ture, stoppered, and kept overnight. The acetic acid was distilled off under reduced pressure. The pale-white solid residue was washed twice with 25-ml portions of acetone and crystallized from mixed acetone–methanol solvent.

1,1,4,4-Tetraphenyl-2,5-di-*tert*-butyl-1,4-diphosphoniacyclohexadiene 2,5-dichloride (8) had mp 285–287°; yield 73%; ir (KBr) 6.12 (C=C), 6.95 μ (PC_6H_5); nmr (TFA) δ 8.45 (t, J = 28 Hz, 2 H, vinyl), 7.94 (m, 20 H, phenyl), 1.33 (s, 18 H, *tert*-butyl groups).

A methanol solution of **8** on treatment with a methanol solution of sodium picrate produced an orange, crystalline precipitate of dipicrate. The precipitate was recrystallized from methanol, mp 278–279°.

Anal. Calcd for $C_{48}H_{44}N_6O_{14}P_2$ (picrate): C, 57.60; H, 4.43; N, 8.40; P, 6.19. Found: C, 58.00; H, 4.54; N, 8.35; P, 5.96.

1,4-Di-*n*-butyl-1,2,4,5-tetraphenyl-1,4-diphosphoniacyclohexadiene 2,5-dichloride (10) had mp 257–259°; ir (KBr) 6.48 (C=C), 6.96 μ (PC_6H_5); nmr (TFA) 8.17 (t, J = 29 Hz, 2 H, vinyl), 7.21–8.65 (m, 20 H, phenyl), 3.11 (m, 4 H, PCH_2), 1.69 (m, 8 H, methylenes), 1.01 (t, J = 7 Hz, 6 H, methyl). The dipricrate of **10** was prepared as described under **8**, mp 265–267°.

Anal. Calcd for $C_{48}H_{44}N_6O_{14}P_2$: C, 57.60; H, 4.43; N, 8.40; P, 6.19. Found: C, 57.76; H, 54.2; N, 8.46; P, 6.33.

1,4-Di-*n*-butyl-1,4-diphenyl-1,4-diphosphonia-2,5-dipropylidenecyclohexane dichloride (11a) had mp 240–241°; yield 32%; ir 6.19 (C=C), 6.96 μ (PC_6H_5); nmr δ 7.10 (2 H, vinyl), 4.27 (t, J = 13 Hz, 4 H, ring methylenes), 3.02 (m, 4 H, PCH_2), 2.49 (d, J = 7 Hz, 4 H, allylic), 1.58 (m, 8 H methylenes), 1.22 (two t, J = 7.5 Hz, 12 H, methyl).

1,4-Di-*n*-butyl-1,4-diphenyl-1,4-diphosphonia-2,5-dibutylidenecyclohexane dichloride (11b) had mp 249–251°; yield 27%; ir 6.20 (C=C), 7.01 μ (PC_6H_5); nmr (TFA) δ 7.95 (m, 10 H, phenyl), 7.08 (crude d of t, J_{PH} = 20, J_{HH} = 7 Hz, 2 H, vinyl), 4.25 (t, J = 13 Hz), 4 H, ring methylenes), 2.98 (m, 4 H, PCH_2), 2.48 (d, J = 7 Hz, 4 H, allylic), 1.56 (m, 12 H, methylenes), 1.02 (12 H, methyls).

1,4-Di-*n*-butyl-1,4-diphenyl-2,5-di-*n*-propyl-1,4-diphosphoniacyclohexadiene 2,5-Dichloride (12).—*n*-Butylphenylpentynyl-1-phosphine (1.16 g, 0.005 mol) was dissolved in 25 ml of glacial acetic acid and cooled to 0°. A slow stream of HCl was passed through the solution for 1 hr with continuous stirring while the temperature was kept at 0°. The acetic acid was stripped off under reduced pressure at room temperature. The residue on trituration with acetone gave the desired product in 20% yield, melting at 229–235°. The ir spectrum (KBr) showed characteristic absorption bands of 6.21 (C=C) and 6.98 μ (PC_6H_5) and the nmr spectrum (AcOH) exhibited the characteristic pseudotriplet (J = 27 Hz) at δ 8.24 and all the other proton resonance signals also checked with the assigned structure. Similarly, the nmr spectrum in methanol was found to be in agreement with the structure. However, nmr spectrum in TFA showed that **12** had isomerized to **11a**. Also when **12** was refluxed with acetic acid for 1 hr, the nmr spectra in all the three solvents, AcOH, TFA, and methanol, showed that **12** had isomerized to the exocyclic form **11a**. Compounds described here are available from Strem Chemical Co., Danvers, Mass.

Registry No.—**7,** 33730-51-7; **8,** 38565-20-7; **8** dipicrate, 38565-21-8; **9a,** 38592-33-5; **9b,** 38565-22-9; **9c,** 38565-23-0; **10,** 38565-24-1; **10** dipicrate, 38565-25-2; **11a,** 38565-26-3; **11b,** 38565-27-4; **12,** 38565-28-5; 3,3-dimethylbutyryllithium, 37892-71-0; diphenylphosphinous chloride, 1079-66-9; phenylethyne, 536-74-3; 1-pentyne, 627-19-0; 1-hexyne, 693-02-7.

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The Reaction of Phenylphosphonic Dichloride with Dimethyl Sulfoxide[1]

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Dimethyl sulfoxide (DMSO) will convert chlorides of pentavalent phosphorus into their acids.[2] To date this reaction has been used only with monochlorides, but we find it to be a convenient method for the single-step conversion of phenylphosphonic dichloride (I) into methyl phenylphosphonate (II).

$$\underset{\text{I}}{\text{PhPOCl}_2} \xrightarrow[2.\ \text{MeOH}]{1.\ \text{DMSO}} \underset{\text{II}}{\text{PhPO(OH)OMe}}$$

Experimental Section

DMSO (2 g, 0.0256 mol) in CH_2Cl_2 (15 ml, dried over CaH_2) was added to stirred phenylphosphonic dichloride (5 g, 0.0256 mol) in dry CH_2Cl_2 (100 ml) during a period of 5 min. The reaction was followed by ir spectroscopy using matched NaCl cells and CH_2Cl_2 as a reference. After *ca.* 30 min, the absorptions at 1258 (P=O) and 1110 cm^{-1} (PPh) due to the phosphonic dichloride had reached a minimum and a new absorption at 1230 cm^{-1} (P=O) had reached a maximum. A fivefold excess of MeOH was then added and after several hours the solvent was removed on a rotary evaporator. The residue, dissolved in dry Me_2CO, was neutralized with cyclohexylamine (Congo Red). The cyclohexylammonium salts of II and phenylphosphonic acid precipitated. (A small amount of dimethyl phenylphosphonate remained in solution, and was identified by nmr.)

Cyclohexylammonium methyl phenylphosphonate (III) was extracted with hot Me_2CO, in which the salt of the diacid is insoluble. The cyclohexylammonium methyl phenylphosphonate (III) had mp 156–158° after recrystallization from Me_2CO, and the overall yield was 52%. *Anal.* Calcd: C, 57.5; H, 8.2; N, 5.2. Found: C, 57.4; H, 8.4; N, 5.0. It had a strong P=O stretch at 1188 cm^{-1}, and the barium salt had a P=O stretch at 1220 cm^{-1}. [That of barium phenylphosphonate is at 1258 cm^{-1}, and that of the free acid is at 1145 cm^{-1}, and the dichloride shows strong absorptions at 1258, 1110, and 580 cm^{-1} (PCl)]. The 60-MHz nmr spectrum of III (in D_2O, Varian T-60) had a multiplet (cyclohexyl) at δ 0.86–1.96 (10.9), a doublet (OMe) at 3.22 and 3.40 (J = 11 Hz, 3.0),[5] and a multiplet (phenyl) at 7.31–7.76 (5.2). The values in parentheses are peak areas. Dimethyl phenylphosphonate in $CDCl_3$ had a doublet (methoxy) at δ 3.69 and 3.87 (J = 11 Hz) and a multiplet (phenyl) at 7.41–8.08.

In an initial experiment the reaction mixture was left for 1 hr after addition of DMSO under N_2 and the yield of III was 40% after recrystallization, but only the salt of the diacid was isolated from an experiment using an twofold excess of DMSO.

Results

This reaction appears to provide a simple alternative to the usual method of dealkylation with halide ion for the preparation of monomethyl phosphates or

(1) Support of this work by the Arthritis and Metabolic Diseases Institute of the USPHS is gratefully acknowledged.

(2) E. H. Amonoo-Neizer, S. K. Ray, R. A. Shaw, and B. C. Smith, *J. Chem. Soc.*, 4296 (1965); 6250 (1965). For general discussion see ref 3, 4.

(3) N. Kharasch and B. S. Thyagarajan, *Quart. Rep. Sulfur Chem.*, **1**, 16 (1966).

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(5) This $^{31}P-^{1}H$ coupling is typical of compounds of this general structure.[6]

(6) J. F. Nixon and R. Schmutzler, *Spectrochim. Acta*, **22**, 565 (1966).

related compounds.[7] We have not tested its general applicability, but it gives better results than the direct reaction of the dichloride with MeOH. The general course of the reactions of DMSO with acid chlorides has been discussed extensively.[2-4]

The reaction generates chloromethyl methyl sulfide, which can react further with DMSO, but this reaction is slower than that of DMSO with a phosphonic dichloride, *cf.* ref 8, and causes no problems.

Registry No.—I, 824-72-6; III, 38555-73-6; DMSO, 67-68-5.

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Isomeric 2,4,6-Tris(3,3,4,4,5,5,6,6,6-nonafluorohexyl)-2,4,6-trimethylcyclotrisiloxanes

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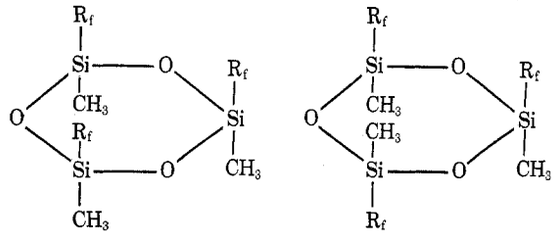
Diorganocyclosiloxanes are an important segment of silicone chemistry and have been studied extensively;[1] however, fluorine-containing diorganocyclosiloxanes are a relatively new class of compounds.[2] Although numerous studies involving diorganocyclosiloxanes have been described in the literature,[1] the isolation and characterization of the stereoisomeric diorganocyclosiloxanes are limited to methylphenylsiloxane[3] and methyl-(3,3,3-trifluoropropyl)siloxane[4] systems. We now wish to report the synthesis and characterization of the *cis*- and *trans*-2,4,6-tris(3,3,4,4,5,5,6,6,6-nonafluorohexyl)-2,4,6-trimethylcyclotrisiloxanes (1 and 2).

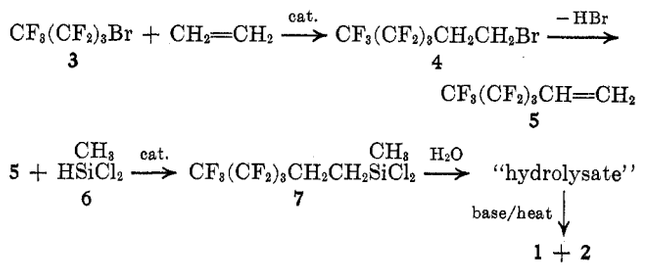


1, cis 2, trans

$R_f = CF_3CF_2CF_2CF_2CH_2CH_2$

The synthetic route for the preparation of the cyclotrisiloxanes 1 and 2 is shown in Scheme I. The free radical catalyzed addition of ethylene to the bromide 3[5] followed by dehydrobromination of the resulting adduct 4 gave the olefin 5 in high yield. In the ethylene addition, some of the higher telomers and a small amount of 1,1,1,2,2,3,3,4,4-nonafluorohexane (8) were formed in addition to the adduct 4. The silane 7 was prepared in 86% yield by the addition of silane 6 to olefin 5 using chloroplatinic acid as a catalyst at reflux temperature. The base-induced "cracking" of the hydrolysate of silane 7 at 225–250° yielded a mixture of two stereoisomeric cyclotrisiloxanes (1 and 2), a high-melting crystalline solid (mp 36–37°), and a low-melting liquid [mp 22–23°, bp 96° (0.17 mm)], in a ratio (glc) of approximately 1:2, respectively. The stereoisomers were both isolated in gas chromatographically pure form by crystallization from pentane and by fractional distillation, respectively. Both isomers gave a satisfactory elemental analysis and molecular weight for 2,4,6-tris(3,3,4,4,5,5,6,6,6-nonafluorohexyl)-2,4,6-trimethylcyclotrisiloxane. The characteristic cyclotrisiloxane band (Si–O, 9.8 μ)[6] was observed in the infrared absorption spectra of the isomers.

SCHEME I



On the basis of thermodynamic considerations[7] and the measurement of the dipole moments (high-melting form, 5.67 D, and low-melting form, 2.75 D),[8] the high-melting form was assigned the cis configuration (1) while the low-melting isomer was assigned the trans configuration (2). In the infrared absorption spectra, bands at 12.7 and 12.4 μ have been observed for the cis and trans isomers 1 and 2, respectively. Bands at 12.7 and 12.4 μ were also observed for the *cis*- and *trans*-2,4,6-tris(3,3,3-trifluoropropyl)-2,4,6-trimethylcyclotrisiloxanes, respectively, and appear to be characteristic bands for the respective stereoisomers.[9] It may be of interest to note that the trans isomer was found to be the high-melting solid in the case of 2,4,6-tris(3,3,3-trifluoropropyl)-2,4,6-trimethylcyclotrisiloxanes.[4a]

Experimental Section

All melting points and boiling points are uncorrected. All melting points were measured by placing a sample in a cooling device and the observations were made using a Lietz hot stage microscope. Infrared absorption spectra were determined on a Perkin-Elmer Model 521 grating infrared spectrophotometer. The ^{19}F resonance spectra were measured on a Varian high-

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(7) The stronger reciprocal repulsions of the bulky and electronegative nonafluorohexyl groups would tend to make the formation of the cis isomer less favorable than that of the trans isomer. The trans/cis ratio observed is approximately two.

(8) Since all electronegative nonafluorohexyl groups in the cis isomer are on the one side of the plane of the siloxane ring, a greater dipole moment should be expected for the cis isomer than for the trans isomer.

(9) H. M. Klimisch and R. R. Buch, unpublished results.