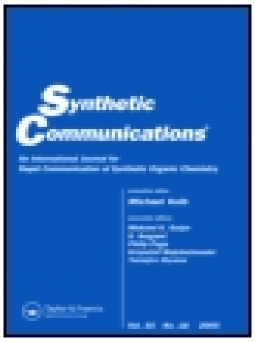

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A NEW SYNTHESIS OF α-ACYLPHOSPHORANE

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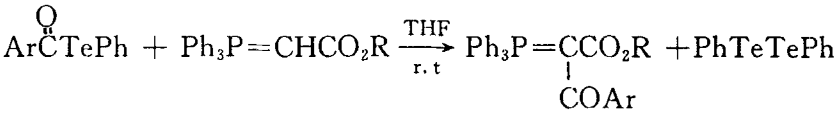
Abstract: Tellurol esters can readily react with phosphoranes to give α-acylphosphoranes and diphenyl ditellurides.

In recent years, with the development of selenium and tellurium untility in organic synthesis, selenol esters and tellurol esters have been attracted considerable interest. But so far, comparing with many reports on selenol esters, only a few literatures about the chemical behavior of tellurol esters have been published. It was reported that tellurol esters can undergo photosubstitution reaction [1], oxidative reaction[2] and a ligand exchange reaction with a palladium complex[3]. They were also shown to be an effective source of acyl, aroyl and carbarmoyllithium intermediates which react in situ with different electrophiles to give α-hydroxy ketones[4], α-hydroxyamides or α-oxoamides[5]. Tellurol esters not only can react with lithium dialkyl cuprates to give the corresponding ketones[6], but also can undergo hydrolysis or alcoholysis reaction to give the corresponding carboxylic acids or esters under treatment with sodium hydroxide or copper(II) chloride dihydrate[7-8].

Considering that phosphorane is a nucleophilic reagent, it could react with tellurol esters. So we deeply investigated the reactive properties of tellurol esters. The experimental results show that tellurol esters 1 and equivalent phosphoranes 2 in THF can undergo acylating reactions at room temperature to give α-acylphosphoranes 3 . The advantages of this method are milder conditions and simpler manipulation. So we think that this reaction gives a new synthesis of α-acylphosphorane.

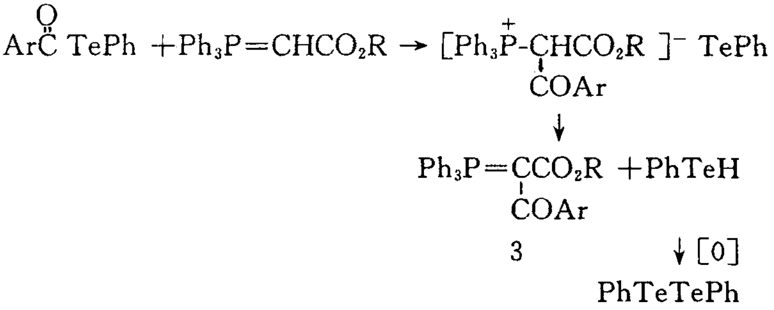


$$\mathrm{Ar}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{TePh} + \mathrm{Ph_3P{=}CHCO_2R} \xrightarrow[\mathrm{r.t}]{\mathrm{THF}} \mathrm{Ph_3P{=}}\underset{\mathrm{COAr}}{\underset{|}{\mathrm{C}}}\mathrm{CO_2R} + \mathrm{PhTeTePh}$$

1 2 3

Ar	R	Ar	R
3a : C_6H_5	C_2H_5	3e : C_6H_5	CH_3
3b : p-BrC_6H_4	C_2H_5	3f : p-ClC_6H_4	CH_3
3c : p-ClC_5H_4	C_2H_5	3g : p-$NO_2C_6H_4$	CH_3
3d : p-$NO_2C_6H_4$	C_2H_5		

The possible mechanism of this reaction is that phosphorane as a nucleophilic reagent could make an attack on tellurol ester to give phosphorane 3 and PhTeH. Then PhTeH could be converted into diaryl ditelluride by oxidation.



$$\mathrm{Ar}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\ \mathrm{TePh} + \mathrm{Ph_3P{=}CHCO_2R} \rightarrow [\mathrm{Ph_3}\overset{+}{\mathrm{P}}\text{-}\underset{\mathrm{COAr}}{\underset{|}{\mathrm{C}}}\mathrm{HCO_2R}\ ]^-\ \mathrm{TePh}$$

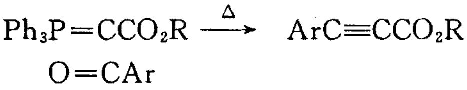
$$\downarrow$$

$$\underset{3}{\mathrm{Ph_3P{=}}\underset{\mathrm{COAr}}{\underset{|}{\mathrm{C}}}\mathrm{CO_2R}} + \mathrm{PhTeH}$$

$$\downarrow [\mathrm{O}]$$

$$\mathrm{PhTeTePh}$$

α-Acylphosphorane is an important intermediate of organic synthesis . It was reported that it can be converted into varied alkynes by treatment with heating to aford a method for the synthesis of alkynes[9].



$$\underset{O=CAr}{Ph_3P=CCO_2R} \xrightarrow{\Delta} ArC\equiv CCO_2R$$

EXPERIMENTAL

The IR spectra were recorded on Perkin Elmer 683 spectrophotometer. The ^1H NMR spectra were recorded on Varian Em-360A Fx-90Q. The microelemental analyses were carried out on Carlo Erba. Melting points were uncorrected.

Tellurol esters were prepared as described[3].

Phosphoranes were prepared as described[10].

General procedure: the mixture of tellurol ester (lmmol) and phosphorane (lmmol) in 10ml anhydrous THF is stirred at room temperature for more than 40hrs. The color of the solution turns red gradually. The reaction is monitored by TLC until tellurol ester disappears. Then the mixture is treated with brine, extracted with chloroform (3xl0ml), the extract dried with magnesium sulfate and concentrated under vacumn to give oil product which is purified by chromatography on silicagel (pet ether: ethyl acetate $=3:5$).

3a: yield 51%; m. p. 136-138℃ (136-137℃[11]); IR(KBr) υ_{max}: 1310, 1550, 1600, 1680; NMR($CDCl_3$) δ: 8. 0-7. 2 (m, 20H), 3. 8-3. 4(d, 2H), 0. 5-0. 7(t, 3H).

3b: yield 44. 2%; m. p. 154-156℃; IR(KBr) υ_{max}: 1310, 1560, 1590, 1660; NMR($CDCl_3$) δ: 8. 0-7. 2(m, 19H), 3. 8-3. 5(d, 2H), 0. 5-0. 7(t, 3H); $C_{29}H_{24}BrO_3P$, Calcd. C: 65. 74, H: 4. 65, Found C: 65. 66, H: 4. 53.

3c: yield 47. 8%; m. p. 150-152℃; IR(KBr) υ_{max}: 1310, 1560, 1600, 1660; NMR($CDCl_3$) δ: 7. 9-7. 1(m, 19H), 3. 8-3. 5(d, 2H), 0.

5-0. 7(t,3H);$C_{29}H_{24}ClO_3P$,Calcd. C:71. 68,H:4. 94,Found C: 71. 71,H:4. 81.

3d:yield 49. 2%;m. p. 169-170℃;IR(KBr)υ_{max}:1100,1340, 1530,1680;NMR($CDCl_3$)δ:8. 1-7. 1(m,19H),3. 7-3. 2(d,2H),0. 7-0. 5(t,3H);$C_{29}H_{24}NO_4P$,Calcd. C:70. 00,H:4. 80,N:2. 69, Found C:69. 53,H:4. 63. N:2. 81.

3e:yield 52. 6%;m. p. 134-136℃ (135-136℃[11]);IR(KBr) υ_{max}:1320,1560. 1590,1630,1680;NMR($CDCl_3$)δ:8. 0-7. 2(m, 20H),3. 1(s,3H).

3f:yield 46. 5%;m. p. 188-189℃(186℃[11]);IR(KBr)υ_{max}: 1310,1550,1600,1640,1680;NMR($CDCl_3$)δ:8. 1-7. 1(m,19H),3. 1(s,3H).

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