trans-6,7-epoxy-2-methylheptadecane, 52260-04-5; *cis*-7,8-epoxy-2-methyloctadecane, 29804-22-6; *trans*-7,8-epoxy-2-methyloctadecane, 42991-03-7; vinyldimethylethoxysilane, 5356-83-2; isopropyl chloride, 75-29-6; tetramethylbis[1-(3-methyl-1-(*E*)-butenyl)]disiloxane, 52260-05-6.

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Notes

Products and Rates of Reaction of Trifluoroacetic Anhydride with Aldehydes. A Nuclear Magnetic Resonance Study

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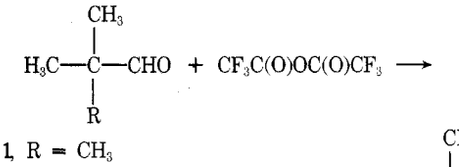
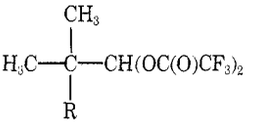
The reaction of carboxylic acid anhydrides with carbonyl compounds has been known since the beginning of this century.[1] These reactions appear to involve initial formation of a *gem*-bisester, $RC[OC(O)R']_2$, but may proceed to form other compounds, including enol esters.[2] While studies[3] have appeared on the synthetic aspects of this reaction, comparatively little has been done to elucidate the mechanism(s) of these reactions. The most extensive study to date appears to be that of Mazur and coworkers[4] on the reaction of ketones with trichloroacetic anhydride.

The broad application of trifluoroacetic anhydride (TFAA) to synthetic organic chemistry,[5] the greater reactivity of TFAA compared to trichloroacetic anhydride, TCAA, and the suitability of TFAA as an nmr solvent have prompted our investigation into the reaction(s) of TFAA with carbonyl compounds.[6] This report deals with the reaction of nonenolizable aliphatic and aromatic carboxaldehydes with TFAA.

Aliphatic Carboxaldehydes. Nonenolizable aliphatic carboxaldehydes were selected for study because they could not readily lose trifluoroacetic acid and would, therefore, lead to stable adducts.[7] The aldehydes selected for examination were 2,2-dimethylpropanol (pivalaldehyde, **1**), 2-methyl-2-phenylpropanal (**2**), and 2-methyl-2-*p*-methoxyphenylpropanal (**3**). These aldehydes reacted with excess TFAA to yield the anticipated 1,1-bis(trifluoroacetoxy)-2,2-dimethylpropane (**4**), 1,1-bis(trifluoroacetoxy)-2-methyl-2-phenylpropane (**5**), and 1,1-bis(trifluoroacetoxy)-2,2-dimethylpropane (**4**), 1,1-bis(trifluoroacetoxy)-tively. No other products could be detected by nmr; these products appear to be stable indefinitely in TFAA at 25°.



1, R = CH_3
2, R = C_6H_5
3, R = *p*-$CH_3OC_6H_4$



4, R = CH_3
5, R = C_6H_5
6, R = *p*-$CH_3OC_6H_4$

The rate of adduct formation was followed by integration of both the decreasing carboxaldehyde resonance and the new methine resonance in the product. The reaction exhibited pseudo-first-order behavior. The half-lives, $t_{1/2}$, for the reactions are similar but suggest some steric hindrance to adduct formation in going *from* **1** *to* **2** and **3** ($t^1_{1/2}$ = 20 min, $t^2_{1/2}$ = 125 min, $t^3_{1/2}$ = 130 min).[8]

The pmr spectra of these adducts are included in Table I. It is noteworthy that adduction "shifts" the aldehydic resonance upfield by *ca.* 2 ppm, since this, when necessary, can serve as a useful diagnostic tool for the presence of the carboxaldehyde group.

Aromatic Carboxaldehydes. Benzaldehydes, like the nonenolizable aliphatic carboxaldehydes, react with TFAA to produce *gem*-bis(trifluoroacetates). Again, these esters

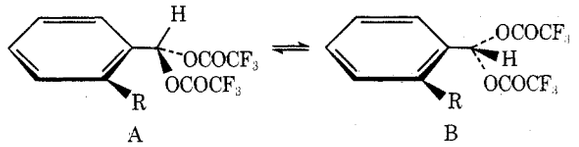
Table I
Proton Chemical Shifts for *gem*-Bis(trifluoroacetates)[a]

R = $(CF_3CO_2)_2CH$– R′ = $(CF_3CO_2)_2CHC(CH_3)_2$–

Compd	Registry no.	X	Chemical shifts				
			$(CF_3CO_2)_2CH$-[b]	C-2,6H[c]	C-3,5H[c,d]	Others	
1-R-4-X-Benzenes	52195-50-3	H	7.82	7.35–7.65			
	52195-51-4	F	7.87	7.66	7.16		
	52195-52-5	Cl	7.83	7.58	7.43		
		Cl[e]	7.80	7.52	7.46		
	52195-53-6	Br	7.82	7.51	7.61		
	52195-54-7	CN[f]	7.97	7.80	7.80		
	52195-55-8	NO_2	7.96	7.88	8.36		
	52195-56-9	OCH_3	7.80	7.53	6.94	OCH_3	3.71
	52217-40-0	CH_3	7.79	7.48	7.25	CH_3	2.33
	52195-57-0	$N(CH_3)_2$	7.72	7.43	6.75	$N(CH_3)_2$	2.92
			$(CF_3CO_2)_2CH$–	C-2,4,5,6 H			
1-R-3-X-Benzenes	52195-58-1	OCH_3	7.80	6.90–7.35		OCH_3	3.80
	52195-59-2	CH_3	7.75	7.21–7.45		CH_3	2.31
	52195-60-5	NO_2	8.01	7.70–8.60			
			$(CF_3CO_2)_2CH$–	C-3,4,5,6 H			
1-R-2-X-Benzenes	52195-61-6	OCH_3	8.25	6.95–7.60		OCH_3	3.88
	52195-62-7	CH_3	8.02	7.10–7.65		CH_3	2.60
			$(CF_3CO_2)_2CH$–	C-3,5 H	C-2,6 CH_3	C-4 CH_3	
1-R-2,4,6-X-Benzene	52195-63-8	CH_3	8.29	6.87	2.55	2.24	
			$(CF_3CO_2)_2CH$–				
1-R-2,3,4,5,6-X-Benzene	52195-64-9	F	8.13				
			$(CF_3CO_2)_2CH$–	C-10 H	C-1,8 H	C-2,7 H	C-3,6 H	C-4,5 H
9-R-Anthracene	52195-65-0	F	9.40	8.21	8.54	7.50	7.30	7.72
			$(CF_3CO_2)_2CH$–	C-2,6 H	C-3,5 H			
1-R′-4-X-Benzenes	52195-66-1	H	7.08	7.15–7.50		R′CH_3	1.55
	52195-67-2	OCH_3[c]	7.02	7.36	6.86	R′CH_3	1.53
						OCH_3	3.68
			$(CF_3CO_2)_2CH$–			Others	
R-X	52195-68-3	CH_3	7.13 q (J = 5.5 Hz)		CH_3	1.74	
	52195-69-4	C_2H_5	6.97 t (J = 5.5 Hz)		CH_3	1.11	$-CH_2-$ 2.08
	52195-70-7	$C(CH_3)_3$	6.76 s		CH_3	1.12	

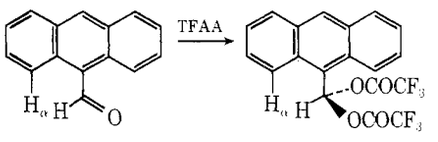
[a] All chemical shifts are reported in parts per million (δ) downfield from internal tetramethylsilane. [b] The methine proton, $(CF_3CO_2)_2CH$–, is a singlet except where indicated. [c] The aromatic chemical shifts in the *para*-substituted compounds were estimated by analyzing the spectrum as a two-spin AB system. [d] Verification of the aromatic assignments was obtained by plotting the C-3,5 H chemical shifts *vs.* the semiempirical parameter, Q, as shown by W. B. Smith and J. L. Roark, *J. Amer. Chem. Soc.*, 89, 5018 (1967). [e] These chemical shifts were taken from the isolated compound in $CDCl_3$. [f] The reaction between 4-cyanobenzaldehyde and TFAA is complex and will be discussed in a future communication.

exhibit the benzylic methine resonance, Ar**C**H[O-C(O)CF_3]$_2$, *ca.* 2 ppm upfield from the resonance of the corresponding aldehyde (Table I). Although the chemical shift of the benzylic methine proton is not readily correlated with the electronic nature of the ring, it is at lower field when a given substituent is ortho to the carboxaldehyde group than when it is para or meta. For example, this resonance occurs at δ 7.79 for the *p*-tolualdehyde adduct but at δ 8.02 for the *o*-tolualdehyde adduct. This suggests a conformational change which places that proton, on the average, closer to the aromatic plane in the ortho-substituted benzaldehyde (B favored at the expense of A, below). Such an alteration should reduce the repulsion between the ortho substituent and the trifluoroacetoxy groups.



A B

When 9-anthraldehyde is dissolved in trifluoroacetic anhydride it rapidly forms the corresponding bis(trifluoroacetate) (7). The pmr spectrum of this adduct contains a



7

methine resonance at δ 9.4. This resonance undergoes an 18% nuclear Overhauser enhancement[9] when the aryl protons adjacent to it (C-H_α) are irradiated. Observation of the NOE suggests an average conformation for the adduct which is similar to that of the parent aldehyde[10] and which possesses its "benzylic" hydrogen close to, or in, the aryl plane. Furthermore, these results are consistent with the ortho effect noted above.

The rate of reaction of aryl carboxaldehydes, studied by pmr, followed pseudo-first-order kinetics. While some compounds (*e.g.*, *p*-$CH_3OC_6H_4CHO$) reacted too rapidly for accurate kinetic study, the logarithm of the observed half-lives (Table II) produced a straight line when plotted against the σ constant for the substituent but not when plotted against σ^+. The ρ value for the reaction was found to be −2.5.[11]

While the *gem*-bis(trichloroacetates) are reported[4] to be comparatively stable and capable of purification by distil-

Table II
Reactivity of Aldehydes with Trifluoroacetic Anhydride[a,b]

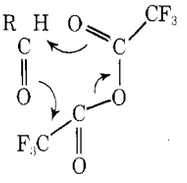
Compd	$t_{1/2}$ (32°), min	Registry no.
p-Anisaldehyde	<1	123-11-5
o-Anisaldehyde	<1	135-02-4
p-Dimethylaminobenzaldehyde	<1[c]	100-10-7
p-Tolualdehyde	9	104-87-0
o-Tolualdehyde	10	529-20-4
m-Tolualdehyde	17	620-23-5
Benzaldehyde	34	100-52-7
p-Fluorobenzaldehyde	35	459-57-4
m-Anisaldehyde	41	591-31-1
p-Chlorobenzaldehyde	70	104-88-1
p-Bromobenzaldehyde	84	1122-91-4
m-Nitrobenzaldehyde	800	99-61-6
p-Nitrobenzaldehyde	1970	555-16-8
Pentafluorobenzaldehyde	~7 days	653-37-2

[a] In each instance the product was identified as the bis(trifluoracetate) by proton and fluorine magnetic resonance spectroscopy. [b] Registry no., 407-25-0. [c] Amide formation prevented use of the isomeric aminobenzaldehydes.

lation, *gem*-bis(trifluoroacetates) are easily converted to carbonyl compounds and TFAA. Thus, attempts at removal of TFAA from solutions of these esters in TFAA by distillation (bp 40°) normally afforded only starting aldehyde. However, diesters could be isolated by removing the excess of TFAA at reduced temperature (below 0°) and pressure. For example, α,α-bis(trifluoroacetoxy)-*p*-chlorotoluene could be separated from TFAA and dissolved in deuteriochloroform to afford an nmr spectrum consistent with the assigned structure (Table I).

Mechanism. There are two mechanisms which could account for *gem*-bisester formation. One (A, below) involves a

$$RCHO + [CF_3C(O)]_2O \longrightarrow [R^+CHOC(O)CF_3CF_3CO_2^-] \longrightarrow RCH[OC(O)CF_3]_2 \quad (A)$$



$$\rightleftharpoons RCH(OCOCF_3)_2 \quad (B)$$

nucleophilic attack by the carbonyl group upon TFAA to form a carbocation and a trifluoroacetate anion. While not discussed by Mazur[4] in their study of TCAA, this could not be ruled out, *a priori*, for reactions of TFAA because trifluoroacetate is a better leaving group than is trichloroacetate. However, the absence of rearrangement during the reaction of **1**, **2**, *and* **3** and the virtually identical rates of reaction of **2** and **3** would appear to rule this mechanism out. One might have imagined that even a moderate increase in positive charge at the carbonyl carbon would have resulted in participation by the *p*-methoxyphenyl group in **3**. Furthermore, if a free carbocation were involved one would have anticipated that the rate of reaction of substituted benzaldehydes would have followed σ^+ rather than σ.

These data argue in favor of a fairly concerted addition, one which may be viewed as a cycloaddition reaction of TFAA across the carbonyl group (B).

Experimental Section

Instruments and Techniques. Spectra were recorded on a Varian HA-100 spectrometer. The nuclear Overhauser enhancement experiments were performed using a Hewlett-Packard 200CD oscillator. The per cent enhancement was determined by comparing the intensity of the enhanced spectra to the intensity of the spectrum during off-resonance irradiation. An average of ten values was used to calculate the NOE.

All samples were prepared in an excess of TFAA (*ca.* 10:1 v/w). Trifluoroacetic anhydride and tetramethylsilane were vacuum distilled from calcium hydride into the nmr tube containing the sample. The tubes were then sealed under vacuum. Progress of the reaction was followed by integrating the aldehydic and the adduct proton resonances at appropriate intervals. The initiation time, t_0, was obtained by extrapolating the linear plot (per cent reaction *vs.* time) back to 0% reaction. The half-life, $t_{1/2}$, was taken from the plot at the point where the reaction was 50% complete. Reactions were normally followed through 3 half-lives.

Syntheses. Most of the aldehydes were available commercially and were purified by recrystallization or distillation. Solid samples were dried *in vacuo* over phosphorus pentoxide; liquids were dried over calcium hydride. All commercial samples were homogeneous (nmr) after such treatment.

2-*p*-Methoxyphenyl-2-methylpropanal. The procedure of Kuntzel, Wolf, and Schaffner[12] was used to prepare 2-*p*-methoxyphenyl-2-methylpropanoic acid in 44% yield. (The work-up was altered slightly by refluxing the crude product in 10% sodium hydroxide to saponify residual ester.)

A solution of 12.2 g (0.0628 mol) of 2-*p*-methoxyphenyl-2-methylpropanoic acid in 20 ml of thionyl chloride was refluxed for 20 min. After removal of volatiles, vacuum distillation afforded 11.1 g (0.0515 mol) of 2-*p*-methoxyphenyl-2-methylpropanoyl chloride, bp 125–135° (0.1 Torr). Reduction of the acid chloride was accomplished by slowly adding a cooled (0°) solution of 12.5 g of lithium aluminum tri-*tert*-butoxyhydride in 40 ml of tetrahydrofuran to 11.0 g of acid chloride dissolved in 120 ml of cold (−68°) tetrahydrofuran. After addition was completed, the reaction mixture was allowed to warm to 10°. The desired product was isolated by pouring the reaction mixture over an equal volume of ice, acidifying with 50 ml of dilute hydrochloric acid, and extracting with methylene chloride (2 × 100 ml). Drying of the extract, followed by removal of solvent, afforded 7.9 ml of yellow oil shown (nmr) to be 70% aldehyde and 30% alcohol. Distillation yielded 4.9 g (0.0275 mol, 53% yield) of 2-*p*-methoxyphenyl-2-methylpropanal, bp 90–95° (0.1 Torr) [lit.[12] bp 143–148° (10 Torr)].

2-Phenyl-2-methylpropanal. The preparation of 2-phenyl-2-methylpropanal was similar to that used to prepare 2-*p*-methoxyphenyl-2-methylpropanal. The desired product was obtained in about 50% yield, based upon the acyl halide, bp 92–96° (0.2 Torr) [lit.[12] bp 105–120° (10 Torr)].

Acknowledgment. We are grateful to the Robert A. Welch Foundation for the support of this research through Grant Y-484 (including a postdoctoral fellowship for Dennis Deavenport). The nmr spectrometer used in this research was purchased with the aid of a grant from the Research Corporation.

Registry No.—**2**, 3805-10-5; **3**, 32454-14-1; 2-*p*-methoxyphenyl-2-methylpropanoic acid, 2955-46-6; 2-*p*-methoxyphenyl-2-methylpropanoyl chloride, 40919-14-0; 2-phenyl-2-methylpropanoyl chloride, 36293-05-7.

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(7) Aldehydes possessing α hydrogens react as do these compounds but the first-formed bisesters may undergo loss of trifluoroacetic acid to enol esters. Under proper conditions these may react further (unpublished results). See also ref 4, and references cited therein.
(8) Pivaladehyde reacts at a rate comparable to that of propanal ($t_{1/2}$ = 11 min), suggesting that, in general, the reaction of aldehydes with acid anhydrides is not subject to *severe* steric requirements.

(9) Related NOE's have been observed for 9,10-dihydroanthracene and thioxanthene derivatives: A. W. Brinkmann, M. Grodon, R. G. Harvey, P. W. Rabideau, J. B. Stothers, and A. L. Ternay, Jr., *J. Amer. Chem. Soc.*, **92**, 5912 (1970); A. L. Ternay, Jr., and S. A. Evans, *J. Org. Chem.*, in press.
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(11) In his study of the reaction of ketones with TCAA, Mazur[3] noted that added trichloroacetic acid (20%) diminished the reaction rate, suggesting that ". . . the carbonyl in its protonated form does not react with anhydride." We have noted, by way of contrast, that the addition of trifluoroacetic acid (as much as 20%) to solutions of aldehydes in TFAA does not appear to have a significant effect upon the rate of adduct formation. For example, $t_{1/2}$ (32°) for *m*-anisaldehyde in TFAA and in 90% TFAA–10% TFA are within experimental error of one another (41 ± 1 min).
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Phase Transfer Catalysis. The Acetoacetic Ester Condensation

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Great interest has developed in recent years in phase transfer processes, especially liquid–liquid phase transfer.[1,2] The elegant paper of Starks[1] on the usefulness of several liquid–liquid phase transfer catalysts gives several examples of how the process may be used as a routine synthetic tool. We have extended this work to a solid–liquid phase transfer process using the acetoacetic ester condensation as a representative example of this principle.

The catalyst used in this study was a long-chained aliphatic quaternary ammonium salt, "Alaquat 336,"[1,3] which consists of mixed trialkylmethylammonium chlorides (average molecular weight 503[1]). It is insoluble in water and soluble in all common organic solvents. The basic process was to generate a solid reactive anion which is normally insoluble in organic solvents, use the phase transfer catalyst to transport this anion into the organic phase, then allow this anion to react in the organic phase. The reactive anion generated in this study was the methyl acetoacetate anion. Once dissolved by the phase transfer catalyst in the organic solvent, this anion reacted with an alkylating agent to give the traditional acetoacetic ester alkylated product.

There have been numerous studies[4,5] directed at the alkylation pattern of ambident ions in both protic solvents (usually alcohols) and polar aprotic solvents. The major difference in these two systems seems to be that carbon alkylation is favored in protic solvents while O-alkylation is favored in polar aprotic solvents [especially in hexamethylphosphoramide[4a] (HMPA)]. In our study it was found that alkylation of the acetoacetate anion in benzene using benzyl chloride as the alkylation reagent gave predominantly (>99%) carbon alkylation with no detectable oxygen alkylation.[6] Thus, this process offers a reversal of the usually observed results in aprotic solvents in that carbon alkylation is favored, thereby giving an alternative to the usual procedure of using protic solvents to favor carbon alkylation. It also offers the advantage that no solvolysis products arising from alkylating reagent–solvent interactions are possible, thus eliminating a major side product of reactions run in protic solvents. This advantage is especially important when small amounts of valuable alkylating reagents are required, such as geranyl bromide.

The experimental conditions using this solid–liquid phase transfer process are exceedingly simple. The concentration of catalyst has an effect on the rate of reaction.

Table I
Catalyst Concentration Using Benzyl Chloride as the Alkylating Reagent

Ratio[a,b]	Yield,[c,d] %
No catalyst	25
25:1	61
20:1	70
10:1	85

[a] Standard conditions consist of benzene as solvent; 8-hr reflux; sodium methyl acetoacetate/benzyl chloride ratio 2:1; the reaction was protected from moisture during the reaction. [b] Molar ratio of catalyst to alkylating agent. Catalyst av mol wt 503. [c] Isolated yields by distillation. [d] Gc analysis shows only one peak >99% purity by integration.

Table II
Solvent Effects on Alkylation Yields

Solvent[a]	Yield,[b] %
Benzene	85
Toluene	82
Chloroform	56
Carbon tetrachloride	42
Hexane	40

[a] Standard conditions: 8-hr reflux, sodium methyl acetoacetate/benzyl chloride/catalyst ratio 20:10:1. [b] Isolated monoalkylated yields by distillation.

Table III
Alkylation Products

Alkylating agent[a]	Product,[b,c] %
Allyl bromide	85
Benzyl chloride	85
Geranyl bromide	85
Dimethylallyl chloride	37
Allyl chloride	30

[a] Standard conditions: 8-hr reflux, benzene solvent; sodium methyl acetoacetate/alkylating agent/catalyst ratio 20:10:1. [b] Product isolated by distillation. [c] Only monocarbon alkylation observed.

Using benzene as a solvent and 8-hr reflux as a standard condition, we found that a 10:1 alkylating reagent/catalyst molar ratio gave consistently high yields. All reactions with catalyst were accelerated over control experiments without catalyst. These results are tabulated in Table I. We also found that benzene was not the only solvent one could use. In effect, all commonly used solvents ranging from benzene to hexane may be used. These results are tabulated in Table II. One might note that in hexane the monocarbon alkylated product was obtained in 40% yield. The alkylation in hexane, without added catalyst, gave essentially no alkylation product (<5%). The reaction using different alkylating reagents is shown in Table III.

It is interesting to speculate on the anion species in solution. The initial transfer would give a quaternary ammonium methyl acetoacetate species which is soluble in nonpolar solvents because of the large hydrophobic properties and symmetry of the transfer reagent.[7] In our system, we looked for not only oxygen alkylation but dialkylation, both carbon–carbon and carbon–oxygen. Again we found very little, if any, of either product.[4,6] In the studies of alkylation in aprotic solvents two factors seem to control the alkylation pattern, that of the nature of the alkylating reagent and the tightness of the generated ion pair. The latter[4] seems to be most important in the control of these reactions. For example, in solvents like HMPA very loose ion pairs are formed, thus favoring the formation of O-al-