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A FACILE PREPARATION OF TELLUROL ESTERS FROM PHENYLTELLUROTRIMETHYLSILANE AND ACYL CHLORIDES[1)]

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Phenyltellurotrimethylsilane cleanly reacted with acyl chloride, giving tellurol ester in an excellent yield. The high reactivity of tellurol ester toward lithium organocuprate was demonstrated.

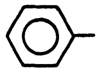
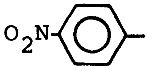
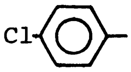
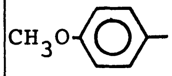
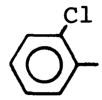
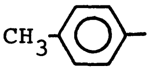
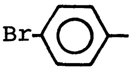
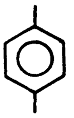
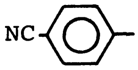
In recent years, chalcogenoesters such as thiol esters[2)] and selenol esters[3)] have attracted considerable interest as activated esters in synthetic as well as biological reactions. On the other hand, there has been so far known no chemical behavior of tellurol esters except for a photosubstitution reaction,[4)] a ligand-exchange reaction with a palladium complex,[5)] and a degradation with phenylhydrazine.[5)] Tellurol esters have generally been prepared by sodium tellurorate with acyl chlorides or anhydrides, but the yields are moderate because of partial decomposition during work-up.[5,6)] The development of ready access of tellurol ester would prompt its synthetic potential as an active acyl-transfer agent. Here we report a facile preparation of tellurol ester 3 from phenyltellurotrimethylsilane 1[7)] and acyl chloride 2.

$$\underset{1}{\mathrm{PhTeSiMe_3}} + \underset{2}{\mathrm{RCOCl}} \longrightarrow \underset{3}{\mathrm{RCOTePh}} + \underset{4}{\mathrm{Me_3SiCl}}$$

When 1 was treated with 2 in dry tetrahydrofuran at room temperature, an exchange reaction smoothly occurred to give tellurol ester 3 and trimethylsilyl chloride 4. The advantage of this method is that almost pure product 3 can be obtained in nearly quantitative yield after evaporation of the solvent, excess reagent 1, and another product 4. The tellurol esters of aryl carboxylic acids are relatively stable, and the analytical grade samples can be obtained by further recrystallization or column chromatography. Some examples are summarized in Table 1. On the other hand, those of aliphatic carboxylic acids such as acetic acid and stearic acid were synthesized in a similar manner, but too unstable to be isolated in pure forms.

A typical procedure is illustrative for the synthesis of Te-phenyl tellurobenzoate 3 (R=Ph). Phenyltellurotrimethylsilane 1 2.10 cm^3 (10.9 mmol) was added into a stirred solution of benzoyl chloride 1.42 g (10.1 mmol) in 30 cm^3 of dry tetrahydrofuran under an argon atmosphere. The mixture was stirred for 3 h at room temperature and concentrated under a reduced pressure. The residual Te-phenyl tellurobenzoate 3 (R=Ph) was purified by recrystallization from pentane

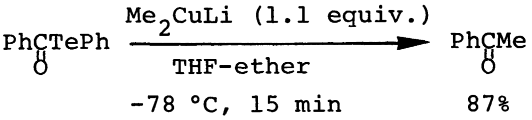
Table 1. Preparation of tellurol esters RCOTePh from phenyltellurotrimethylsilane and acyl chlorides

Compound R	Yield[a] %	Crystal Form	Mp θm/°C	Compound R	Yield[a] %	Crystal Form	Mp θm/°C
	87	yellow needles[d]	71-72 70-72[b] 66-70[c]		79	red plates[f]	107-108
	87	yellow crystals[d]	65		62	pale yellow plates[d]	105-106 103-105[b] 100-103[c]
	85	yellow needles[d]	41-42 42-44[c]		91	yellow needles[d]	71 69-71[b]
	88	yellow crystals[d]	83 77-79[b]		85	orange crystals[e]	144-145
	83	orange needles[e]	120				

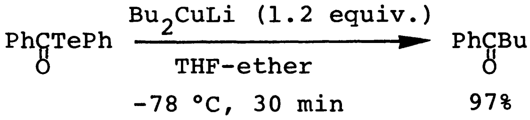
a) Isolated yield. b) Reference 5. c) Reference 6.
Recrystallization solvent: d) pentane; e) pentane-ether; f) ether.

to give yellow needles, yield 2.71 g (87%), IR (KBr disc) $\nu_{C=O}$ 1670 cm^{-1}.

Treatment of Te-phenyl tellurobenzoate with a soft metal reagent, lithium dimethylcuprate or dibutylcuprate, bearing a strong affinity for tellurium gave the corresponding ketone in a high yield. Thus tellurol ester has turned out to serve as a promising agent for acyl transformation. Further investigation on this scope is now in progress.



$$PhC(=O)TePh \xrightarrow[\text{THF-ether, } -78\ ^\circ C,\ 15\ min]{Me_2CuLi\ (1.1\ equiv.)} PhC(=O)Me\quad 87\%$$



$$PhC(=O)TePh \xrightarrow[\text{THF-ether, } -78\ ^\circ C,\ 30\ min]{Bu_2CuLi\ (1.2\ equiv.)} PhC(=O)Bu\quad 97\%$$

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