphetan ring is attached in an *endo*-configuration to C(2) and C(3) of a norbornane skeleton. Unexpectedly the phosphetan ring is puckered with an angle of only 4.6(8)°, the usual range being 19—26°.[5] The bond angles around the phosphorus atom are considerably distorted from their tetrahedral value, as is usual in a phosphetan ring. The internal angle at the phosphorus atom is 81.65° (mean value). The P=O bond length of 1.486 Å (mean value) and P–C(methyl) bond length of 1.787 Å (mean value) agree well with known values.[3,5] Formation of stereoisomer (3a) rather than (3b) can be easily understood on the basis of less steric crowding in structure (3a).

The second compound isolated in 25% yield was the chlorophosphine oxide (4a), m.p. 83—84 °C. Its ^1H n.m.r. ^{13}C n.m.r., and mass spectra (see Experimental section) are consistent with this structure. In particular, attachment of phosphorus to the more substituted carbon of the double bond is clearly demonstrated by the presence of four methyls instead of three in (3) as shown by the ^1H and ^{13}C n.m.r. spectra. Hydrolysis by dilute sulphuric acid at room temperature gives the phosphinic acid (4b), m.p. 184—185 °C, δ 9.3 (OH) disappearing in D_2O. The acid (4b) was isolated instead of (4a) in one experiment where during the work-up procedure silica gel was used for chromatography instead of Florisil. Its mass spectrum shows peaks corresponding to dimeric species. This behaviour of phosphinic acids has previously been noted by Dimroth[6] and Trippett.[4] The methyl ester (4c) was obtained from (4a) by refluxing in anhydrous methanol for 3 h.



(4)

a; Y = Cl
b; Y = OH
c; Y = OMe

Structure (4a) was confirmed and the steric configuration established by single-crystal *X*-ray analysis. The molecule is shown in Figure 2. The angles of the bonds around the phosphorus atom agree well with tetrahedral co-ordination. The P=O bond length of 1.485(10) Å and the P–Cl bond length of 2.051(6) Å are very similar to corresponding values previously found for disubstituted chlorophosphine oxides.[7-9] The P–C(11) bond length of 1.821(14) Å is in the usual range. The methylchlorophosphoryl group is in a staggered conformation with respect to the bonds attached to C(2) of the norbornane skeleton.

The formation of chlorophosphine oxides as by-products in the reaction of the $PCl_2R-AlCl_3$ complex with olefins has already been reported[10,11] but its mechanism still remains obscure. The occurrence of a transient phosphiranium ring has been postulated[11,12] but a re-examination[13] of the reaction with tetramethylethylene[12] led to the tentative interpretation shown in

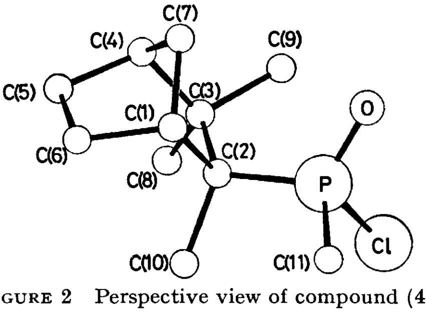
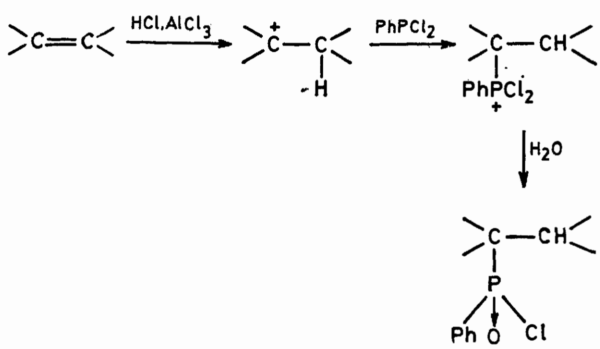
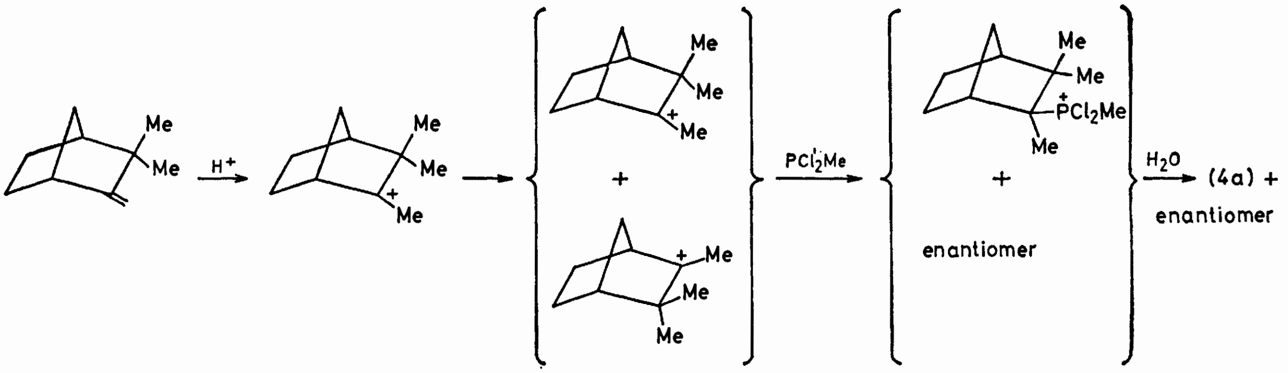


FIGURE 2 Perspective view of compound (4a)

Scheme 4. The source of the hydrogen in the newly formed C–H bond was supposed to be HCl, present in $AlCl_3$. This view seems to us to be valid since it is substantiated (*i*) by Kashman's observation that the yield of chlorophosphine oxide is increased when small amounts of water are added to the PCl_2R–$AlCl_3$ complex;[11,14] and (*ii*) by the optical activity of our products. The camphene we used had a specific rotation $[\alpha]_D$ +30° (optically pure camphene has $[\alpha]_D$ +84°). The phosphetan (3a) has $[\alpha]_D$ −9.4°, whereas the chlorophosphine oxide and the related acid are optically inactive at two different wave lengths. This finding corroborates Quin's hypothesis that protonation of the double bond must occur before phosphorus becomes attached to the intermediate carbenium ion (Scheme 5).



SCHEME 4



SCHEME 5

Thus the two compounds formed in the reaction seem to be the result of the competition for the most electron-rich carbon of the double bond in camphene, between the electrophilic phosphorus atom of the complex PClMe–Cl–$AlCl_3$,* leading to the optically active phosphetan (3) (Scheme 3) on the one hand, and the protons present in the medium, leading to racemized chlorophosphine oxide (4a) (Scheme 5) on the other hand.

EXPERIMENTAL

Melting points were measured using a capillary melting point Büchi apparatus. N.m.r. spectra were run on Cameca 250 and Bruker WP 60 spectrometers for solutions in deuteriochloroform; resonance positions are in p.p.m. relative to $SiMe_4$ as internal reference. Mass-spectral measurements were performed on Hewlett–Packard 5992 A GC/MS System. T.l.c. silica gel plates were developed with either (*A*) chloroform–methanol (98 : 2 or 95 : 5), or (*B*) ethyl acetate–pyridine–acetic acid–water (60 : 20 : 6 : 11). Compounds were revealed by iodine or/and Dittmer's reagent.[15]

Reaction of Dichloromethylphosphine with Camphene.—To anhydrous $AlCl_3$ (6.65 g, 0.05 mol) suspended in CH_2Cl_2 (50 ml) was added PCl_2Me (5.85 g, 0.05 mol). The mixture was stirred until homogeneous, and cooled to 5 °C while camphene (6.8 g, 0.05 mol) in CH_2Cl_2 (30 ml) was added dropwise (1 h). The reaction was conducted under nitrogen. The mixture was allowed to warm to room temperature and was stirred overnight. The reaction mixture was poured onto ice–water, the two phases separated, and the aqueous solution extracted several times with CH_2Cl_2; the organic layer was washed with water, aqueous $NaHCO_3$, and water, dried, and evaporated to yield a viscous oil (5.8 g) which was distilled in a Kugelrohr distillation apparatus. The fraction boiling at 150 °C at 0.5 mmHg was collected and chromatographed on a Florisil column. Elution with $CHCl_3$ gave *compound* (4a) [R_F 0.08 (*A*)], m.p. 83—84 °C (ether) (Found: C, 56.35; H, 8.5; Cl, 14.75; P, 13.4. $C_{11}H_{20}ClOP$ requires C, 56.28; H, 8.58; Cl, 15.08; P, 13.24%); whereas compound (3a) [R_F 0.65 (*A*)], m.p. 67—69 °C (ether–pentane) needed methanol–chloroform (2 : 98) to be eluted (Found: C, 66.3; H, 9.65; P, 15.25. $C_{11}H_{19}OP$ requires C, 66.64; H, 9.66; P, 15.63%). Chromatography of the adduct on a silica gel column [MeOH–$CHCl_3$ (1 : 99)] gave compound (4b) [R_F 0.62 (*B*)], m.p. 184—185 °C (ether) (Found: C, 59.95; H, 9.6; P, 13.95. $C_{11}H_{21}O_2P$ requires C, 61.09; H, 9.79; P, 14.32%); and compound (3a).

Spectral Data.—Compound (3a); *m/e* 198 (M^+, 38%), 183 (M^+ − Me, 20), 135 [M^+ − P(OH)Me, 14], 131 (100%, see earlier), and 107 [M − $P(O)C_3H_8$, 14%); δ_H 1.05 (d, 3 H), 1.15 (d, 3 H), 1.58 (d, 3 H), 1.3—1.5 (m, 4 H), 1.92 (m, 2 H), 2.05 (br s, 1 H), 2.32 (br s, 1 H), and 2.6—2.75 (m, 2 H); δ_C 15.2 (d, C-11, J_P 50 Hz), 18.6 (s, C-9), 23.1 (d, C-8, J_{PCCH} 12 Hz), 40.3 (d, C-10, J_{PCH_2} 53 Hz), 42.1 (C-3), 46.1 (d, C-2, J_{PC} 56 Hz).

Compound (4a); *m/e* 234 (M^+, 1.3%); 219 (M − Me, 5), 199 (M^+ − Cl, 6), 137 [M^+ − P(O)ClMe, 80), and 81 (base, 137 − C_4H_8); δ_H 1.07 (s, 3 H), 1.28 (d, 3 H, J_{HCCP} 22 Hz), 1.58 (s, 3 H), 1.98 (d, 3 H, J_{HCP} 12 Hz); δ_C 18.1 (d,

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* Quin[13] has shown by ^{31}P n.m.r. spectroscopy that the PCl_2R–$AlCl_3$ complex does not have the ion-pair structure $\overset{+}{P}ClR$–$AlCl_4^-$.

Me, q in off-resonance, J_{PCCC} 3.8 Hz), 20.9 (d, Me, q in off-resonance, J_{PC} 64 Hz), 22.9 (s, Me, q in off-resonance), 24.6 (d, Me, q in off-resonance, J_{PCC} 14 Hz), 45.03 (d in off-resonance, C-1), 45.4 (d, C-4), 51.00 (d, s in off-resonance, J_{PC} 25 Hz), and 51.04 (s, s in off-resonance).

Compound (4b); M^+ at *m/e* 216 non-detectable, *m/e* 375 ($2M^+ - C_4H_9$, 2.5%), 332 ($375 - C_3H_7$, 1.6), 275 ($332 - C_4H_9$, 1.7), and 257 ($275 - H_2O$, 1); δ_H 1.02 (s, 3 H), 1.27 (d, 3 H, J_{HCP} 21 Hz), 1.58 (s, 3 H), 1.95 (d, 3 H, J_{HCP} 12 Hz), and 9.28 (br s, 1 H).

Hydrolysis of (4a) *to* (4b).—Compound 4a (100 mg) solubilized in dioxan–water (60 ml) (50 : 10) was left overnight in the presence of 0.1N (10 ml) H_2SO_4; the solution was then extracted several times with ether. The combined ethereal extracts were washed with water, dried, and evaporated to give a white solid which was recrystallized from ether, m.p. 183—185 °C, identical with the phosphinic acid obtained directly by chromatography of the adduct on the silica gel column (see above).

Methanolysis of (4a).—Compound (4a) (50 mg) was refluxed in anhydrous methanol for 3 h. The solvent was then removed and the residue diluted with CH_2Cl_2, washed several times with water, and dried. The product obtained following evaporation of the solvent was an amorphous white *solid* which failed to crystallize (Found: C, 62.6; H, 9.68; P, 13.38. $C_{12}H_{23}O_2P$ requires C, 62.63; H, 9.99; P, 13.46%).

X-*Ray Diffraction Study*.—*Compound* (3a). Repeated crystallization from ether–pentane provided suitable crystals for the *X*-ray diffraction study; data were collected for a small white crystal (size 0.3 × 0.3 × 0.2 mm) on a Philips PW 1100 diffractometer (graphite-monochromated Cu-K_α radiation). Unit-cell dimensions and orientation matrix were obtained by least-squares analysis from the settng angles of 25 reflections. The intensities of reflections with $\theta < 68°$ were measured by an ω—2θ scan at a scan speed of 0.040° s^{-1} and an ω-scan angle of 1.20°. Background measurements of 8 s were made on both sides of each scan. 2 522 Reflections with $I > 3\sigma(I)$ were corrected for Lorentz and polarization factors.

The structure was solved by direct methods using the XGIF 79 package,[16] a new phase program including the NQEST figure of merit.[17] 22 of the 26 non-hydrogen atoms were correctly identified from an *E* map based on 294 reflections. The missing atoms were subsequently found from a Fourier synthesis. The non-methyl H atoms were fitted geometrically and the methyl-group H atoms were found from a difference-Fourier synthesis. The H atoms were included in the structure-factor calculations with the thermal parameters of the bonded atoms.

Crystal data. Triclinic, space group $P\bar{1}$, $a = 13.221(4)$, $b = 11.942(3)$, $c = 7.501(2)$ Å, $\alpha = 90.90(7)$, $\beta = 92.30(7)$, $\gamma = 112.20(9)°$, $U = 1\,095$ Å^3, $Z = 2$, $D_c = 1.19$ g cm^{-3}. Cu-K_α radiation ($\lambda = 1.541\,8$ Å).

The full-matrix least-squares refinement of the non-hydrogen atoms with anisotropic thermal parameters converged at *R* 0.048 (*R'* 0.051). The minimized function was $\Sigma\omega(|F_o| - |F_c|)^2$ with $\omega = 1/\sigma(F_o)^2$.* The atomic co-ordinates are listed in Table 1.

TABLE 1

Fractional atomic co-ordinates (×10^4), with estimated standard deviations for non-hydrogen atoms for compound (3a)

Atom	*x*	*y*	*z*
C(1)	2 313(3)	−953(3)	6 654(5)
C(2)	2 815(3)	−1 661(3)	5 462(5)
C(3)	1 757(3)	−2 585(3)	4 376(4)
C(4)	819(3)	−2 316(3)	5 226(5)
C(5)	779(3)	−1 106(4)	4 665(5)
C(6)	1 822(3)	−178(3)	5 589(5)
C(7)	1 255(3)	−2 003(4)	7 147(5)
C(8)	3 510(3)	−2 168(4)	6 594(6)
C(9)	1 559(3)	−3 928(3)	4 509(5)
C(10)	2 060(3)	−2 134(3)	2 477(5)
C(11)	4 392(3)	−1 640(4)	2 798(6)
P(1)	3 375(1)	−1 058(1)	3 330(1)
O(1)	3 728(2)	243(2)	2 943(4)
C(12)	2 932(4)	4 147(4)	−1 122(5)
C(13)	3 155(3)	3 381(3)	383(4)
C(14)	1 951(3)	2 530(3)	825(4)
C(15)	1 232(3)	2 866(4)	−593(5)
C(16)	1 199(5)	4 098(5)	−172(6)
C(17)	2 360(5)	4 969(4)	−456(6)
C(18)	1 957(4)	3 165(4)	−2 154(5)
C(19)	3 922(4)	2 795(4)	−230(6)
C(20)	1 690(3)	1 159(3)	697(5)
C(21)	1 957(3)	2 950(3)	2 783(5)
C(22)	4 172(3)	3 278(3)	3 935(5)
P(2)	3 380(1)	3 954(1)	2 702(1)
O(2)	3 742(2)	5 269(2)	3 173(3)

TABLE 2

Compound 4*a*: $C_{11}H_{20}ClOP$. Fractional atomic co-ordinates (×10^4), with estimated standard deviation for non-hydrogen atoms, for compound (4a)

Atom	*x*	*y*	*z*
C(1)	1 687(18)	1 017(13)	1 823(12)
C(2)	778(15)	2 191(15)	1 532(9)
C(3)	2 459(16)	3 042(14)	1 642(10)
C(4)	3 944(16)	2 283(16)	2 085(11)
C(5)	3 733(19)	1 864(17)	3 126(12)
C(6)	2 125(19)	993(14)	2 947(12)
C(7)	3 496(17)	1 150(15)	1 514(12)
C(8)	2 192(19)	4 138(14)	2 262(12)
C(9)	2 913(19)	3 512(14)	635(11)
C(10)	−709(16)	2 491(15)	2 186(10)
C(11)	−2 362(16)	1 080(14)	340(11)
Cl	−1 594(5)	3 491(4)	−101(3)
P	−404(4)	1 970(3)	307(3)
O	651(12)	1 555(8)	−440(7)

Compound (4a). The sample used was recrystallized from ether; the data were collected for a small white crystal (dimensions *ca.* 0.4 × 0.3 × 0.2 mm) (for method and conditions see above). Background measurements of 15 s were made on both sides of each scan. 1 261 Reflections with $I > 3\sigma(I)$ were corrected for Lorentz and polarization factors. The structure was solved by direct methods;[16, 17] 13 of the 14 non-hydrogen atoms were correctly identified from an *E* map based on 285 reflections. The missing atom was subsequently found from a Fourier synthesis. The non-methyl H atoms were fitted geometrically. The methyl-group H atoms were not revealed from difference-Fourier synthesis after partial refinement.

Crystal data. Monoclinic, space group $P2_1/C$, $a = 7.559(3)$, $b = 11.814(3)$, $c = 13.921(1)$ Å, $\beta = 98.66(1)°$, $U = 1\,229$ Å^3, $Z = 4$, $D_c = 1.27$ g cm^{-3}, Cu-K_α radiation ($\lambda = 1.541\,8$ Å). The full-matrix least-squares refinement of the non-hydrogen atoms with anisotropic thermal parameters converged at *R* 0.140 (*R'* 0.142). The minimized function was $\Sigma\omega(|F_o| - |F_c|)^2$ with $\omega = 1/\sigma(F_o)^2$.* The atomic co-ordinates are listed in Table 2.

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* Lists of structure factors, thermal parameters, bond distances and angles have been deposited in Supplementary Publication No. SUP 22818 (27 pp). See Notice to Authors No. 7, *J.C.S. Perkin I*, 1979, Index issue, for details.

The difference syntheses showed no peaks higher than 1.2 e Å^{-3} and no coherent chemical features, arising from a possible disorder or the presence of solvent, could be deduced. Probably the failure to grow better crystals led to a structure less well defined than the authors would have liked but the chemical problem is solved without ambiguity.

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