Reaction of 1,7,7-trimethylbicyclo[2.2.1]heptane-2,3-dione with hexaethyltriamidophosphite in the presence of diethylammonium chloride. Synthesis and the three-dimensional structure of (1,7,7-trimethyl-2-oxobicyclo[2.2.1]hept-3-yloxy)tris(diethylamino)phosphonium chloride

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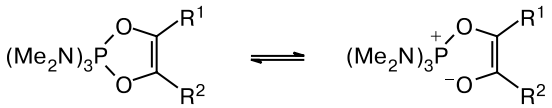
The reaction of 1,7,7-trimethylbicyclo[2.2.1]heptane-2,3-dione with hexaethyltriamidophosphite in the presence of diethylammonium chloride afforded a stable quasiphosphonium salt, *viz.*, (1,7,7-trimethyl-2-oxobicyclo[2.2.1]hept-3-yloxy)tris(diethylamino)phosphonium chloride, as one diastereomer (racemate, 1*R**,3*S**,4*S**).

Key words: 1,7,7-trimethylbicyclo[2.2.1]heptane-2,3-dione (camphoroquinone), diethylammonium chloride, hexaethyltriamidophosphite, quasiphosphonium salt.

It is known[1—6] that derivatives of tricoordinate phosphorus, *viz.*, total amides of phosphorous acid, can react with α,β-dicarbonyl compounds, including *ortho*-quinones, to form phosphoranes or betaine-type phosphonium salts. For example, studies of the reactions of hexamethyltriamidophosphite with α-diketones demonstrated[1—4] that the resulting phosphoranes **1** are in rapid equilibrium with the corresponding quasiphosphonium salts **2** (Scheme 1).

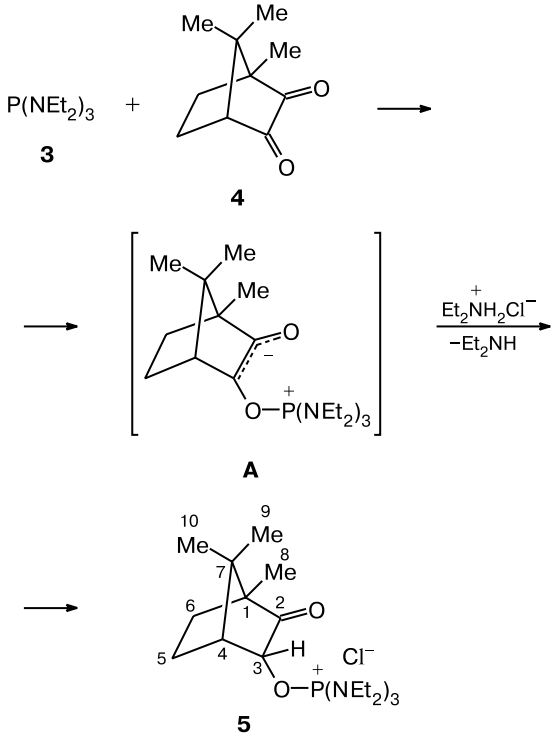
Scheme 1



1 **2**

We demonstrated for the first time that hexaethyltriamidophosphite (**3**) slowly reacts with *d*,*l*-camphoroquinone (**4**) in the presence of diethylamine hydrochloride (Scheme 2) to give a crystalline compound, which is characterized by a singlet at δ_P 37.8 in the $^{31}P—\{^1H\}$ NMR spectrum. This chemical shift is indicative of the formation of a phosphonium salt. Analysis of the ^1H NMR spectrum of the reaction product revealed a low-field signal for the proton (δ 4.91, dd, $^3J_{P,O,C,H}$ = 9.6 Hz,

Scheme 2



3 **4** **A** **5**

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$^3J_{H,C,C,H}$ = 5.0 Hz) corresponding to the O—CH environment. This is consistent with the formation of a quasiphosphonium salt containing the P—OC bond. The $^{13}C—\{^1H\}$ NMR spectrum shows two low-field signals, *viz.*, a singlet of the carbonyl C(2) atom (δ_C 212.91) and a doublet of the C atom of the POC(3)H fragment (δ_C 80.67). In the proton-coupled spectrum, the latter signal is transformed into a doublet of multiplets with the additional constant $^1J_{H,C}$ = 151.2 Hz. These facts are indicative of the formation of relatively stable quasiphosphonium salt **5** containing the P—O—C fragment as one diastereomer.

The reaction proceeds, apparently, through the intermediate bipolar ion **A**, which is protonated by diethylammonium chloride to give the final product **5** and diethylamine. Generally, the quasiphosphonium salts $R_3P^+OR'X^-$ are very unstable and are readily transformed into compounds containing the phosphoryl group (Arbuzov reaction).[7] Compound **5** is relatively stable due, apparently, to steric shielding of the C(3) atom by the bicycloheptane fragment, which hinders the attack of the chloride anion on this atom according to the dealkylation step in the Arbuzov reaction by the S_N2 mechanism.

The structure of quasiphosphonium salt **5** was confirmed also by X-ray diffraction (Fig. 1). Compound **5** crystallizes in a noncentrosymmetric nonpolar space group (*Cc*), *i.e.*, exists as a racemate. The oxyphosphonium group is in an equatorial position in the five-membered ring C(1)C(2)C(3)C(4)C(7) and has an *endo* configuration at the bicyclo[2.2.1]heptane cage. The phosphorus atom has a distorted tetrahedral configuration. In the crystal structure of compound **5**, numerous nonclassical both intermolecular (C—H...O and C—H...Cl) and intramolecular (C—H...N) hydrogen bonds are present. Molecules **5** form chains along the crystallographic axis 0*z* due to the involvement of each molecule in two C—H...Cl contacts. The C—H...O interactions act in the perpendicular direction due to which the molecules are linked to each other to form zigzag chains. The simultaneous influence of these contacts gives rise to bilayer supramolecular structures parallel to the crystallographic plane *x*0*z*.

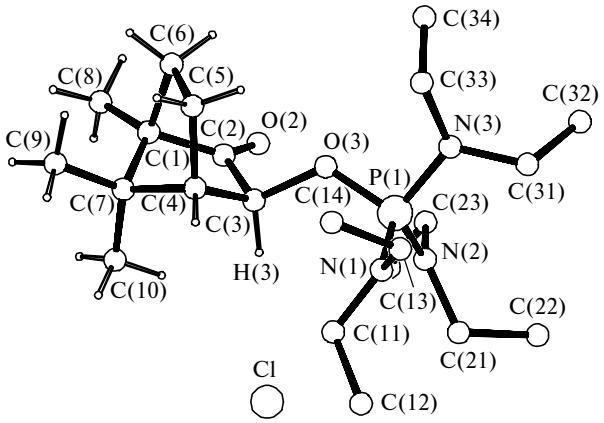

Fig. 1. Geometry of quasiphosphonium salt **5** (H atoms of the Et_2N groups are omitted). Selected geometric parameters of the molecule are given below. Bond lengths (*d*/Å): P(1)—O(3), 1.570(9); P(1)—N(1), 1.621(8); P(1)—N(2), 1.605(8); P(1)—N(3), 1.62(1); O(2)—C(2), 1.24(1); O(3)—C(3), 1.50(2); N(1)—C(11), 1.43(2); N(1)—C(13), 1.50(2); N(2)—C(21), 1.47(1); N(2)—C(23), 1.45(2); N(3)—C(31), 1.44(2); N(3)—C(33), 1.46(2); C(1)—C(2), 1.46(2); C(1)—C(6), 1.70(3); C(1)—C(7), 1.49(2); C(1)—C(8), 1.48(2); C(2)—C(3), 1.52(2); C(3)—C(4), 1.52(1); C(4)—C(5), 1.52(3); C(4)—C(7), 1.60(2); C(5)—C(6), 1.41(4); C(7)—C(9), 1.56(2). Bond angles (ω/deg): O(3)—P(1)—N(1), 115.2(4); O(3)—P(1)—N(2), 109.6(5); O(3)—P(1)—N(3), 99.8(5); N(1)—P(1)—N(2), 108.2(4); N(1)—P(1)—N(3), 111.0(6); N(2)—P(1)—N(3), 113.0(4); P(1)—O(3)—C(3), 123.9(6); P(1)—N(1)—C(13), 121.0(7); P(1)—N(2)—C(21), 123.9(7); C(2)—C(1)—C(7), 104(1); C(2)—C(1)—C(8), 120(1); C(6)—C(1)—C(7), 99(1); C(7)—C(1)—C(8), 122(1); O(2)—C(2)—C(1), 128(1); O(2)—C(2)—C(3), 124(1); C(1)—C(2)—C(3), 108.2(9); O(3)—C(3)—C(2), 108.4(8); O(3)—C(3)—C(4), 110(1); C(2)—C(3)—C(4), 102.1(9). Torsion angles (τ/deg): N(3)—P(1)—O(3)—C(3), −176.1(7); N(3)—P(1)—N(1)—C(11), 178.9(7); P(1)—O(3)—C(3)—C(2), −140.5(7); P(1)—O(3)—C(3)—C(4), 108.7(8); O(2)—C(2)—C(3)—O(3), 57(2); O(2)—C(2)—C(3)—C(4), 173(1).

Experimental

The ^1H, ^{13}C, $^{13}C—\{^1H\}$, ^{31}P, and $^{31}P—\{^1H\}$ NMR spectra were recorded on Bruker Avance-600 (600 MHz for ^1H and 150.9 MHz for ^{13}C) and Bruker CXP-100 (36.48 MHz for ^{31}P) instruments in $CDCl_3$ at 25 °C on the δ scale relative to Me_4Si; the signals of the residual protons of the deuterated solvent or the carbon nuclei of $CDCl_3$ (^1H and ^{13}C) were used as the internal standard; H_3PO_4 was used as the external standard.

(1,7,7-Trimethyl-2-oxobicyclo[2.2.1]hept-3-yloxy)tris(diethylamino)phosphonium chloride (5). A solution of hexaethylamidophosphite (**3**) (1.2 mL, 4.6 mmol), which was distilled over calcium hydride, and diethylammonium chloride (0.33 g, 3 mmol) in CH_2Cl_2 (5 mL) was added dropwise with cooling (−20 °C) to a solution of camphoroquinone (**4**) (0.5 g, 3 mmol) in CH_2Cl_2 (10 mL) under argon. The reaction mixture was kept at 20 °C for 7 days. The solvent was removed *in vacuo*. Hexane (10 mL) was added to the resulting oily liquid. After 1 day, a crystalline precipitate was obtained. The precipitate was filtered off and dried *in vacuo* (40—50 °C, 12 Torr). The yield was 0.8 g (60%), m.p. 120 °C. Found (%): C, 59.02; H, 10.33; P, 7.23. $C_{22}H_{45}ClN_3O_2P$. Calculated (%): C, 58.73; H, 10.01; P, 6.90. $^{31}P—\{^1H\}$ NMR, δ_P: 37.8 (s). ^1H NMR, δ: 4.91 (dd, H(3), $^3J_{P,O,C,H}$ = 9.6 Hz, $^3J_{H,C,C,H}$ = 5.0 Hz); 3.13 (dq, NCH_2, $^3J_{H,C,C,H}$ = 7.0 Hz, $^3J_{P,N,C,H}$ = 11.0 Hz); 2.53 (br.s, H(4)); 1.76—1.77 (two m, $C(5)H_2$); 1.62 (m, H(6A), $^3J_{H,C,C,H}$ = 9.5 Hz); 1.29 (m, H(6B), $^3J_{H,C,C,H}$ = 9.5 Hz, $^2J_{H,C,H}$ = 9.5 Hz);

1.11 (t, PNCMe, $^3J_{H,C,C,H}$ = 7.0 Hz); 0.95 (s, C(10)H_3); 0.89 (s, C(9)H_3); 0.85 (s, C(8)H_3). ^{13}C NMR, δ:* 212.91 (m [s], C(2)); 80.67 (dm [d], C(3), $^1J_{H,C}$ = 151.2 Hz, $^2J_{P,O,C}$ = 9.0 Hz); 58.41 (m [s], C(1)); 48.10 (br.d [br.s], C(4), $^1J_{H,C}$ = 146.6 Hz); 43.15 (m [s], C(7)); 40.45 (tm [d], NCH_2, $^1J_{H,C}$ = 138.8 Hz, $^2J_{P,N,C}$ = 4.2 Hz, $^2J_{H,C,C}$ = 4.2 Hz); 32.03 (br.tm [s], C(6), $^1J_{H,C}$ = 134.7 Hz); 20.20 (qq [s], C(10), $^1J_{H,C}$ = 125.5 Hz, $^3J_{H,C,C,C}$ = 4.8 Hz); 18.69 (br.tt [s], C(5), $^1J_{H,C}$ = 132.9 Hz, $^2J_{H,C(6),C(5)}$ = 0.8 Hz); 18.45 (qq [s], C(9), $^1J_{H,C}$ = 126.2 Hz, $^3J_{H,C,C,C}$ = 4.5 Hz); 13.40 (qdt [br.s], NCCH_3, $^1J_{H,C}$ = 127.0 Hz, $^3J_{P,N,C,C}$ = 2.8 Hz, $^2J_{H,C,C}$ = 2.8 Hz); 9.08 (qd [s], C(8), $^1J_{H,C}$ = 126.6 Hz, $^3J_{H,C,C,C}$ = 2.2 Hz).

X-ray diffraction study of compound 5 was carried out on an automated four-circle Enraf-Nonius CAD-4 diffractometer (Cu-Kα radiation, 20 °C). Crystals of compound **5** are monoclinic. At 20 °C, a = 9.976(8) Å, b = 30.46(2) Å, c = 9.169(15) Å, β = 107.07(10)°, V = 2663(5) Å^3, Z = 4, d_{calc} = 1.12 g cm^{-3}, space group *Cc*. The intensities of 2944 reflections were measured, of which 1928 reflections were with $I \geq 2\sigma$ (ω-scanning technique, variable θ-scan rate, 1—16.4 deg min^{-1}, $\theta \leq 74.20°$). The intensities of check reflections showed no decrease in the course of X-ray data collection. No absorption correction was applied. The structure was solved by direct methods using the SIR program[8] and refined first isotropically and then anisotropically against F^2 with the use of the SHELX-97 program package[9]. The coordinates of the H atoms were calculated based on the stereochemical criteria and refined using a riding model. The final R factors were as follows: R = 0.058, R_w = 0.143 for 1528 observed reflections with $F^2 \geq 2\sigma$. All calculations were carried out using the MolEN[10] and WinGX programs.[11] Intermolecular contacts, including hydrogen bonds in the crystals, were analyzed using the PLATON package.[12]

* The multiplicities of the signals in the ^{13}C—{^{1}H} NMR spectrum are given in brackets.

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