Addition of Elemental Sulfur to Phosphonate Carbanions and Its Application for Synthesis of α-Phosphoryl Organosulfur Compounds. Synthesis of Aromatic Ketones[1]

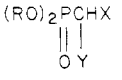
Marian Mikołajczyk,* Sławomir Grzejszczak, Anna Chefczyńska, and Andrzej Zatorski

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

Received March 30, 1979

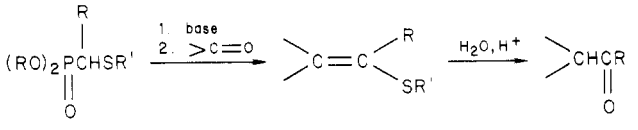
It was found that elemental sulfur reacts with phosphonate carbanions to give α-phosphoryl thiols which upon alkylation are converted into α-phosphoryl sulfides. A new synthesis of *S,S*- and *O,S*-thioacetals of formylphosphonates which involves sulfur addition to carbanions from α-phosphoryl sulfides and α-phosphoryl ethers followed by alkylation is described. Synthesis of aromatic ketones involving the Horner–Wittig reaction of α-phenyl-α-phosphoryl methyl sulfide with aldehydes and subsequent hydrolysis of the vinyl sulfides formed is also reported.

The application of organic sulfur compounds in organic synthesis and particularly in reversal (umpolung) of normal reactivity of nucleophilic and electrophilic centers is a subject of considerable current interest.[2] Recent studies have shown α-phosphoryl-substituted organosulfur compounds (**1**) to be useful reagents for effecting a variety of synthetic transformations. Thus far the following α-phosphoryl organic sulfur compounds have been described: α-phosphoryl sulfides (**1a**),[3] α-phosphoryl sulfoxides (**1b**),[4] α-phosphoryl sulfones (**1c**),[3d,5] monothio- and dithioacetals of formylphosphonates (**1d**[6] and **1e**[6c,7]), and α-phosphorylsulfonium and -sulfoxonium salts (**1f**[8] and **1g**[9]). Among these, α-phosphoryl sulfides (**1a**) have attracted special attention because they are key reagents in the synthesis of ketones.[3b] This method, which may be in general classified as a nucleophilic acylation with elaboration at the electrophilic center, involves the Horner–Wittig reaction of an α-phosphoryl sulfide (**1a**),

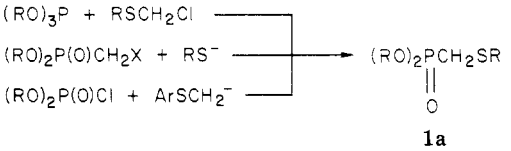


1a, X = SR; Y = H, alkyl, aryl
b, X = S(O)R; Y = H, alkyl, aryl
c, X = $S(O)_2R$; Y = H, alkyl, aryl
d, X = SR; Y = OR
e, X = Y = SR
f, X = $\overset{+}{S}R_2$; Y = H
g, X = $\overset{+}{S}(O)R_2$; Y = H

bearing an alkyl or aryl group on the α-carbon atom, with a carbonyl component. Subsequent hydrolysis of the intermediate α,β-unsaturated sulfide condensation product affords the desired ketone end product.



It should be noted, however, that the primary limitation of this scheme involves the synthesis of the α-phosphoryl sulfides **1a** containing the alkyl and aryl α-substituent R. Whereas the unsubstituted sulfides **1a** are readily available by any of three routes, Arbuzov reaction of trialkyl phosphites with α-halo sulfides,[3a] condensation of dialkyl (chloromethyl)phosphonates with alkyl mercaptides[3g] or the recently described reaction of dialkyl phosphorochloridates with carbanions derived from alkyl aryl sulfides,[3h] the desired α-substituted-α-phosphoryl sulfides **1a** still required development of a convenient route.



1a

Corey and Shulman[3b] solved this problem in part by alkylation of the lithio derivative of the unsubstituted sulfide **1a**. However, the introduction of an aromatic group into the α position by this method was not possible. Very recently Grayson and Warren[10] have described the reaction of lithio derivatives of primary alkyldiphenylphosphine oxides with dimethyl and diphenyl disulfides, affording sulfenylated phosphine oxides (**2**) which were subsequently employed for the synthesis of some aliphatic ketones.

In the course of our studies aimed at overcoming the difficulties mentioned above and developing a convenient

(1) Part 23 of the series Organosulfur Compounds; Part 22, J. Drabowicz and M. Mikolajczyk, *Synthesis*, submitted for publication.

(2) D. Seebach and M. Kolb, *Chem. Ind. (London)*, 687 (1974); D. Seebach and K. H. Geiss, *J. Organomet. Chem. Libr.*, 1 (1976); O. W. Lever, Jr., *Tetrahedron*, **32**, 1943 (1976); B. T. Gröbel and D. Seebach, *Synthesis*, 357 (1977).

(3) (a) M. Green, *J. Chem. Soc.*, 1324 (1963); (b) E. J. Corey and J. I. Shulman, *J. Org. Chem.*, **35**, 777 (1970); (c) E. J. Corey and J. I. Shulman, *J. Am. Chem. Soc.*, **92**, 5522 (1970); (d) I. Shahak and J. Almog, *Synthesis*, 170 (1970); (e) I. Shahak and J. Almog, *ibid.*, 145 (1970); (f) J. Vlattas, L. D. Vecchia, and A. O. Lee, *J. Am. Chem. Soc.*, **98**, 2008 (1976); (g) B. A. Arbuzov and N. P. Bogonostseva, *Zh. Obshch. Khim.*, **26**, 2419 (1956); **27**, 2360 (1957); (h) D. L. Comins, A. F. Jacobine, J. L. Marshall, and M. M. Turnbull, *Synthesis*, 309 (1978); (i) N. Kreutzkamp and J. Pluhatsch, *Arch. Pharm.*, **292**, 159 (1957).

(4) (a) M. Mikolajczyk and A. Zatorski, *Synthesis*, 669 (1974); (b) M. Mikolajczyk, S. Grzejszczak, and A. Zatorski, *J. Org. Chem.*, **40**, 1979 (1975); (c) M. Mikolajczyk, W. Midura, S. Grzejszczak, A. Zatorski, and A. Chefczynska, *ibid.*, **43**, 473 (1978).

(5) I. C. Popoff, J. L. Dever, and G. R. Leader, *J. Org. Chem.*, **34**, 1128 (1969); G. H. Posner and D. J. Brunelle, *ibid.*, **37**, 3547 (1972); H. Fillion, M. H. Pera, J. L. Rappa, and C. Lun-Duc, *J. Heterocycl. Chem.*, **15**, 753 (1978).

(6) (a) M. Mikolajczyk, B. Costisella, S. Grzejszczak, and A. Zatorski, *Tetrahedron Lett.*, 477 (1976); (b) M. Mikolajczyk, A. Zatorski, S. Grzejszczak, B. Costisella, and W. Midura, *J. Org. Chem.*, **43**, 2518 (1978); (c) M. Mikolajczyk, S. Grzejszczak, A. Zatorski, B. Mlotkowska, H. Gross, and B. Costisella, *Tetrahedron*, **34**, 3081 (1978).

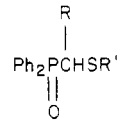
(7) (a) M. Mikolajczyk, S. Grzejszczak, A. Zatorski, and B. Mlotkowska, *Tetrahedron Lett.*, 2731 (1976); (b) B. Mlotkowska, H. Gross, B. Costisella, M. Mikolajczyk, S. Grzejszczak, and A. Zatorski, *J. Prakt. Chem.*, **319**, 17 (1977); (c) K. Ishikawa, K. Akiba, and N. Inamoto, *Tetrahedron Lett.*, 3695 (1976); (d) C. G. Kruse, N. L. J. M. Broekhof, A. Wijsman, and A. van der Gen, *ibid.*, 885 (1977); (e) K. Akiba, K. Ishikawa, and N. Inamoto, *Synthesis*, 861 (1977).

(8) K. Kondo and D. Tunemoto, *J. Chem. Soc., Chem. Commun.*, 952 (1972); K. Kondo, Y. Liu, and D. Tunemoto, *J. Chem. Soc., Perkin Trans. 1*, 1279 (1974).

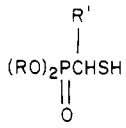
(9) O. I. Kolodiazhnyi, V. P. Lysenko, and J. G. Gololobov, *Zh. Obshch. Khim.*, **45**, 703 (1975); O. I. Kolodiazhnyi, V. P. Lysenko, M. G. Tretjak, R. A. Loktinova, and J. G. Gololobov, *Khim. Elementoorg. Sojedn.*, 178 (1976).

(10) J. I. Grayson and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 2263 (1977).

0022-3263/79/1944-2967$01.00/0



2, R = alkyl; R′ = Me, Ph

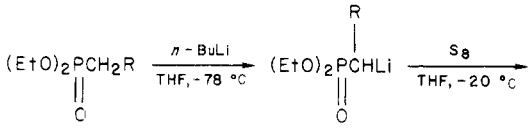


3, R′ = alkyl, aryl

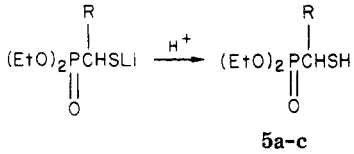
route for aromatic ketones, we explored addition of the elemental sulfur to phosphonate carbanions. The reaction proceeded smoothly and cleanly[11] to the α-phosphoryl thiols (**3**), a previously little known class of compounds.[12] The synthesis of α-phosphoryl thiols (**3**), in combination with their alkylation, provides a new entry not only to variously substituted sulfides (**1a**) but also to other classes of α-phosphoryl organosulfur compounds. We now report the results of these studies, and in addition the synthesis of aromatic ketones using a suitably substituted α-phosphoryl sulfide **1a** as an acyl anion equivalent.

Results and Discussion

Synthesis of α-Phosphoryl Thiols 5, Disulfides 8, and Sulfides 9. It was found that carbanions of diethyl phosphonates **4a–c**, formed with *n*-butyllithium in tetrahydrofuran at −78 °C, react readily with elemental sulfur. Dissolution of sulfur was observed to take place at and above −20 °C, thus affording the corresponding lithium mercaptides. The mercaptides were separated from the reaction mixture by extraction with water. Acidification of the water phase, followed by extraction with chloroform and removal of solvent, affords the crude α-phosphoryl thiols **5a–c** in an analytically pure state. Their structures were confirmed by ^1H and ^{31}P NMR spectra and elemental analyses.



4a, R = H
b, R = CH_3
c, R = Ph



5a–c

It should be noted that sulfur reacts readily with the lithium derivatives of both the unsubstituted **4a** and substituted **4b** and **4c** phosphonates. In all cases the corresponding α-phosphoryl thiols **5** were obtained in yields exceeding 80% (see Table I).

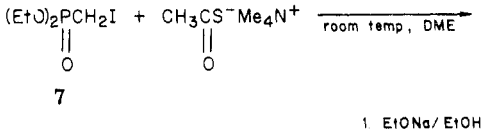
The preparation of α-phosphoryl thiols by this method requires two additional comments. The first is that diethyl phosphonates and not dimethyl phosphonates should be used as substrates, since the phosphonate methoxy function undergoes a secondary reaction (demethylation[13]) with the generated lithium mercaptide. Secondly, the ratio of elemental sulfur to the lithium derivative of **4** is of great importance and, therefore, stoichiometric amounts of elemental sulfur, or a slight excess, must be used in order to prevent the formation of sulfide and disulfide products according to the reactions illustrated below.

$$RLi + S \rightarrow RSLi$$

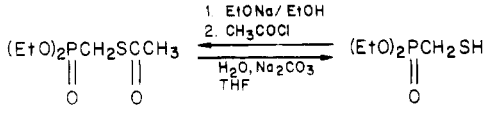
$$2RSLi + S \rightarrow RSSR + Li_2S$$

$$RSSR + RLi \rightarrow RSLi + RSR$$

An alternative approach to the synthesis of the unsubstituted α-phosphoryl thiol **5a** was also developed. This alternative is the alkaline hydrolysis of (diethylphosphoryl)methyl thiolacetate (**6**) obtained from the reaction between the tetramethylammonium salt of thioacetic acid and diethyl iodomethylphosphonate (**7**).

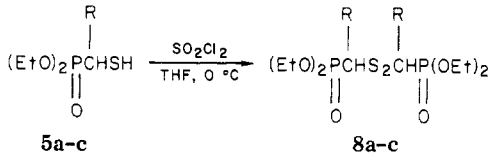


7



6 **5a**

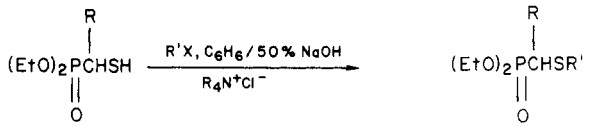
Besides spectral identification, the α-phosphoryl thiols **5** were further characterized as the corresponding disulfides **8**. The conversion of **5** to **8** was achieved with sulfuryl chloride. The yields and observed ^{31}P NMR chemical shifts of **8** are collected in Table I.



5a–c **8a–c**

It is interesting to note that disulfides **8b** and **8c** contain two identical chirality centers and may exist in two diastereomeric forms, meso and *dl*. As expected, the $^{31}P(^1H)$ NMR spectra of **8b** and **8c** revealed the presence of both diastereomers in the ratios 55:45 and 57:43, respectively.

From the synthetic viewpoint the most important products which can be obtained from the α-phosphoryl thiols **5** are the corresponding α-phosphoryl sulfides **9**,



5a–c **9a–h**, R′ = Me, Et, $PhCH_2$

since their anions function as an acyl anion equivalent in ketone synthesis. Although sulfides **9** may be prepared from phosphonates **4** in one step by in situ alkylation of the lithium α-phosphorylmethyl mercaptides, we have found that better results, i.e., a higher yield and purity, are obtained when alkylation (R′X = MeI, EtI, $PhCH_2Cl$) of the isolated thiols **5** is performed under phase-transfer catalytic conditions.[14] Examples of the preparation of **9** are presented in Table I.

Clearly, our method provides a very simple and convenient synthesis of α-phosphoryl sulfides substituted at the α-carbon atom with an alkyl or aryl group.

Synthesis of Aromatic Ketones. Our successful synthesis of α-phosphoryl α-phenyl methyl sulfides **9f–h**

(11) This method is of practical importance in only a few cases, such as the preparation of thiophenols and heteroaromatic and acetylenic thiols. However, addition of elemental sulfur to lithioalkyls was found to afford a complicated mixture of products. See, for example: B. J. Wakefield, "The Chemistry of Organolithium Compounds", Pergamon Press, New York, 1974, pp 192–196.

(12) α-Phosphoryl thiols have been mentioned only in the patent literature as products of the reactions between acylphosphonates and hydrogen sulfide and hydrogen in the presence of catalysts: G. H. Birum, U.S. Patent 2 879 285; *Chem. Abstr.*, **53**, 16965 (1959).

(13) The mercaptide anions are known to be strong dealkylating agents; see, for example, M. E. Peach in "The Chemistry of the Thiol Group", Vol. 2, S. Patai, Ed., Wiley, London, 1974, p 721.

(14) A. W. Herriott and D. Picker, *Synthesis*, 447 (1975).

Table I. Preparation and ^{31}P NMR Data of α-Phosphoryl Thiols (5), α-Phosphoryl Disulfides (8), and α-Phosphoryl Sulfides (9)

no.	structure	yield,[a] %	^{31}P NMR ($CDCl_3/H_3PO_4$)
5a	$(C_2H_5O)_2P(O)CH_2SH$	84	26.3
5b	$(C_2H_5O)_2P(O)CH(CH_3)SH$	80	28.2
5c	$(C_2H_5O)_2P(O)CH(Ph)SH$	81	24.2
8a	$(C_2H_5O)_2P(O)CH_2SSCH_2P(O)(OC_2H_5)_2$	95	22.8
8b	$(C_2H_5O)_2P(O)CH(CH_3)SSCH(CH_3)P(O)(OC_2H_5)_2$	91	27.7; 27.3[b]
8c	$(C_2H_5O)_2P(O)CH(Ph)SSCH(Ph)P(O)(OC_2H_5)_2$	96	20.7; 21.4[b]
9a	$(C_2H_5O)_2P(O)CH_2SCH_3$	83	23.4
9b	$(C_2H_5O)_2P(O)CH_2SCH_2CH_3$	86	25.5
9c	$(C_2H_5O)_2P(O)CH_2SCH_2Ph$	84	25.3
9d	$(C_2H_5O)_2P(O)CH(CH_3)SCH_3$	81	26.6
9e	$(C_2H_5O)_2P(O)CH(CH_3)SCH_2CH_3$	84	27.5
9f	$(C_2H_5O)_2P(O)CH(Ph)SCH_3$	80	21.1
9g	$(C_2H_5O)_2P(O)CH(Ph)SCH_2CH_3$	87	23.2
9h	$(C_2H_5O)_2P(O)CH(Ph)SCH_2Ph$	82	23.0

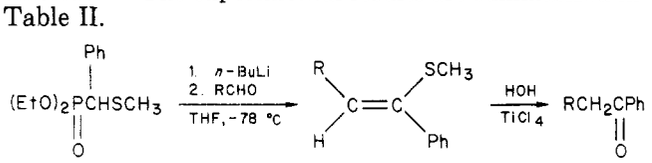
[a] Yield of analytically pure products. [b] Two diastereomers.

Table II. Preparation and Hydrolysis of α,β-Unsaturated Sulfides (10)

	product				products of hydrolysis		
starting aldehyde	no.	structure	yield,[a] %	E/Z ratio	no.	structure	yield,[a] %
benzaldehyde	10a	$PhCH{=}C(Ph)SCH_3$	82	11:89	11a	$PhCH_2COPh$	80
acetaldehyde	10b	$CH_3CH{=}C(Ph)SCH_3$	78	32:68	11b	CH_3CH_2COPh	78
butyrylaldehyde	10c	$CH_3(CH_2)_2CH{=}C(Ph)SCH_3$	76	22:78	11c	$CH_3(CH_2)_3COPh$	74

[a] Yield of analytically pure products.

paved the way for the synthesis of aromatic ketones according to the principles discussed above. In the present experiments sulfide **9f** was used as a starting agent. Its metalation was found to occur easily in tetrahydrofuran solution at −78 °C using a small molar excess of *n*-butyllithium. Moreover, it should be stressed, as revealed by the low-temperature ^{31}P NMR spectra, that the formation of the lithio derivative of **9f**, as well as those from the other sulfides **9**, occurs immediately after mixing the reagents at −78 °C. Lithiation does not require 5 h of stirring as has been stated in the literature.[3b] The resulting lithio derivative of **9f** reacts with aldehydes to give the corresponding vinyl sulfides **10a–c**. Unfortunately, sulfide **9f** did not give Horner–Wittig products with ketones. All of the vinyl sulfides **10** were hydrolyzed to the corresponding ketones **11** in the presence of titanium tetrachloride.[15] The experimental results are summarized in Table II.

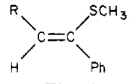
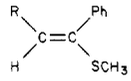


(*E* + *Z*)-**10a**, R = Ph
b, R = Me
c, R = Pr-*n*

11a-c

Crude vinyl sulfides **10** were purified by column chromatography on silica gel. They were obtained as mixtures of *E* and *Z* geometrical isomers. The isomeric compositions of **10** were determined from ^1H NMR spectra. For assignment of *E* and *Z* configurations to respective isomers of **10**, the additive increments method[16] was applied. The observed and calculated vinyl proton resonance positions of (*Z*)-**10** and (*E*)-**10** corresponding to proposed configurations are shown in Table III. Although in the case of the *E* isomers of sulfides **10b** and **10c** there are substantial

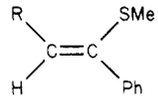
Table III. Structural Assignments to Geometrical Isomers in α,β-Unsaturated Sulfides (10) Using Additive Shielding Increments

	no.	R	δ calcd	δ obsd	Δδ[a] (reversing assignments)
	10a	Ph	6.86	6.75	−0.11 (−0.46)
	10b	CH_3	5.93	5.89	−0.04 (−0.23)
	10c	$CH_3(CH_2)_2$	5.93	5.80	−0.13 (−0.35)
(*Z*)-**10**					
	10a	Ph	6.27	6.40	0.13 (0.48)
	10b	CH_3	5.34	5.70	0.36 (0.23)
	10c	$CH_3(CH_2)_2$	5.34	5.58	0.24 (0.35)
(*E*)-**10**					

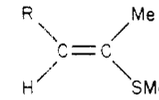
[a] Δδ denotes experimental value − calculated value.

differences between the calculated and observed δ values, the configurational assignments seem to be justified by our previous experience.[4b]

Regarding the steric course of the Horner–Wittig reaction of sulfide **9f**,[17] it is interesting that in all cases the predominant isomer was (*Z*)-**10**, in which the phenyl group



(*Z*)-**10**, R = Me, Pr-*n*, Ph



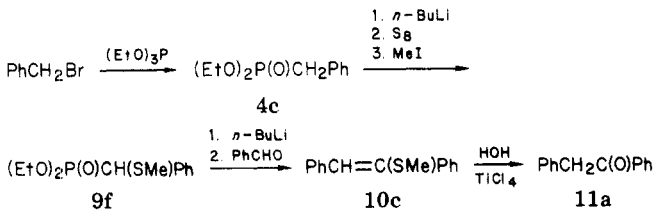
(*E*)-**12**, R = pentyl, Ph

and vinyl proton are cis situated. In an analogous reaction of sulfide **9d** described by Corey and Shulman,[3b] vinyl sulfides **12** were produced which contained the *E* isomers as the major isomers. In these isomers the methylthio group was cis related to the vinyl proton, i.e., situated on the less sterically crowded side of the double bond.

These observations suggest the order of increasing steric requirements of the substituents Me < MeS < Ph, assuming that the steric factor is mainly responsible for the

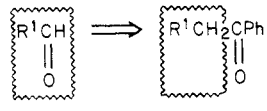
(15) D. Seebach and H. Neumann, *Chem. Ber.*, **107**, 847 (1974).
(16) C. Pascual, J. Meier, and W. Simon, *Helv. Chim. Acta*, **49**, 164 (1966); V. E. Matter, C. Pascual, E. Pretsch, W. Simon, and S. Sternhell, *Tetrahedron*, **25**, 691 (1969).
(17) For recent reviews see: J. Boutagy and R. Thomas, *Chem. Rev.*, **74**, 87 (1974); W. S. Wadsworth, Jr., *Org. React.*, **25**, 73 (1977).

Scheme I

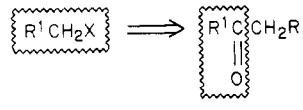


ratio of geometrical isomers formed in the Horner–Wittig reaction.

In summary, the efficient synthesis of vinyl sulfides **10** followed by hydrolysis can be regarded as a new method for the conversion of any aldehyde into an aromatic ketone as schematically illustrated.

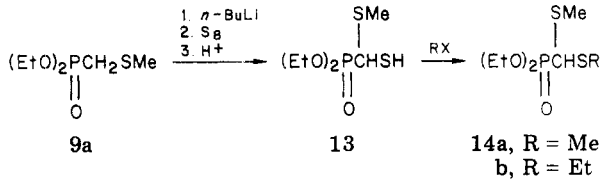


Moreover, since phosphonates **4** used for the corresponding thiols **5** are obtained from alkyl halides by means of the Michaelis–Becker or Arbuzov reaction, it is thus possible to convert an alkyl halide into a ketone as shown schematically.



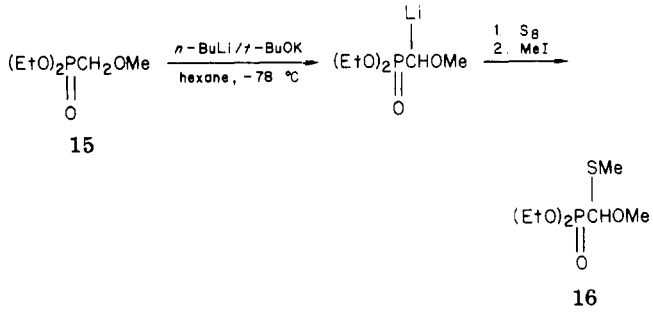
The latter case is exemplified by the conversion of benzyl bromide into benzyl phenyl ketone in an overall 47% yield (Scheme I).

Synthesis of *S,S*- and *O,S*-Thioacetals of Formylphosphonates. In an extension of the present studies, addition of sulfur to the lithio derivative of α-phosphoryl sulfide **9a** was investigated in the hope of obtaining the corresponding hemithioacetal **13**. The latter upon alkylation should give *S,S*-thioacetals of diethyl formylphosphonate **14**, which became the reagents of choice for the synthesis of ketene thioacetals.[6c] As expected, addition of sulfur to **9a** occurs readily under the conditions already elaborated. However, only half of the molar equivalent of **9a** is converted into **13** because of competing proton transfer from **13** to the lithio derivative of **9a**. Fortunately, separation of **13** from the unreacted substrate is very simple due to a good water solubility of hemithioacetal **13**. Alkylation of **13** under two-phase system[14] conditions gives rise to *S,S*-thioacetals **14**. Furthermore, this method

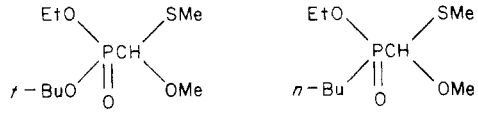


makes it possible to prepare not only symmetrical thioacetals such as **14a** but also unsymmetrical systems such as **14b**, which are not readily accessible by other methods.

Finally, we were able to convert in similar fashion diethyl methoxymethylphosphonate **15** into the *O,S*-thioacetal of diethyl formylphosphonate (**16**).[18] Since some difficulties in generating the carbanion of **15** were encountered, a more effective base was required. Thus, reacting a mixture of potassium *tert*-butoxide and *n*-butyllithium[19] in hexane at −78 °C with **15**, and then addition of sulfur followed by methyl iodide, gave after the usual workup thioacetal **16** in 53% yield. However, this reaction is very sensitive to



experimental conditions. For instance, the reverse addition of the reagents, i.e., addition of the base to **15**, afforded a mixture of **16** and **17**. Similarly, when *n*-butyllithium was used alone for anion generation a mixture of **16** and **18** was obtained.



Experimental Section

^{1}H NMR spectra were recorded at 60 MHz with an R12B Perkin-Elmer spectrometer; chemical shifts are reported in parts per million downfield from Me_4Si as an internal standard. ^{31}P NMR spectra were run on a Jeol C-60H or Jeol JNM-C-60H1 spectrometer with H_3PO_4 as an external standard. In this paper the new convention of positive ^{31}P NMR signals to low field from H_3PO_4 is used. Column chromatography was done on Merck silica gel, 100–200 mesh.

Solvents and Reagents. Solvents and commercial reagents were distilled and dried before use. *n*-Butyllithium purchased from Fluka AG was titrated before use. Reagent-grade tetrahydrofuran (THF) was distilled from lithium aluminum hydride. Diethyl methylphosphonate (**4a**) was obtained from diethyl phosphonate and methyl iodide. Diethyl ethylphosphonate (**4b**) and diethyl benzylphosphonate (**4c**) were obtained from triethyl phosphite and ethyl iodide and benzyl bromide, respectively.

General Procedure for Synthesis of α-Phosphoryl Thiols (5). To a stirred solution of phosphonate **4** (0.01 mol) in 10 mL of dry THF a solution of *n*-butyllithium (0.01 mol) in hexane was added dropwise under an argon atmosphere at −78 °C. The solution was stirred at −78 °C for 5 min and then dried and powdered sulfur (0.32 g, 0.01 mol) was added. The mixture was warmed slowly to −20 °C. A clear, dark red solution obtained was treated with water (30 mL). The bulk of the solvents was removed and the remaining aqueous solution was extracted with chloroform (2 × 15 mL). An aqueous layer was cooled to 0 °C, acidified by 1 N hydrochloric acid, and extracted with chloroform (3 × 15 mL). The chloroform extract was washed with water (10 mL), dried over anhydrous $MgSO_4$, and concentrated, giving the pure α-phosphoryl thiol (**5**) as a yellow oil. The physical and ^{1}H NMR data of the products obtained follow.

5a: n^{24}_D 1.4658; ^{1}H NMR ($CDCl_3$) δ 1.33 (t, 6, CH_3CH_2OP, J_{HH} = 7.0 Hz), 2.16 (t, 1, SH, J_{HH} = 8.7 Hz), 2.70 (dd, 2, PCH_2–, J_{PH} = 13.7 Hz), 4.18 (dq, 4, CH_3CH_2OP, J_{PH} = 8.7 Hz). Anal. Calcd for $C_5H_{13}O_3PS$: C, 32.62; H, 7.06; P, 16.82. Found: C, 32.90; H, 7.08; P, 16.91.

5b: n^{24}_D 1.4631; ^{1}H NMR ($CDCl_3$) δ 1.34 (t, 6, CH_3CH_2OP, J_{HH} = 7.0 Hz), 1.49 (dd, 3, CH_3CHP, J_{PH} = 17.7, J_{HH} = 7.7 Hz), 2.02 (d, 1, SH, J_{HH} = 8.3 Hz), 3.10 (m, 1, PCH), 4.13 (dq, 4, CH_3CH_2OP, J_{PH} = 7.1 Hz). Anal. Calcd for $C_6H_{15}O_3PS$: C, 36.37; H, 7.57; P, 15.63. Found: C, 36.67; H, 7.60; P, 15.91.

(18) The synthesis of **16** has been described in a preliminary communication; see ref 6a.

(19) M. Schlosser and J. Hartmann, *Angew. Chem., Int. Ed. Engl.*, **12**, 508 (1973); J. A. Favre and R. J. Sonnenfeld, *J. Organomet. Chem.*, **55**, 221 (1973).

5c: n^{24}_D 1.5284; ^{1}H NMR ($CDCl_3$) δ 1.10 and 1.30 (t, 6, nonequivalent CH_3CH_2OP, J_{HH} = 7.4, J_{PH} = 14.1 Hz), 2.62 (dd, 1, PCH, J_{PH} = 11.4, J_{HH} = 8.7 Hz), 3.55 (d, 1, SH), 4.10 (dq, 4, CH_3CH_2OP, J_{PH} = 7.8 Hz), 7.15–7.50 (m, 5, aromatic). Anal. Calcd for $C_{11}H_{17}O_3PS$: C, 50.78; H, 6.53; P, 11.90. Found: C, 50.42; H, 6.73; P, 11.78.

(Diethylphosphoryl)methyl Thiolacetate (6). To a suspension of 1.49 g (0.01 mol) of the dry tetramethylammonium salt of thioacetic acid in dimethoxyethane (15 mL) diethyl (iodomethyl)phosphonate (2.5 g, 0.009 mol) was added. The reaction mixture was stirred for 2 h at room temperature and then filtered. The filtrate was washed with water, dried over anhydrous $MgSO_4$, and evaporated. The residue was purified by column chromatography [benzene–acetone (9:1)] to give 1.65 g (81% yield) of **6**. Thiolacetate **6** was also obtained from diethyl phosphorylmethylthiol (**5a**) by the following procedure. To sodium diethyl phosphorylmethyl mercaptide [prepared from 1.84 g (0.01 mol) of **5a** and sodium ethoxide] was added a solution of 0.79 g (0.01 mol) of acetyl chloride in 15 mL of THF at 0 °C. The reaction mixture was stirred for 1 h at room temperature. Then, the solvent was evaporated. The residue was treated with water (20 mL), extracted with chloroform (3 × 15 mL), and dried over anhydrous $MgSO_4$. The chloroform solution was evaporated to afford the crude thiol ester **6**, which was purified by column chromatography to yield 1.42 g (70%) of **6**: n^{24}_D 1.4849; ^{31}P NMR ($CDCl_3$) δ 23.8; ^{1}H NMR ($CDCl_3$) δ 1.30 (t, 6, CH_3CH_2OP, J_{HH} = 8.0 Hz), 2.36 (s, 3, $CH_3C(O)S$), 3.17 (d, 2, PCH_2, J_{PH} = 14.6 Hz), 4.11 (dq, 4, CH_3CH_2OP, J_{PH} = 8.2 Hz). Anal. Calcd for $C_7H_{15}O_4PS$: C, 38.90; H, 6.94; P, 14.33. Found: C, 38.70; H, 6.92; P, 14.38.

Hydrolysis of 6 to 5a. **6** was hydrolyzed by an aqueous sodium carbonate in THF solution at 60 °C for 15 min. From the resulting sodium diethylphosphorylmethyl mercaptide, thiol **5a** was isolated according to the previously described procedure (yield 71%).

Synthesis of α-Phosphoryl Disulfides (8). General Procedure. To a solution of **5** (0.01 mol) in THF (15 mL) under an argon atmosphere at −5 °C sulfuryl chloride (0.68 g, 0.005 mol) was added. The resulting solution was stirred at −5 to 0 °C for an additional 1 h. Then the solvent was removed in vacuo to give α-phosphoryl disulfide (**8**). An analytically pure sample of **8** was obtained by column chromatography using benzene–acetone (9:1) as the solvent. The physical and ^{1}H NMR data of **8** are given below.

8a: n^{26}_D 1.4894; ^{1}H NMR ($CDCl_3$) δ 1.28 (t, 12, CH_3CH_2OP, J_{HH} = 6.8 Hz), 3.19 (d, 4, PCH_2, J_{PH} = 12.9 Hz), 4.06 (dq, 8, CH_3CH_2OP, J_{PH} = 7.1 Hz). Anal. Calcd for $C_{10}H_{24}O_6P_2S_2$: C, 32.79; H, 6.55; P, 16.91. Found: C, 32.97; H, 6.47; P, 16.80.

8b: mixture of two diastereoisomers in ratio 55:45; ^{31}P NMR δ 27.3 and 27.7, respectively; n^{26}_D 1.4901; ^{1}H NMR ($CDCl_3$) δ 1.31 (t, 12, CH_3CH_2OP, J_{HH} = 6.9 Hz), 1.50 (dd, 6, CH_3CHP, J_{PH} = 17.7, J_{HH} = 7.7 Hz), 3.28 (m, 2, PCH), 4.15 (dq, 8, CH_3CH_2OP, J_{PH} = 7.4 Hz). Anal. Calcd for $C_{12}H_{28}O_6P_2S_2$: C, 35.56; H, 7.10; P, 15.71. Found: C, 35.63; H, 7.13; P, 15.68.

8c: mixture of two diastereoisomers in ratio 57:43; ^{31}P NMR δ 21.4 and 20.7, respectively; n^{26}_D 1.5409; ^{1}H NMR ($CDCl_3$) δ 1.09 (t, CH_3CH_2OP, J_{HH} = 7.3 Hz) for first diastereoisomer and 1.29 (dt, CH_3CH_2OP, J_{PH} = 2.0, J_{HH} = 7.3 Hz) for the second one, 3.96 (d, 2, PCH, J_{PH} = 19.9 Hz), 3.5–4.1 (m, 8, CH_3CH_2OP), 7.25–7.40 (m, 10, aromatic). Anal. Calcd for $C_{22}H_{32}O_6P_2S_2$: C, 50.96; H, 6.22; P, 11.95. Found: C, 50.67; H, 6.10; P, 11.80.

Preparation of α-Phosphoryl Sulfides (9). All the α-phosphoryl sulfides (**9**) listed in Table I were obtained according to Herriot and Picker[14] from corresponding thiols **5** and alkyl halides under two-phase system catalytic conditions. The physical and ^{1}H NMR data of the products follow.

9a: n^{20}_D 1.4650; ^{1}H NMR ($CDCl_3$) δ 1.29 (t, 6, CH_3CH_2OP, J_{HH} = 6.7 Hz), 2.22 (s, 3, CH_3S), 2.61 (d, 2, PCH_2, J_{PH} = 12.6 Hz), 4.09 (dq, 4, CH_3CH_2OP, J_{PH} = 7.2 Hz). Anal. Calcd for $C_6H_{15}O_3PS$: C, 36.41; H, 7.62; P, 15.63. Found: C, 36.20; H, 7.60; P, 15.78.

9b: n^{24}_D 1.4671; ^{1}H NMR ($CDCl_3$) δ 1.71 (t, 3, CH_3CH_2S, J_{HH} = 7.3 Hz), 1.30 (t, 6, CH_3CH_2OP, J_{HH} = 6.8 Hz), 2.51 (q, 2, CH_3CH_2S), 3.15 (d, 2, PCH_2, J_{PH} = 13.0 Hz), 4.18 (dq, 4, CH_3CH_2OP, J_{PH} = 7.4 Hz). Anal. Calcd for $C_7H_{17}O_3PS$: C, 39.63; H, 8.02; P, 14.60. Found: C, 39.47; H, 7.78; P, 14.61.

9c: n^{24}_D 1.5356; ^{1}H NMR ($CDCl_3$) δ 1.32 (t, 6, CH_3CH_2OP, J_{HH} = 7.7 Hz), 2.53 (d, 2, PCH_2, J_{PH} = 13.3 Hz), 3.90 (s, 2, $PhCH_2S$), 4.17 (dq, 4, CH_3CH_2OP, J_{PH} = 7.3 Hz). Anal. Calcd for $C_{12}H_{19}O_3PS$: C, 52.56; H, 6.93; P, 11.29. Found: C, 52.41; H, 6.88; P, 11.22.

9d: n^{20}_D 1.4630; ^{1}H NMR ($CDCl_3$) δ 1.35 (t, 6, CH_3CH_2OP, J_{HH} = 7.2 Hz), 1.46 (dd, 3, CH_3CHP, J_{PH} = 16.4, J_{HH} = 7.0 Hz), 2.26 (s, 3, CH_3S), 2.70 (m, 1, PCH), 4.18 (m, 4, CH_3CH_2OP, J_{PH} = 7.8 Hz). Anal. Calcd for $C_7H_{17}O_3PS$: C, 39.63; H, 8.02; P, 14.60. Found: C, 39.50; H, 8.10; P, 14.82.

9e: n^{24}_D 1.4656; ^{1}H NMR ($CDCl_3$) δ 1.32 (t, 6, CH_3CH_2OP, J_{HH} = 7.0 Hz), 1.34 (t, 3, CH_3CH_2S, J_{HH} = 8.2 Hz), 1.45 (dd, 3, CH_3CHP, J_{PH} = 16.2, J_{HH} = 8.2 Hz), 2.79 (q, 2, CH_3CH_2S), 3.22 (m, 1, PCH), 4.11 (dq, 4, CH_3CH_2OP, J_{PH} = 7.0 Hz). Anal. Calcd for $C_8H_{19}O_3PS$: C, 42.29; H, 8.40; P, 13.69. Found: C, 42.30; H, 8.21; P, 13.50.

9f: n^{25}_D 1.5288; ^{1}H NMR (CCl_4) δ 1.09 and 1.28 (t, 6, nonequivalent, CH_3CH_2OP, J_{HH} = 7.0 Hz), 2.02 (s, 3, CH_3S), 3.86 (d, 1, PCH, J_{PH} = 20.3 Hz), 4.09 (dq, 4, CH_3CH_2OP, J_{PH} = 7.2 Hz). Anal. Calcd for $C_{12}H_{19}O_3PS$: C, 52.54; H, 6.98; P, 11.29. Found: C, 52.42; H, 6.90; P, 11.20.

9g: n^{24}_D 1.5208; ^{1}H NMR ($CDCl_3$) δ 1.12 and 1.34 (t, 6, nonequivalent, CH_3CH_2OP, J_{HH} = 7.3 Hz), 1.24 (t, 3, CH_3CH_2S, J_{HH} = 7.9 Hz), 2.51 (q, 2, CH_3CH_2S), 3.10 (d, 1, PCH, J_{PH} = 21.2 Hz), 3.98 (dq, 4, CH_3CH_2OP, J_{PH} = 7.3 Hz). Anal. Calcd for $C_{13}H_{21}O_3PS$: C, 54.18; H, 7.28; P, 10.74. Found: C, 54.18; H, 7.36; P, 10.74.

9h: n^{24}_D 1.5618; ^{1}H NMR ($CDCl_3$) δ 1.51 and 1.62 (t, 6, nonequivalent, CH_3CH_2OP, J_{HH} = 8.0 Hz), 4.00 (s, 2, $PhCH_2$), 4.28 (d, 1, PCH, J_{PH} = 20.0 Hz), 4.31 (dq, 4, CH_3CH_2OP, J_{PH} = 8.0 Hz). Anal. Calcd for $C_{18}H_{23}O_3PS$: C, 61.73; H, 6.57; P, 8.84. Found: C, 61.73; H, 6.63; P, 8.54.

General Procedure for Synthesis of α,β-Unsaturated Sulfides (10). To a stirred solution of α-(diethylphosphoryl)-benzyl methyl sulfide (**9f**; 2.74 g, 0.01 mol) in dry THF (20 mL) at −78 °C a solution of *n*-butyllithium (0.01 mol) in hexane was added dropwise under an argon atmosphere. The solution was stirred at −78 °C for 5 min and then a solution of aldehyde (0.01 mol) in THF (10 mL) was added. The mixture was warmed to room temperature and refluxed for 2 h. After removal of solvents the residue was treated with water (50 mL) and extracted with chloroform (3 × 25 mL). The chloroform solution was washed with aqueous ammonium chloride solution and water, dried, and evaporated to afford the crude product, which was chromatographed (hexane) to give analytically pure vinyl sulfide (**10**). The physical and ^{1}H NMR data of **10** follow.

1-(Thiomethyl)-1-phenyl-2-phenylethylene (10a): colorless oil; *E*/*Z* ratio 11:89; n^{22}_D 1.6361; ^{1}H NMR (CCl_4) (*Z*)-**10a** δ 1.92 (s, 3, CH_3S), 6.75 (s, 1, =CH), 7.1–7.8 (m, 10, aromatic); ^{1}H NMR (CCl_4) (*E*)-**10a** 2.11 (s, 3, CH_3S), 6.40 (s, 1, =CH). Anal. Calcd for $C_{15}H_{14}S$: C, 79.60; H, 6.23. Found: C, 79.64; H, 6.20.

1-(Thiomethyl)-1-phenylpropene (10b): colorless oil; *E*/*Z* ratio 32:68; n^{19}_D 1.5654. For pure (*Z*)-**10b** isomer: n^{20}_D 1.5581; ^{1}H NMR (CCl_4) δ 1.83 (s, 3, CH_3S), 1.92 (d, 3, CH_3C=, J_{HH} = 6.8 Hz), 5.89 (q, 1, =CH), 7.1–7.5 (m, 5, aromatic). Anal. Calcd for $C_{10}H_{12}S$: C, 73.12; H, 7.36. Found: C, 73.01; H, 7.30. ^{1}H NMR (CCl_4) for isomer (*E*)-**10b**: δ 1.64 (d, 3, CH_3C=, J_{HH} = 6.8 Hz), 1.98 (s, 3, CH_3S), 5.73 (q, 1, = CH).

1-(Thiomethyl)-1-phenyl-1-pentene (10c): colorless oil; *E*/*Z* ratio 22:78 n^{21}_D 1.5462; ^{1}H NMR (CCl_4) (*Z*)-**10c** δ 1.82 (s, 3, CH_3S), 0.7–2.5 (m, 7, CH_3CH_2C=), 5.85 (t, 1, =CH, J_{HH} = 7.3 Hz), 7.0–7.5 (m, 5, aromatic); ^{1}H NMR (CCl_4) (*E*)-**10c** δ 1.96 (s, 3, CH_3S), 5.58 (t, 1, =CH, J_{HH} = 7.3 Hz). Anal. Calcd for $C_{12}H_{16}S$: C, 77.38; H, 5.41. Found: C, 77.21; H, 5.40.

Hydrolysis of Vinyl Sulfides (10) to Ketones (11). All the sulfides **10** were hydrolyzed to the corresponding aryl ketones **11** according to the Seebach and Neumann[15] procedure using titanium(IV) chloride.

Addition of Sulfur to (Dimethylphosphoryl)methyl Methyl Sulfide (9a). α-Phosphoryl sulfide (**9a**) was reacted with *n*-butyllithium and then with sulfur under similar conditions to those described for phosphonates **4** to give hemithioacetal **13** in 78% yield: n^{20}_D 1.5080, ^{31}P NMR ($CDCl_3$) δ 19.7; ^{1}H NMR (CCl_4) δ 1.36 (t, 6, CH_3CH_2OP, J_{HH} = 7.3 Hz), 2.22 (d, 1, SH, J_{HH} = 9.2 Hz), 2.32 (s, 3, SCH_3), 2.60 (dd, 1, PCH, J_{PH} = 10.7 Hz), 4.22 (dq, 4, CH_3CH_2OP, J_{PH} = 8.6 Hz). Anal. Calcd for $C_6H_{15}O_3PS_2$: C, 31.42; H, 6.59; P, 13.11. Found: C, 31.21; H, 6.40; P, 12.81.

Preparation of *S*,*S*-Thioacetals of Diethyl Formylphosphonate (14). The thioacetals **14** were prepared from **13**

and alkyl halides in the same manner as sulfides **9**.

***S,S*-Dimethylthioacetal of diethyl formylphosphonate (14a)** was obtained in 72% yield from **13** and methyl iodide: n^{24}_D 1.5200; ^{31}P NMR ($CDCl_3$) δ 20.0; ^{1}H NMR ($CDCl_3$) δ 1.32 (t, 6, CH_3CH_2OP, J_{HH} = 7.3 Hz), 2.22 (s, 3, CH_3S), 3.69 (d, 1, PCH, J_{PH} = 18.0 Hz), 4.18 (dq, 4, CH_3CH_2OP, J_{PH} = 8.2 Hz) (lit.[7b] n^{20}_D 1.5212).

***S*-Methyl-*S*-ethylthioacetal of diethyl formylphosphonate (14b)** was obtained in 70% yield from **13** and ethyl iodide: n^{26}_D 1.4946; ^{31}P NMR ($CDCl_3$) δ 18.5; ^{1}H NMR (CCl_4) δ 1.22 (t, 6, CH_3CH_2S, J_{HH} = 7.3 Hz), 1.25 (t, 6, CH_3CH_2OP, J_{HH} = 7.9 Hz), 2.25 (s, 3, SCH_3), 2.52 (q, 4, CH_3CH_2S), 3.58 (d, 1, PCH, J_{PH} = 17.7 Hz), 4.10 (dq, 4, CH_3CH_2OP, J_{PH} = 8.1 Hz). Anal. Calcd for $C_8H_{19}O_3PS_2$: C, 37.19; H, 7.41; P, 11.94. Found: C, 36.98; H, 7.30; P, 11.81.

Preparation of *O,S*-Dimethylthioacetal of Diethyl Formylphosphonate (16). To the freshly prepared mixture of potassium *tert*-butoxide (0.01 mol) in THF (15 mL) and *n*-butyllithium (0.01 mol) in hexane diethyl (methoxymethyl)-phosphonate (1.82 g, 0.01 mol) was added under an argon atmosphere at −78 °C. The reaction mixture was stirred at −78 °C for 30 min. Then sulfur (0.32 g, 0.01 mol) and methyl iodide (1.42 g, 0.01 mol) were added. The reaction mixture was warmed to room temperature. The bulk of the solvents was removed and the residue was treated with chloroform (50 mL) and washed with water. The chloroform solution was dried and evaporated to afford the crude **16**, which was chromatographed [benzene–acetone (9:1)] to give 1.2 g (53%) of pure **16**: n^{24}_D 1.4622; ^{31}P NMR ($CDCl_3$) δ 16.5; ^{1}H NMR ($CDCl_3$) δ 1.34 (t, 6, CH_3CH_2OP, J_{HH} = 7.4 Hz), 2.18 (s, 3, CH_3S), 3.46 (s, 3, CH_3O), 4.16 (dq, 4, CH_3CH_2OP, J_{PH} = 7.4 Hz), 4.33 (d, 1, PCH, J_{PH} = 11.8 Hz) (lit.[6b] n^{24}_D 1.4622).

Registry No. 4a, 683-08-9; **4b**, 78-38-6; **4c**, 1080-32-6; **5a**, 70660-05-8; **5b**, 70660-06-9; **5c**, 70660-07-0; **6**, 70660-08-1; **7**, 10419-77-9; **8a**, 70660-09-2; *dl*-**8b**, 70660-10-5; *meso*-**8b**, 70660-11-6; *dl*-**8c**, 70660-12-7; *meso*-**8c**, 70660-13-8; **9a**, 28460-01-7; **9b**, 54091-78-0; **9c**, 41760-64-9; **9d**, 22966-40-1; **9e**, 70660-14-9; **9f**, 70660-15-0; **9g**, 70660-16-1; **9h**, 70660-17-2; (*E*)-**10a**, 70660-18-3; (*Z*)-**10a**, 2764-94-5; (*E*)-**10b**, 70660-19-4; (*Z*)-**10b**, 70660-20-7; (*E*)-**10c**, 70660-21-8; (*Z*)-**10c**, 70660-22-9; **11a**, 451-40-1; **11b**, 93-55-0; **11c**, 1009-14-9; **13**, 70660-23-0; **14a**, 62999-70-6; **14b**, 70660-24-1; **15**, 32806-04-5; **16**, 59590-52-2; **17**, 70660-25-2; **18**, 70660-26-3; diethyl phosphonate, 762-04-9; triethyl phosphite, 122-52-1; thioacetic acid tetramethylammonium salt, 62698-51-5; benzaldehyde, 100-52-7; acetaldehyde, 75-07-0; butyrylaldehyde, 123-72-8; sulfur, 10544-50-0; sulfuryl chloride, 7791-25-5.

Pyrylium Salts from Friedel–Crafts Acetylation of Isoparaffins

Michel Arnaud, Annette Pedra, Christian Roussel,* and Jacques Metzger

I.P.S.O.I., Centre Universitaire St Jérôme, 13013 Marseille, France

Received February 21, 1979

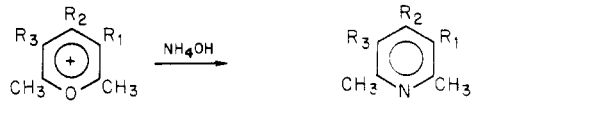
The first synthesis of pyrylium salts from acetylation of isoparaffins (isopentane, 2-methylpentane, 3-methylpentane, and 2,3-dimethylbutane) under Friedel–Crafts conditions is reported. The pyrylium salts are converted into the corresponding pyridines and the selectivity of the reaction is discussed. The influence of the $AcCl/AlCl_3$ ratio on the apparent selectivity is demonstrated.

Pyrylium salts are versatile synthons in preparative organic chemistry since they can be converted to several benzenoid derivatives and heterocyclic compounds.[1,2] Among the various synthetic routes, the diacylation of alkenes is a standard method for the preparation of alkyl-substituted pyrylium salts bearing two identical α substituents.[2] Various alkene precursors, such as alcohols or *tert*-alkyl halides, have been used with success.[2-6] We report the first examples of pyrylium salt synthesis from isoalkanes under Friedel–Crafts conditions. This study opens new prospects for the utilization of isoparaffins.

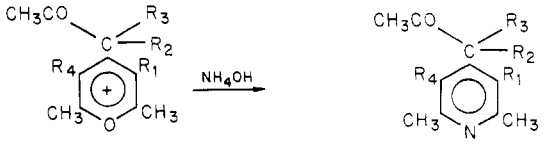
Results and Discussion

The acetylations were performed by acetyl chloride and aluminum chloride on four isoparaffins: isopentane, 2-methylpentane, 3-methylpentane, and 2,3-dimethylbutane, with and without chloroform. The isomeric hexanes were chosen to investigate possible rearrangements and fragmentations in the Friedel–Crafts medium.

Scheme I



1a, R_1 = H, R_2 = Me, R_3 = H
b, R_1 = H, R_2 = Et, R_3 = H
c, R_1 = H, R_2 = *i*-Pr, R_3 = H
d, R_1 = Me, R_2 = Me, R_3 = H
e, R_1 = H, R_2 = Pr, R_3 = H
f, R_1 = Et, R_2 = Me, R_3 = H
g, R_1 = Me, R_2 = Et, R_3 = H
h, R_1 = Me, R_2 = Me, R_3 = Me



2a, R_1 = H, R_2 = H, R_3 = H, R_4 = H
b, R_1 = H, R_2 = H, R_3 = Me, R_4 = H
c, R_1 = H, R_2 = Me, R_3 = Me, R_4 = H
d, R_1 = H, R_2 = H, R_3 = Et, R_4 = H
e, R_1 = Me, R_2 = H, R_3 = H, R_4 = H
f, R_1 = Me, R_2 = H, R_3 = Me, R_4 = H
g, R_1 = Et, R_2 = H, R_3 = H, R_4 = H
h, R_1 = Me, R_2 = H, R_3 = H, R_4 = Me

The conversion of alkylpyrylium salts into the corresponding pyridines is almost quantitative[1-6] and thus the pyridine mixture obtained upon treatment of the crude reaction medium by NH_4OH is representative of the

(1) S. V. Krivun, O. F. Alferova, and S. V. Sayapina, *Russ. Chem. Rev. (Engl. Transl.)*, **43**, 835 (1974).
(2) A. T. Balaban, W. Schroth, and G. Fisher, *Adv. Heterocycl. Chem.*, **10**, 241 (1969); A. T. Balaban, book dedicated to Professor Tilak's 60th birthday, in preparation.
(3) G. N. Dorofeenko, Yu. A. Zhdanov, and L. N. Etmetchenko, *Khim. Geterosikl. Soedin.*, **5**, 781 (1969); M. Arnaud, C. Roussel, and J. Metzger, *Tetrahedron Lett.*, 1795 (1979).
(4) (a) A. T. Balaban, A. Bota, F. Chiraleu, E. Sliam, A. Hanes, and C. Draghici, *Rev. Roum. Chim.*, **22**, 1003 (1977), and references therein; (b) A. T. Balaban and C. D. Nenitzescu, *Justus Liebigs Ann. Chem.*, **625**, 74 (1959); *J. Chem. Soc.*, 3553 (1961).
(5) A. G. Anderson and P. J. Stang, *J. Org. Chem.*, **41**, 3034 (1976).
(6) P. F. G. Praill and A. L. Whitear, *J. Chem. Soc.*, 3573 (1961).

0022-3263/79/1944-2972$01.00/0