Tetrahedron Letters,Vol.25,No.11,pp 1111-1114,1984
Printed in Great Britain

0040-4039/84 $3.00 + .00

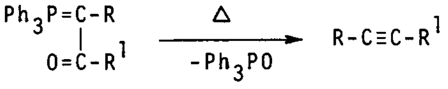
PYROLYSIS OF α-ACYL,α-THIO PHOSPHORANES → THIOACETYLENES

Antonio L. Braga, João V. Comasseto* and Nicola Petragnani

Instituto de Química
Universidade de São Paulo
Caixa Postal 20.780
São Paulo - S.P.
Brasil

Summary: Pyrolysis of α-acyl,α-thio phosphoranes affords thioacetylenes in good yield. The thio acetylenes are precursors of terminal and alkyl disubstituted acetylenes.

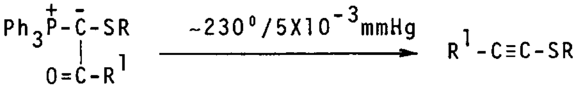
Thermolysis of α-acyl phosphoranes is a useful method of synthesizing acetylenes:



$$\mathrm{Ph_3P{=}\underset{\underset{O=C-R^1}{|}}{C}-R} \xrightarrow[-\mathrm{Ph_3PO}]{\Delta} \mathrm{R-C{\equiv}C-R^1}$$

However, the fragmentation reaction proceeds satisfactorily only when R is an electron withdrawing group such as CO_2R,[1,2,3,4] Ar[5,6] and CN[2,7]. No acetylene is obtained when R is hydrogen or an alkyl group.

In this work we have prepared thioacetylenes (2) through the pyrolysis of α-acyl, α-thio methylenetriphenylphosphoranes (1), taking advantage of the well known ability of sulfur to stabilize carbanions.[8]



$$\mathrm{Ph_3\overset{+}{P}-\underset{\underset{O=C-R^1}{|}}{\overset{-}{C}}-SR} \xrightarrow{\sim 230^{\circ}/5X10^{-3}\,\mathrm{mmHg}} \mathrm{R^1-C{\equiv}C-SR}$$

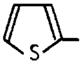
(1) (2)

This reaction complements a recently developed methodology to the preparation of acetylenes based on the pyrolysis of selenophosphoranes,[9] since (2) can lead to terminal or alkyl disubstituted acetylenes, as will be discussed below. In the selenophosphorane method the reaction gives good results only when R^1 is an aryl or electron withdrawing group, tarry products being formed when R^1 is an alkyl group. The thiophosphorane route is of general applicability as can be seen in Table 2.

The starting α-acyl, α-thio methylenetriphenylphosphoranes (1) are easily obtained through a transylidation reaction between a α-thio methylenetriphenylphosphorane and an appropriate acid chloride or anhydride (Table 1).

Table 1

$$2Ph_3P{=}CHSR \xrightarrow[\text{benzene, r.t.}]{R'COX} (1) + Ph_3\overset{+}{P}\text{-}CH_2SR\ X^-$$

R	R^1	X	m.p.°C	yield %[a,b]
CH_3	Ph	Cl	183-6	61
CH_3	p-CH_3Ph	Cl	200-3	64
CH_3		Cl	177-9	74
Ph	Ph	Cl	206-8	65
Ph	p-CH_3Ph	Cl	170-4	68
Ph	CF_3	$COCF_3$	216-8	68
Ph	CH_3	Cl	218-2	69
Ph	$(CH_3)_3C$	Cl	153-5	66
Ph	n-C_5H_{11}	Cl	130-2	70

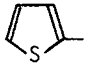
[a]Recrystallized yield; [b]All compounds gave satisfactory IR and NMR spectral data and elemental analyses.

When heated in a kugelrohrofen under vaccum (~230°/5X10^{-3}mmHg) the α-acyl, α-thio methylenetriphenylphosphoranes (1) decompose to give the thioacetylenes (2) in moderate to good yields (Table 2).

Reaction of (2) with n-butyl lithium affords the corresponding lithium acetylides, which can be trapped with electrophiles to give terminal or disubstituted acetylenes (3).[10] On the other hand, the thioacetylenes are easily oxidized to sulfones,[11] which by treatment with alkyllithiums or Grignard reagents lead directly to the disubstituted acetylenes (4).[12] In this way the acetylenic

Table 2

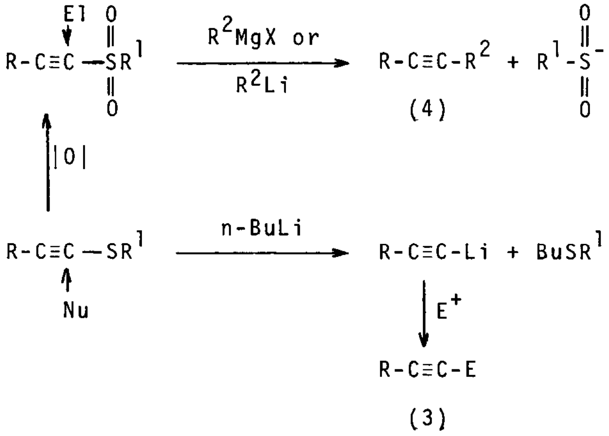
$$(1) \xrightarrow[\text{-PhPO}]{\sim 230/5X10^{-3}\text{mmHg}} (2)$$

R	R^1	b.p.°C/mmHg[a]	yield (%)[b,c]
CH_3	Ph	70/0.5	80
CH_3	p-CH_3PH	60/0.4	68
CH_3		70/1	69
Ph	Ph	70/0.3	71
Ph	p-CH_3PH	78/0.3	69
Ph	CF_3	60/3	74
Ph	CH_3	60/0.5	41
Ph	$(CH_3)_3C$	65/0.3	43
Ph	n-C_5H_{11}	70/0.3	45

[a] Distilled in kugelrohrofen; [b] yields refer to pure and isolated products, purity >98% in all cases determined by G.L.C.|(SE 30,3% in chromosorb W)|; [c] All compounds gave satisfactory IR and NMR spectral data and elemental analyses.

carbon atom linked to the sulfur moiety can formally act both as an electrophilic or a nucleophilic center (Scheme 1).

Scheme 1



Our results show that the α-acyl, α-thio methylenetriphenylphosphoranes are valuable synthons of protected terminal acetylenes, which can lead to terminal or disubstituted acetylenes, that could not be obtained through the pyrolysis of α-acyl methylenetriphenylphosphoranes. The sequence of reactions (1) → (2) → (3) or (4) could become a valuable route to some naturally occuring acetylenes.[13] Finally it must be emphasized that the acetylenic sulfones, obtained by oxydation of the corresponding thioacetylenes,[11,14] are valuable intermediates in a number of synthetic transformations.[14]

REFERENCES AND NOTES

1. G. Märkl, Chem.Ber., 94, 3005 (1961).
2. S.T.D. Gough and S. Trippett, J.Chem.Soc., 543 (1964).
3. H.J. Bestmann and C. Geismann, Justus Liebigs Ann. Chem., 282 (1977).
4. N. Petragnani and G. Schill, Chem.Ber., 97, 3293 (1964).
5. S.T.D. Gough and S. Trippett, J.Chem.Soc., 2333 (1962).
6. Y. Kobayashi, T. Yamashita, K. Takahashi, H. Kurada and I. Kumadaki, Tetrahedron Lett., 23, 342 (1982).
7. Y.Z. Huang, Y. Shen, W. Ding and J. Zheng, Tetrahedron Lett., 22, 5883 (1981).
8. B.T. Gröbel and D. Seebach, Synthesis, 257 (1977).
9. A.L. Braga, J.V. Comasseto and N. Petragnani, Synthesis (in press).
10. Compound (2d) (1 mmol) in THF (5 ml) was treated with n-BuLi (1,05 mmol) at -78°C. After 3 hr stirring at room temperature the mixture was quenched with water, worked up in the usual way and distilled, affording phenyl butyl sulfide (74%) and phenyl acetylene (66%); treatment of a solution of (2d) and n-BuLi (prepared as above) with a stream of carbon dioxide, followed by extraction of the organic phase with sodium hydroxide solution and acidification of the aqueous phase with concentrated hydrochloric acid gave phenyl propiolic acid (69%). Phenyl butyl sulfide was isolated from the organic phase in 79% yield.
11. G. Pourcelot and P. Cadiot, Bull, Soc.Chem.Fr., 3024 (1966).
12. R.L. Smorada and W.E. Truce, J. Org. Chem., 44, 3445 (1979).
13. F. Bohlmann, T. Burkhardt and C. Zdero, "Naturally Occurring Acetylenes", Academic Press, London, 1973.
14. T.G. Back, S. Collins and R.G. Kerr, J.Org.Chem., 48, 3077 (1983) and references cited therein.

(Received in USA 12 December 1983)