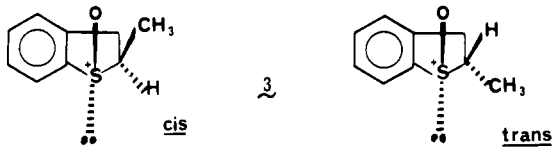
groups in each isomer. From X-ray data of analogous cyclic sulfonium salts,[9] the anion would be predicted to be oriented in an area roughly in the plane of the thiophene ring as close to the positive sulfur as is sterically allowable. In addition, the negatively charged anion would remain oriented as far away as possible from the π-electron cloud of the aromatic ring and the electron pair on sulfur.

The results of the LIS study on **2** are given in Figure 2. These results are consistent with a complexation at or with the anion and not with the lone pair on sulfur.[10] If the lone pair is the site of complexation, then the SCH_3 of both the cis and trans isomers would be approximately equidistant from the LSR, but the CCH_3 of the trans isomer would be much closer to the praseodymium than would the CCH_3 of the cis isomer. There should be a large difference in shift between these latter two methyl groups.[12] Note for comparison the difference in shift of the *C*-methyl groups of the corresponding sulfoxides **3**. The $\Delta\Delta\nu$ at a



1:1 molar ratio of the shift reagent to the substrate for the *C*-methyl of each of the isomers is ca. 5 ppm.[8] As we see from Figure 2, the sulfonium salts do not exhibit shift differences of this magnitude ($\Delta\Delta\nu$ = 0.47 ppm for *S*-methyl and 0.81 ppm for *C*-methyl). If, on the other hand, the complexation were occurring at the anion, the results would be expected to be quite different. In this case, the SCH_3 groups of both the cis and trans isomers would be approximately equidistant from the anion as would be the CCH_3 groups of both of these isomers. No significant difference in the magnitude of the shifts of these two isomeric methyl pairs would be observed. This is consistent with our findings. It appears that the site of complexation is at the anion. The nature of this complexation is presently under investigation in our laboratories. Preliminary UV results indicate that no direct covalent complex is forming but do not disprove the possible involvement of a weak complexation between the lanthanide ion and the tetrafluoroborate anion. We hope to have answers to these questions in the near future.

In summary, LIS studies may be used in the investigation of the structure of sulfonium salts. In these applications, the McConnel-Robertson equation holds, with the complexation apparently occurring primarily at the anion of the salt.

Acknowledgment. The authors wish to express their appreciation to Ms. Moira Casey and Mr. L. Blattner for their help on this project. Also, thanks are extended to Mr. J. Gaudiello, Mr. A. Fierschnaller, and Mr. J. Sosnowski for their help in the synthesis of 2,3-dihydrobenzothiophene. This project was supported by a grant from the Towson State University Faculty Research Committee; their aid is greatly appreciated.

(9) For example, S. M. Johnson, C. A. Maier, and I. C. Paul, *J. Am. Chem. Soc. B*, 1603 (1970).
(10) This investigation does not rule out the possibility of complexation occurring at both sites [see, for example, C. C. Hinkley, M. R. Klotz, and F. Patil, *J. Am. Chem. Soc.*, **93**, 2147 (1971)].
(11) All spectra were recorded as mixtures of the cis and trans isomers, consisting of an ca. 80:20 trans/cis ratio as determined by NMR.
(12) When the radial (R) and angular (θ) factors are taken into account, and if complexation is occurring solely at the lone pair on sulfur, calculations show that the induced shift of the CCH_3 of the trans isomer should be larger than that of the cis by a factor of ca. 1:2 cis/trans.

Registry No. *cis*-**2** BF_4^-, 55563-68-3; *trans*-**2** BF_4^-, 55563-67-2; dimethyl-*p*-tosylsulfonium tetrafluoroborate, 51404-78-5.

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Synthesis of Aromatic Esters, Lactones, Anhydrides, and Heterocycles via Thallation-Carbonylation of Arenes

Summary: The thallation and subsequent palladium-catalyzed carbonylation of simple arenes, benzylic and β-phenethyl alcohols, benzoic and phenylacetic acids, benzamide, and acetanilide afford benzoate esters, phthalides, 3,4-dihydroisocoumarins, phthalic and homophthalic anhydrides, phthalimide, and acetylanthranil, respectively. The carbonylation reaction proceeds in excellent yield at room temperature and atmospheric pressure and is highly stereo- and regioselective.

Sir: In recent years a substantial number of important new synthetic procedures have been developed which utilize organothallium intermediates.[1,2] Our interest in the application of carbonylation reactions in organic synthesis,[3] and particularly in the synthesis of biologically active lactones,[4] prompted us to examine the carbonylations of arylthallium compounds. At this time we wish to report that thallation and subsequent palladium-catalyzed carbonylation of arenes provides a highly convenient new route to a wide variety of aromatic esters, lactones, anhydrides, and heterocycles.

The direct carbonylation of arylthallium compounds has been studied and requires high temperatures and pressures.[5] We have observed, however, that carbonylation can be effected at room temperature under 1 atm of carbon monoxide simply by employing *catalytic* amounts of palladium chloride. Thus by utilizing essentially the same thallation conditions as Taylor and McKillop,[6,7] replacing the solvent by methanol, adding lithium chloride, magnesium oxide, and 10% palladium chloride, and flushing with carbon monoxide, we observe the facile conversion of arenes to the corresponding methyl benzoate esters (eq 1). Some representative examples are presented in Table

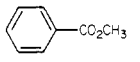
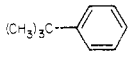
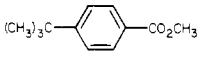
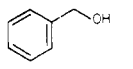
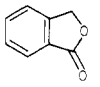
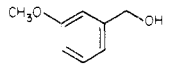
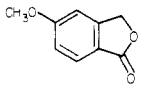
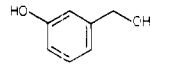
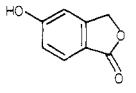
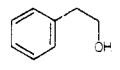
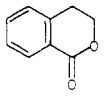
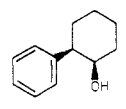
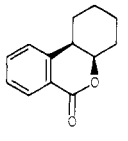
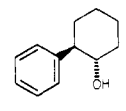
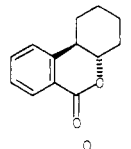
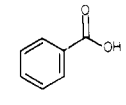
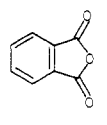
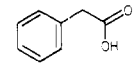
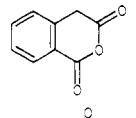
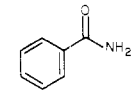
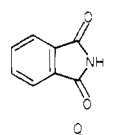
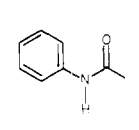
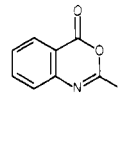
$$\mathrm{ArH} \xrightarrow{\mathrm{Tl(O_2CCF_3)_3}} \mathrm{ArTl(O_2CCF_3)_2} \xrightarrow[\substack{\mathrm{LiCl/MgO}\\ \mathrm{CH_3OH}}]{\substack{\mathrm{CO}\\ 10\%\ \mathrm{PdCl_2}}} \mathrm{ArCO_2CH_3} \quad (1)$$

I (entries 1 and 2). It is particularly noteworthy that only catalytic amounts of palladium chloride are required and that no additional reoxidant for palladium need be added.

(1) McKillop, A.; Taylor, E. C. *Chem. Br.* **1973**, *9*, 4-11.
(2) McKillop, A.; Taylor, E. C. *Adv. Organomet. Chem.* **1973**, *11*, 147-206.
(3) Larock, R. C. *J. Org. Chem.* **1975**, *40*, 3237-42.
(4) Larock, R. C.; Riefling, B.; Fellows, C. A. *J. Org. Chem.* **1978**, *43*, 131-7.
(5) Davidson, J. M.; Dyer, G. *J. Chem. Soc. A* **1968**, 1616-7.
(6) McKillop, A.; Hunt, J. D.; Zelesko, M. J.; Fowler, J. S.; Taylor, E. C.; McGillivray, G.; Kienzle, F. *J. Am. Chem. Soc.* **1971**, *93*, 4841-4.
(7) Taylor, E. C.; Kienzle, F.; Robey, R. L.; McKillop, A.; Hunt, J. D. *J. Am. Chem. Soc.* **1971**, *93*, 4845-50.

0022-3263/80/1945-0363$01.00/0

Table I. Thallation-Carbonylation of Arenes

entry	arene	product	% yield[a]
1			52
2			80
3			33
4			89 (47)
5			(95)
6			62
7			88
8			77 (43)
9			44
10			(56)
11			83
12			(40)

[a] Percent yield based on starting alcohol determined by gas chromatographic analysis using an internal standard (isolated, purified yield in parentheses).

The thallium(III) salt present in the reaction mixture apparently serves this role. The following mechanism is suggested (eq 2–5).[8]

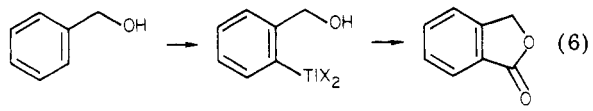
$$ArTlX_2 + PdX_2 \rightarrow ArPdX + TlX_3 \quad (2)$$

$$ArPdX + CO \rightarrow ArCOX + Pd \quad (3)$$

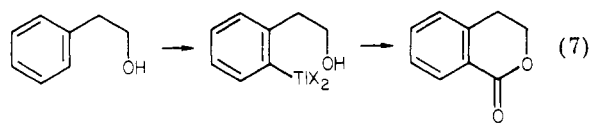
$$ArCOX + ROH \rightarrow ArCO_2R + HX \quad (4)$$

$$Pd + TlX_3 \rightarrow PdX_2 + TlX \quad (5)$$

The thallation–carbonylation sequence also provides a highly convenient route to a variety of aromatic lactones. For example, one can take advantage of the strong ortho-directing effect of the oxygen atom in benzylic and β-phenethyl alcohols[7] to activities. ortho-thallated products which are readily carbonylated to phthalides and 3,4-dihydroisocoumarins, respectively (Table I, entries 3–8) (eq 6 and 7). Such lactones comprise a large class of naturally



(6)

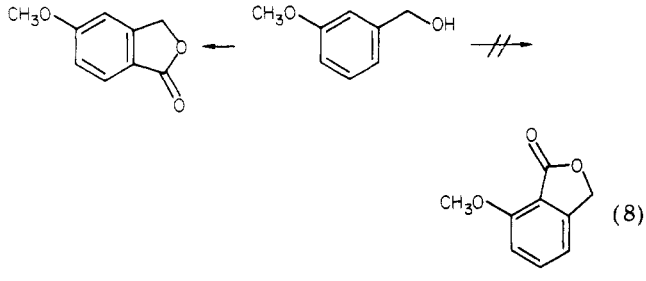


(7)

occurring, physiologically active compounds[9,10] with interesting fungicidal, bacteriocidal, herbicidal,[11] analgesic,[12] diuretic, and hypotensive–antihypertensive[13] activities.

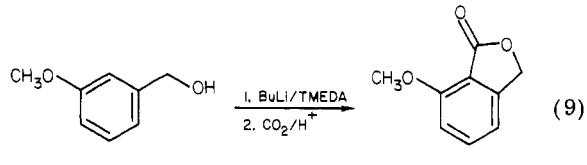
Our results indicate that benzylic alcohols possessing groups which activate the ring toward electrophilic aromatic substitution give higher yields of phthalides and that β-phenethyl alcohols having alkyl substituents on the side chain, which hold the hydroxyl group in a more rigid conformation, give increased yields of 3,4-dihydroisocoumarins.

The reactions are also highly stereo- and regiospecific. Thus, thallation–carbonylation of *cis*- and *trans*-2-phenylcyclohexanols (entries 7 and 8) provides exclusively the cis and trans fused tricyclic lactones, respectively, compounds easily distinguished by NMR spectroscopy. Substituents on the aromatic ring are also observed to effect a very pronounced directive effect. For example, thallation–carbonylation of *m*-methoxybenzyl alcohol affords the 5-methoxyphthalide in 89% yield and only a trace of the 7-methoxyphthalide (entry 4) (eq 8). Simi-



(8)

larly, *m*-hydroxybenzyl alcohol affords a 95% isolated yield of pure 5-hydroxyphthalide (entry 5). It is important to note that this procedure nicely complements the present literature procedure for the conversion of *m*-methoxybenzyl alcohol to the 7-methoxy isomer[14] (eq 9), and simplifies recent carbonylation procedures employing *o*-halobenzyl and *o*-phenethyl alcohols.[15,16]



(9)

The phthalides and 3,4-dihydroisocoumarins were prepared according to the following representative procedure. One millimole of aryl alcohol was thallated according to

(8) For a previous example of arylthallium–palladium transmetalation, see: Spencer, T.; Thorpe, F. G. *J. Organomet. Chem.* **1975**, *99*, C8–C10.
(9) Dean, F. M. "Naturally Occurring Oxygen Ring Compounds"; Butterworths: London, 1963.
(10) Barry, R. D. *Chem. Rev.* **1964**, *64*, 229–60.
(11) Lacova, M. *Chem. Zvesti* **1973**, *27*, 525–35; *Chem. Abstr.* **1974**, *80*, 59757.
(12) Elderfield, R. C. "Heterocyclic Compounds"; Wiley: New York, 1951; pp 91–122.
(13) Houlihan, W. J.; Nadelson, J. *British Patent* 1374337, 1974; *Chem. Abstr.* **1975**, *83*, 43196.
(14) Uemura, M.; Tokuyama, S.; Sakan, T. *Chem. Lett.* **1975**, 1195–8.
(15) Mori, M.; Chiba, K.; Inotsume, N.; Ban, Y. *Heterocycles* **1979**, *12*, 921–4.
(16) Stille, J. K., private communication.

the published procedure[7] by using a 1 M solution of thallic trifluoroacetate in trifluoroacetic acid [1–1.2 equiv of $Tl(O_2CCF_3)_3$]. The procedure was modified for aryl alcohols with one or more activating groups on the ring by diluting the solution with 5 mL of tetrahydrofuran and stirring overnight at room temperature. The solvents were then removed under vacuum and the arylthallium intermediates carbonylated without further purification. Palladium chloride (0.1 mmol), anhydrous lithium chloride (2 mmol), magnesium oxide (2 mmol), and 5 mL of methanol were placed in a round-bottomed flask with a septum inlet. The system was flushed with carbon monoxide and the arylthallium compound dissolved in 5 mL of methanol was added, after which the system was again flushed with carbon monoxide and maintained under a 1 atm pressure. After the reaction had stirred overnight at room temperature, the product was isolated by standard extractive and recrystallization procedures, or the yield was determined by gas chromatography using an internal standard.

This thallation–carbonylation procedure has proven to be quite general for a variety of other aromatic compounds as well. Thus, thallation–carbonylation of benzoic and phenylacetic acids yields phthalic and homophthalic anhydrides, respectively (entries 9 and 10), and benzamide affords phthalimide in excellent yield (entry 11). In a similar fashion, acetanilide[17] is cyclocarbonylated to acetylanthranil (entry 12). The versatility of this procedure should prove useful in the synthesis of a large variety of interesting heterocyclic systems. At present we are examining further applications of these ortho-thallated intermediates in organic synthesis.

Acknowledgment. We gratefully acknowledge the generous financial support of the National Institutes of Health and also Matthey Bishop Inc. and Engelhard Industries for supplying the palladium chloride.

Registry No. Benzene, 71-43-2; methyl benzoate, 93-58-3; *tert*-butylbenzene, 98-06-6; methyl *tert*-butylbenzoate, 26537-19-9; benzenemethanol, 100-51-6; 1(3*H*)-isobenzofuranone, 87-41-2; 3-methoxybenzenemethanol, 6971-51-3; 5-methoxy-1(3*H*)-isobenzofuranone, 4741-62-2; 3-hydroxybenzenemethanol, 620-24-6; 5-hydroxy-1(3*H*)-isobenzofuranone, 55104-35-3; benzeneethanol, 60-12-8; 3,4-dihydro-1*H*-2-benzopyran-1-one, 4702-34-5; *cis*-2-phenylcyclohexanol, 16201-63-1; *cis*-1,2,3,4,4a,10b-hexahydro-6*H*-dibenzo[*b*,*d*]pyran-6-one, 72331-10-3; *trans*-2-phenylcyclohexanol, 2362-61-0; *trans*-1,2,3,4,4a,10b-hexahydro-6*H*-dibenzo[*b*,*d*]pyran-6-one, 72331-11-4; thallic trifluoroacetate, 23586-53-0.

(17) For a recent report on the direct palladation of acetanilide, see: Horino, H.; Inoue, N. *Tetrahedron Lett.* **1979**, 2403–6.

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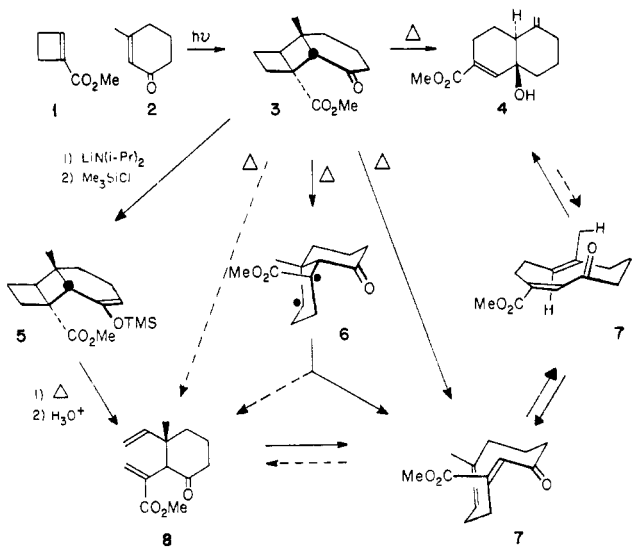
Received November 13, 1979

Olefin Metathesis–Transannular Ene Sequence. A Method for the Stereocontrolled Synthesis of *trans*-Decalin Derivatives. 1. Total Synthesis of (±)-Calameon[1]

Summary: The salient mechanistic and synthetic features of a method for the stereocontrolled synthesis of *trans*-decalin derivatives based on the thermolysis of photoadducts derived from methyl cyclobutenecarboxylate and 3-alkylcyclohex-2-enones are presented.

Scheme I



Sir: Synthetic approaches to various steroids, alkaloids, and terpenes draw heavily on methodology for the synthesis of *trans*-decalin derivatives. The most commonly used approaches to these derivatives include the reduction of octalones derived from Robinson annelations, epimerization of *cis*-decalin derivatives prepared from Diels–Alder cycloadditions, polyene cyclizations, and Michael additions to enones followed by enolate trapping.[2] These strategies which involve the elaboration of a latent ring-junction bond are topologically differentiated from an approach in which the ring-junction bond and stereochemistry are simultaneously established through transannular closure of a medium-ring precursor.[3] While the synthetic potential of this approach can be appreciated from a consideration of its role in the biosynthesis of various *trans*-decalin natural products[4] and of studies on transannular reactions,[5] its use in synthesis is limited by the paucity of methodology for the facile preparation of suitably functionalized medium-ring intermediates. We describe herein a method for the synthesis of *trans*-decalin derivatives based on the closure of cyclodecadienones easily derived from readily available precursors by a photothermal olefin metathesis sequence.[6]

(1) Presented in part at the ACS/CSJ Chemical Congress, Honolulu, Hawaii, Apr 1–6, 1979, No. ORGN 115.

(2) For representative applications of these strategies in terpene synthesis, see: Heathcock, C. H. "The Total Synthesis of Natural Products"; ApSimon, J., Ed.; Wiley: New York, 1973; Vol. 2, pp 197–558.

(3) For an analysis of design considerations pertinent to the synthesis of polycyclic structures, see: Corey, E. J.; Howe, W. J.; Orf, H. W.; Pensak, D. A.; Petersson, G. *J. Am. Chem. Soc.* **1975**, *97*, 6116.

(4) See, for example: Cordell, G. A. *Chem. Rev.* **1976**, *76*, 425.

(5) For studies pertinent to the work presented herein, see: (a) Terada, Y.; Yamamura, S. *Tetrahedron Lett.* **1979**, 1623. Niwa, M.; Iguchi, M.; Yamamura, S. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 3148. (b) Oppolzer, W.; Snieckus, V. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 476. (c) Scovell, E. G.; Sutherland, J. K. *J. Chem. Soc., Chem. Commun.* **1978**, 529.

(6) Recently, independent studies on (a) the pyrolysis of the piperitone photoadduct **13** (Lange, G. L.; McCarthy, F. C. *Tetrahedron Lett.* **1978**, 4749) and (b) the pyrolysis of the photoadduct (i) derived from methylcyclobutene and piperitone (Williams, J. R.; Callahan, J. F. *J. Chem. Soc., Chem. Commun.* **1979**, 404, 405) have been reported. The product stereochemistry presented in the former study differs from that expected on the basis of the mechanistic analysis and the supporting calameon synthesis presented herein (cf. ref 5a, 6b, and 8, and references cited therein). With respect to synthetic utility, it is notable that the photoadducts derived from ester **1** are converted to *trans*-decalin derivatives in significantly higher yields than the corresponding photoadducts derived from (i). Our studies on this point suggest that relative to the methyl group the ester subunit may serve to facilitate the cycloreversion reaction, activate the ketone carbonyl for the ene reaction, and stabilize the product (cf. ref 18).

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