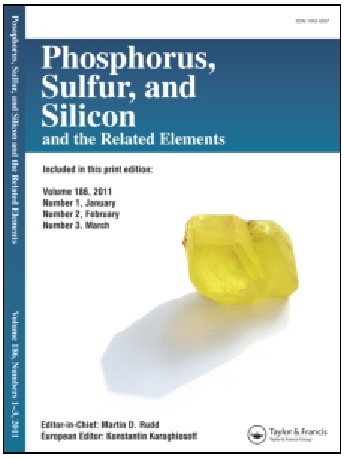

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INFLUENCE OF NUCLEOPHILIC REAGENTS ON THE REACTIONS OF PHOSPHORUS SULFIDES AND ALKYL HOMOLOGUES OF DAVY'S REAGENT WITH ALKYL HALIDES AND DIALKYL DISULFIDES

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Use of potassium carbonate, sodium sulfide and sodium alkylthiolates results in the reactivity enhancement of phosphorus sulfides (P_4S_{10}, P_4S_7 and P_4S_5) and alkyl homologues of Davy's reagent in their reactions with alkyl halides and dialkyl disulfides.

Keywords: Phosphorus sulfides; homologues of Davy's reagent; potassium carbonate; sodium sulfide; sodium alkylthiolates; alkyl halides; dialkyl disulfides; organothiophosphorus compounds

INTRODUCTION

During the past few years we have become interested in the problem of reactivity enhancement of lower and higher phosphorus sulfides (P_4S_{10}, P_4S_7, P_4S_5 and P_4S_3) and their organic derivatives of 2,4-bis(substituted) 2,4-dithioxo-1,3,2λ^5,4λ^5-dithiadiphosphetane structure (Lawesson and Davy-like reagents) in their reactions with organic compounds. Thus, the reactions of tetraphosphorus trisufide and tetraphosphorus decasulfide with alkyl chlorides proceed under severe conditions (160–330°C) to form alkyl dichlorodithiophosphates and dialkyl chlorotrithiophosphates in the absence of any additives.[1,2] The reactions of tetraphosphorus trisulfide, tetraphosphorus pentasulfide (P_4S_5),

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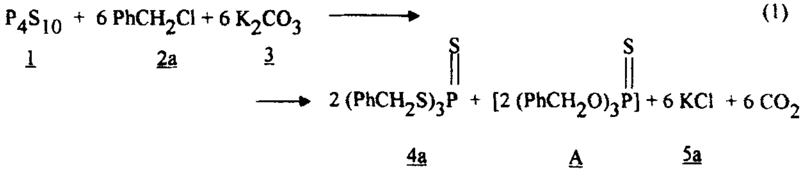
Lawesson and Davy-like reagents with dialkyl disulfides and thioacetals occured sometimes at 100-200°C (up to 22 h) and are accompanied by resinous materials.[3–6] In order to increase reactivity of phosphorus sulfides and Lawesson and Davy-like reagents in the reactions with disulfides, thioacetals, aminals and sulfenamides we have previously developed efficient methods of facilitation of these reactions by involvement of organic amines and benzoyl peroxide,[3] and iodine.[7,8] UV and ultrasonic irradiations have been shown to be effective methods of promoting the reactions of tetraphosphorus trisilfide, tetraphosphorus pentasulfide (P_4S_5), Lawesson and Davy-like reagents with organic disulfides, thioacetals, acetals, bis(tributylstannyl)sulfide and (isobutylthio)tributylstannane.[4,9–11] In continuation of these works we involved potassium carbonate, sodium sulfide and sodium alkylthiolates in the reactions of phosphorus sulfides (P_4S_{10}, P_4S_7 and P_4S_5) and alkyl homologues of Davy's reagent in their reactions with alkyl halides and dialkyl disulfides and present the results in this article.

RESULTS AND DISCUSSION

Additions of inorganic salts such as sodium sulfide, Na_2S,[12] sodium carbonate, Na_2CO_3,[12–15] sodium hydrogen-carbonate, $NaHCO_3$,[12,15] and calcium fluoride, CaF_2, [16] to the reaction mixture of tetraphosphorus decasulfide with carbonyl compounds were reported to accelerate the sulfurization of carbonyl groups. Salts of 1,2,3,5,6,7,4,8-hexathiadiphosphocane-4,8-dithioxo-4,8-dithiolic acid were obtained in the reaction of tetraphosphorus decasulfide with tetraalkylammonium bromides in the presence of sodium azide, NaN_3, in glyme.[17] Treatment of Lawesson's reagent (and its homologues) with potassium fluoride,[18] potassium azide,[18] potassium cyanide[19] and alkali thiocyanates[20] in ketones or acetonitrile as solvents results in the formation of the alkali salts of the corresponding phosphonodithioic acids. 4-Methoxyphenyl dithiophosphonate derivatives were prepared by treatment of Lawesson's reagent with sodium and potassium salts of carboxylic and xanthogenic acids[21] or sodium alkoxides[22] in their subsequent interactions with alkyl halides or benzoyl chlorides. Obviously these salts lead to the increase of nucleophilic reactivity of tetraphosphorus decasulfide or Lawesson's reagent via the formation of some reactive and thermal instable organothiophosphorus intermediates. We assumed that involvement of nucleophilic reagents such as potassium carbonate, sodium sulfide and sodium alkylthiolates in the reactions of phosphorus sulfides and 1,3,2,4-dithiadiphosphetane-2,4-disulfides with alkyl halides and dialkyl disulfides may result in the formation of organothiophosphorus products under milder reaction conditions.

Indeed, we have found that the reaction of tetraphosphorus decasulfide **1** with benzyl chloride **2a** in the presence of dried potassium carbonate **3** in anhydrous acetonitrile proceeds at 60–70 °C for 2 h and gives tribenzyl tetrathiophosphate **4a** (Equation (1), and Tables (I) and (II)).



$$\underset{\underline{1}}{P_4S_{10}} + 6\,\underset{\underline{2a}}{PhCH_2Cl} + 6\,\underset{\underline{3}}{K_2CO_3} \longrightarrow \tag{1}$$

$$\longrightarrow 2\,\underset{\underline{4a}}{(PhCH_2S)_3\overset{\overset{S}{\|}}{P}} + \underset{\underline{A}}{[2\,(PhCH_2O)_3\overset{\overset{S}{\|}}{P}]} + 6\,KCl + 6\,\underset{\underline{5a}}{CO_2}$$

TABLE I Experimental data and yields of tetrathiophosphates **4**

Initial compounds	*Reaction conditions*[a] *Temp., °C / Time, h*	*Product (Yield, %)*
P_4S_{10} **1**, $PhCH_2Cl$ **2a**, K_2CO_3 **3**	60–70/2	$(PhCH_2S)_3P(S)$ **4a** ($51^b/26^c$)
$(EtSPS_2)_2$ **8a**, $PhCH_2Cl$ **2a**, K_2CO_3 **3**	60–70/2	$EtSP(S)(SCH_2Ph)_2$ **4b** ($56^b/19^c$)
$(EtSPS_2)_2$ **8a**, BuBr **2b**, K_2CO_3 **3**	60–70/1	$EtSP(S)(SBu)_2$ **4c** ($71^b/33^c$)
$(i\text{-}BuSPS_2)_2$ **8b**, BuBr **2b**, K_2CO_3 **3**	60/1	$i\text{-}BuSP(S)(SBu)_2$ **4d** (55^c)
$(EtSPS_2)_2$ **8a**, EtSSEt **12a**, K_2CO_3 **3**	70/1	$(EtS)_3P(S)$ **4e** (51^d)
$(i\text{-}BuSPS_2)_2$ **8b**, i-BuSSBu-1 **12b**, K_2CO_3 **3**	60/1	$(i\text{-}BuS)_3P(S)$ **4f** (66^d)
$(i\text{-}BuSPS_2)_2$ **8b**, PrSSPr **12c**,K_2CO_3 **3**	60/1	$i\text{-}BuSP(S)(SPr)_2$ **4g** (50^c)
P_4S_{10} **1**, $PhCH_2Cl$ **2a**, Na_2S **15**	50–60/2	$(PhCH_2S)_3P(S)$ **4a** ($54^b/23^c$)
$(EtSPS_2)_2$ **8a**, $PhCH_2Cl$ **2a**, Na_2S **15**	20/4.5	$EtSP(S)(SCH_2Ph)_2$ **4b** ($21^b/g^c$)
P_4S_5 **16**, PrSSPr **12c**, Na_2S **15**	20/2	$(PrS)_3P(S)$ **4h** ($46^b/32^d$)
P_4S_7 **18**, PrSSPr **12c**, Na_2S **15**	20/6	$(PrS)_3P(S)$ **4h** ($22^b/19^d$)
P_4S_{10} **1**, i-BuSSBu-i **12b**, Na_2S **15**	20/6	$(i\text{-}BuS)_3P(S)$ **4f** ($39^b/21^d$)
$(EtSPS_2)_2$ **8a**, PrSSPr **12c**, Na_2S **15**	20/6	$EtSP(S)(SPr)_2$ **4i** (25^d)
P_4S_7 **18**, PrSSPr **12c**, NaSPr-i **17b**	20/1	$i\text{-}PrSP(S)(SPr)_2$ **4j** ($10^b/7^d$)

[a] In MeCN.
[b] Yield of crude product.
[c] Yield of crude product purified by column chromatography.
[d] Yield of crude product purified by distillation.

TABLE II Physical, analitical and the ^{31}P NMR data of tetrathiophosphates $RSP(S)(SR')_2$

Prod.	*R*	*R'*	*R_f Value (C_6H_6)*	n_D^{20}	*^{31}P NMR δ_P ppm (C_6H_6)*	*Molecular formula (Mol.mass)*	*Found Calc.'%*			
							C	*H*	*P*	*S*
4a	$PhCH_2$	$PhCH_2$	0.82	1.6569	90.5	$C_{21}H_{21}PS_4$ (432.1)	58.08 58.33	5.60 4.91	7.01 7.17	29.13 29.60
4b[a]	Et	$PhCH_2$	0.80	1.6478	92.1	$C_{16}H_{19}PS_4$ (370.0)	51.52 51.89	5.05 5.19	8.20 8. 37	34.44 34. 56
4c	Et	Bu	0.84	1.5859	91.2	$C_{10}H_{23}PS_4$ (302.1)	39.50 39.72	7.80 7.69	10.53 10.25	42.44 42.33
4d	i-Bu	Bu	0.86	-	94.0	$C_{12}H_{27}PS_4$ (330.1)	43.96 43.62	8.01 8.26	9.56 9.38	38.98 38.74
4g	i-Bu	Pr	0.89	1.5802	93.9	$C_{10}H_{23}PS_4$ (302.1)	39.50 39.72	7. 24 7.69	10.44 10.25	42.61 42. 33
41[b]	Et	Pr	-	1.5805	94.0	$C_8H_{19}PS_4$ (274.0)	35.32 35.04	7.21 7.00	11.21 11.30	46. 34 46. 67
4j[c]	i-Pr	Pr	-	1.5872	94.9	$C_9H_{21}PS_4$ (288.1)	37.01 37.49	7.48 7.36	10.32 10.75	44.61 44.39

[a] B.p. 195–198 °C (0.07 mm Hg).
[b] B.p 98–100 °C (0.07 mm Hg).
[c] B.p. 136–138 °C (0.02 mm Hg).

The structure of tetrathiophosphate **4a** has been established by IR (Table III), ^1H NMR (Table IV), ^{31}P NMR (Table II), mass spectral data (Table V) as well as elemental analyses (Table II) and by comparing its NMR spectral data with literature ones.[23] The ^{31}P NMR spectrum of product **4a** (C_6H_6) reveals resonance at δ_P 90.5 ppm (cf. Lit.[23] δ_P 90.2 ppm). The electron impact mass spectrum of **4a** shows a mass peak of the molecular ion $[M]^{+\cdot}$ m/e 432.

TABLE III IR spectral data (ν, cm^{-1}) of tetrathiophospates **4**

Prod.	*=C-H^a, Ar*	*$CH_3{}^a$ as, s; $CH_2{}^a$as, s.*	*C=C^a, Ar*	*δ^b(CH_3 as)*	*P=S^a, PS^a as*	*PS$^a{}_2$ s, P-SC^a*
4a	3096, 3060π, 3040	2985, 2940, 2882	1605, 1500	1450	709, 685	570 525, 465
4b	3090, 3060, 3040	2985, 2940, 2882	1605, 1500	1450	709, 685	530
4c		2970, 2938, 2880		1460	690	532
4d		2965, 2930, 2882		1470	695	540
4g		2935, 2910, 2880		1468	692	500
4i		2970, 2933, 2910, 2880		1460	690	530
4j		2980, 2940, 2930, 2880		1460	690	530

[a] Valence vibrations.
[b] Deformation vibrations.

TABLE IV ^1H NMR data of tetrathiophosphates **4**

Prod.	*CCl_4, δ, ppm, J, Hz*
4a	4.05 (d, 3H, $\underline{CH}_2SP$, $^3J_{P\text{-}H}$ 14.0); 6.93–7.27 (m, 15H, $C_6\underline{H}_5$).
4b	1.23 (t, 3H, $\underline{CH}_3CH_2SP$, $^3J_{H\text{-}H}$ 7.5) ; 2.86 (dq, 2H, $CH_3\underline{CH}_2SP$, $^3J_{H\text{-}H}$ 7.5, $^3J_{P\text{-}H}$ 16.5) ; , 3.88 (d, 4H, $\underline{CH}_2C_6H_5$, $^3J_{P\text{-}H}$14.0) ; 6.97–7.26 (m, 10H, $C_6\underline{H}_5$. ·
4c	0.98 (t, 3H, $\underline{CH}_3CH_2SP$, $^3J_{H\text{-}H}$ 7.5) ; 1.46 (t, 6H, $\underline{CH}_3CH_2CH_2CH_2S$, $^3J_{H\text{-}H}$ 7.5) ; 1.37–1.90 and 2.69–3.33 (m, 2H, $CH_3\underline{CH}_2S$ + m, 12H, $CH_3\underline{CH_2CH_2CH}_2S$).
4d	0.55–2.02 (m, $\underline{CH}_3CHCH_2SP$ + $CH_3\underline{CH}CH_2SP$ + C_4H_9SP) ; 2.90 (dd, 2H, $CH_3CH\underline{CH}_2$, $^3J_{H\text{-}H}$ 7.0, $^3J_{P\text{-}H}$15.0)
4g	1.03 (t, 6H, $\underline{CH}_3CH_2CH_2$, $^3J_{H\text{-}H}$ 7.0) ; 1.09 (d, 6H, $\underline{CH}_3CHCH_z$, $^3J_{H\text{-}H}$ 7, 0) ; (1.40–2.07 (m, 4H, $\underline{CH}_3CHCH_2$, $^3J_{H\text{-}H}$ 7.0); 1.40-2.07 (m, 4H, $CH_3\underline{CH}_2CH_2S$ + m, 1H, $CH_3\underline{CH}CH_2S$) ; 2.48–3.18 (m, 4H, $CH_3CH_2\underline{CH}_2SP$ + m, 2H, $CH_3CH\underline{CH}_2SP$).
4i	0.94 (t, 3H, $\underline{CH}_3CH_2SP$, $^3J_{H\text{-}H}$ 7.5) ; 1.39 (t, 6H, $\underline{CH}_3CH_2CH_2S$, $^3J_{H\text{-}H}$ 7.5) ; 1.28–1.83 (m, 4H, $CH_3\underline{CH}_2CH_2SP$) ; 2.63–3.27 (m, 2H, $CH_3\underline{CH}_2SP$) ; 2.93 (dt, 4H, $CH_3CH_2\underline{CH}_2SP$, $^3J_{H\text{-}H}$ 7.5, $^3J_{P\text{-}H}$ 24.0).
4j	1.02 (t, 6H, $\underline{CH}_3CH_2CH_2SP$, $^3J_{H\text{-}H}$ 7.0) ; 1.43 (d, 6H, $\underline{CH}_3CHSP$, $^3J_{H\text{-}H}$ 7.0) ; 1.25–2.05 (m, 4H, $CH_3\underline{CH}_2CH_2SP$) ; 2.42–3.38 (m, 1H, $CH_3\underline{CH}SP$) ;2.93 (dt, 4H, $CH_3CH_2\underline{CH}_2SP$, $^3J_{H\text{-}H}$ 7.0, $^3J_{P\text{-}H}$ 17.0).

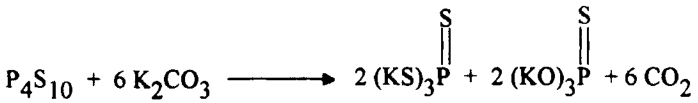
TABLE V Mass spectral data of tetrathiophosphates **4**

Prod.	*i-C_4H_{10}, m/e (I_{rel}, %)*
4a[a]	433 $[M + H]^+$ (25), 310 $[M + H - PhCH_2\text{-} S]^+$ (25), 246 $[M + H - PhCH_2 - 3S]^+$ (100).
4a[b]	432 $[M]^{+\bullet}$ (13), 309 $[M - PhCH_2 - S]^{+\bullet}$ (16), 277 $[M - PhCH_2 - 2S]^+$ (25).
4b[a]	371 $[M + H]^+$ (30) ; 310 $[M + H - Et - S]^+$ (55) ; 338 $[M - S]^+$ (30).
4b[b]	309 $[M - Et - S]^{+\bullet}$ (28) ; 280 $[M - 2Et \text{-} S]^{+\bullet}$ (10), 247 $[M - PhCH_2 - S]^{+\bullet}$ (100), 218 $[M - Et - S - PhCH_2]^{+\bullet}$(51), 123 $[M \text{-} Et - 3S - PhCH_2]^{+\bullet}$ (71).
4c[a]	303 $[M + H]^+$ (44) ; 274 $[M + H - Et]^+$(100).
4c[b]	302 $[M]^{+\bullet}$ (5) ; 273 $[M - Et]^{+\bullet}$(41), 245 $[M - Bu]^{+\bullet}$(44), 241 $[M - Et - S]^{+\bullet}$ (22), 213 $[M - Bu - S]^{+\bullet}$ (66).
4d[a]	331 $[M + H]^+$ (52), 274 $[M + H - Bu]^+$(100), 242 $[M + H - Bu - S]^+$ (39).
4f[b]	330 $[M]^{+\bullet}$ (10), 273 $[M - Bu]^{+\bullet}$(70).
4j[a]	289 $[M + H]^+$ (100).

[a] Chemical ionization, 100 eV.
[b] Electron impact, 70 eV.

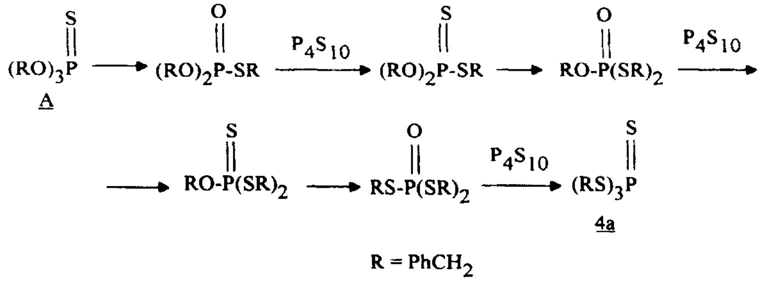
The reaction (Equation (1)) was accompained by the evolution of carbon dioxide and formation of a precipitate of potassium chloride **5a,** which was removed by washing with water. The product **4a** was not decomposed by washing with water. Tetrathiophosphate **4a** was consequently purified by column chromatography. It should be noted that unlike with the literature data on the reactions of tetraphosphorus decasulfide with alkyl halides[2] the involvement of potassium carbonate in the reaction studied (Equation (1)) lead not only to decrease in reaction temperature but the change of the reaction route gave a different synthetic result.

Some assumptions may be suggested concerning the structures of the intermediates and initial products of the interactions of phosphorus sulfide **1** with chloride **2a** in the presence of carbonate **3**. It would seem to be reasonable to assume that the degradation of the cage-like molecule of tetraphosphorus decasulfide is a multi-step process. A nucleophilic attack of the oxygen atom of the K-O fragment of the carbonate **3** upon a phosphorus atom of **1** would be expected to lead to the rupture of the P-S bond and consequent migration of the potassium ion to the sulfur atom neighbouring the P-S fragment. It seems that this proposed mechanism is similar to that suggested by Roesky and Remmers for the reactions of tetraphosphorus decasulfide with trimethylsilyldimethylamine in which a nucleophilic nitrogen atom attacks a phosphons atom.[24] Finally, a series of consequent transformations involved of the elimination of the carbon dioxide molecule and the formation of tripotassium thiophosphate **7** and tripotassium trithiophosphate **6** (Equation (2)).



$$\underset{\underline{1}}{P_4S_{10}} + \underset{\underline{3}}{6\,K_2CO_3} \longrightarrow \underset{\underline{6}}{2\,(KS)_3\overset{S}{\overset{\|}{P}}} + \underset{\underline{7}}{2\,(KO)_3\overset{S}{\overset{\|}{P}}} + 6\,CO_2 \qquad (2)$$

The interaction of benzyl chloride **2a** with this reaction mixture (Equation (2)) is assumed to result in alkylation of these tripotassium thiophosphate **7** and tripotassium trithiophosphate **6** and/or some precursor intermediates containing P-S-K and P-O-K bonds formed in earlier reaction steps with formation of tribenzyl tetrathiophosphate **4a** and tribenzyl thiophosphate **A.** Thiophosphate **A** is likely to undergo S,O-exchange transformations in accordance with the Pishchimuka rearrangement with exchange of a phosphoryl group is a thiophosphoryl one under the effect of tetraphosphorus decasulfide **1** (Equation (3)). These exchange thionation processes seem to lead to formation of tetrathiophosphate **4a** as the only final organothiophosphorus product in accordance with ^{31}P and ^{1}H NMR spectral data.



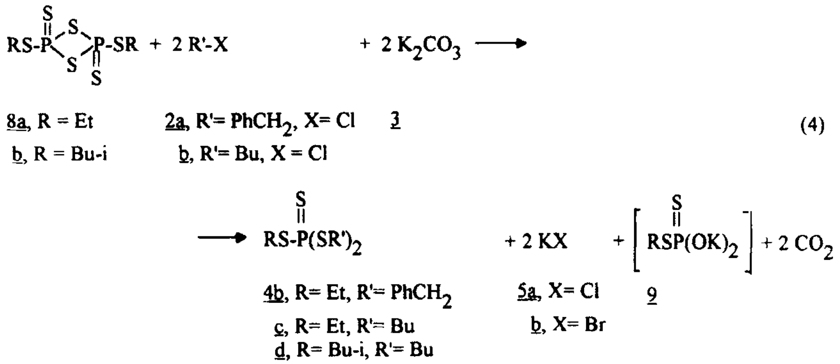
(3)

Scheeren and co-authors suggested that the solutions of tetraphosphorus decasulfide with inorganic salts (Na_2CO_3, $NaHCO_3$ and Na_2S) in organic solvents contain the anions $X_2PS_2^-$ (where X is the monovalent anion in the salt used) in monomeric or polymeric forms.[12] We have observed that the ^{31}P NMR spectrum of the crude reaction mixture of tetraphosphorus decasulfide **1** with potassium carbonate **3** in acetonitrile after evoluation of carbon dioxide (20 °C, 2 h) shows two main signals at δ_P 117.8 and 87.7 ppm in the ratio 1 : 1 (Table VI), It is known that the ^{31}P NMR spectrum of trisodium thiophosphate reveals resonance at δ_P 87.7 ppm.[25] The signal at δ_P 87.7 ppm observed in the reaction of tetraphosphorus decasulfide **1** with potassium carbonate **3** may be attributed to tripotassium thiophosphate **7.** Other small intensity signals (δ_P 128.4 and 91.9 ppm, Table VI) may be attributed to some intermediates with P-S-K and P-O-K bonds. The treatment of this mixture with benzyl chloride **2a** leads to the appearence of the signal of tetrathiophosphate **4a** (δ_P 90.5 ppm).

TABLE VI 31_p NMR data of reaction mixtures of phosphorus sulfides **1**, **16**, **18** and dithiadiphosphetane **8a** c K_2CO_3 3, Na_2S **15** and thiolate **17b**

Initial		δ_p *(MeCN), ppm* (I_{rel})
1	**3**	19.7 (4), 25.2 (5), 56.2 (7), 87.7 (30), 91.9 (10), 117.8 (29), 128.4 (8).
8a	**3**	89.5 (10), 97.1 (30).
1	**15**	38.4 (42), 115.4 (12), 120.3 (23).
8a	**15**	-17.9 (58), 38.3 (92), 120.8 (22).
16	**15**	37.8 (26), 39.0 (45), 41.1 (25), 118.0 (10).
18	**15**	-18.1 (21), 39.0 (46), 40.4 (68), 41.9 (73.5), 115.8 (28), 141 (20).
18	**17b**	36.9 (25).

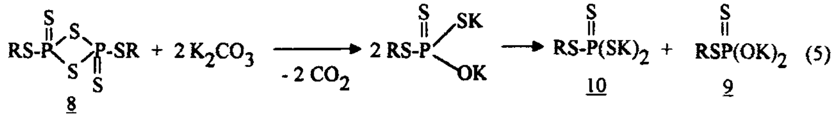
Use of inorganic salts has been shown to be an effective means of promoting the reactions of phosphorus sulfides with organic compounds. We extended this approach to the alkyl homologues of Davy's reagent. Thus, the 2,4-bis(alkylthio)-2,4-dihioxo-1,3,2λ^5,4λ^5-dithiadiphosphetanes **8a,b** react with alkyl chlorides **2a,b** in the presence of carbonate **3** in MeCN at 60–70 °C for 1–3 h to form tetrathiophosphates **4b-d** with mixed substituents (R =/= R') (Equation (4), Tables (I)-(V)).



(4)

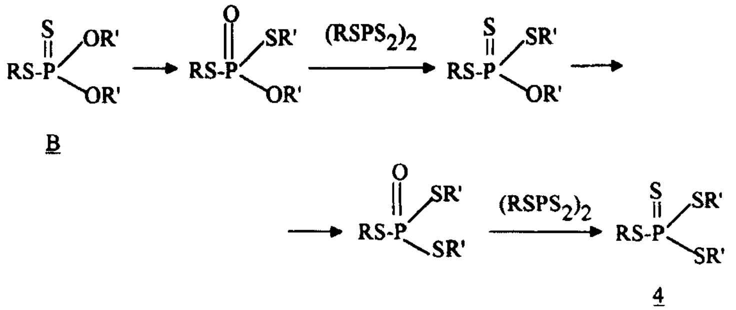
The ^{31}P NMR spectra of the products **4b-d** reveal the signals at δ_P 92.1–94.0 ppm. Most of the known tetrathiophosphates appear in the same region.[25] The chemical ionization mass spectrum of tetrathiophosphate **4b** shows the mass peak of molecular ion $[M + H]^+$ m/e 371.

In this case we also assumed an initial nucleophilic attack of the oxygen atom of the K-O fragment of carbonate **3** upon a phosphorus atom of dithiadiphosphetanes **8** with subsequent elimination of carbon dioxide. A subsequent symmetrization of the intermediate O,S-dipotassium alkyltrithiophosphates seems to lead to the formation of dipotassium alkyldithiophosphates **9** and dipotassium alkyltetrathiophosphates **10** (Equation (5)).



(5)

Similarly interaction of alkyl cldorides **2a,b** with this reaction mixture (Equation (5)) is likely to occur by alkylation of the salts **9** and **10** and/or some intermediates containing P-S-K and P-O-K bonds with the formation of tetrathiophosphates **4b-d** and S-alkyl-O,O'-dialkyldithiophosphates **B**. The latter seems to undergo S,O-exchange processes in accordance with the Pishchimuka reaction with subsequent exchange of a phosphoryl group to a thiophosphoryl one under the effect of dithiadiphosphetanes **8** with the formation of final tetrathiophosphates **4b-d** as the only final organothiophosphorus products (Equation (6)).

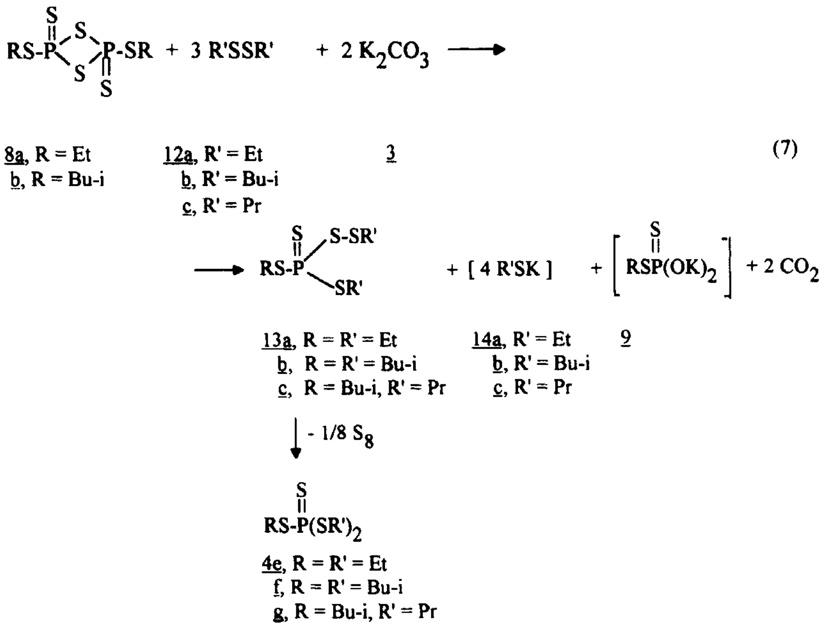


(6)

The ^{31}P NMR spectrum of the crude reaction mixture of dithiadiphosphetanes **8** with potassium carbonate **3** in acetonitrile at 20 °C after evoluation of carbon dioxide shows two signals at δ_P 97.1 and 89.5 ppm in the ratio 3 : 1 (Table VI) which may be attributed to salts **9** and **10.**

We have previously shown that the reaction of dithiadiphosphetanes **8** with dialkyl disulfides proceeds at 90-100 °C for 1–1.5 h to form S,S'-dialkyl S“,S”-alkyltetrathiolothionophosphates with an S-S bridge bond.[6] This reaction was also facilitated when carbonate **3** was employed. Thus, the reaction of dithiadiphosphetanes **8a,b** with disulfides **12a-c** in the presence of an equimolar amount of carbonate 3 occurs in MeCN at 60–70 °C for 1 h (Equation (7), Tables (I) and (II)).

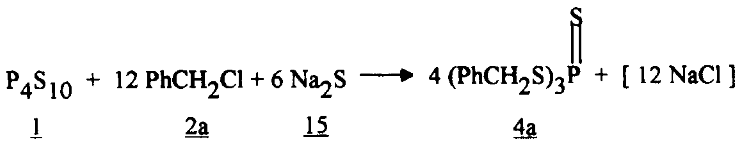
This reaction (Equation (7)) proceeds via the initial formation of pentathiophosphates **13a-c**. Their intermediate formation was confirmed by the ^{31}P NMR spectra of the crude reaction mixtures indicating the signals at δ_P (C_6H_6) 98 and 100 ppm (Reference 6: δ_P (C_6H_6) **13a** 98.0 ppm, and **13b** and 100.5 ppm). The ^{31}P NMR spectrum of pentathiophosphate **13c** reveals resonance at δ_P (C_6H_6) 100.7 ppm. The chemical ionization mass spectrum of pentathiophosphate **13a**



(7)

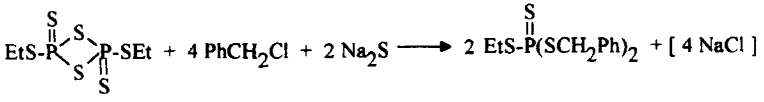
shows the mass peak of molecular ion $[M + H]^+$ m/e 279. There is the mass peak $[M]^+$ m/e 362 in the electron impact mass spectrum of compound **13b** which may be attributed to its molecular ion. We have previously shown that the penthiophosphates **13** with S-S thiol bond are thermally unstable compounds.[4] Products **13a-c** formed in the reaction (7) are unstable during distillation as well and tetrathiophosphates **4e-g** were isolated in pure form (distilled or chromatographed) from the reaction mixtures (Tables (I)-(IV)).

We assumed that tetrathiophosphates may be also formed in the reactions of phosphorus sulfides with alkyl halides in the presence of sodium sulfide. Indeed, the reaction of tetraphosphorus decasulfide **1** with benzyl chloride **2a** in the presence of sodium sulfide **15** in anhydrous acetonitrile at 50–60 °C for 2 h gave tribenzyl tetrathiophosphate **4a** (Equation (8), and Table (I)).



$$\underset{\underline{1}}{P_4S_{10}} + \underset{\underline{2a}}{12\,PhCH_2Cl} + \underset{\underline{15}}{6\,Na_2S} \longrightarrow \underset{\underline{4a}}{4\,(PhCH_2S)_3\overset{\overset{S}{\|}}{P}} + [\,12\,NaCl\,] \qquad (8)$$

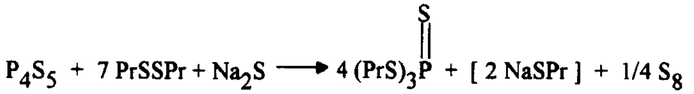
Thus sodium sulfide has proved to be a more effective promoter as regards phosphorus sulfides. Thus tetrathiophosphate **4b** was also obtained in the reaction of dithiadiphosphetane **8a** with chloride **2a** under mild conditions (20 °C, 4.5 h, MeCN) when sodium sulfide **15** was employed (Equation (9), and Table (I)).



(9)

8a 2a 15 4b

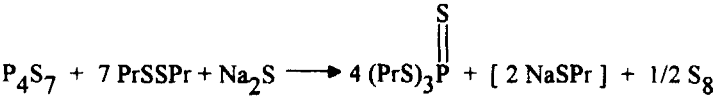
We extended this technique to the reactions of phosphorus sulfides (P_4S_{10}, P_4S_7 and P_4S_5) and dithiadiphosphetanes **8** with dialkyl disulfides because these reactions traditionally proceed under severe conditions (100-160 °C).[4,7,8] Thus, the formation of tetrathiophosphate **4h** occurred already at 20 °C for 2 h in the reaction of tetraphosphorus pentasulfide (P_4S_5) **16** in the presence of an equimolar amount of sodium sulfide **15** in MeCN (Equation (10), and Table (I)).



$$P_4S_5 + 7\,PrSSPr + Na_2S \longrightarrow 4\,(PrS)_3\overset{\overset{S}{\|}}{P} + [\,2\,NaSPr\,] + 1/4\,S_8 \qquad (10)$$

16 12b 15 4h 17a

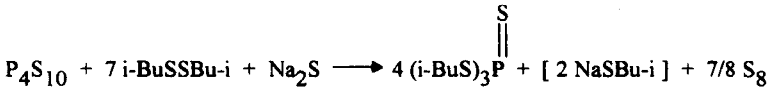
Similarly tetrathiophosphate **4h** was also formed in the reaction of tetraphosphorus heptasulfide (P_4S_7) **18** with disulfide **12c** and sodium sulfide **15** at 20 °C for 6 h in MeCN (Equation (11), and Table (I))



$$P_4S_7 + 7\,PrSSPr + Na_2S \longrightarrow 4\,(PrS)_3\overset{\overset{S}{\|}}{P} + [\,2\,NaSPr\,] + 1/2\,S_8 \qquad (11)$$

18 12c 15 4h 17a

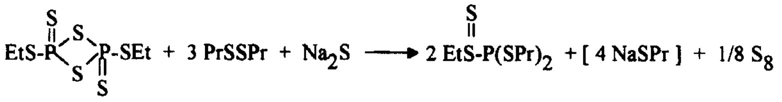
Both reactions (10) and (11) proceed via the intermediate formation of pentathiophosphate **13d** (R = R' = Pr) (δ_P (C_6H_6) 100.2 ppm). Similar formation of pentathiophosphate **13b** was also observed in the reaction of tetraphosphorus decasulfide 1 with disulfide **12b** in the presence of sodium sulfide **15** at 20 °C for 6 h in MeCN. Tetrathiophosphate **4f** was isolated from the reaction mixture by distillation (Equation (12), and Tables (I)and (II)).



$$P_4S_{10} + 7\,i\text{-BuSSBu-}i + Na_2S \longrightarrow 4\,(i\text{-BuS})_3\overset{S}{\overset{\|}{P}} + [\,2\,NaSBu\text{-}i\,] + 7/8\,S_8 \qquad (12)$$

1 12b 15 4f 17c

Tetrathiophosphate **4i** with mixed substituents was isolated in the reaction of dithiadiphosphetane **8a** with disulfide **12c** in the presence of an equimolar amount of sodium sulfide **15** under mild conditions (20 °C, 2 h, MeCN) (Equation (13), and Tables (I)-(IV)).

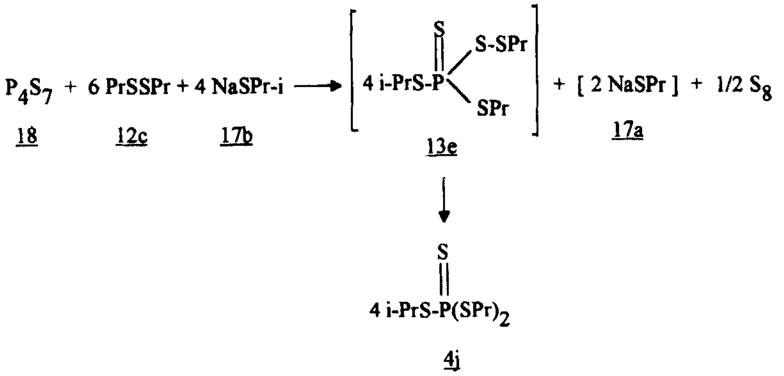


(13)

8a 12c 15 4i 17a

We have recorded the ^{31}P NMR spectra of the crude reaction mixtures of phosphorus sulfides and dithiadiphosphetane **8a** with sodium sulfide **15** in MeCN in the absence of organic reagents at 20 °C (Table (VI)). These signals may be attributed to some intermediates with P-S-Na bonds. It seems the treatment of this mixture with alky halides or disulfides leads to the formation of the final tetrathiophosphates **4.**

In accordance with the stoichiometry of reactions of phosphorus sulfides (P_4S_{10}, P_4S_7 and P_4S_5) and dithiadiphosphetane **8a** with disulfides **12** in the presence of potassium carbonate and sodium sulfide (Equations (7) and (10)-(13)) they should be accompanied by the formation of potassium or sodium alkylthiolates **14** or **17.** It seemed of interest to study the influence of alkaline alkylthiolates on the reactivity of phosphorus sulfides. We carried out the reaction of tetraphosphorus heptasulfide (P_4S_7) **18** with disulfide **12c** in the presence of sodium isopropylthiolate **17b** in MeCN at 20 °C for 1 h and obtained tetrathiophosphate **4j** with mixed substituents (Equation (14), Tables (I)-(V)).



(14)

The intermediate formation of pentathiophosphate **13e** was confirmed by the ^{31}P NMR spectrum of the crude reaction mixture (Equation (14)) (signal at δ_P (C_6H_6) 104.8 ppm) and by the chemical ionization mass spectrum data of the reaction mixture (molecular ion $[M + H]^+$ m/e 321). Tetrathiophosphate **4j** has different alkyl substituents (n- and i-propyl) that have been established by its ^1H NMR spectrum. The $\underline{CH_3}CH_2CH_2$ protons appear as a triplet at δ 1.02 ppm ($^3J_{H\text{-}H}$7.0 Hz), while the $\underline{CH_3}CH$ protons of thioisopropyl group appear as a doublet at δ 1.43 ppm ($^3J_{H\text{-}H}$ 7.0 Hz). The spectrum also shows double triplets of the $CH_3CH_2\underline{CH_2}SP$ protons at δ 2.93 ppm ($^3J_{H\text{-}H}$ 7.0 Hz, $^3J_{P\text{-}H}$ 17.0 Hz).

In spite of the moderate yields of the final products the application of potassium carbonate, sodium sulfide and sodium alkylthiolates in the phosphorus sulfides and alkyl homologues of Davy's reagent in their reactions with alkyl halides and dialkyl disulfides has resulted in an enhanced reactivity of phosphorus sulfides, reduction in reaction temperature and reaction time. It should be noted that the reactions studied are the three component interactions and their mechanisms seem to be very complicated.

EXPERIMENTAL

The ^{31}P NMR spectra were recorded with a Bruker CXP-100 (36.5 MHz) instrument in C_6H_6, reference external H_3PO_4 (85%). The ^1H NMR spectra were run on a Varian T-60 (60 MHz) spectrometer in CCl_4, reference internal $(Me_3Si)_2O$ and a Bruker WM-250 (250 MHz) spectrometer in C_6D_6. The IR spectra were obtained in a KBr pellet with a UR-20 infrared spectrophotometer. The mass spectra (EI, 70 eV; CI, 100 eV) were determined on a M 80 B Hitachi chromato-mass spectrometer.

Reaction of Tetraphosphorus Decasulfide 1 with Benzyl Chloride 2a in the Presence of Potassium Carbonate 3. Typical Procedure

Dried carbonate **3** (3.7 g, 26.8 mmol) was added portionwise to a stirred suspension of **1** (2.0 g, 4.5 mmol) in 10 mL of anhydrous acetonitrile at 20 °C. The mixture was stirred at 100 °C for 0.5 h. Chloride **2a** (6.9 g, 54.5 mmol) was added dropwise with stirring at 20 °C to the mixture and stirring was continued for 2 h at 60–70 °C. The mixture was filtered. The precipitate was extracted with benzene. The extractions and filtrate were combined and evaporated at reduced pressure (0.04 mm Hg) at 70°C for 5 h and gave crude tetrathiophosphate **4a** (2.0 g, 26%). The residue was diluted with 50 mL of benzene and washed with water. The organic layer was dried ($MgSO_4$) and filtered. The filtrate was evaporated under vacuum (0.1 and 0.02 mm Hg) at 50°C for 2 h. The residue was chromatographed on Al_2O_3 column with benzene as eluant and gave pure **4a** (1.0 g, 13%) (See Tables I-V).

Similarly dithiadiphosphetane **8a** (3.0 g, 9.6 mmol), chloride **2a** (4.9 g, 38.7 mmol) and carbonate **3** (2.7 g, 19.5 mmol) (reaction conditions: 60-70 °C, 3 h, 10 mL MeCN) gave crude S-ethyl S',S"-dibenzyltetrathiophosphate **4b** (2.0 g, 28%). Pure **4b** (0.7 g, 10%) was isolated from the residue by means of column chromatography (Al_2O_3, benzene).

Similarly dithiadiphosphetane **8a** (2.5 g, 8.0 mmol), bromide **2b** (4.4 g, 32.1 mmol) and carbonate **3** (2.2 g, 15.9 mmol) (reaction conditions: 60-70 °C, 1 h, 10 mL MeCN) gave crude S-ethyl S',S"-dibutyltetrathiophosphate **4c** (1.7 g, 35%) and pure (chromatographed) **4c** (0.8 g, 17%).

Similarly dithiadiphosphetane **8b** (5.2 g, 16.7 mmol), bromide **2b** (9.1 g, 66.4 mmol) and carbonate **3** (4.6 g, 33.3 mmol) (reaction conditions: 60 °C, 1 h, 10 mL MeCN) gave crude S,S'-dibutyl-S"-isobutyltetrathiophosphate **4d** (3.0 g, 27%).

Similarly dithiadiphosphetane **8a** (4.9 g, 15.7 mmol), disulfide **12a** (5.8 g, 47.5 mmol) and carbonate **3** (2.2 g, 15.9 mmol) (reaction conditions: 70 °C, 1 h, 10 mL MeCN) gave distilled triethyltetrathiophosphate **4e** (2.0 g, 26%), b.p. 110 °C (0.03 mm Hg), n_D^{20} 1.6207. The ^{31}P NMR (C_6H_6) δp: 91.7 ppm. The mass spectrum (EI, 70 eV), m/e (I_{rel}, %): 246 $[M]^{+\cdot}$ (28) (Reference 26: b.p. 124-125 °C (1.5 mm Hg), n_D^{20} 1.6201. The ^{31}P NMR δp: 91.7 ppm).

Similarly dithiadiphosphetane **8b** (3.2 g, 8.7 mmol), disulfide **12b** (4.6 g, 25.8 mmol) and carbonate **3** (1.2 g, 8.7 mmol) (reaction conditions: 60 °C, 1 h, 10 mL MeCN) gave distilled triisobutyltetrathiophosphate **4f** (1.9 g, 33%), b.p. 130 °C (0.03 mm Hg), n_D^{20} 1.5559. The ^{31}P NMR (C_6H_6) δp 93.9 ppm. The mass spectrum (El, 70 eV), m/e (I_{rel}, %): 330 $[M]^{+\cdot}$ (43) (Reference 4: b.p. 136-137 °C (0.02 mm Hg), n_D^{20} 1.5549. The ^{31}P NMR (C_6H_6) δp: 92.8 ppm).

Similarly dithiadiphosphetane **8b** (2.0 g, 5.4 mmol), disulfide **12c** (2.4 g, 16.0 mmol) and carbonate **3** (0.8 g, 5.8 mmol) (reaction conditions: 70 °C, 1 h, 10 mL MeCN) gave crude S,S'-dipropyl-S"-isobutyltetrathiophosphate **4g** (2.0 g, 61%) which was chromatographed (Al_2O_3 column, benzene) and gave pure **4g** (0.8 g, 24%).

Reaction of Tetraphosphorus Decasulfide 1 with Benzyl Chloride 2a in the Presence of Sodium sulfide 15. Typical Procedure

Dried sulfide **15** (2.4 g, 30.8 mmol) was added portionwise to a stirred suspension of **1** (2.3 g, 5.2 mmol) in 10 mL of anhydrous acetonitrile at 20 °C. Chloride **2a** (7.9 g, 62.4 mmol) was added dropwise with stirring at 20 °C to the mixture and stirring was continued for 2 h at 50-60 °C. The mixture was diluted with 40 mL of MeCN and washed with water. The organic layer was dried ($MgSO_4$) and filtered. The filtrate was evaporated under vacuum (0.1 and 0.07 mm Hg) at 50 °C for 2 h and gave crude tetrathiophosphate **4a** (4.9 g, 54%). The residue was chromatographed on Al_2O_3 column with benzene as eluant and gave pure **4a** (2.1 g, 23%) (See Tables I-V).

Similarly dithiadiphosphetane **8a** (4.5 g, 14.4 mmol), chloride **2a** (7.3 g, 57.7 mmol) and sulfide **15** (2.3 g, 29.5 mmol) (reaction conditions: 20 °C, 4.5 h, 15 mL MeCN) gave crude tetrathiophosphate **4b** (2.2 g, 21%). Distillation of the residue gave pure **4b** (1.0 g, 9%), b.p. 195–198 °C (0.07 mm Hg) (See Tables I-V).

Similarly tetraphosphorus pentasulfide (P_4S_5) **16** (2.7 g, 9.5 mmol), disulfide **12c** (10.0 g, 66.6 mmol) and sulfide **15** (0.74 g, 9.5 mmol) (reaction conditions: 20 °C, 2 h, 10 mL MeCN) gave crude tetrathiophosphate **4h** (5.1 g, 46%) and distilled **4h** (3.5 g, 32%), b.p. 128-130 °C (0.04 mm Hg), n_D^{20} 1.5892. The ^{31}P NMR (C_6H_6) δp: 92.0 ppm. The mass spectrum (CI, 100 eV), m/e (I_{rel}, %): 289 $[M + H]^+$ (100) (Reference 14: b.p. 131–132 °C (0.5 mm Hg), n_D^{20} 1.5885. The ^{31}P NMR δp: 92.5 ppm).

Similarly tetraphosphorus heptasulfide (P_4S_7) **18** (4.5 g, 12.9 mmol), disulfide **12c** (13.6 g, 90.6 mmol) and sulfide **15** (1.0 g, 12.8 mmol) (reaction conditions: 20 °C, 6 h, 10 mL MeCN) gave crude tetrathiophosphate **4h** (3.3 g, 22%) and distilled **4h** (2.8 g, 19%).

Similarly dithiadiphosphetane **8a** (5.2 g, 16.7 mmol), disulfide **12c** (7.5 g, 50.0 mmol) and sulfide **15** (1.3 g, 16.7 mmol) (reaction conditions: 20 °C, 2 h, 10 mL MeCN) gave distilled tetrathiophosphate **4i** (2.3 g, 25%) (See Tables I-IV).

Reaction of Tetraphosphorus heptasulfide 18 with Dipropyl Disulfide 12c in the Presence of Sodium Isopropylthiolate 17b

Dried thiolate **17b** (3.5 g, 35.7 mmol) was added portionwise to a stirred suspension of **18** (3.1 g, 8.9 mmol) in 10 mL of anhydrous acetonitrile at 20 °C. Disulfide **12c** (8.0 g, 53.3 mmol) was added dropwise with stirring at 20 °C to the mixture and stirring was continued for 1 h at 20 °C. The mixture was washed with water. The organic layer was dried ($MgSO_4$) and evaporated under vacuum (0.1 and 0.03 mm Hg) at 50°C for 3 h and gave crude tetrathiophosphate **4j** (1.0 g, 10%). Distillation of the residue gave pure **4j** (0.7 g, 7%) (See Tables I-V).

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