atom is bonded to oxygen atoms of neighboring molecules in such a way that molecules are linked indefinitely along the *a* and *c* axes, but not along *b*. The oxygen and thallium atoms are buried within the interior of the crystals with a consequent exposure of the carbon backbone of acetylacetone units at the crystal surface. It is attractive to postulate that the extraordinary specificity observed in alkylation and acylation reactions may be directly related to the crystal structure of the complexes and to the rigid geometry imposed on the transition states for reaction as a consequence of the tetragonal-pyramidal structure of the tetracoordinate thallium complex. Certainly heterogeneity in the above reactions is a critical requirement for specificity. Further speculations at this time on the relevance of structure to chemical reactivity and specificity, however, would be premature.

Table II. Acylation of Thallium(I) Salts of β-Dicarbonyl Compounds

Tl^+ salt of	Yield, %, of O-Acetyl derivative[a]	Yield, %, of C-Acetyl derivative[b]
Ethyl acetoacetate	90	95
Acetylacetone	90	95
2-Carbethoxycyclopentanone	90	95
Ethyl benzoylacetate	90	98
3-Methylpentane-2,4-dione	95	95

[a] Prepared by treatment of the salt in ether with acetyl chloride at −78°. [b] Prepared by treatment of the salt in ether with acetyl fluoride at room temperature.

Representative experimental procedures are as follows. **Acetylacetonatothallium(I):** Acetylacetone (0.11 mole) is stirred in 50 ml of petroleum ether and 0.10 mole of thallium(I) ethoxide added all at once. The mixture is stirred for 2–3 min, chilled, and filtered; the yield of acetylacetonatothallium(I) is quantitative; mp 160.5°.[8–10] **3-Methylpentane-2,4-dione:** A suspension of 0.10 mole of acetylacetonatothallium(I) in 85 ml of methyl iodide is heated under reflux with stirring for 4 hr, cooled, and filtered. The filtrate is passed through a short column of Florisil to remove traces of thallium(I) iodide, concentrated, and distilled (68–70° (26 mm)). The yield is quantitative. **Triacetylmethane:** Acetyl fluoride is bubbled into a suspension of 0.10 mole of acetylacetonatothallium(I) in 200 ml of ether at a rate of 0.2 l./min for 30 min. The thallium(I) fluoride is removed by filtration and the filtrate concentrated and distilled (95–97° (1.0 mm)). The yield of triacetylmethane is >95%.

(8) E. Kurowski, *Ber.*, **43**, 1078 (1910).
(9) G. H. Christie and R. C. Menzies, *J. Chem. Soc.*, 2372 (1925).
(10) G. T. Morgan and H. W. Moss, *ibid.*, 195 (1914).

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Thallium in Organic Synthesis. II. Acylation, Aroylation, and Tosylation of Phenols and Carboxylic Acids[1]

Sir:

Thallium(I) salts of phenols are readily prepared in quantitative yield by the addition of thallium(I) ethoxide[2] to a solution of the phenol in a solvent such as benzene or ethanol. They are crystalline, sharp-melting, stable solids which may be conveniently recrystallized from water or aqueous ethanol.[3–5] We have found that treatment of a suspension of these phenol salts in anhydrous ether with an equimolar quantity of an acyl or aroyl halide for 1 hr at room temperature, followed by filtration of the thallium(I) halide and evaporation of solvent, affords pure phenol esters in yields seldom lower than 97%. In every case investigated this procedure is the method of choice. Representative examples are given in Table I.

Table I

$ROTl + R'COCl \longrightarrow R'COOR + TlCl$

R	Yield, %, for R' = CH_3	$(CH_3)_3C$	C_6H_5
C_6H_5	98	96	98
$p\text{-}NO_2C_6H_4$	98	100	100
$o\text{-}CHOC_6H_4$	98	83	97
$p\text{-}CH_3OC_6H_4$	100	98	100
$\beta\text{-}C_{10}H_7$	96	97	97

Treatment of the thallium(I) salts of phenols with tosyl chloride in dimethylformamide or dimethylacetamide for 15 min at room temperature, removal of thallium(I) chloride by filtration, and dilution of the filtrate with water, followed by extraction with benzene and evaporation, gives crystalline phenol tosylates in 92–96% yield. Representative conversions are given in Table II.

Table II

$ROTl + TsCl \longrightarrow ROTs + TlCl$

R	Yield, %
C_6H_5	96
$p\text{-}NO_2C_6H_4$	95
$o\text{-}CHOC_6H_4$	92
$o\text{-}CH_3OC_6H_4$	94

Thallium(I) salts of carboxylic acids can also be readily prepared in quantitative yield by the addition of thallium(I) ethoxide to a solution of the acid in a suitable solvent such as ether or ethanol. These salts are crystalline, light-insensitive, sharp-melting, stable solids.[3] We have found that treatment of these thallium(I) carboxylates in ether suspension with a stoichiometric amount of an acyl or aroyl chloride, removal of thallium(I) chloride by filtration, and evaporation of the ether solvent at <30° afford carboxylic anhydrides in

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[1] We gratefully acknowledge the financial support of this work by the Smith Kline and French Laboratories, Philadelphia, Pa.
[2] G. Brauer, Ed., "Handbook of Preparative Inorganic Chemistry," Vol. 1, 2nd ed, Academic Press Inc., New York, N. Y., 1963, p 877.
[3] R. C. Menzies and E. M. Wilkins, *J. Chem. Soc.*, **125**, 1148 (1924).
[4] G. H. Christie and R. C. Menzies, *ibid.*, **127**, 2369 (1925).
[5] C. M. Fear and R. C. Menzies, *ibid.*, **129**, 937 (1926).

virtually quantitative yield. Representative examples are given in Table III.

Table III

$RCO_2Tl + R'COCl \longrightarrow RCOOCOR' + TlCl$				
R	R′	Temp, °C	Time, hr[a]	Yield, %[b]
C_6H_5	CH_3	5	0.25	95
C_6H_5	$(CH_3)_2CH$	25	6	100
C_6H_5	$(CH_3)_3C$	25	8	99
C_6H_5	C_6H_5	35	4	100
$(CH_3)_3C$	CH_3	5	0.25	97
$(CH_3)_3C$	$(CH_3)_2CH$	25	1	98
$(CH_3)_3C$	$(CH_3)_3C$	25	1	100
$(CH_3)_2CH$	CH_3	5	0.25	96
$(CH_3)_2CH$	$(CH_3)_2CH$	25	1	99
$(CH_3)_2CH$	$(CH_3)_3C$	25	1	98
H	CH_3	5[c]	3	67[d]

[a] Completion of the reaction was established by examination of the ir spectra of aliquots removed from the reaction mixture at suitable intervals and observation of the disappearance of bands characteristic of the acyl or aroyl halide employed. [b] Spectral examination (ir, nmr) of the mixed anhydrides revealed the presence of traces (1–3%) of the corresponding symmetrical anhydrides. [c] Reaction allowed to warm up gradually to 25°. [d] Recovery was 77%. The product must be distilled to remove disproportionation products. Extended reaction times gave lower yields.

Although symmetrical anhydrides can be prepared by the above procedure, a much more convenient synthesis which does not require the intermediacy of the acid chloride is the reaction of the thallium(I) carboxylate with thionyl chloride in ether at room temperature.[6] The intermediate diacyl or diaroyl sulfite spontaneously loses sulfur dioxide; evaporation of the ether gives the anhydride in 96–98% yield after distillation. Representative examples are given in Table IV.

Table IV

$2RO_2Tl + SOCl_2 \longrightarrow (RCO)_2O + SO_2 + 2TlCl$	
R	Yield, %
CH_3	98
$(CH_3)_2CH$	97
$(CH_3)_3C$	96
C_6H_5	97

The conventional synthetic procedures for anhydride formation,[7,8] even those utilizing other metal carboxylate salts, are not generally suitable for the preparation of mixed anhydrides because of the ease with which the latter may disproportionate above room temperature[9] either during the conditions of their formation or in the course of purification. The present method, which employs stoichiometric amounts of both reactants and proceeds quantitatively at room temperature or below, appears to utilize the minimal conditions requisite for mixed anhydride formation and preservation. Disproportionation can be observed even with the present method, however, if the mixed anhydride formed is more reactive than the acid chloride. It is therefore important to employ as reactant the carboxylate salt of the weaker acid.

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[6] This procedure is analogous to but much superior to the use of silver carboxylates; see W. S. Denham and H. Woodhouse, *ibid.*, **103**, 1861 (1913).

[7] M. F. Ansell and R. H. Gigg in "Rodd's Chemistry of Carbon Compounds," S. Coffey, Ed., Elsevier Publishing Co., New York, N. Y., 1965, p 156.

[8] R. B. Wagner and H. D. Zook, "Synthetic Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1953, p 558.

[9] C. D. Hurd and M. F. Dull, *J. Am. Chem. Soc.*, **54**, 3427 (1932).

Thallium in Organic Synthesis. III. Coupling of Aryl and Alkyl Grignard Reagents[1]

Sir:

Biaryls are customarily prepared from aryl halides either by the classical Ullmann reaction[2] or by coupling of aryl Grignard reagents with halides of such metals as Co, Cu, Hg, Ni, Ag, Au, etc.[3] Unless activating substituents such as a nitro group are present in the nucleus, the Ullmann reaction requires the use of the relatively expensive aryl iodide, but is of special value in the coupling of *ortho*-substituted halides. Previously described procedures for the coupling of Grignard reagents lead to mixtures of products, and the reactions are difficult to control.

We wish to report a simple, general procedure for the coupling of aryl- and *sec*-alkylmagnesium bromides using thallium(I) bromide.[4] The experimental procedure is illustrated by the conversion of 4-bromotoluene to 4,4′-dimethylbiphenyl.

A mixture of 0.135 mole of thallium(I) bromide and 0.0675 mole of 4-tolylmagnesium bromide in 40 ml of tetrahydrofuran–benzene (1 : 1) was stirred and refluxed under nitrogen for 4 hr, cooled, acidified with dilute hydrochloric acid, and filtered. The filtrate was concentrated and passed through a short column of alumina and the crude product, obtained by further concentration, recrystallized from benzene to give 4,4′-dimethylbiphenyl, mp 121°, in 91% yield.

Typical conversions are given in Table I.

As can be seen from Table I, secondary alkyl Grignard reagents give coupled products in moderate yields. On the other hand, primary aliphatic Grignard reagents give only traces of coupled alkanes; the major products of the reaction are the corresponding dialkylthallium(III) bromides. This reaction represents the method of choice for the preparation of these previously difficultly accessible compounds and will be described elsewhere.[5] Similarly, *ortho*-substituted aryl Grignard reagents fail to give coupled products under the above conditions; mesitylmagnesium bromide, for example, gives only dimesitylthallium(III) bromide. The anomalous course taken by this class of Grignard reagent has not yet been

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[1] We gratefully acknowledge the financial support of this work by the Smith Kline and French Laboratories, Philadelphia, Pa.

[2] (a) P. E. Fanta, *Chem. Rev.*, **38**, 139 (1946); (b) P. E. Fanta, *ibid.*, **64**, 613 (1964).

[3] M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Non-Metallic Substances," Constable and Co., Ltd., London, 1954, Chapter 5.

[4] Optimum conditions require 1.5–2.0 moles of thallium(I) bromide per mole of Grignard reagent.

[5] A. McKillop, L. F. Elsom, and E. C. Taylor, to be submitted for publication.