Evaporation of the solvent gave crude **10**, which upon recrystallization from benzene–petroleum ether gave (*R,R*)-(+)-**10** as colorless prisms (25 g, 53%): mp 138–140 °C; $[\alpha]_D$ +57.7° (*c* 4.0, $CHCl_3$); IR 1630 cm^{-1} (CO); 0.83–2.67 (br, 44 H), 3.40 (s, 6 H), 4.53 (s, 2 H). Anal. Calcd for $C_{30}H_{52}O_4N_2$: C, 71.38; H, 10.38; N, 5.55. Found: C, 71.44; H, 10.13; N, 5.51.

Optical Resolution of 11 by Complexation with Optically Active 7. When a solution of (*R,R*)-(+)-**7** (4.06 g, 17.5 mmol) and *rac*-**11** (5.0 g, 17.5 mmol) in benzene (20 mL)–hexane (5 mL) was kept at room temperature for 12 h, a 1:1 complex of (*R,R*)-(+)-**7** and (−)-**11** (4.1 g) was formed, which upon recrystallization from benzene gave a pure complex as colorless prisms (3.70 g, 82%): mp 149–150 °C; $[\alpha]_D$ +61.5° (*c* 1.0, $CHCl_3$)). Column chromatography of the complex on silica gel using benzene as a solvent gave (*S*)-(−)-**11** of 100% ee[19] (1.8 g, 72%);[20] $[\alpha]_D$ −33.2° (*c* 1.1, THF). The filtrate left after separation of a 1:1 complex of (*R,R*)-(+)-**7** and (−)-**11** was chromatographed on silica gel to give (+)-**11** (2.7 g, $[\alpha]_D$ +21° (*c* 1.1, THF)). Complexation of the crude (+)-**11** (2.7 g) with (*S,S*)-(−)-**7** (2.19 g) followed by recrystallization gave a 1:1 complex of (*S,S*)-(−)-**7** and (+)-**11** as colorless prisms (2.70 g, 60%): mp 150–151 °C; $[\alpha]_D$ −43.9° (*c* 1.0, $CHCl_3$). Column chromatography of the complex on silica gel using benzene as a solvent gave (*R*)-(+)-**11** of 100% ee (1.48 g, 59%); $[\alpha]_D$ +33.2° (*c* 1.1, THF).

Decomposition of a 1:1 Complex of 7 and 11 with Hydrazine. For example, when a solution of a 1:1 complex of (*S,S*)-(−)-**7** and (*R*)-(+)-**11** (3.15 g) in benzene (20 mL) was treated with 64% aqueous NH_2NH_2 (5 mL) at room temperature for 5 min, a 1:1 complex of (*R*)-(+)-**11** and NH_2NH_2 was formed as colorless needles (1.78 g), mp 135–142 °C. Decomposition of the complex with dilute HCl gave (*R*)-(+)-**11** (1.7 g, 98%).

Optical Resolution of 12 by Complexation with Optically Active 8. When a solution of (*R,R*)-(+)-**8** (1.26 g, 5.16 mmol) and *rac*-**12** (1.0 g, 2.59 mmol) in EtOH (20 mL) was kept at room temperature for 12 h, a 2:1 complex of (*R,R*)-(+)-**8** and (−)-**12** (1.03 g) was formed, which upon recrystallization from EtOH gave a pure complex as colorless prisms (0.85 g, 75%): mp 178–180 °C; $[\alpha]_D$ −23.9° (*c* 1.0, $CHCl_3$). Column chromatography of the complex on silica gel using benzene as a solvent gave (*S*)-(−)-**12** of 100% ee (0.37 g, 74%); $[\alpha]_D$ −81.1° (*c* 1.2, $CHCl_3$). The filtrate left after separation of a 2:1 complex of (*R,R*)-(+)-**8** and (−)-**12** was concentrated to half-volume to give a 1:1 complex of (*R,R*)-(+)-**8** and (+)-**12** (0.8 g). The complex was recrystallized from EtOH, and chromatography on silica gel using benzene as a solvent gave (*R*)-(+)-**12** of 100% ee (0.4 g, 80%); $[\alpha]_D$ +81.1° (*c* 1.2, $CHCl_3$).

Decomposition of a 2:1 Complex of 8 and 12 with Ammonia. For example, when NH_3 gas was bubbled for 30 min at room temperature through a solution of a 2:1 complex of (*R,R*)-(+)-**8** and (*S*)-(−)-**12** (4.0 g) in MeOH (20 mL), a 2:2:1 coplex of (*S*)-(−)-**12**, NH_3, and MeOH was obtained as colorless prisms (1.6 g). Heating of the complex in vacuo gave (*S*)-(−)-**12** (1.48 g, 84%).

Optical Resolution of 13 by Complexation with Optically Active 10. When a solution of (*R,R*)-(+)-**10** (0.58 g, 1.15 mmol) and *rac*-**13** (0.4 g, 1.15 mmol) in EtOH (5 mL) was kept at room temperature for 12 h, a 1:1 complex of (*R,R*)-(+)-**10** and (+)-**13** was obtained (0.51 g), which upon recrystallization from EtOH gave a pure complex as colorless prisms (0.45 g, 92%), mp 238–243 °C. Treatment of a solution of the complex in benzene with 3% aqueous NaOH gave an aqueous NaOH solution of (+)-**13**, which on acidification with dilute HCl gave (+)-**13** of 100% ee (0.18 g, 90%); $[\alpha]_D$ +27.1° (*c* 0.88, MeOH).

Registry No. **5**, 87-91-2; (+)-**6**, 26549-65-5; (−)-**6**, 63126-52-3; (+)-**7**, 26549-29-1; (*R,R*)-(+)-**7**·(−)-**11**, 114596-73-5; (−)-**7**, 63126-53-4; (*S,S*)-(−)-**7**·(+)-**11**, 114596-76-8; (*R,R*)-(+)-**8**, 63126-29-4; (*R,R*)-(+)-**8**·(+)-**12**, 114596-74-6; 2(*R,R*)-(+)-**8**·(−)-**12**, 114614-19-6; (*S,S*)-(−)-**8**, 111828-49-0; (*R,R*)-(+)-**9**, 7305-62-6; (*R,R*)-(+)-**9** (acid chloride), 114596-70-2; (*S,S*)-(−)-**9**, 6984-37-8; (+)-**10**, 114596-71-3; (+)-**10**·(+)-**13**, 114596-75-7; (−)-**10**, 114596-72-4; *rac*-**11**, 41024-90-2; (+)-**11**, 18531-94-7; (−)-**11**, 18531-99-2; *rac*-**12**, 95119-70-3; (+)-**12**, 95033-75-3; (−)-**12**, 95033-74-2; *rac*-**13**, 73100-16-0; (+)-**13**, 107955-86-2; (−)-diethyl tartrate, 13811-71-7; dimethylamine, 124-40-3; 2,2-dimethoxypropane, 77-76-9; dicyclohexylamine, 101-83-7.

(19) The optical purities (% ee) of **11**, **12**, and **13** were determined by HPLC using columns containing optically active solid phases, Chiralcel OC and OT(+), respectively, which are available from Daicel Chemical Industries, Ltd., Himeji, Japan. Accuracy of values of the % ee is more than 0.5%.

(20) All yields of the optical resolution were calculated on the basis of the theoretical amount of the optical isomer contained in the initial (±) compound.

Conformation of 2-(Diphenylphosphinoyl)-5,5-dimethyl-1,3-dioxane. A Contrasting Conformational Behavior of 2-Phosphoryl-Substituted 1,3-Dithianes and 1,3-Dioxanes

Marian Mikołajczyk* and Piotr Graczyk

Center of Molecular and Macromolecular Studies, Polish Academy of Sciences, Department of Organic Sulfur Compounds, 90-362 Łódź, Boczna 5, Poland

Michał W. Wieczorek and Grzegorz Bujacz

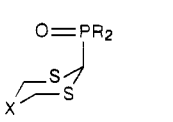
Institute of General Chemistry, Technical University, 90-924 Łódź, Żwirki 36, Poland

Yurij T. Struchkov and Michail Y. Antipin

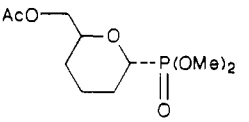
Institute of Organoelement Compounds, Academy of Sciences of USSR, Moscow 117312, Vavilov Str. 28, USSR

Received December 7, 1987

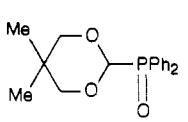
As part of our ongoing interest in the chemistry and stereochemistry of α-heterosubstituted phosphonates and related compounds,[1,2] we have undertaken a systematic investigation of the conformational preferences of various types of organophosphorus substituents in the 1,3-di- and 1,3,5-trithiane rings.[3] The first evidence that the 2-diphenylphosphinoyl group is axial in the 1,3-dithiane **1** was provided by Juaristi et al.[4] As a result of our investigations, a strong axial preference of the dimethoxyphosphoryl group in the 1,3,5-trithiane **2**[5] and 1,3-dithiane **3**[6] has also been found.



1, X=CH_2, R=Ph
2, X=S, R=MeO
3, X=CH_2, R=MeO



4



5

Very recently, on the basis of the accumulated spectroscopic and X-ray analysis data as well as theoretical calculations, we proposed[3,7] a new explanation for a strong

(1) Mikołajczyk, M. In *Current Trends in Organic Synthesis*; Nozaki, H., Ed.; Pergamon: New York, 1983.

(2) Mikołajczyk, M. In *Proceedings of the International Conference on Chemistry and Biotechnology of Biologically Active Products*; Vlahov, R., Ed.; Publishing House of the Bulgarian Academy of Sciences: Sofia, 1985; Vol. 2.

(3) Mikołajczyk, M. *Pure Appl. Chem.* **1987**, *59*, 983.

(4) (a) Juaristi, E.; Valle, L.; Mora-Uzeta, C.; Valenzuela, B. A.; Joseph-Nathan, P.; Fredrich, M. F. *J. Org. Chem.* **1982**, *47*, 5038. (b) Juaristi, E.; Valle, L.; Valenzuela, B. A.; Aguilar, M. A. *J. Am. Chem. Soc.* **1986**, *108*, 2000.

(5) Mikołajczyk, M.; Bałczewski, P.; Wróblewski, K.; Karolak-Wojciechowska, J.; Miller, A.; Wieczorek, M. W.; Antipin, M. Y.; Struchkov, Y. T. *Tetrahedron* **1984**, *23*, 4855.

(6) Engelhardt, M.; Hägele, G.; Mikołajczyk, M.; Bałczewski, P.; Wendisch, D. *Magn. Reson. Chem.* **1985**, *23*, 18.

0022-3263/88/1953-3609$01.50/0

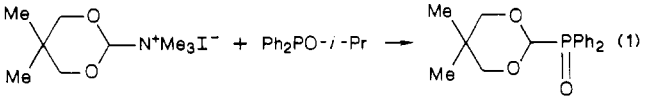
anomeric effect operating in 2-phosphorylpolythianes which is believed to be due to repulsive interactions between the nonbonded electron pairs on the endocyclic sulfur atom and on the phosphoryl oxygen atom in the equatorial conformation. Moreover, the axial position of the phosphoryl group may additionally be stabilized by attractive interactions (weak hydrogen bonding) between the phosphoryl oxygen atom and the axial hydrogens at C-4 and C-6. The role of the $n_X-\sigma_{C-P}^*$ overlapping, which may be considered to be responsible for the anomeric effect, is rather neglegible in this case.[8]

In spite of the fact that the analogy between the P(O) and C(O) group is rather formal, the latter shows also the predominant axial orientation in 1,3-di and 1,3,5-trithiane rings.[9-11] On the other hand, in the case of oxane and 1,3-dioxane, the carbonyl-containing substituents at C-2 tend to be situated equatorially.[12,13] Therefore, we became interested in comparing the conformational preference of the phosphoryl group at the anomeric carbon atom in 1,3-dithiane with that in 1,3-dioxane. In this context, it is of interest that the only work dealing with this problem has been published by Thiem et al.,[14] who showed that the anomeric effect of the dimethoxyphosphoryl group in the oxane 4 is small and equal to 0.53 kcal/mol.

In the present paper we would like to report the results of our studies on a solution and solid-state conformation of 2-(diphenylphosphinoyl)-5,5-dimethyl-1,3-dioxane (5) as a model compound.

Results and Discussion

The dioxane 5 was prepared in 78% yield according to the slightly modified procedure described by Costisella and Gross,[15] which involves the Arbuzov reaction of isopropyl diphenylphosphinite with (5,5-dimethyl-1,3-dioxan-2-yl)-trimethylammonium iodide (eq 1).



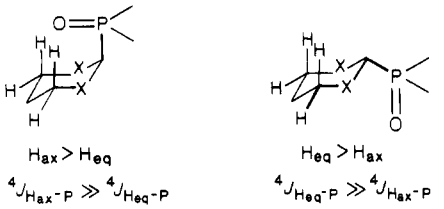
5

The ^1H NMR spectrum (250 MHz, $CDCl_3$) of 5 shows at high field two well-separated singlets at δ 0.72 and 1.03 corresponding to the geminal methyl groups. In the range between δ 3.4 and 3.8 one observes two groups of signals due to the methylene protons. A high-field signal centered at δ 3.48 appears as a doublet with the coupling constant $^2J_{H-H}$ = 11.0 Hz whereas the low-field signal centered at δ 3.74 consists of a doublet of doublets with the same geminal coupling constant, $^2J_{H-H}$ = 11.0 Hz, and a small one, $^4J_{H-P}$ = 1.5 Hz, due to a long-range coupling with phosphorus.

These data for 5, however, do not allow us to make an unambigous assignment of these two signals to the axial and equatorial methylene protons, because, independently of the predominant conformation in a solution, the long-range coupling with phosphorus would be expected for the low-field signal. Such a situation is schematically shown below (for the sake of simplicity the methyl groups are omitted).

Table I. Solvent Effect on the Chemical Shift Difference, $\Delta\delta$, for the Methylene Protons and Chemical Shift of the Methine Proton at C-2 in 5

solv	$\Delta\delta$	δH(C-2)
DMSO-d_6	0.33	5.42
CD_3CN	0.16	5.28
CD_3OD	0.14	5.32
$(CD_3)_2CO$	0.13	5.26
CD_2Cl_2	0.24	5.16
$CDCl_3$	0.26	5.27
C_6D_6	0.41	5.06



Nevertheless, a small chemical shift difference between the axial and equatorial methylene protons, $\Delta\delta$ = 0.26, strongly indicates that the diphenylphosphinoyl group in 5 is occupying predominantly the equatorial position. Therefore, it is reasonable to ascribe the signals at δ 3.74 to the equatorial methylene protons and their coupling with phosphorus as a *W*-type.

Further support for this assignment was provided by the ^{13}C NMR spectra (62.89 MHz, $CDCl_3$) of 5. On the basis of the off-resonance experiments the doublet at δ 78.38 is ascribed to the C-4 and C-6 carbon atoms. A large coupling constant, $^3J_{C-P}$ = 10.4 Hz, indicates that phosphorus and carbon C-4 (or C-6) are in antiperiplanar orientation. Furthermore, in accord with the observed relationship[7] between the orientation of the phosphoryl group at C-2 in 1,3-dithianes and the magnitude of the γ-effect, the γ-effect value for 5 equal to -0.72 ppm[16] is consistent with the prevailing equatorial position of the $Ph_2P(O)$ groups in the 1,3-dioxane ring.

The change in a conformational equilibrium may be reflected in the magnitude of the chemical shift difference, $\Delta\delta$, between the axial and equatorial protons at C-4 and C-6. For example, Ōki et al.[17] observed an increase of the $\Delta\delta$ values with increasing population of the axially substituted conformer for 2-(phenylthio)- and 2-(methylthio)-1,3,5-trithianes. A similar simple dependence of the chemical shift of the methine proton at C-2 on conformational equilibrium has also been noted in the literature. Eliel et al.[11] showed that the axial proton at C-2 resonates at lower field than the equatorial one in anancomeric 2-(hydroxymethyl)-*cis*-4,6-dimethyl-1,3-dithianes. The corresponding changes of the chemical shift of the methine proton depending on a conformational equilibrium were observed by Ōki et al. for 2-(phenylthio)-1,3,5-trithiane. Our observations (see Table I) of phenomena taking place in a solution of 5 in different solvents are in line with that mentioned above.

Thus, one observes the gradual decrease of the $\Delta\delta$ values and increase of the $\delta_{H(C-2)}$ values with increasing dielectric

(7) Mikołajczyk, M.; Graczyk, P.; Bałczewski, P. *Tetrahedron Lett.* **1987**, *28*, 573.
(8) The absence of the deuterium isotope effect on the conformational equilibrium in 2-deuterio-1,3-dithiane led Anet and Kopelevich to the same conclusion: Anet, F. A. L.; Kopelevich, M. *J. Chem. Soc., Chem. Commun.* **1987**, 595.
(9) Arai, K.; Iwamura, H.; Ōki, M. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3319.
(10) Juaristi, E.; Tapia, J.; Mendez, R. *Tetrahedron* **1986**, *42*, 1253.
(11) Eliel, E. L.; Hartmann, A. A.; Abatjoglou, A. G. *J. Am. Chem. Soc.* **1974**, *96*, 1807.
(12) Anderson, C. B.; Sepp, D. T. *J. Org. Chem.* **1968**, *33*, 3272.
(13) Bailey, W. F.; Eliel, E. L. *J. Am. Chem. Soc.* **1974**, *96*, 1798.
(14) Thiem, J.; Mayer, B.; Paulsen, H. P. *Chem. Ber.* **1978**, *111*, 3325.
(15) Costisella, B.; Gross, H. *J. Prakt. Chem.* **1977**, *319*, 8.
(16) The values of the ^{13}C NMR chemical shifts for 5,5-dimethyl-1,3-dioxane as a reference compound were taken from the work of Eliel et al.; Jones, A. J.; Eliel, E. L.; Grant, M. O.; Knoeber, M. C.; Bailey, W. F. *J. Am. Chem. Soc.* **1971**, *93*, 4772.
(17) Ōki, M.; Sugawara, T.; Iwamura, H. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2457.

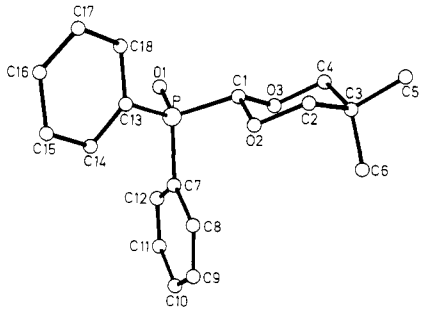
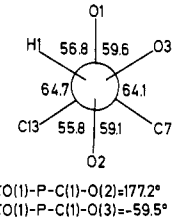


Figure 1. Atom numbering scheme and solid-state conformation of 2-(diphenylphosphinoyl)-5,5-dimethyl-1,3-dioxane (**5**).



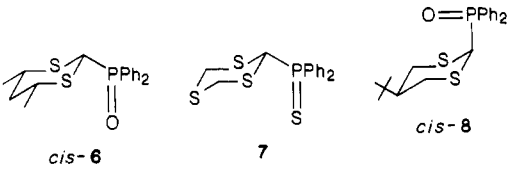
∢O(1)-P-C(1)-O(2)=177.2°
∢O(1)-P-C(1)-O(3)=-59.5°

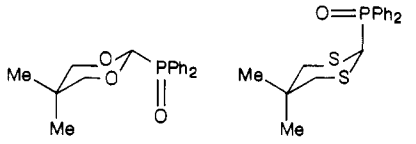
Figure 2. Newman projection around the C-1–P bond showing the relevant torsion angles in **5**.

constant of the medium. Such changes result from the conformational equilibrium shift in favor of the equatorial conformer of **5** on going from nonpolar to polar solvents.[18] The only exception is DMSO, in which a rather high value of $\Delta\delta$ is observed. This may be due to a specific solvation of **5** by this highly polar, aprotic solvent.

All the spectroscopic data presented above points to a strong preferential equatorial orientation of the diphenylphosphinoyl group in the 1,3-dioxane ring of **5** in a solution. This is additionally confirmed by temperature invariance of the ^{31}P NMR spectrum of **5** down to −90 °C. There was no decoalescence at low temperature, as would be expected if there existed in palpable equilibrium between two conformers. The equatorial orientation of the $Ph_2P(O)$ group in **5** was also found in the crystal state. The crystal structure of **5** was solved by direct methods. Refinement of atomic parameters converged to $R = 0.051$ over 2697 reflections. A view of the solid-state conformation of **5** with the numbering system is shown in Figure 1. It reveals that the 1,3-dioxane ring has a chair conformation with the diphenylphosphinoyl group being equatorial. A Newman projection (Figure 2) along the anomeric carbon–phosphorus bond shows that the phosphoryl oxygen atom, O-1, is antiperiplanar and synclinal to the ring oxygen atoms O-2 and O-3, respectively. The nonbonding distance between O(1) and O(3) is rather short and equal to 3.138 Å. The bond length between the anomeric carbon and phosphorus [C-1–P] in **5** of 1.846 Å is very similar to that in the *cis*-1,3-dithiane **6** [1.840 Å][19] and close to the corresponding value of 1.829 Å in the 1,3,5-trithiane **7**[20] with the thiophosphoryl group in the equatorial position. However, it is significantly longer than the corresponding C-1–P distances found in **1** [1.825 Å],[4a] **2** [1.812 Å],[5] *cis*-**8** [1.824 Å][20] where the phosphoryl group is axial.

The results presented above clearly show that the phosphoryl group in **5** is occupying an equatorial position both in solution and in the crystal. This finding is a sharp contrast with 2-(diphenylphosphinoyl)-5,5-dimethyl-1,3-dithiane (**9**), which exists in a chair conformation with the phosphoryl group at C-2 being axial.[7]





Most probably, due to a shorter distance between the anomeric carbon atom and the endocyclic oxygen atoms in **5**, as compared with the C–S bond in **9**, the diphenylphosphinoyl group behaves normally as a bulky substituent preferring the equatorial position in the 1,3-dioxane ring. In other words, the steric effect (1,3-syn axial, repulsive interaction in the axial conformation of **5**) is much stronger than any other stereoelectronic effects and determines the conformational equilibrium of **5**. Further experimental studies and theoretical calculations to understand this contrasting conformational behavior of 2-phosphoryl-1,3-dioxanes and 1,3-dithianes are under way in this laboratory.

Experimental Section

^1H NMR spectra of 3–4% solution in appropriate deuteriated solvents were recorded at 80 and 250.13 MHz on Tesla and Bruker WP 250 spectrometers, respectively. The ^{13}C NMR spectra were measured at 62.89 MHz on the Bruker instrument. The ^{31}P NMR chemical shifts were measured on a Jeol INM-FX 60 spectrometer at 24.3 MHz with 85% H_3PO_4 as external standard. Mass spectra were recorded with an LKB 2091 mass spectrometer. Anhydrous hydrocarbons and diethyl ether were distilled from $LiAlH_4$. Methylene chloride was distilled from P_2O_5. Melting points are uncorrected.

2-(Diphenylphosphinoyl)-5,5-dimethyl-1,3-dioxane (5). A mixture of freshly prepared (5,5-dimethyl-1,3-dioxan-2-yl)trimethylammonium iodide (3.01 g, 10.0 mmol) and isopropyl diphenylphosphinite (2.23 mL, 2.44 g, 10.0 mmol) in toluene (30 mL) was refluxed for 3 h. The reaction mixture was then cooled, filtered, and concentrated to about 10 mL. Petroleum ether (bp 40–60 °C, 40 mL) was added, and the mixture was left to stand overnight. The solid thus obtained was recrystallized from benzene–petroleum ether to afford 2.82 g (78.0%) of white crystals, mp 140.8–141.8 °C. Recrystallization from methylene chloride–diethyl ether gave the analytically pure sample of **5**: mp 142.0–143.0 °C (lit.[15] mp 139–141 °C); ^1H NMR (250 MHz, $CDCl_3$) δ 0.72 (s, 3 H), 1.03 (s, 3 H), 3.48 (d, $^2J_{H-H}$ = 11.0 Hz, 2 H), 3.74 (dd, $^2J_{H-H}$ = 11.0 Hz, $^4J_{H-P}$ = 1.5 Hz, 2 H), 5.27 (d, $^2J_{H-P}$ = 5.9 Hz, 1 H), 7.4–8.0 (m, 10 H); ^{31}P NMR (24.3 MHz, $CHCl_3$) δ 23.16; ^{13}C NMR (62.89 MHz, $CDCl_3$) δ 21.92 (s, CH_3), 22.90 (s, CH_3), 30.97 (s, $(CH_3)_2C$), 78.38 (d, $^3J_{P-C}$ = 10.4 Hz, CH_2), 101.31 (d, $^1J_{P-C}$ = 118.1 Hz, CHP), 128.26 (d, $^3J_{P-C}$ = 12.0 Hz, $C_{Ar\ meta}$), 129.38 (d, $^1J_{P-C}$ = 100.9 Hz, PC_{Ar}), 132.22 (s, $C_{Ar\ ortho}$), 132.38 (s, $C_{Ar\ para}$); IR (KBr) 1087 (vs), 1190 (vs) cm^{-1}; MS (70 eV) m/e (relative intensity) 115 (100), 69 (67), 45 (28), 41 (20). Anal. Calcd for $C_{18}H_{21}PO_3$: C, 68.34; H, 6.69; P, 9.79. Found: C, 68.45; H, 7.12; P, 9.57.

Crystal Data. $C_{18}H_{21}O_3P$, M_r 318.31, monoclinic, a = 11.178 (3) Å, b = 9.607 (4) Å, c = 15.475 (6) Å, β = 91.86 (2)°, V = 1660.8 (9) Å^3, Z = 4, d_{calcd} = 1.265 g cm^{-3}, absorption coefficient for Mo K_α (λ = 0.7107 Å), μ = 1.806 cm^{-1}, space group $P2_1/c$.

Intensities were measured on a Syntex $P2_1$ diffractometer with graphite monochromated Mo K_α radiation. The θ–2θ scan technique was used, $\theta 2_{max}$ = 52°. Of 2853 reflections measured, 2697 with $I > 1.96^*(I)$ were retained for the structure analysis.

(18) Fuchs, B.; Ellencweig, A.; Tartakovsky, E.; Aped, P. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 287.
(19) Juaristi, E.; Valenzuela, B. A.; Valle, L. *J. Org. Chem.* **1984**, *49*, 3026.
(20) Mikołajczyk, M.; Bałczewski, P.; Graczyk, P.; Wieczorek, M.; Bujacz, G., unpublished results.

Structure Analysis and Refinement. The crystal structure was solved by direct methods using the MULTAN-76 program. The structure was refined by the full-matrix least-squares method for non-H atoms with anisotropic temperature factors and with isotropic temperature factors for H atoms, which were located in a difference map in the expected positions. The final R value was 0.051, R_w = 0.061. Final atomic positional and thermal parameters are listed in Tables II and III (supplementary material).

Acknowledgment. This work was financially supported by the Polish Academy of Sciences and Ministry of Education within the project CPBP-01-13 and RP-II-10.

Registry No. 5, 20570-22-3; (5,5-dimethyl-1,3-dioxan-2-yl)-trimethylammonium, 62999-89-7; isopropyl diphenylphosphinite, 1706-91-8.

Supplementary Material Available: Final atomic coordinates and temperature factors (Tables II and III), bond lengths and angles (Tables IV and V), torsion angles (Table VI), displacements of atoms from selected least-squares planes and angles between normals to planes (Table VII) for compound **5** (6 pages); a list of observed and calculated structure factors (Table VIII) for compound **5** (20 pages). Ordering information is given on any current masthead page.

Easy One-Step General Synthesis of Acylsilanes

Antonella Capperucci, Alessandro Degl'Innocenti,* Cristina Faggi, and Alfredo Ricci

Centro CNR sulla Chimica e la Struttura dei Composti Eterociclici e loro Applicazione, c/o Dipartimento di Chimica Organica dell'Università, via G. Capponi 9, 50121 Firenze, Italy

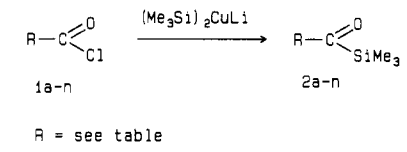
Pasquale Dembech and Giancarlo Seconi

Istituto CNR dei Composti del Carbonio Contenenti Eteroatomi, via Tolara di Sotto 69, 40089 Ozzano Emilia, Italy

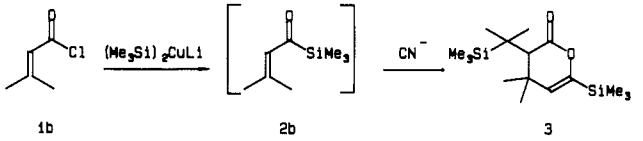
Received November 3, 1987

Acylsilane chemistry has seen an increasing interest in the recent years,[1] due to the emerging potentialities of these compounds as valuable building blocks for the synthesis of more complex molecules.[2] Acylsilanes in fact may undergo a number of synthetically useful transformations, such as Brook reactions,[3] oxidation to carboxylic acids,[4] fluoride-promoted conversion to aldehydes,[5] and catalyzed nucleophilic acylation.[6]

Scheme I



Scheme II



Since the first discovery of acylsilanes by A. G. Brook, several synthetic methods have been developed, but most of them suffer of lengthy procedures[7] or involve the use of expensive or not easily available starting materials.[8] Moreover, none of the present synthetic methods seem to be of a general nature, often being applied to the preparation of a specific series of acylsilanes. We report here a simple one-pot synthesis of acyltrimethylsilanes, through the reaction of (trimethylsilyl)cuprate with a variety of acyl chlorides, as depicted in Scheme I.

All the reactions were performed with (trimethylsilyl)-cuprate generated from (trimethylsilyl)lithium and CuCN, following Fleming's procedure.[9] The results are summarized in Table I.

The use of (trimethylsilyl)cuprate proved to be essential, in order to achieve a clean reaction, since treatment of (trimethylsilyl)lithium itself with several acyl chlorides led to complex reaction mixtures where only traces of the wanted compounds could be detected.

Reactions proceed smoothly and under mild conditions, usually affording, after the workup, the required acylsilane with a high degree of purity.

An outstanding feature of this new preparation of acylsilanes is its generality: as shown in Table I, this synthetic approach may be used with a wide variety of acyl halides, leading to a simple, direct synthesis of either aliphatic, aromatic, or heteroaromatic acylsilanes from commercially available starting materials.

Items 5 and 9–12 in Table I point out an even more interesting feature of this reaction, which affords the preparation of several novel mono- and bis(acylsilanes), otherwise not easily obtainable by known common routes. Thus for instance, whereas the literature methods failed when applied to the synthesis of the sterically hindered acylsilane **2e**, this compound could be obtained with good yields by following the silylcuprate procedure. In the particular case of item 2, the silylcuprate was prepared by using CuI instead of CuCN. The high reactivity of the expected 3-methyl-1-(trimethylsilyl)-2-buten-1-one in the presence of catalytic amounts of cyanide ion, as already pointed out in a previous paper,[6c] led to the formation of compound **3**, as shown in Scheme II.

The use of CuI turned out to minimize, even if it did not completely inhibit, the formation of **3**, allowing the isolation of **2b** in reasonable yield.

(1) (a) Reich, H. J.; Eisenhart, E. K.; Olson, R. E.; Kelly, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 7791. (b) Danheiser, R. C.; Fink, D. M. *Tetrahedron Lett.* **1985**, *26*, 2509. (c) Ricci, A.; Fiorenza, M.; Degl'Innocenti, A.; Seconi, G.; Dembech, P.; Witzgall, K.; Bestmann, H. J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1068. (d) Page, P. C. B.; Rosenthal, S. *Tetrahedron Lett.* **1986**, *27*, 5421. (e) Reich, H. J.; Holtan, R. C.; Borkowsky, S. L. *J. Org. Chem.* **1987**, *52*, 312.

(2) Reich, H. J.; Eisenhart, E. K. *J. Org. Chem.* **1984**, *49*, 5282. Ricci, A.; Degl'Innocenti, A.; Borselli, G.; Reginato, G. *Tetrahedron Lett.* **1987**, *28*, 4093.

(3) Brook, A. G. *Acc. Chem. Res.* **1974**, *7*, 77.

(4) (a) Miller, J. A.; Zweifel, G. *J. Am. Chem. Soc.* **1981**, *103*, 6217. (b) Zweifel, G.; Backlund, S. J. *J. Am. Chem. Soc.* **1977**, *99*, 3184.

(5) (a) Brook, A. G. *J. Am. Chem. Soc.* **1957**, *79*, 4373. (b) Sato, T.; Arai, M.; Kuwajima, I. *J. Am. Chem. Soc.* **1977**, *99*, 5827. (c) Shinzer, D.; Heathcock, C. H. *Tetrahedron Lett.* **1981**, *22*, 1881.

(6) (a) Degl'Innocenti, A.; Pike, S.; Walton, D. R. M.; Seconi, G.; Ricci, A.; Fiorenza, M. *J. Chem. Soc., Chem. Commun.* **1980**, 1201. (b) Ricci, A.; Degl'Innocenti, A.; Chimichi, S.; Fiorenza, M.; Rossini, G.; Bestmann, H. J. *J. Org. Chem.* **1985**, *50*, 130. (c) Ricci, A.; Degl'Innocenti, A.; Mordini, A.; Reginato, G.; Colotta, V. *Gazz. Chim. Ital.* **1987**, *117*, 645.

(7) (a) Brook, A. G.; Duff, J. M.; Jones, P. F.; Davis, N. R. *J. Am. Chem. Soc.* **1967**, *89*, 431. (b) Brook, A. G. *Adv. Organomet. Chem.* **1968**, *7*, 95. (c) Corey, E. J.; Seebach, D.; Freedman, R. *J. Am. Chem. Soc.* **1967**, *89*, 434.

(8) (a) Yamamoto, K.; Suzuki, S.; Tsuji, J. *Tetrahedron Lett.* **1980**, *21*, 1653. (b) Aoyama, T.; Shioiri, T. *Tetrahedron Lett.* **1986**, *27*, 2005. (c) Kang, J.; Lee, J. H.; Kim, K. S.; Jeong, J. U.; Pyun, C. *Tetrahedron Lett.* **1987**, *28*, 3261.

(9) Ager, D. J.; Fleming, I.; Patel, S. K. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2521.

0022-3263/88/1953-3612$01.50/0