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Alkylation of α-Formyl Esters via Their Thallium(I) Salts

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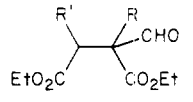
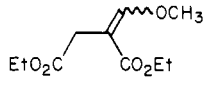
Treatment of the thallium(I) salt of β-diketones and β-keto esters with alkyl halides had been shown to be a useful method for the regioselective C-alkylation of these compounds. This approach, however, has apparently not been examined for α-formyl esters. In an effort to determine the applicability of this method to aldehyde substrates, the reaction with α-formyl esters which covers a range of properties for α-substituents has been examined. In addition, the effects of various solvents and Et_3N catalysis on the course of the reaction were evaluated. The overall yields and ratios of C/O alkylation were determined by using ^1H NMR integration. In no case did exclusive C-alkylation result and, furthermore, the results obtained indicate that previous explanations for the observed regioselectivity may not have been accurate and the preference for C-alkylation may be related to the covalent nature of the thallium salt in solution as opposed to reaction on the crystal surface. It is concluded that this method represents a useful synthetic procedure only for cases where the α-formyl ester has a relatively low enolization tendency and the steric demand of the electrophile is small.

While engaged in a program directed toward the synthesis of small ring heterocycles as potential anticonvulsants the aldehyde **1** was desired as a key intermediate.





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1, R = CH_3; R′ = H
2, R = H; R′ = H
4, R = H; R′ = CH_3

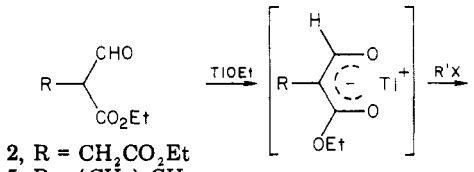
It had been reported that a logical precursor to the desired compound, the known diethyl α-formylsuccinate (**2**),[1] could not be successfully alkylated in the desired α position with either methyl or ethyl iodide, utilizing various basic catalysts and solvents.[2] The products from the attempted alkylation with MeI were reported to consist of the corresponding O-alkylated enol ether **3** and diethyl α-methylsuccinate which was suggested to arise from either **1** or the β-methyl analogue **4**. Since the starting aldehyde is known to exist substantially in its enol form,[3] one would expect standard alkylating procedures to generate significant amounts of O-alkylated products and possibly aldol-type products.[4]

Alkylations of reactive aldehydes via hindered enamines[5] or imine magnesium salts[6] represent indirect procedures for the alkylation of aldehydes; however, a facile, one-step procedure would be more desirable and, in the present case, hydrolysis of the alkylated enamine in aqueous mineral acid would likely result in decarboxylation which is known to occur readily with this type of aldehyde.[3,7]

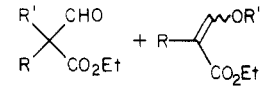
Early observations on the reaction of organothallium salts with alkyl halides were not pursued.[8] In 1968, however, Taylor and McKillop extended this work and reported the exclusive mono C-alkylation of thallium(I) salts of β-dicarbonyl compounds in nearly quantitative yields.[9] A search of the literature, however, failed to reveal any published reports concerning the application of this procedure to the alkylation of α-formyl esters, and therefore a study was embarked upon to ascertain the feasibility of this approach for C-alkylation of these substrates.

It has been proposed,[10] based on X-ray crystallographic studies of the thallium(I) salts of β-dicarbonyl compounds,[11] that reaction occurs at the crystal surface where the carbanionic centers are exposed, with the oxygen and thallium atoms buried within the interior of the complex,

Scheme I



2, R = CH_2CO_2Et
5, R = $(CH_2)_3CH_3$
6, R = C_6H_5



R′X = MeI, EtI, EtBr, *i*-PrI

and that the crystal is literally "peeled away" until the reaction is complete.

This contention that heterogeneity is a prerequisite for regiospecific C-alkylation may not be valid. On reexamination of some of this work, Hooz and Smith[12] were unable to obtain the complete regiospecificity previously observed. Furthermore, the degree of regioselectivity observed did not seem to correlate with the apparent heterogeneity as previously postulated. Because of the disparity in results obtained previously and the lack of utilization of alternative solvent systems, it was reasoned that exploration of different solvents of varying polarity, which should retain the presumably requisite surface reaction characteristics, was also warranted.

The use of a polar, protic solvent which might hopefully retain some of the desirable characteristics of the thallium(I) salt was also of interest since selective solvation of the oxygen atom of an enolate is known to play a role in

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Table I. Alkylation of the Thallium(I) Salt of Diethyl α-Formylsuccinate (2)

solvent	dielectric constant, 20 °C[a]	electrophile	products, relative %[b] aldehyde (1)	products, relative %[b] enol ether (3)	time, h (temp, °C)	yield, %[c]
CH_3I	7.00	CH_3I	75 (9.13)	25 (7.40)	4 (45)	76
hexane	1.89	CH_3I	3	97	8 (68)	79
benzene	2.28	CH_3I	9	91	6 (80)	69
THF	7.58	CH_3I	57	43	9 (65)	75
CH_2Cl_2	9.08	CH_3I	74	26	30 (40)	48
ethanol	24.30[d]	CH_3I	55	45	6 (78)	64
C_2H_5I	7.82	C_2H_5I	37 (9.77)	63 (7.62)	6 (45)	56
C_2H_5Br	9.39	C_2H_5Br	6	91[e]	14 (45)	42
$(CH_3)_2CHI$	8.19	$(CH_3)_2CHI$	18.5 (9.80)	78.5[e] (7.51)	30 (55)	27

[a] R. L. Schneider, *Eastman Org. Chem. Bull.*, 47, 1 (1975). [b] Determined by integration of the ^1H NMR spectrum after distillation. δ values in parentheses are the chemical shift of the aldehydic and vinylic protons. [c] Yields are of distilled product mixture based on the amount of TlOEt used. [d] Measured at 25 °C. [e] The remainder corresponds to unreacted starting material.

the site of ambident anion alkylation.[13] A solvent which could hydrogen bond with the oxygen of the enolate might still represent a satisfactory system for C-alkylation.

The general reaction investigated is shown in Scheme I. Reaction conditions were explored in an attempt to optimize the C/O alkylation ratio of **2** with MeI. The methylation of the thallium(I) salt of **2** in MeI was studied in order to ascertain the applicability of the procedure to this substrate. The methylation of **2** in aprotic solvents of increasing polarity, as evidenced by their dielectric constants, was also evaluated and EtOH was chosen as the polar, protic solvent for these initial studies.

As noted in Table I, refluxing the thallium(I) salt of **2** in excess MeI yielded the most favorable combination of C/O alkylation ratio and net yield. This procedure had originally been stated[9] to result in 100% C-alkylation of β-dicarbonyl compounds; however, in our hands we were unable to achieve better than 75% C-alkylation of the α-formyl ester as determined by ^1H NMR integration of the areas under the aldehydic (δ 9.13) and vinylic (δ 7.40) proton resonances for the C- and O-alkylated products **1** and **3**, respectively. It was even more surprising that with the methods of refluxing the thallium(I) salt of **2** with excess MeI in hexane and benzene nearly complete O-alkylation was observed. One might have expected that in these solvents the heterogeneity presumably necessary for C-alkylation would have been maintained. With the more polar solvent THF, a moderately biased ratio of 57% C-alkylation to 43% O-alkylation was observed. In CH_2Cl_2, the most polar, aprotic solvent employed, essentially the same C/O alkylation ratio was obtained (74:26) as when the electrophile itself was used as its own solvent. In this case, however, there was a dramatic increase in reaction time and decrease in yield due to significant polymerization. Refluxing the thallium(I) salt in EtOH with excess MeI afforded significant polymerization (producing a relatively low yield of alkylation products) although the C- to O-alkylation ratio (~55:45) was reasonable. Apparently, the use of the alkylating agent as the solvent is not an absolute prerequisite for C-alkylation in the case of α-formyl esters. However, these results seem to indicate that a polar solvent, as evidenced by its dielectric constant, is necessary for some regioselectivity toward C-alkylation whether the solvent is the alkyl halide itself or another suitable solvent. This desirable effect of a solvent on regioselectivity seems to be at a maximum when its dielectric constant is similar to that of the alkyl halide and it is less likely to have some interaction with the thallium salt, as suggested by comparison of the results in CH_2Cl_2 and THF.

Table II. Effect of Et_3N Catalysis on Alkylation of Diethyl α-Formylsuccinate (2)

electrophile	amount of Et_3N	products, relative %[a] aldehyde	products, relative %[a] enol ether	reaction time, h	yield, %[b]
C_2H_5Br	none	6	91[c]	14	42
C_2H_5Br	catalytic	9	91	7	65
C_2H_5Br	0.5 equiv	11	89	11	57
C_2H_5I	none	37	63	6	56
C_2H_5I	catalytic	27	73	1.5	69
C_2H_5I	0.5 equiv	27	71[c]	4	64
CH_3I	none	75	25	4	76
CH_3I	catalytic	63	37	1.5	69

[a] Determined by integration of the ^1H NMR spectrum after distillation. [b] Yields are of distilled product mixture based on the amount of TlOEt used. [c] The remainder corresponds to unreacted starting material.

With the bulkier EtI and *i*-PrI acting as both electrophile and solvent, drastic reductions in both percent C-alkylation and yield were observed with attendant increases in reaction time and polymerized materials, more in line with the observations of Hooz and Smith[12] than those of Taylor and co-workers.[9]

In previous work on β-dicarbonyl alkylations, it was reported that alkyl bromides could be used as the alkylating agent; however, their lowered reactivity necessitates higher reaction temperatures and/or the use of triethylamine as a catalyst, with a resulting decrease in yield.[9] In the present case, as can be seen in Table II, the use of EtBr in the alkylation of **2** also resulted in an increase in reaction time with a concomitant reduction in yield and C/O alkylation ratio. Employing a catalytic amount of Et_3N in an attempt to shorten this reaction time and possibly improve the isomer ratio did result in a decreased reation time with an increase in yield apparently due to a decrease in polymerized side products (Table II). This surprising improvement in yield was not accompanied by any real increase in the C/O alkylation ratio. When 0.5 equiv of Et_3N was used, a lesser reduction in reaction time and an increase in yield were observed and no significant change in the C/O alkylation ratio took place.

Et_3N catalysis was also explored with the alkyl iodides since it appeared to at least improve yields and reduce reaction times. Reaction with the corresponding alkyl iodide, EtI, and the use of a catalytic amount of Et_3N and 0.5 equiv of Et_3N, respectively, again resulted in an increase in yield; however, in both cases approximately a 10% decrease in the relative C/O alkylation ratio occurred

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Table III. Alkylation of the Thallium(I) Salts of 5 and 6

compd	electrophile	products, relative %[a] aldehyde	products, relative %[a] enol ether	reaction time, h[b]
5	CH_3I	82 (9.70)	18 (7.13, 7.22)	6
5	C_2H_5I	45 (9.87)	44[c] (7.13, 7.33)	18
5	$(CH_3)_2CHI$	33 (9.95)	50[c] (7.37, 7.40)	>48
5	C_2H_5Br	20	75[c]	24
6	CH_3I	0	100 (7.42)	24
6	C_2H_5I	0	92[c] (7.47, 7.87)	45

[a] Determined by integration of the ^1H NMR spectrum after distillation. δ values in parentheses are the chemical shift of the aldehydic and vinylic protons. [b] All reactions conducted at 45 °C (bath temperature) except with *i*-PrI at 55 °C. [c] The remainder corresponds to unreacted starting material.

(Table II). Since catalytic Et_3N seemed to yield the greatest reduction in reaction time with an accompanying increase in yield, it was applied to the alkylation of **2** with MeI. In this case a dramatic reduction in reaction time was observed; however, the overall yield was not improved and a slight reduction in regioselectivity for C-alkylation was observed.

Since there was a potential that the second ester moiety in **2** may have played a role in the observed reaction course, it was decided to expand the scope of this investigation by employing additional substrates which would enable a more general exploration of the applicability of this procedure to the alkylation of α-formyl esters. Ethyl α-formylcaproate[14] (**5**) and ethyl α-formylphenylacetate[15] (**6**) were thus selected as substrates having R groups presumably not capable of any direct interactions which could possibly be influencing the site of alkylation. In addition, these R groups might be expected to have extremes of influence on the degree of enolizability of the α-formyl moiety. As can be seen in Table III, the course of the alkylation with the electrophile as the solvent is strongly influenced by the nature of the substrate, with only the α-alkyl derivative **5** providing any C-alkylated product. As is the case with **2**, an increase in the amount of time necessary to affect alkylation was observed with increasing steric bulk of the electrophile. Along with this increase in reaction time an analogous reduction in regioselectivity for C-alkylation was observed. In contrast to the results with **2** and **5**, even with the small, reactive electrophile MeI, no C-alkylation of the aromatic α-formyl ester **6** was observed.

In accordance with the findings of Hooz and Smith on the alkylation of β-dicarbonyls,[12] it appears that with α-formyl esters regiospecific C-alkylation cannot be obtained via alkylation of their thallium(I) salts. Nonetheless, at least in the case of the reaction of **2** and **5** with MeI, significant preference for C-alkylation can be obtained. The utilization of a nonpolar solvent system appears to reduce this selectivity to a great extent. However, from this data it would appear that the relative C/O alkylation ratios increase with the increasing polarity of the solvent employed, provided the solvent is not likely to directly influence the nature of the thallium(I) salt. The results obtained from the use of Et_3N catalysis also seem to show that the reaction rate enhancement it brings about greatly

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Table IV. Comparison of Methylation Products of α-Formyl Esters and Enolization of Substrate

compd	% enol[a]	% aldehyde
2	40	75
5	25	82
6	>90	0

[a] Determined by integration of the ^1H NMR spectrum in $CDCl_3$ of the aldehydic and vinylic protons of the starting material.

reduces polymerization, although in most cases it also increases O-alkylation (at least with the more reactive alkyl iodides and **2**) which may result from an enhancement of the degree of dissociation of the thallium salts as discussed below.

The observations that in all cases some O-alkylation is seen and in many cases significant polymerization occurs (probably via poly-aldol reactions) and that starting material can be reisolated strongly suggest the possibility that in the case of α-formyl esters, as also for β-dicarbonyls,[12] the organothallium salt or the nature of the reaction may somehow differ from that originally proposed.[9] Previous workers have described these organothallium salts as being white, crystalline, filterable solids.[9,12] In the present experiments a crystalline, filterable thallium salt was obtained only with **6**, a substrate yielding only O-alkylation, whereas compounds **2** and **5**, which gave rise to regioselective C-alkylation, formed amorphous salts. Particularly in the experiments with these amorphous salts, completely heterogeneous systems were not observed with the alkyl halide as the solvent, and, in fact, in the methylation of **2** in CH_2Cl_2, a solvent promoting C-alkylation, the solution appeared completely homogeneous in the initial stages of the reaction. Furthermore, at least in the case of the α-formyl esters examined in the present study, there appears to be an inverse correlation between the tendency toward enolization of the starting materials, as shown by their ^1H NMR spectra in $CDCl_3$, and the amount of C-alkylation that occurs (Table IV). It should also be noted that the most obviously heterogeneous reaction system encountered was with the thallium salt of **6** which afforded complete O-alkylation.

It also seems noteworthy that in the nonpolar solvents hexane and benzene, which were most likely to maintain heterogeneity, the maximum amount of O-methylation of **2** occurs, lending credence to the suggestion[12] that this "apparent heterogeneity" of thallium salt alkylations is not the essential factor promoting C-alkylation, exclusive or otherwise, and, in fact, a certain degree of homogeneity may be necessary to observe some regioselectivity for the C-alkylation of both β-dicarbonyls and α-formyl esters.

A possible explanation for these observations is that C-alkylation occurs principally with the solubilized, intact organothallium complex and is highly dependent upon the covalent character of the thallium bond(s) in the complex. It seems reasonable to expect that the ionic character of the complex would increase as the tendency toward enolization of the starting material increased, indicating a greater delocalization of electrons in the enolate. This would result in a reduced solubility and a greater proportion of the reaction taking place on the solid surface. The net result would be similar in cases where a solvent system incapable of solubilizing even the more covalent complexes was employed. Finally, the use of solvents capable of direct interaction with the thallium atom (e.g., THF and EtOH), although producing sufficient solubility, might tend to decrease or disrupt the covalent character

of the complex and facilitate O-alkylation and polymerization.

In conclusion, it would appear that for α-formyl esters under the conditions employed, this procedure only represents a synthetically useful method for the relatively selective C-alkylation of less extensively enolized α-formyl esters such as **2** and **5** with small, reactive, alkylating agents. With bulkier and less reactive electrophiles and/or more extensively enolized α-formyl esters, we have been unable to achieve a selective C-alkylation. However, for these more labile substrates, this procedure may be more useful than indirect procedures when the intact dicarbonyl is desired.

Experimental Section

All melting points, determined with a Thomas-Hoover apparatus, and boiling points are uncorrected. ^{1}H NMR spectra were recorded on a Varian Associates T-60 spectrometer in $CDCl_3$ with Me_4Si as an internal standard. IR spectra were determined with a Perkin-Elmer 237B grating infrared spectrometer as liquid films. UV spectra were recorded in MeOH on a Cary 118 recording spectrophotometer. TLC was performed on silica gel 60 F_{254} from EM Reagents. All solvents were appropriately dried prior to use.

General Procedure. To a magnetically stirred solution of the α-formyl ester (10 mmol) in 50 mL of dry hexane, in a one-necked round-bottom flask equipped with a reflux condenser and $CaSO_4$ drying tube, was added TlOEt (0.65 mL, 9 mmol) all at one. The salt which immediately precipitated was stirred for 15 min and the hexane decanted. The alkyl halide (160 mmol or 40 mmol plus 50 mL of solvent) was added to the residue and the suspension stirred at reflux on a water bath during which time (when an alkyl iodide was employed) it proceeded through gradual color changes from yellow to dark orange and then rapidly to bright yellow as Tl(I)[16] plated out. The Tl(I) halide was removed by suction filtration with ether rinsing. The ethereal filtrate was dried through $MgSO_4$, concentrated to a crude oil, and distilled under reduced pressure to afford the product mixture as a clear oil. **Caution**: Tl(I) salts are known to be extremely toxic. All procedures were conducted in the fume cupboard and the collected Tl(I) halide was immediately oxidized with concentrated HNO_3.

Characterization of Diethyl α-Formyl-α-methylsuccinate (1) and Diethyl α-(Methoxymethylene)succinate (3). In order to characterize the aldehyde and enol ether products of these alkylations, the clear oil resulting from the alkylation of **2** with MeI was eluted on a silica gel column with $CHCl_3$–MeOH (9:1). The earlier fractions which showed R_f 0.58 on TLC ($CHCl_3$–MeOH 95:5) were combined and evaporated to give **1**: NMR δ 1.07–1.38 (m, 6, CH_2CH_3), 1.37 (s, 3, CCH_3), 2.87 (s, 2, CH_2C), 3.87–4.43 (m, 4, CH_2CH_3), 9.13 (s, 1, CHO); IR 2980, 1715, 1630 cm^{-1}; UV λ_{max} 237 nm (ε 6000). The orange 2,4-DNP derivative was prepared according to standard procedures, mp 103–104 °C (EtOH).

The enol ether **3** was obtained in approximately 97% purity as the distilled product mixture after methylation of **2** in hexane; bp 81–105 °C (0.1 mm) [lit.[2] bp 103–104 °C (1 mm)]. TLC ($CHCl_3$–MeOH 95:5) showed the major product **3** at R_f 0.48 and a minor amount of material with R_f 0.58 corresponding to **1**: NMR δ 1.13–1.38 (m, 6, CH_2CH_3), 3.23 (s, 2, CH_2C), 3.85 (s, 3, OCH_3), 3.97–4.37 (m, 4, CH_2CH_3), 7.40 (s, 1, vinyl); IR 2960, 1783, 1715, 1640 cm^{-1}; UV λ_{max} 238 nm (ε 6320).

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Registry No. 1, 73587-50-5; 1 2,4-DNP derivative, 73587-51-6; 2, 5472-38-8; 2 Tl(I) salt, 73587-43-6; 3, 73587-52-7; 5 Tl(I) salt, 73587-44-7; 6 Tl(I) salt, 73597-06-5; diethyl α-ethyl-α-formylsuccinate, 73587-53-8; diethyl α-(ethoxymethylene)succinate, 70145-31-2; diethyl α-formyl-α-isopropylsuccinate, 73587-54-9; diethyl α-(isopropoxymethylene)succinate, 73587-55-0; ethyl α-formyl-α-methylcaproate, 73587-56-1; ethyl α-(methoxymethylene)-caproate, 73587-57-2; ethyl α-ethyl-α-formylcaproate, 73587-58-3; ethyl α-(ethoxymethylene)caproate, 73587-59-4; ethyl α-formyl-α-isopropylcaproate, 73587-60-7; ethyl α-(isopropoxymethylene)-caproate, 73587-61-8; ethyl α-(methoxymethylene)phenylacetate, 15937-30-1; ethyl α-(ethoxymethylene)phenylacetate, 15937-27-6.

(16) When employing alkyl bromides as the alkylating agent, the precipitation of the light yellow TlBr is more difficult to visualize. However, the end point of the reaction can be determined to be when the suspension separates into a light yellow (TlBr) precipitate and a light orange supernatant.

Preparation of Allylic Alcohols from Epoxides Using Iodotrimethylsilane

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The transformation of epoxides into allylic alcohols by use of iodotrimethylsilane and 1,5-diazabicyclo-[5.4.0]undec-5-ene is described. The scope and limitations of this reaction are examined. This method is complementary to the method of Sharpless in the case of trisubstituted epoxides and proceeds under milder reaction conditions than the method employing lithium dialkylamides.

Synthetic studies required the regioselective conversion of an epoxide into an allylic alcohol. Although this transformation might be accomplished by the use of lithium dialkylamides,[1] the basic reaction conditions that must be employed can promote undesired side reactions. A recent improvement on this reaction by Yamamoto[2] involves the use of dialkylaluminum amides. Sodium phenyl selenide has been used for the opening of epoxides under mildly basic reaction conditions.[3] Subsequent oxidative elimination affords allylic alcohols. With trisubstituted epoxides this method is regioselective and produces the more hindered allylic alcohol. While this work was in progress, Noyori and co-workers[4] reported the use of trimethylsilyl trifluoromethanesulfonate and 1,5-diazabicyclo[5.4.0]undec-5-ene (DBN) to effect the epoxide to allylic alcohol transformation. Although this reaction proceeds

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