$Cl(CH_2)_2O(CH_2)_2O(CH_2)_2O(CH_2)_2Cl$, 638-56-2; $PhCH_2NH_2$, 100-46-9; PhCHO, 100-52-7; $H_2N(CH_2)_3O(CH_2)_2O(CH_2)_2O(CH_2)_3NH_2$, 4246-51-9; $Cl(CH_2)_2O(CH_2)_2O(CH_2)_2Cl$, 112-26-5; $H_2N(CH_2)_2NEt_2$, 100-36-7; $H_2N(CH_2)_2N((CH_2)_2NH_2)_2$, 4097-89-6; $AcNH(CH_2)_2N((CH_2)_2NHAc)_2$, 124764-08-5.

Supplementary Material Available: ^1H NMR spectra for compounds **16**, **17**, **20–22**, **36**, and **38** (8 pages). Ordering information is given on any current masthead page.

Triorganothallium Reagents in Organic Chemistry. 1. A Simple, Efficient, and Versatile Preparation of Ketones from Acid Chlorides†

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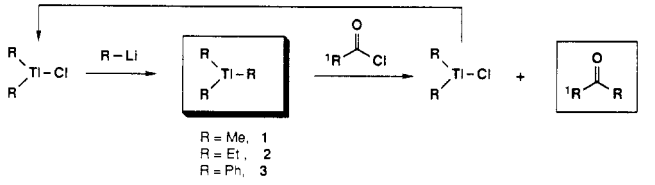
Although the transformation of a carboxylic acid into the corresponding ketone is a useful functional group transformation,[1] a simple and versatile procedure is still required. Organometallics[2] usually employed to produce ketones from acid chlorides include organocopper[3] and organocadmium[4] derivatives, but they suffer from limitations.[5]

We now report that triorganothallium derivatives such as trimethylthallium[6] (TMT, **1**), triethylthallium[7] (TET, **2**), and triphenylthallium[8] (TPT, **3**), react cleanly with acid chlorides at room temperature, giving methyl or phenyl ketones in high yields (eq 1, Table I).

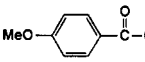
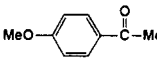


(1)

The thallium(III) compounds are readily prepared from the corresponding diorganothallium halides,[9] which are among the least reactive organometallic reagents known. Diorganothallium halides are usually solids, unaffected by water, oxygen, light, and acids, and insoluble in most organic solvents as well as in water. They can be conveniently handled and stored for months without decomposition. Addition of an organolithium compound to an ethereal suspension of a diorganothallium halide—or of a Grignard reagent to a THF suspension[10]—generates the soluble and highly reactive triorganothallium derivative.[11] When an acid chloride is added to such a solution, rapid (seconds for entries 1–4, 8, and 9, minutes for entries 5–9 and 10) precipitation of the diorganothallium chloride occurs with concomitant formation of the ketone. Filtration of the thallium(III) salt gives in high yields nearly pure ketones, which can be further purified by distillation or chromatography.

The reaction is general (Table I) for both aliphatic and aromatic substrates. It is highly chemoselective. The triorganothallium reagents react selectively with acid chlorides in the presence of other functional groups such as olefins, esters, and ketones.[12] It is noteworthy that no tertiary alcohol, which might conceivably result from overaddition of the triorganothallium derivative to the ketone, could be detected, even in the presence of excess of reagent.

Table I. Synthesis of Ketones from Acid Chlorides Using Triorganothallium Reagents[a]

entry	substrate	reagent	product	yields[g]
1	$C_9H_{19}COCl$ [a]	Me_3Tl[d]	$C_9H_{19}COMe$	85%
2	$CH_2{=}CH(CH_2)_8COCl$ [a]	Me_3Tl	$CH_2{=}CH(CH_2)_8COMe$	73%
3	 [a]	Me_3Tl		76%
4	$CH_3O(CO)(CH_2)_8(CO)Cl$ [c]	Me_3Tl	$CH_3O(CO)(CH_2)_8(CO)Me$	92%
5	$PhCOCl$ [b]	Me_3Tl	$PhCOMe$	78%
6	 [b]	Me_3Tl		82%
7	$PhCOCl$ [b]	Et_3Tl[e]	$PhCOEt$	88%
8	$C_9H_{19}COCl$ [a]	Et_3Tl	$C_9H_{19}COEt$	91%
9	CH_3COCl [b]	Ph_3Tl[f]	CH_3COPh	87%
10	$PhCOCl$ [b]	Ph_3Tl	$PhCOPh$	85%

[a] Prepared from the corresponding carboxylic acid and $SOCl_2$ in refluxing $CHCl_3$. (b) The commercially available acid chloride was distilled before use. (c) Prepared by Fisher esterification, partial saponification with 1 equiv of KOH in MeOH and reaction with $SOCl_2$. (d) Prepared in situ by adding MeLi to a suspension of Me_2TlCl in ether at 20 °C. (e) Prepared in situ by adding EtLi to a suspension of Et_2TlCl in ether at 20 °C. (f) Prepared in situ by adding PhLi to a suspension of Ph_2TlBr in ether at 0 °C. (g) All yields are for isolated, pure material and are based on the starting acid chloride.

† Dedicated fondly to Dr. S. Goldstein.

(1) (a) House, H. O. *Modern Synthetic Reactions*; W. A. Benjamin, Inc.: London, 1972. (b) March, J. *Advanced Organic Chemistry*; J. Wiley and Sons: New York, 1985.

(2) For some leading references discussing the scope and the use of organometallic reagents, other than organocadmium and organocopper, in the transformation of acid chlorides into ketones, see: Collman, J. P., Hegedus, L. S., Norton, J. R., Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

(3) (a) Posner, G. H. *Organic Reactions*; J. Wiley and Sons: New York, 1975; Vol. 22, p 253. (b) Castro, C. E.; Havlin, R.; Honwad, V. K.; Malte, A.; Moje, S. *J. Am. Chem. Soc.* **1969**, *91*, 6464.

(4) Cason, J.; Fessenden, R. *j. Org. Chem.* **1960**, *25*, 477.

(5) Typical problems associated with this simple transformation are (a) the overaddition of the organometallic reagent, leading to tertiary alcohols, (b) decomposition or racemization of the starting material under the rigorous conditions required for some reagents, e.g., organocadmiums, (c) instability of the organometallic reagent, e.g., organocuprates, (d) difficulties in preparing branched organometallic reagents and therefore in forming branched ketones. Numerous branched triorganothallium compounds have been prepared (ref 9) by classical organometallic reactions. They are much more stable than their copper, cadmium, and zinc counterparts. Ketone synthesis using these branched derivatives will be reported in due course.

(6) (a) Gilman, H.; Jones, R. G. *J. Am. Chem. Soc.* **1946**, *68*, 517. (b) Gilman, H.; Jones, R. G. *J. Am. Chem. Soc.* **1950**, *72*, 1760.

(7) (a) Groll, H. P. A. *J. Am. Chem. Soc.* **1930**, *52*, 2998. (b) Rochow, E. G.; Dennis, L. M. *J. Am. Chem. Soc.* **1935**, *57*, 486. (c) Birch, S. F. *J. Chem. Soc.* **1934**, 1132.

(8) (a) Birch, S. F. *J. Chem. Soc.* **1934**, 1132. (b) Gilman, H.; Jones, R. G. *J. Am. Chem. Soc.* **1939**, *61*, 1513.

(9) (a) Lee, A. G. *The Chemistry of Thallium*; Elsevier: Barking, U.K. 1971. (b) Kurosawa, H. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, 1982; Vol. 1, p 725.

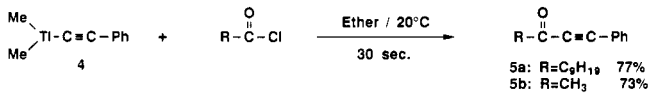
(10) Okhlobystin, O. Y.; Bilevitch, K. A.; Zakharkin, L. J. *J. Organomet. Chem.* **1964**, *2*, 281.

0022-3263/90/1955-3368$02.50/0

The organometallic byproduct from the ketone-forming reaction is a diorganothallium(III) chloride. This is also the starting material used to prepare triorganothallium derivatives (vide supra). After filtration, washing, and drying (see Experimental Section) this salt can be recovered in high yields and reused in another reaction.

In order to develop this ketone synthesis, an investigation of the reaction of the mixed triorganothallium derivative **4** was undertaken. Dimethyl(phenylacetenyl)-thallium(III) (**4**),[13] easily prepared from trimethylthallium and phenylacetylene, was reacted with decanoyl chloride and acetyl chloride. The acetylenic ketones **5a** (77% yield) and **5b** (73%) were formed rapidly at room temperature.

No 2-undecanone or acetone, which would result from a competitive methyl transfer, could be detected in the ^1H NMR spectrum of the crude reaction mixtures (eq 2). This observation suggests that a selective group transfer from a mixed triorganothallium derivative can occur.[14]



(2)

In conclusion, we have described a novel, efficient, and versatile preparation of ketones from acid chlorides using triorganothallium derivatives. The method possesses several advantages over preexisting ones. These are the following: (1) the rapidity and cleanliness of the reaction, (2) the mildness of the reaction conditions, (3) the absence of overaddition products, even when employing excess reagent, and (4) the easy and almost quantitative recycling of the diorganothallium(III) halide, stable precursor of the highly reactive triorganothallium reagents.

Further studies to determine the scope, limitations, and mechanism of this efficient and flexible ketone synthesis[15] are under active investigation and will be reported in due course.

Warnings. Thallium and its compounds are toxic and must be handled with care. Although thallium is classed as a cumulative poison, as are lead and mercury, it must be emphasised that it is gradually excreted from the body as a result of soft-tissue turnover.[16]

Experimental Section

Melting points were taken on a Kofler hot stage micro melting point apparatus and are uncorrected. Proton NMR spectra were recorded on a Perkin-Elmer 220-MHz or Bruker 250-MHz spectrometers. IR spectra were taken on a Perkin-Elmer 157 G instrument while mass spectral data were collected on a Kratos MS25 instrument. Analytical TLC plates employed were kieselgel 60 F254 plates on aluminum. Ether was distilled from sodium/benzophenone ketyl prior to use. each ketone product was compared with an authentic sample, either commercially available or prepared by known procedure. Standard workup represents separating the organic layer from the aqueous one, drying it over $MgSO_4$, and removing the solvent in vacuo.

1. Preparation of Dimethylthallium Chloride. In a flamed-dried, three-necked flask, maintained under a positive pressure of argon, were placed 24 g (0.072 mol) of TlI, 11.3 mL (0.18 mol) of MeI, and 25 mL of dry ether. To the well-stirred yellow suspension was added MeLi (100 mL of a 1.4 M solution in ether, 0.14 mol) dropwise, at 20 °C, over 6–7 h. As each drop of MeLi reached the reaction mixture, a black-colored spot was formed, which readily disappeared. Gradually, the solid dissolved and, at the end of the addition, a nearly transparent, light brown solution was obtained, which was left to stand overnight, protected from light by using aluminum foil. The solution was transferred by filtration into another flask and cooled to 0 °C, and a 1.0 M aqueous HCl solution was added dropwise until pH = 1–2 was reached. The white precipitate of dimethylthallium chloride was removed by filtration, washed several times with water, and dried in a desiccator over phosphorus pentoxide. Yield: 15.8 g (81%).

2. Preparation of 2-Undecanone. In a flamed-dried, three-necked flask, maintained under a positive pressure of argon, were placed 5 g (18.5 mmol) of dimethylthallium chloride and 100 mL of dry ether. To the stirred suspension was added MeLi (13.2 mL of a 1.4 M solution in ether, 18.5 mmol) dropwise at 20 °C. On addition of the MeLi, the white suspension yielded a colorless solution of trimethylthallium. Decanoyl chloride (3.4 g, 18 mmol) dissolved in 10 mL of ether was added all at once. An immediate precipitation of dimethylthallium chloride took place. After an additional 5 min of stirring, 10 mL of 0.1 M HCl was added and the heterogeneous reaction mixture filtered. The solid was washed several times with ether. The combined organic layers were separated from the aqueous layer and dried over $MgSO_4$, and the solvent was removed in vacuo. The crude 2-undecanone (3.7 g) was purified further by chromatography over silica gel (eluant, 1:4 ethyl acetate/light petroleum ether) to give 3.4 g (85% yield) of pure material: MS, EI 170, 155, CI, 171, 188; IR (neat, cm^{-1}) 2915, 2845, 1730; 220-MHz NMR ($CDCl_3$) δ 2.41 (2 H, t, J = 7 Hz), 2.13 (3 H, s), 1.6 (2 H, m), 1.27 (12 H, m), 0.87 (3 H, t, J = 7.8 Hz).

The crude, precipitated dimethylthallium chloride was washed successively and portion-wise with 100 mL of CH_2Cl_2, 100 mL 0.1 M HCl, and 100 mL of water. After drying in vacuo, dimethylthallium chloride (4.75 g, 95%) was recovered. It can be used in another reaction without further purification.

3. Preparation of Diphenylthallium Bromide. (a) $TlBr_3$. To a stirred suspension of TlBr (3 g, 10.5 mmol) in 60 mL of dry acetonitrile was added bromine (3.1 g, 38.8 mmol) dropwise at 20 °C. After 15 min, all the TlBr dissolved and the reaction mixture was left to stand for another 2.5 h. Removal of the solvent and excess of bromine yielded essentially pure $TlBr_3$, which was used immediately without further purification.

(b) Ph_2TlBr. Freshly prepared $TlBr_3$ (4.5 g, 0.01 mol) and benzeneboronic acid (2.48 g, 0.02 mol) were dissolved in 12.4 mL of water and boiled for 2 min. A pale-yellow precipitate formed immediately and was removed by filtration. After being washed with water, the solid diphenylthallium bromide was recrystallized from pyridine, yielding 2 g (47%) of pure material.

4. Preparation of Acetophenone. To a cold (0 °C) suspension of 0.81 g (1.85 mmol) of diphenylthallium bromide in 30 mL of anhydrous ether was added dropwise 0.9 mL (1.85 mmol) of a 2 M solution of phenyllithium in ether. The suspended solid gradually solubilized, giving a colorless solution of triphenylthallium. The cooling bath was removed and the temperature of the reaction mixture was allowed to reach 20 °C. Acetyl chloride (0.15 g, 1.85 mmol) was then added rapidly with concomittant precipitation of diphenylthallium chloride. After an additional 5 min, 0.5 mL of 0.1 M HCl was added and the solid material removed by filtration. A standard workup followed by distillation (94–96 °C/20 mm) gave 0.19 g (87% yield) of pure acetophenone.

5. Preparation of 1-Phenyl-3-oxododec-1-yne. To a solution of trimethylthallium (prepared as described above from 1.8 mmol

(11) Triorganothallium compounds are highly reactive, as exemplified by the weakness of the Tl–C bond, e.g., the mean value for the Tl–C bond dissociation energy in trimethylthallium is 27.4 kcal/mol as compared to 70.5 kcal/mol for monomeric trimethylaluminum.

(12) For example, trimethylthallium reacts with an equimolar mixture of 2-butanone and decanoyl chloride to produce 2-undecanone. No 2-methyl-2-butanol could be detected.

(13) (a) Lee, A. G. *J. Chem. Soc. A* **1970**, 2157. (b) Nast, R., Kab, K. *J. Organomet. Chem.* **1966**, *6*, 456.

(14) Not every mixed triorganothallium reagent transfers their ligands with such high selectivity, e.g., dimethylphenylthallium reacts with decanoyl chloride to give a 2/3 mixture of 2-undecanone and phenyl nonanyl ketone.

(15) Trimethylindium reacts similarly with acid chlorides, giving methyl ketones in high yields. However, in contrast with triorganothallium reagents that transfer only one group—giving the highly stable diorganothallium(III) halides—all three groups of trimethylindium are used in this reaction, leading to indium trichloride (Markó, I. E. Unpublished results).

(16) (a) Browning, E. C. *Toxicity of Industrial Metals*; Butterworths: London, 1961. (b) Grunfeld, O.; Hinostroza, G. *Arch. Int. Med.* **1964**, *114*, 132. (c) Taylor, E. C.; McKillop, A. *Acc. Chem. Res.* **1970**, 338. For antidotes, see: Heydlaug, H. *Eur. J. Pharm.* **1969**, *6*, 340. For useful references concerning the handling of organothallium compounds, see: (c) *Organic Synthesis*, Vol. 6, 348, 488, 709, 791. (d) McKillop, A.; Taylor, E. C. *Comprehensive Organometallic Chemistry*, Vol. 7, 1982.

of dimethylthallium chloride and 1.8 mmol of MeLi) in 20 mL of ether was added dropwise 0.18 g (1.8 mmol) of phenylacetylene and the reaction mixture was stirred for 17 h. Decanoyl chloride (0.34 g, 1.8 mmol) was then added and the heterogeneous mixture that resulted was stirred for an additional 5 min. Addition of 0.5 mL of a 0.1 M aqueous HCl solution followed by filtration and a standard workup gave the crude ketone, which was further purified by reverse-phase HPLC (eluant, 20:80 water/acetonitrile) to afford 0.35 g (75%) of pure material: MS, EI 155, CI 257, 274; IR (neat, cm^{-1}) 2910, 2850, 2190, 1665, 1555; 220-Mz NMR ($CDCl_3$) δ 7.55 (2 H, d, J = 8 Hz), 7.37 (3 H, m), 2.55 (1 H, t, J = 7.5 Hz), 1.75 (2 H, m), 1.25 (12 H, m), 0.85 (3 H, t, J = 8 Hz).

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Registry No. 1, 3003-15-4; 2, 687-82-1; 3, 3003-04-1; **5a**, 84907-66-4; **5b**, 1817-57-8; TlI, 7790-30-9; Me_2TlCl, 16834-14-3; TlBr, 7789-40-4; $TlBr_3$, 13701-90-1; $PhB(OH)_2$, 98-80-6; Ph_2TlBr, 10192-61-7; PhC≡CH, 536-74-3; $C_9H_{19}C(O)Cl$, 112-13-0; H_2C=$CH(CH_2)_8C(O)Cl$, 38460-95-6; $MeOC(O)(CH_2)_8C(O)Cl$, 14065-32-8; PhC(O)Cl, 98-88-4; $MeOC_6H_4$-*p*-C(O)Cl, 100-07-2; MeC(O)Cl, 75-36-5; $C_9H_{19}C(O)Me$, 112-12-9; H_2C=$CH(CH_2)_8C(O)Me$, 5009-33-6; $MeOC(O)(CH_2)_8C(O)Me$, 18993-09-4; PhC(O)Me, 98-86-2; $MeOC_6H_4$-*p*-C(O)Me, 100-06-1; PhC(O)Et, 93-55-0; $C_9H_{19}C(O)Et$, 1534-27-6; PhC(O)Ph, 119-61-9; cyclopentanecarbonyl chloride, 4524-93-0; acetylcyclopentane, 6004-60-0.

Synthesis of 6-Aryl-4,5-dibenzamido-1,2,3,6-tetrahydropyridines

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In 1928 van der Merwe[1] reported the reaction sequence, shown in Scheme I starting with histamine and *p*-anisaldehyde. The three steps are Schiff base formation, reduction of the anil double bond, and a Bamberger ring fission reaction.[2] Information on yields was not provided. Only elemental analyses were given in support of structures **2** and **3**, but that evidence was not convincing because the experimental values van der Merwe reported for the nitrogen content of the dipicrate of the secondary amine **2** (-0.49%) and the carbon content of the Bamberger product **3** (-0.80%) did not check within acceptable limits.

In 1966 we reported[3] on some histamine research that included evidence that compound **1** of van der Merwe's proposed sequence was actually 4-(4-methoxyphenyl)-4,5,6,7-tetrahydro-1*H*-imidazo[4,5-*c*]pyridine (**4a**) formed by thermal cyclization of the Schiff base **1**. In the light of that finding it seemed reasonable to presume that van der Merwe's final step employing Bamberger reaction conditions produced 4,5-dibenzamido-1-benzoyl-6-(4-methoxyphenyl)-1,2,3,6-tetrahydropyridine (**5a**) (Scheme II). The current research was undertaken, in part, to confirm this assumption.

Further motivation for the project came from a literature search that revealed that many substituted 1,2,3,6-tetrahydropyridines exhibit interesting and potentially useful pharmacological properties.[4] Thus, a major objective of the current research was to study the potential of Scheme II as a pathway to a series of new 1,2,3,6-tetrahydropyridines.

Our first effort was simply to repeat van der Merwe's work to allow us to test our assumptions concerning the actual structure of his Bamberger reaction product and to determine the reaction yield. The product we obtained was a solid that, contrary to the expected properties of a Bamberger product such as **3** or **5**, was largely (80-90%) soluble in dilute aqueous acid.

Examination of the small amount of acid-insoluble residue by means of elemental analyses and spectroscopy (^1H NMR and MS) proved it to be the expected Bamberger product **5a**. The corrected melting point of our analytical sample was approximately 12 °C higher than the 205 °C reported by van der Merwe, suggesting our isolation scheme afforded a product of higher purity. The yield, however, was only 10% and various attempts to improve the yield by either manipulating reaction conditions or by using a large excess of benzoyl chloride met with failure. During this phase of our work **4b** was also subjected to the Bamberger reaction. By means of a similar workup, **5b** was isolated in 9% yield.

We then turned our attention to the acid-soluble portion of the Bamberger reaction product. Spectral data (^1H NMR and MS) of this material showed that it was the monobenzoylated derivative 5-benzoyl-4-(4-methoxyphenyl)-4,5,6,7-tetrahydro-1*H*-imidazo[4,5-*c*]pyridine (**6a**). Convincing evidence that the benzoyl group was at the 5-position was provided by the strong downfield shifts of the absorptions of neighboring protons at C-4 and C-6 in the ^1H NMR spectrum.[6] This rapid, initial benzoylation occurring at the more basic (and more nucleophilic) 5-position of the tetrahydropyridine ring[7] evidently produced

(1) van der Merwe, P. *Z. Physiol. Chem.* **1928**, *177*, 30.

(2) For a comprehensive review of the Bamberger reaction, see: Hofmann, K. *Imidazole and Its Derivatives, Part I*, in the series the Chemistry of Heterocyclic Compounds; Weissberger, A.; Ed.; Interscience; New York, 1953; pp 48-49, 156, 273-276.

(3) Stocker, F. B.; Fordice, M. W.; Larson, J. K.; Thorstenson, J. H. *J. Org. Chem.* **1966**, *31*, 2380.

(4) A number of di- and trisubstituted 1,2,3,6-tetrahydropyridines have been shown to have pharmacological activity. See: Boettcher, H.; Fuchs, A.; Seyfried, C. Ger. Pat. DE 1986 3, 438,394 (tranquilizers); *Chem. Abstr.* **1986**, *105*, 97328k. McCall, J. M.; TenBrink, R. E.; Kamdar, B. V.; Skaletzky, L. L.; Perricone, S. C.; Piper, R. C.; Delehanty, P. J. *J. Med. Chem.* **1986**, *29*, 133 (hypotensive agents). Pall, H. S.; Williams, A. C.; Ramsden, D. B. *J. Clin. Hosp. Pharm.* **1986**, *11*, 229 (involvement with Parkinson's disease). Eur. Pat. Appl. EP 1982 60,179 (CL. CO7D211/70); *Chem. Abstr.* **1983**, *98*, 71939k (appetite suppressants). Martin, L. L.; Klioze, S. S.; Worm, M.; Crichlow, C. A.; Geyer, H. M., III; Kruse, H. *J. Med. Chem.* **1979**, *22*, 1347 (anti-depressants). F. Hoffman-La Roche and Co., A.-G. Neth. Pat. Appl. 1965 6,407,413 (Cl. C 07d); *Chem. Abstr.* 1965, *63*, 1774b (analgesics).

(5) When slightly more than 3 equiv of benzoyl chloride was allowed to react with 1 equiv of **4c** in pyridine at 85 °C for 45 min, monobenzoylation at the 5-position occurred in 92% yield. (See Experimental Section.)

(6) The ^1H NMR methylene proton absorption at C-6 was shifted from 3.0 and 3.15 ppm downfield to 3.24 and 3.61 ppm, whereas the methine proton absorption at C-4 was shifted from 4.9 downfield to 6.9 ppm. Reference data from Silverstein et al. [Silverstein, R. M.; Bassler, G. G.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; John Wiley and Sons: New York, 1981; p 220, 222] give a predicted methylene shift of approximately 0.6 ppm and a predicted methine shift of approximately 0.9 ppm. The observed methylene shift is close to the predicted value but the observed methine shift is approximately 1 ppm farther downfield than the predicted value. If one assumes that the bulk 4-methoxyphenyl and the benzoyl groups are trans to one another on the tetrahydropyridine ring, the benzoyl group then is cis to the methine C-4 proton. We surmise that anisotropic deshielding by the nearby benzoyl group is responsible for the unexpectedly large downfield shift of the methine proton.

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