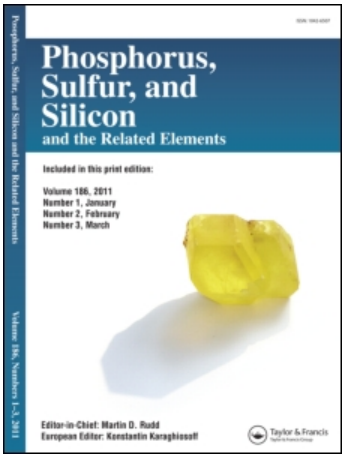

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INFLUENCE OF ULTRASONIC IRRADIATION ON THE REACTIVITY OF TETRAPHOSPHORUS DECASULFIDE AND 2,4-DITHIOXO-1,3,2λ^5,4λ^5-DITHIADIPHOSPHETANES

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Ultrasonic irradiation leads to increased reaction rate and reduction in reaction temperature and time in the reactions of tetraphosphorus decasulfide and 2,4-bis(alkylthio- and 4-methoxyphenyl)-2,4-dithioxo-1,3,2λ^5,4λ^5-dithiadiphosphetanes with dialkyl disulfides, thioacetals, acetals, bis(tributylstannyl)sulfide and tributyl(iso-butylthio)stannane and to increased yields of organothiophosphorus products.

Key words: Ultrasound; tetraphosphorus decasulfide; 2,4-dithioxo-1,3,2λ^5,4λ^5-dithiadiphosphetanes; organothiophosphorus compounds.

INTRODUCTION

Reactions of tetraphosphorus decasulfide and 2,4-bis(substituted)-2,4-dithioxo-1,3,2λ^5,4λ^5-dithiadiphosphetanes proceed sometimes under severe conditions (100–140°C, up to 22 h) and are accompanied by pitching of reaction mixtures which hamper the purification of organothiophosphorus products. In order to increase reactivity of tetraphosphorus decasulfide and Davy's and Lawesson's-like reagents and to decrease the reaction temperature and time we use ultrasonic irradiation in their reactions with organic and organotin derivatives.

RESULTS AND DISCUSSION

Chemical application of ultrasound has seen intense activity in recent years.[9–16] The beneficial effects of synthetic applications of sonochemistry are acceleration of chemical reactions, the use of less forcing conditions, reduction of induction period, reaction temperature and time and ease of experimental technique.[12,16] Reactivity of phosphorus sulfides is determined by their solubilities in liquid organic reagents or in organic solvents and by solid particle sizes.[17] The use of low frequency ultrasound (frequencies 20–100 kHz) may result in reactivity enhancements via the fragmentation and consequent solid particle size reduction, cavitation phenomena, formation of active sites, etc.[12,16] Ultrasound has been found to give increased

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rates for the preparation of thioamides by reaction of their respective amides with tetraphosphorus decasulfide.[18] We decided to use low frequency ultrasound (22 kHz) to previously studied reactions of tetraphosphorus decasulfide, Davy's and Lawesson's-like reagents with dialkyl disulfides, thioacetals, acetals, bis(stannyl)-sulfides and alkylthiostannanes.[1-5]

Reaction of tetraphoshorus decasulfide 1 with dialkyl disulfides 2a,b (Equation (1)) was carried out at 100–110°C for 1 h in the traditional manner[1] and with ultrasound application. Use of low frequency ultrasound (22 kHz, power 130 W) leads to increased yields (from 4–38 to 60%) of 3a,b (non-acoustic,[16] the chemical yields of products are tabulated in Table I) and reduction in reaction temperature (to 75–80°C) and time (to 20–30 min).

$$P_4S_{10} + 6\ RSSR \longrightarrow 4\ (RS)_2\overset{S}{\overset{\|}{P}}S\text{-}SR + 1/4\ S_8 \qquad (1)$$

1 2a, R = Et 3a, R = Et

b, R = Bu-i b, R = Bu-i

TABLE I

Experimental data and yields of the products obtained

Initial cpd.		Prod.	Reaction conditions: temp. (°C) — Methods of synthesis[a] A	B	time (min) — Methods of synthesis[a] A	B	Yield[b], % — Methods of synthesis[a] A	B
1	2a	3a	100	80	60	30	6[c]	34[c]
1	2b	3b	100-110	75	60	20[e]	38[c]	60[c]
4a	2a	3a	100	80	60	10	83[c]	70[c]
4a	5a	6a	20	80-100	900	40	36[c]/27[d]	79[c]/43[d]
4b	5b	6b	20	50-75	720	15[e]	48[d]	53[c]/34[d]
7	2a	8a	120-130	80-100	60[e]	20[e]	56[c]/40[d]	14[c]/12[d]
7	2b	8b	120	75	40	20[e]	46[c]/30[d]	64[c]/47[d]
7	5a	10a	70-80	70	240[e]	15[e]	99[c]/95[d]	76[c]/43[d]
7	9	10b	100	70	60	30[e]	77[c]/63[d]	83[c]/63[d]
1	11	12	140	95	30	5	89[c]/44[d]	99[c]/84[d]
7	11	13	80	60	180	5[e]	69[c]/61[d]	85[c]/70[d]
7	14	15	100-130	105	1320	20	89[d]	90[c]/87[d]

[a]Methods of synthesis: A - in the absence of ultrasound; B - in the presence of ultrasound.

[b]Chemical yield.

[c]Yield of crude product.

[d]Yield of isolated product.

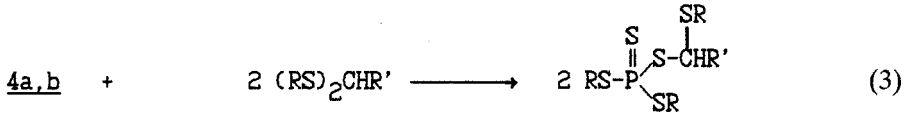
[e]Solvent: toluene.

Pentathiophosphate 3a was also obtained in the reaction of 2,4-bis(ethylthio)-2,4-dithioxo-1,3,2λ^5,4λ^5-dithiadiphosphetane (homologue of Davy's reagent) 4a with 2a (Equation (2), Table I).[1]

4a (2)

A comparison of methods using ultrasonic agitation with those using mechanical stirring showed that the reaction of 4a with 2a (Equation (2)) was complete in 10 min with ultrasound at 80°C, while the preparation of 3a traditionally required 1 h at 100°C.

Reaction of 4a,b with thioacetals 5a,b (Equation (3), Table I) was traditionally performed under mild conditions (20°C)[1] and the formation of S,S′-dialkyl S″-(1-alkylthio)benzyltetrathiophosphates 6a,b required long stirring of the reaction mixture (5–15 h). This reaction was also facilitated when ultrasonic irradiation was employed. Thus 6a,b were obtained in 53–79% yields in 15–40 min compared with 36–48% yields in the absence of ultrasound.



(3)

b, R = Bu-i

5a, R = Et, R′ = H 6a, R = Et, R′ = H

b, R = Bu-i, R′ = Ph b, R = Bu-i, R′ = Ph

The reaction temperatures of the reaction of Lawesson's reagent 7 with 2a,b which leads to S,S-alkyl-S′-alkyl(4-methoxyphenyl)phosphonotrithiolothionoates 8a,b[2,3] (Equation (4)) are reduced from 120–130°C (the traditional method) to 75–100°C in the presence of ultrasound. Besides, ultrasound gave a 2–3-fold increase in reaction rate over a mechanically stirred control reaction and the yield of 8b was increased by up to 64%.

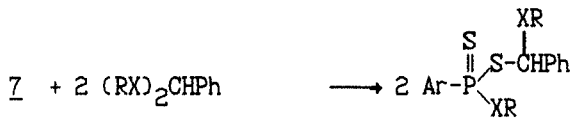
(4)

7, Ar = 4-MeOC$_6$H$_4$

8a, Ar = 4-MeOC$_6$H$_4$, R = Et

b, Ar = 4-MeOC$_6$H$_4$, R = Bu-i

We observed significant improvements both in reaction temperatures and times over conventional methodology (80–120°C, 1–4 h) in the reaction of 7 with thioacetal 5b and acetal 9 which resulted in products of (1-alkylthio)- and (1-alkyloxy)alkyl trithio- and dithiophosphonate structures 10a,b[3] when the reaction (Equation (5)) was carried out in the presence of ultrasound (70°C, 15–30 min). Thus, 83% yield of 10b was obtained after 20 min sonication.

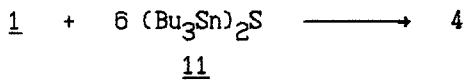


(5)

5b, R = Bu-i, X = S 10a, Ar = 4-MeOC$_6$H$_4$, R = Bu-i, X = S

9, R = Et, X = O b, Ar = 4-MeOC$_6$H$_4$, R = Et, X = O

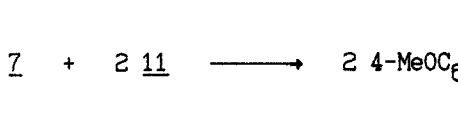
Reaction of 1 with bis(tributylstannyl)sulfide 11 in the absence of ultrasound gives only a moderate yield (44%) of tris(tributylstannyl)tetrathiophosphate 12 and requires severe reaction conditions (140°C, 0.5 h) (Equation (6)).[4]



(6)

The rate of this reaction (Equation (6)) is enhanced 6-fold (95°C) when the reaction is performed under ultrasound.

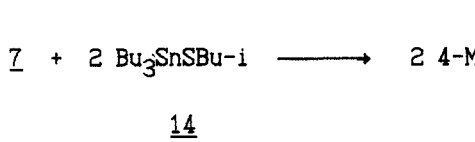
The reaction of 2,4-bis(tert.-butyl)-2,4-dithioxo-1,3,2λ^5,4λ^5-dithiadiphosphetane with bis(trimethylstannyl)sulfide was reported[19] to result in bis(trimethylstannyl) tert.-butylphosphonotrithioate. Similar result was obtained for the preparation of S,S′-bis(tributylstannyl)-4-methoxyphenylphosphonotrithioate 13 from the reaction of 7 with 11. Ultrasound gave substantial rate enhancement in the reaction of 7 with 11 (60°C, 5 min) compared with 3 h (80°C) for non-ultrasonic control (Equation (7)).



(7)

The mechanically stirred reaction 7 with 11 (Equation (7)) gave 69% of 13 whereas the ultrasonic method gave 85% of 13.

S-Iso-butyl-S′-tributylstannyl-4-methoxyphenylphosphonotrithioate 15 was obtained in 90% yield in 20 min at 105°C in the presence of ultrasound compared with the formation of 15 in 22 h at 100–130°C in the absence of ultrasound.



(8)

Thus, ultrasound has been shown to be an effective means of promoting the reactions of tetraphosphorus decasulfide, Davy's and Lawesson's-like reagents with organic compounds and organic derivatives of tin. The application of low frequency ultrasound in these reactions has resulted in enhanced chemical reactivity of tetraphosphorus decasulfide, Davy's and Lawesson's-like reagents, reduction in reaction temperature and time and increased yields of organothiophosphorus products.

EXPERIMENTAL

^{31}P NMR spectra were recorded with a Bruker MSL-400 (162 MHz) and non-serial NMR KGU-4 (10.2 MHz) spectrometers, reference external H_3PO_4 (85%). ^1H NMR spectra were run on a Varian T-60 (60 MHz) spectrometer in CCl_4 with $(Me_3Si)_2O$ as an internal reference. IR spectra were obtained in KBr with a UR-20 infrared spectrophotometer.

The products 3a, 3b, 6a, 6b, 8a, 8b, 10a, 10b, 12 and 15 were obtained in the absence of ultrasound according to References 1–5.

S-Iso-butyl S'-tributylstannyl 4-methoxyphenylphosphonotrithioate 15. *Typical Procedure in the Presence of Ultrasound.* The mixture of 7 (5.0 g, 12.4 mmol) and 14 (9.4 g, 24.8 mmol) in a glass vessel equipped with a water cooler was irradiated with ultrasound generated by an UZDN-A device (22 kHz, 130 W, direct immersion sonic horn) for 20 min at 105°C. The solid 7 disappeared. Removal of the volatile materials from the mixture (0.02 mm Hg, 50°C) resulted in crude 15 (13.0 g, 90%). Product 15 was isolated from the residue by means of thin layer distillation at 160–170°C (0.02 mm Hg), n_D^{20} 1.5980. ^{31}P NMR (neat, δ, ppm): 71 (Lit.[5] b.p. 175–180°C (0.02 mm Hg), n_D^{20} 1.5979).

Other reactions (Equations (1)–(5)) were performed in the presence of ultrasound. Products 3b, 6b, 8a, 8b, 10a and 10b were obtained in toluene.

S,S'-Bis(tributylstannyl) 4-methoxyphenylphosphonotrithioate 13. *(A) Procedure in the Absence of Ultrasound.* 7 (3.4 g, 8.4 mmol) was added portionwise to stirred 11 (10.3 g, 16.8 mmol) at 20°C and stirring was continued for 3 h at 80°C. The mixture was evaporated at reduced pressure (0.04 mm Hg). 13 (8.3 g, 61%) was isolated from the residue by means of thin layer distillation at 190°C (0.02 mm Hg), d_4^{20} 1.2668, n_D^{20} 1.5793. ^{31}P NMR (CCl_4, δ, ppm): 70.0. ^1H NMR (CCl_4, δ, ppm, J, Hz): 0.72–1.90 (m, 54H, C_4H_9Sn), 3.75 (s, 3H, CH_3O), 6.75 (dd, 2H, 3,5-$H_2C_6H_2$), $^3J_{H-H}$ 9.0, $^4J_{P-H}$ 4.0), 7.98 (dd, 2H, 2,6-$H_2C_6H_2$, $^3J_{H-H}$ 9.0, $^3J_{H-H}$ 15.0). IR (ν, cm^{-1}): 3073, 3010 ν (C—H, Ar), 2965, 2930, 2880, 2860 ν (CH_3 as, s; CH_2 as, s); 1595, 1500, 1465 ν (C=O, Ar), 680 ν (P=S), ν (PS_2 as); 540, 512 ν (Sn—C as), ν (P—SC), ν (PS_2 s). Found. %: C 45.65; H 7.60; P 3.61; S 11.76; Sn 29.32. $C_{31}H_{61}OPS_3Sn_2$. Calc. %: C 45.70; H 7.57; P 3.81; S 11.78; Sn 29.17.

(B) In the Presence of Ultrasound. Similarly to the preparation of 15 reagent 7 (3.2 g, 7.9 mmol) and 11 (9.7 g, 15.9 mmol) (reaction conditions: 60°C, 5 min, toluene) yielded 13 (9.0 g, 70%).

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