gave *exo*-2-methylbicyclo[3.2.1]oct-3-ene (*exo*-**21**). No endo product was detected by capillary GC (230-ft column, UCON LB-550-X, 85 °C). A sample was obtained by preparative GC (10 ft × $^3/_8$ in. column, 20% UCON LB-550-X on Chromasorb W, 80 °C): $[\alpha]^{25}_D$ −61.3°, $[\alpha]^{25}_D$ −211° (*c* 1.01, $CHCl_3$). Comparison with published values[26] shows that this is 25 ± 1% optically pure (−)-(1*R*,2*S*,5*S*)-*exo*-**21**.

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE 8108535).

Registry No. *cis*-4-OCONHPh, 84473-17-6; *trans*-4-OCONHPh, 84473-18-7; *cis*-1-D-**5**, 84473-19-8; *dl*-**8**-OH, 84519-62-0; (*R*)-(+)-**8**-OH, 62413-47-2; (*S*)-(−)-)**8**-OH, 81176-43-4; *dl*-**8**-OAc, 82045-04-3; (*R*)-(+)-**8**-OAc, 84519-63-1; (*R*)-(+)-**8**-OCONHPh, 84473-20-1; (*S*)-(−)-**8**-OCONHPh, 84473-21-2; (*R*)-**9** (R = Me), 84519-64-2; (*R*)-**9** (R = *n*-Bu), 84519-65-3; (*S*)-**10** (R = Me), 84519-66-4; (*S*)-**10** (R = *n*-Bu), 84519-67-5; **11** (R = *n*-Bu), 79594-10-8; (*R*)-(−)-**12** (R = Me), 36667-55-7; *dl*-**12** (R = *n*-Bu), 84473-22-3; (*R*)-(−)-**12** (R = *n*-Bu), 84519-68-6; **13**-OH, 84473-23-4; **13**-OCONHPh, 84473-24-5; **14**, 84473-25-6; **15**, 84473-26-7; **16**, 84473-27-8; **16** 2,4-DNP, 84473-28-9; **18**, 16204-62-9; **19**, 84473-29-0; *endo*-**20**-OH, 32222-49-4; (+)-*exo*-**20**-OH, 84519-69-7; *endo*-**20**-OCONHPh, 84473-30-3; (+)-*exo*-**20**-OCONHPh, 84519-70-0; *exo*-**21**, 78965-86-3; $LiCuMe_2$, 15681-48-8; Li, 7439-93-2; CuI, 7681-65-4; MeLi, 917-54-4; *n*-BuLi, 109-72-8; $LiCu(n\text{-}Bu)_2$, 24406-16-4; phenyl isocyanate, 103-71-9; cerium chloride, 7790-86-5; *trans*-1-(2,4,6-trimethylphenyl)-1-buten-3-one, 42811-78-9; *dl*-1-bromo-1-phenylbutane, 84473-31-4; mesitylaldehyde, 487-68-3; (2-methylpropyl)triphenylphosphonium bromide, 22884-29-3; mesitylacetonitrile, 34688-71-6; ethyltriphenylphosphonium iodide, 4736-60-1.

Alkylation of Allylic Derivatives. 5.[1] Loss of Double-Bond Configuration Associated with α-Alkylation of Allylic Carboxylates with Dialkylcuprates

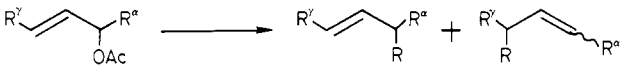
Harlan L. Goering* and Steven S. Kantner[2]

Samuel M. McElvain Laboratories of Organic Chemistry, Department of Chemistry, Univerisity of Wisconsin, Madison, Wisconsin 53706

Received July 20, 1982

Alkylation of *cis*- and *trans*-cinnamyl acetate with $LiCuMe_2$ gives primarily the conjugated α-alkylation product, 1-phenyl-1-butene. Detectable loss of double-bond configuration is observed with the *trans*-acetate and substantial loss of configuration is observed with the *cis*-acetate. The partial loss of double-bond configuration in the α-alkylation product has profound mechanistic implications, which are discussed.

In the earlier work we showed that alkylation of cyclic[3] and acylic[4] allylic carboxylates with dialkylcuprates is nonregiospecific and gives mixtures of α- and γ-alkylation products (eq 1). The double-bond configuration of the

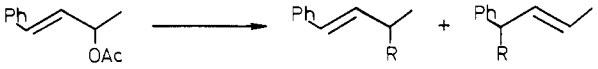


α-alkylation γ-alkylation (1)

α-alkylation product, relative to that of the starting ester, provides important information with regard to the nature of intermediates involved. Put another way, it is necessary to know whether or not double-bond geometry is preserved to distinguish between possible mechanistic pathways.

Our original mechanistic interpretation[5] included bothersome features to accommodate our impression that original double-bond configuration is fully preserved in the unrearranged α-alkylation product. This impression was based on fragmentary evidence such as the report[6] that in the geranyl–neryl system, alkylation of the *E* and *Z* allylic acetates with $LiCuMe_2$ gives α-alkylation without detectable loss of double-bond configuration. The reported[7a] α-alkylation of *cis*-cinnamyl alcohol and (*Z*)-2-buten-1-ol with methyllithium by the Murahashi method without isomerization of the double bond seemed particularly relevant because this reaction is thought to be mechanistically similar to, and involve the same types of intermediates as, alkylation of allylic carboxylates with alkylcuprates.[5,7]

In other work[4] we observed that alkylation of *trans*-α-methyl-γ-phenylallyl acetate (**1**) with dialkylcuprates gives about 95% α-alkylation with preservation of double-bond configuration and about 5% γ-alkylation as illustrated by eq 2. However, in this case the configuration at the outset



1 ~95% ~5% (2)

is the more stable one and retention could result from thermodynamic rather than stereoelectronic factors. In this connection it is noteworthy that in this system γ-alkylation gives only the *E* olefin. Generally, γ-alkylation products are *E*/*Z* mixtures,[1,5,8] but in some cases only the more stable *E* isomer is formed.[4,6]

Conflicting evidence with regard to preservation of double-bond geometry involves the copper(I)-catalyzed alkylation of *E* and *Z* isomeric allylic ethers with methyl Grignard.[9] Presumably this reaction involves a methylcuprate reagent and is mechanistically similar to the alkylation of allylic carboxylates with organocuprates. In the system investigated[9] (disubstituted double bond) the isomeric ethers give the same α-alkylation product (pri-

(1) Previous paper in this series is Goering, H. L.; Kantner, S. S.; Tseng, C. C., preceding paper in this issue.
(2) National Science Foundation Fellow, 1977–1980.
(3) Goering, H. L.; Singleton, V. D., Jr. *J. Am. Chem. Soc.* **1976**, *98*, 7854.
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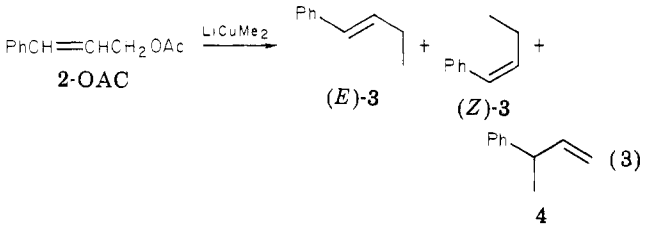
0022-3263/83/1948-0721$01.50/0

marily the more stable trans isomer) together with the common γ-alkylation product.

In this work we have investigated the alkylation of *cis*- and *trans*-cinnamyl acetate (2-OAc) with lithium dimethylcuprate. Alkylation of *cis*-cinnamyl alcohol (*cis*-2-OH) with methyllithium by the Murahashi method[5,7] was also examined. In each case we find substantial loss of double-bond configuration for α-alkylation of the cis isomer.

The three alkylation products derived from **2** are shown by eq 3 and results of key experiments are presented under



trans-2-OAC	0 °C	99%	1%	~0.1%
cis-2-OAc	0 °C	42%	57%	1%
cis-2-OAc	−78 °C	99.5%	0.4%	0.1%

the equation. In these experiments *cis*- and *trans*-2-OAc were alkylated with 2 equiv of $LiCuMe_2$ in ether. Under these conditions alkylation is not regiospecific.[3,4] However, the reaction is regioselective and gives primarily the conjugated α-alkylation product as would be expected from our earlier work with the α-methyl-γ-phenylallyl system.[4] Product distributions were determined by capillary GC and components were identified by comparison with authentic samples.

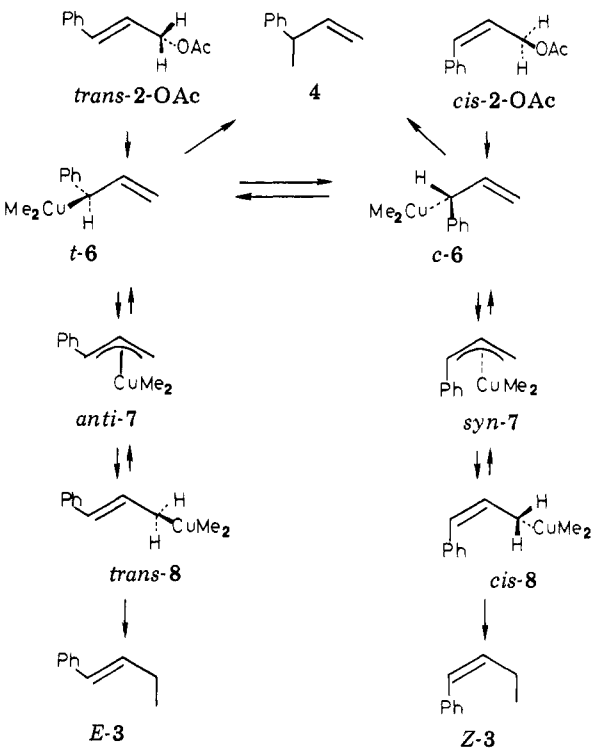
These results show there is substantial loss of double-bond configuration for alkylation of *cis*-2-OAc at 0 °C and loss of configuration is essentially complete at −78 °C. Loss of double-bond geometry is less evident with *trans*-2-OAc because of the thermodynamic bias that tends to preserve the more stable trans arrangement. However, in this case also there is detectable loss of configuration. It should be noted that the small amount of (*Z*)-**3** derived from *trans*-2-OAc does not result from contamination of starting acetate with *cis*-2-OAc. The present results for *trans*-2-OAc are similar to those for *trans*-α-methyl-γ-phenylallyl acetate (1) in which case small amounts (~1%) of the *Z* α-alkylation product are formed.[4] Originally we thought this might result from contamination of starting 1 with the cis isomer.[4] We now tend to feel that as with *trans*-2-OAc, the trace amount of *Z* α-alkylation product derived from 1 results from loss of original double-bond configuration during alkylation.

That loss of configuration does not result from isomerization of starting acetate prior to alkylation was established as follows. Alkylations of *cis*-2-OAc at 0 and −78 °C were carried out with excess acetate. Analysis of the reaction mixtures with 270-MHz NMR showed that the unreacted *cis*-2-OAc contained no detectable *trans*-2-OAc. Control experiments with synthetic mixtures showed that 1% intercontamination of the isomeric acetates (2-OAc) can readily be detected by this method.

The possibility that *trans*-2-OAc does not accumulate in the unreacted acetate because of a high trans/cis rate ratio for the acetates was ruled out as follows. Competitive rate studies to be presented elsewhere[10] show that the trans/cis rate ratio at 0 °C is 2:3. Moreover, the data under eq 3 show that at 0 °C different product-forming intermediates are involved for *cis*- and *trans*-2-OAc. This shows

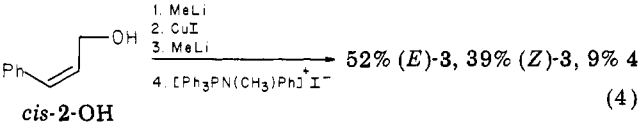
(10) Kantner, S. S.; Seitz, E. P., Jr., unpublished results.

Scheme I. Mechanistic Pathway for Alkylation of Allylic Carboxylates with Dialkylcuprates



that the rate for the cis isomer is not the rate of isomerization to the trans isomer which is immediately consumed. Thus the absence of *trans*-acetate in the unreacted acetate can not result from alkylation as fast as formation. Put another way, if prior *cis*-2-OAc → *trans*-2-OAc isomerization were involved, *trans*-2-OAc would accumulate in the unreacted acetate.

Alkylation of *cis*-cinnamyl alcohol (*cis*-2-OH) with methyllithium by the original Murahashi procedure[7a] also results in substantial loss of double-bond configuration as shown by eq 4. In this experiment 3 equiv of MeLi was

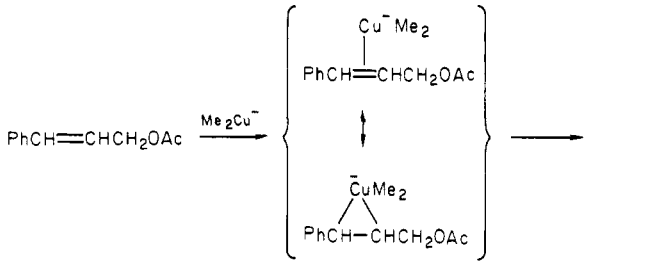


used in step 3 and (methylphenylamino)triphenylphosphonium iodide was used in the last step. Under these conditions the reaction is not regiospecific[5] and it has been shown[7a] that the isomeric cinnamyl alcohols give primarily the conjugated α-alkylation product. The product composition shown in eq 4 was determined by capillary GC. In earlier work[5] we concluded that this process is mechanistically similar to alkylation of allylic carboxylates with cuprates and we now see that the results are similar with regard to partial loss of double-bond configuration. The reason for the discrepancy between the present results and the reported[7a] complete preservation of double-bond geometry is not clear.

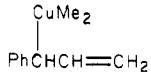
The partial to complete loss of double-bond configuration for alkylation of *cis*-2-OAc indicates that the S_N2' (σ-allyl)copper(III) complex **6** is an intermediate and it is at this stage that bond rotation can result in loss of configuration as indicated in Scheme I. Previously[5] we noted that there is excess γ-alkylation in all cases where regiospecificity is observed and from this we concluded that for these alkylations, oxidative addition of the allyl derivative to the cuprate gives the S_N2' σ-allyl isomer instead of the S_N2 isomer as had been proposed earlier.[6] At that

time we thought that the S_N2' σ-allyl complex **6** could not be involved in α-alkylation because of our misconception regarding preservation of double-bond configuration. This led to the complex proposal[5] that oxidative addition involves simultaneous and irreversible formation of the S_N2' σ-allyl complex **6** (which gives γ-alkylation product) and the (π-allyl)copper(III) complex **7** (which gives α-alkylation product with preservation of double-bond configuration together with γ-alkylation product).

Our original general mechanism[5] can now be simplified because the present results indicate that oxidative addition gives the S_N2' σ-complex **6** and that this intermediate is central to α-alkylation as well as γ-alkylation. The reason for the S_N2' regiochemistry for this step is thought to result from prior complexation of the cuprate with the double bond to give a cuprate–olefin π-complex **5**, which is converted to **6**.[5] The π-complex **5** can be considered to be a hydrid of copper(I) and copper(III) "-ate complexes" as shown in eq 5. The lower resonance structure, which



5



6 (5)

corresponds to oxidative addition of the π bond to the cuprate, is useful with regard to visualizing plausible mechanistic details for the **5** → **6** transformation. It seems reasonable that this pathway, and regiochemistry, will be general for oxidative additions of allylic derivatives with subsequent isomerization of the initially formed σ-allyl complex to the π-allyl complex in those cases where the latter is more stable. The structural illustrations are not meant to imply that only monomeric copper species are involved. It is known that under conditions of these reactions dialkylcuprates are dimeric[11a] and that other copper(I) species exist as aggregates.[11b]

The indicated anti stereochemisty for the S_N2' oxidative addition is based on our stereochemical investigations that show that such alkylations are stereospecific and give anti γ-alkylation and α-alkylation with inversion in both cyclic[3,5] and acyclic systems.[12] Since reductive eliminations (i.e., the **6** → **4** and **8** → **3** transformations) proceed with retention of configuration,[13] configurational relationships are as indicated in Scheme I.

As shown in Scheme I, when equilibration of the rotamers of **6** is slow relative to product formation, original double-bond configuration is preserved. The two rotamers shown in the scheme are those in which the carbon–copper bond is perpendicular to the plane of the double bond. One of these, *t*-**6**, is related to the anti π-allyl complex (*anti*-**7**) and trans product ((*E*)-**3**) and the other, *c*-**6**, to the syn π-allyl complex (*syn*-**7**) and cis product ((*Z*)-**3**). If the *t*-**6** ⇄ *c*-**6** equilibration is rapid relative to product formation, the double-bond configuration is lost and if equilibration is complete, *cis*- and *trans*-**2**-OAc give the same mixture of α-alkylation products.

It should be noted that the fluxional behavior proposed for the (π-allyl)copper(III) complex **7** parallels that observed with more stable π-allyl complexes of transition metals.[14] The most widely accepted mechanism for syn–anti isomerization involves π-allyl to σ-allyl interconversion and bond rotation as shown in Scheme I.

The data under eq 3 show that for reaction of *cis*-**2**-OAc bond rotation in **6** competes with product formation at 0 °C and equilibration of rotamers is complete at −78 °C. This shows that the temperature-dependent activation barrier is larger for conversion of *c*-**6** to product (preservation of geometry) than for bond rotation. The data also show that the barrier for conversion of *t*-**6** to (*E*)-**3** is lower than for conversion of *c*-**6** to (*Z*)-**3**. Thus under conditions where bond rotation in **6** is fast relative to product formation, (*E*)-**3** is the α-alkylation product derived from *cis*-**2**-OAc. This also results in preservation of double-bond geometry for alkylation of *trans*-**2**-OAc.

The partial retention of double-bond configuration for alkylation of *cis*-**2**-OAc at 0 °C suggests that double-bond configuration will be preserved if there is less driving force for isomerization or a higher rotational barrier for the initial S_N2' σ-allyl complex than in the cinnamyl system. Thus the present results are consistent with the earlier observation that double-bond configuration is preserved for alkylation of *E* and *Z* allylic acetates in the geranyl–neryl system.[6] This system involves a trisubstituted double bond and thus there is a high rotational barrier in the σ-allyl complex and little, if any, driving force for isomerization. The earlier report of loss of double bond configuration for alkylation of *E* and *Z* allylic ethers is also now understandable.[9] This system is similar to the present one in that the double bond is disubstituted and both isomers give the same α-alkylation product consisting primarily of the more stable *E* isomer.

Experimental Section

Materials. *trans*-Cinnamyl acetate (*trans*-**2**-OAc), bp 137–139 °C (10 mm), was prepared from freshly distilled *trans*-cinnamyl alcohol (Aldrich) and acetic anhydride. The 270-MHz NMR spectrum showed no signals due to *cis*-**2**-OAc. The distinguishing features of the NMR spectra for the isomers involve the α and β protons. For *cis*-**2**-OAc these signals are centered at δ 4.84 and 5.8, whereas for *trans*-**2**-OAc these signals appear at δ 4.72 and 6.28.

cis-Cinnamyl acetate (*cis*-**2**-OAc), bp 116 °C (6.5 mm), was prepared from acetic anhydride and *cis*-cinnamyl alcohol. The alcohol, bp 103 °C (3 mm), was prepared by atmospheric hydrogenation of 1-phenyl-1-propyn-3-ol[15] in dry pyridine over 5% $Pd/BaSO_4$. The 270-MHz NMR spectrum showed no signals due to *trans*-**2**-OAc. The isomeric purity (>99%) of the starting materials was demonstrated by NMR studies. For example, in the spectrum of *cis*-**2**-OAc with 1% added *trans*-**2**-OAc, signals due to the trans isomer are plainly visible at δ 6.28 and 4.72. The intensity is such that a signal half that strength would still be seen. Hence, if *cis*-**2**-OAc were contaminated with 1% *trans*-**2**-OAc, the latter would be visible in the NMR spectrum.

Alkylation Products. Authentic samples of *cis*- and *trans*-1-phenyl-1-butene (**3**) were obtained as a binary mixture (28:72) from the Wittig reaction[16] of propionaldehyde and benzyltriphenylphosphonium chloride. Samples of the isomers were

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(16) Wittig, G.; Schoelkopf, U. "Organic Syntheses"; Wiley: New York, 1973; Collect. Vol. V, p 751.

separated by preparative GC (10 ft × $^3/_8$ in. column, 15% UCON 50-HB-2000 on Chromosorb P) and identified by their IR and NMR spectra.[17]

3-Phenyl-1-butene (4) was prepared by the Wittig reaction[16] of 2-phenylpropionaldehyde[18] and methyltriphenylphosphonium iodide and purified by preparative GC (10 ft × $^3/_8$ in. column, 15% UCON 50-HB-2000 on Chromosorb P). The NMR spectrum is in agreement with the published values.[19]

The preparation and purification of other reagents and solvents and the standardization of MeLi have been described earlier.[5]

Alkylation of *cis*- and *trans*-Cinnamyl Acetate (2-OAc) with $LiCuMe_2$. In a typical procedure 1.91 g (10 mmol) of CuI was placed in an oven-dried 100-mL round-bottom flask equipped with a magnetic stirrer. The flask was flushed with nitrogen and capped with a septum. Twenty milliliters of dry ether was introduced and the stirred suspension cooled to 0 °C after which 18.5 mL of 1.08 M MeLi was added and the resulting mixture stirred 10 min (0 °C) to obtain homogeneity. A solution of 0.88 g (5 mmol) of *cis*-2-OAc in 10 mL of dry ether was rapidly added and the mixture stirred 105 min at 0 °C under a positive pressure of dry nitrogen. The reaction was quenched with 10 mL of saturated aqueous NH_4Cl and filtered (washing the precipitate well with ether), and the organic layer was dried ($MgSO_4$). After careful concentration by fractional distillation, the product distribution was determined by capillary GC (94-ft column, UCON LB-550-X). Reaction of *trans*-2-OAc was done in a similar fashion. For reaction of *cis*-2-OAc at −78 °C the $LiCuMe_2$ solution was cooled to −78 °C after attaining homogeneity and a prechilled solution of acetate was added. The reaction mixture was stirred 2 h at −78 °C and then gradually warmed over another 30 min. Reactions with excess acetate were performed the same way, using only 2 mmol of $LiCuMe_2$ for 3 mmol of 2-OAc.

Alkylation of *cis*-Cinnamyl Alcohol with MeLi by the Murahashi Method. To a stirred suspension of 0.76 g (4 mmol) of CuI in 10 mL of dry THF was added a solution of 4 mmol of alkoxide (prepared at 0 °C by adding 3.4 mL of 1.19 M MeLi to 0.54 g (4 mmol) of *cis*-cinnamyl alcohol). The reaction mixture was stirred 30 min at room temperature and cooled to −78 °C, after which 10 mL of 1.19 M MeLi was added. After being stirred 4 min, a solution of 1.75 g (4 mmol) of (methylphenylamino)-triphenylphosphonium iodide[5] in 20 mL of dry DMF was added dropwise over 15 min. The solution was stirred 1 h at −78 °C, warmed to room temperature, and stirred 3 more h. The reaction was quenched by addition of 10 mL of saturated aqueous NH_4Cl and filtered, and the aqueous layer was extracted with pentane (25 mL). The combined organic layers were washed with 5% HCl (10 mL), saturated aqueous $NaHCO_3$ (10 mL), and brine (10 mL), dried ($MgSO_4$), and carefully concentrated by fractional distillation. The product distribution was determined by capillary GC (94-ft column, UCON LB-550-X).

Acknowledgment. This work was supported by the National Science Foudation (Grant CHE 8108535).

Registry No. *cis*-2-OAc, 77134-01-1; *trans*-2-OAc, 21040-45-9; $LiCuMe_2$, 15681-48-8; *cis*-cinnamyl alcohol, 4510-34-3; 1-phenyl-1-propyn-3-ol, 1504-58-1.

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Acetyl Hypofluorite, a New Moderating Carrier of Elemental Flourine and Its Use in Fluorination of 1,3-Dicarbonyl Derivatives

Ori Lerman and Shlomo Rozen*

Department of Chemistry, Tel Aviv University, Tel Aviv 69978, Israel

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Elemental fluorine and most of the fluoroxy reagents do not react efficiently or cleanly with 1,3-dicarbonyl derivatives or with their corresponding metal enolates even at −75 °C. It has been found that a suspension of sodium acetate in $CFCl_3$ or in $CFCl_3$–AcOH, when treated with elemental fluorine, forms a new electrophilic fluorinating reagent, CH_3COOF (1), which reacts with substrates without further isolation or purification. This reagent is milder than F_2, CF_3OF, or CF_3COOF and reacts successfully where the other reagents fail. When 1 reacts with 1,3-dicarbonyl compounds, the main product is the 1,3-dioxo-2-fluoro derivative in reasonable yields. When, however, the corresponding sodium enolates were treated with 1, the yields of the monofluoro derivatives were considerably higher. In the case of 1,3-dicarbonyl derivatives with low enol content, only the sodium enolates react with 1 to produce good to very good yields of the corresponding 2-monofluoro derivatives. Thus 1 can be considered as a moderating carrier of the highly reactive F_2.

Very few works have been published in the last decade dealing with perchloryl fluoride ($FClO_3$). The main reasons are its treacherous nature[1] and the introduction of alternative electrophilic fluorinating agents that are more potent, efficient, and easy to handle such as CF_3OF,[2] CF_3CF_2OF and CF_3COOF,[3] F_2,[4] and XeF_2.[5] These reagents, with the exception of elemental fluorine, were also used successfully for synthesis of α-fluoro ketones from the corresponding enol ethers,[2] enol acetates,[2,6,7] or silylenol ethers.[8] Direct fluorination of ketones by F_2 has also been tried, but success was limited to a few pyruvic acid derivatives.[9]

While there are reports of perchloryl fluoride reacting with certain metal enolates of 1,3-dicarbonyl compounds to produce fluorocarbonyl derivatives, no such reactions have been reported with the new generation of the above electrophilic fluorinating agents.[10] It seems to us that the

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