Table I

	MLB × 10^6	1/MLB	maximum yield of DNA, %	charge passed in 2 h in C	maximum current efficiency, %
B[*a*]P control	149	6.71×10^3	100.0		
B[*a*]P electrolysis	3031	3.30×10^2	40.6	51.2	3.5[a]
6-MeB[*a*]P electrolysis	1584	6.31×10^2	9.4	28.3	2.2[b]
DNA electrolysis			0.9	79.3	
I_2 activation[c]	9	1.09×10^5			

[a] Based on a 6-electron process according to ref 7. [b] Based on a 2-electron process according to ref 6. [c] This sample was washed with distilled phenol according to ref 11.

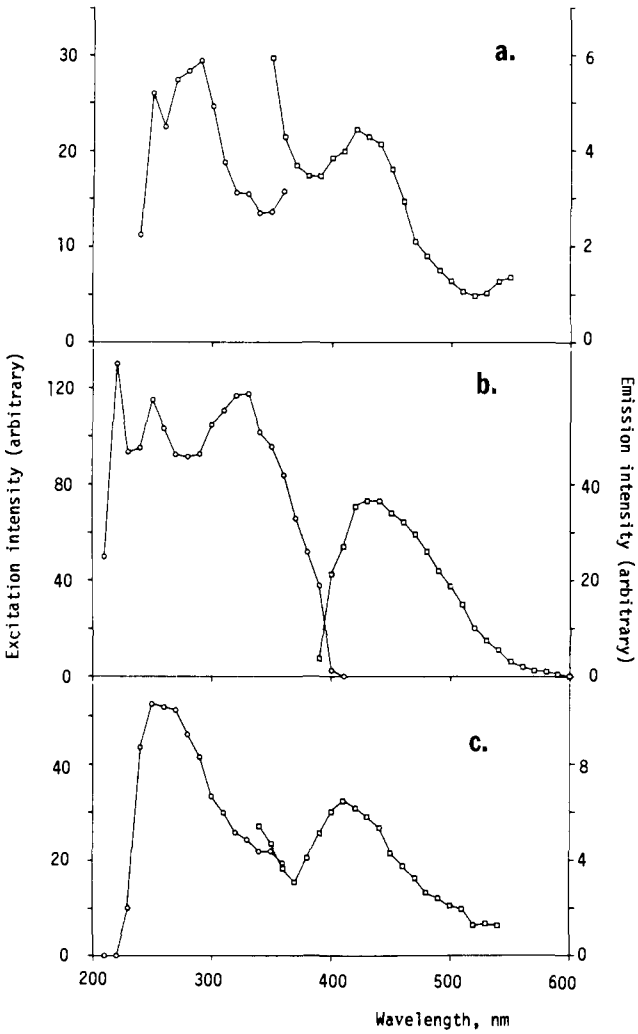

Figure 1. Corrected fluorescence excitation and emission spectra for DNA in 50% ethanol solutions which are initially 0.3 mM heat-denatured DNA, 0.005 M phosphate buffer, 0.015 M TBAP, and 0.1 mM hydrocarbon. (a) B[*a*]P stirred with DNA for 2 h; (b) B[*a*]P electrolyzed at +1.15 V vs. Ag reference for 2 h; (c) 6-MeB[*a*]P electrolyzed at +1.03 V vs. Ag reference for 2 h. The emission spectra were excited at 300, 360, and 300 nm for (a), (b), and (c), respectively, while the excitation spectra were monitored at 410, 425, and 410 nm, respectively.

replenished B[*a*]P several times during the course of the reaction. Also, differences in washing procedures, low quantum yield, or the presence of TBAP could account for this difference. In any case, it seems that electrochemically activated binding is also more efficient than I_2-activated binding by about 2 orders of magnitude.

Another aspect of these experiments is the nature of the electrolytic process. As seen in Table I, the maximum current efficiencies (assuming total consumption of hydrocarbon) are extremely low. The bulk of the current seems to be channeled into another process, possibly oxidation of ethanol and/or DNA. The detailed mechanism for these processes are being studied.

It is highly unexpected that the total charge passed should be actually less with hydrocarbon than with an electrolysis experiment in which hydrocarbon was absent. This result is also supported by cyclic voltammograms in which the anodic current is suppressed upon addition of B[*a*]P. This suppression could be accounted for by the tendency of B[*a*]P and B[*a*]P cation radical to adsorb onto Pt.[7]

The fact that the recovery of DNA was the highest with B[*a*]P electrolysis points toward an unexplained process in which the destruction of DNA, possibly by reactive products of ethanol oxidation or by the electrode itself, is decelerated by this adsorption. One reason for the difference is protective ability of B[*a*]P and 6-MeB[*a*]P could be that B[*a*]P, with its demonstrated tendency to catalytically regenerate itself during oxidation,[7,11] together with the greater number of electrons required for its consumption, remains in solution for a longer time and can exert its protective effect longer.

One could draw a final conclusion in the light of this argument about the relative MLB values of B[*a*]P and 6-MeB[*a*]P. Since they are of the same order of magnitude and since we would expect that B[*a*]P would have much more opportunity to form cation radicals, 6-MeB[*a*]P binding may not result from a cation radical but rather from the more stable benzylic carbonium ion. The carbonium ion would form as a result of loss of a proton and an electron from the cation radical and has been postulated as a reactive intermediate in the reaction of 7-methylbenz[*a*]anthracene cation radical with pyridine.[12,13]

(11) Park, S.-M.; Michnovicz, J. J.; Daub, G. H. *Anal. Biochem.* **1978**, *90*, 374-388.
(12) Cavalier, E.; Roth, R. *J. Org. Chem.* **1976**, *41*, 2679-2684.
(13) Lorentzen, R. J.; Ts'o, P. O. P. *Biochemistry* **1977**, *16*, 1467-1473.

Acyl-Transfer Reactions in the Gas Phase. The Question of Tetrahedral Intermediates

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Esterification and hydrolysis reactions of carboxylic acids and derivatives commonly proceed by mechanisms in which an acyl group is transferred to the attacking nucleophile by way of tetrahedral intermediates. Evidence supporting addition–elimination mechanisms refers almost entirely to solution-phase reactions catalyzed by acids, bases, or enzymes.[1] Although related gas-phase reactions have been observed in the ion–molecule chemistry of acyl compounds by using ion cyclotron resonance (ICR) techniques,[2-4] certain features of these reactions are inconsistent

(1) For a review, see E. K. Euranto in "The Chemistry of Carboxylic Acids and Esters", S. Patai, Ed., Interscience, New York, 1969, Chapter 11.
(2) For a review, see N. M. M. Nibberring, *NATO Adv. Study Inst. Ser., Ser. B*, **40** 165-197 (1979).

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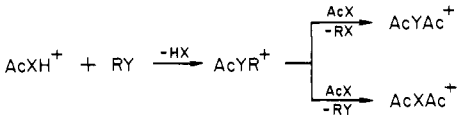
Table I. Summary of Gas-Phase Acylation Reactions



reactant ion[a] $AcXH^+$ (m/z)	neutral RY or AcX	product ions[b] $AcYR^+$ (m/z)	$AcYAc^+$ (m/z)	$AcXAc^+$ (m/z)
$AcOH_2^+$ (61)	CH_3OH[d]	$(AcOCH_3)H^+$ (75)[c]		
	CH_3SH[d]	$(AcSCH_3)H^+$ (91)[c]		
	$(CH_3)_2O$	$AcO(CH_3)_2^+$ (89)[e]		
	$(CH_3)_2S$	$AcS(CH_3)_2^+$ (105)[f]		
	AcOH			$(AcOH)Ac^+$ (103)
$AcSH_2^+$ (77)	CH_3OH	$(AcOCH_3)H^+$ (75)[c]		
	CH_3SH	$(AcSCH_3)H^+$ (91)[c]		
	$(CH_3)_2O$	$AcO(CH_3)_2^+$ (89)[e]		
	$(CH_3)_2S$	$AcS(CH_3)_2^+$ (105)		
	AcSH			$(AcSH)Ac^+$ (119)
$(AcOCH{=}CH_2)H^+$ (87)	CH_3OH[g,d]	$(AcOCH_3)H^+$ (75)	$(AcOCH_3)Ac^+$ (117)	
	CH_3SH[d]	$(AcSCH_3)H^+$ (91)	$(AcSCH_3)Ac^+$ (133)	
	$(CH_3)_2O$	$AcO(CH_3)_2^+$ (89)		$(AcOCH{=}CH_2)Ac^+$ (129)
	$(CH_3)_2S$	$AcS(CH_3)_2^+$ (105)		
	$CD_3OC_2H_5$	$AcOC_3H_5D_3^+$ (106)		
	$AcOCH{=}CH_2$			$AcOCH{=}CH_2)Ac^+$ (129)
$(AcOC(CH_3){=}CH_2)H^+$ (101)	CH_3OH	$(AcOCH_3)H^+$ (75)	$(AcOCH_3)Ac^+$ (117)	
	CH_3SH	$(AcSCH_3)H^+$ (91)	$(AcSCH_3)Ac^+$ (133)	
	$(CH_3)_2O$	$AcO(CH_3)_2^+$ (89)		
	$(CH_3)_2S$	$AcS(CH_3)_2^+$ (105)[f]		
	$CD_3OC_2H_5$	$AcOC_3H_5D_3^+$ (106)		
	$AcOC(CH_3){=}CH_2$			$Ac^+(AcOC(CH_3){=}CH_2)$ (143)
$(AcOAc)H^+$ (103)	CH_3OH	$(AcOCH_3)H^+$ (75)	$(AcOCH_3)Ac^+$ (117)	
	CH_3SH	$(AcSCH_3)H^+$ (91)	$(AcSCH_3)Ac^+$ (133)	
	$(CH_3)_2O$	$AcO(CH_3)_2^+$ (89)		$(AcOAc)Ac^+$ (145)
	$(CH_3)_2S$	$AcS(CH_3)_2^+$ (105)[f]		$(AcOAc)Ac^+$ (145)
	AcOAc			$(AcOAc)Ac^+$ (145)
$(AcSAc)H^+$ (119)	CH_3OH	$(AcOCH_3)H^+$ (75)	$(AcOCH_3)Ac^+$ (117)	
	CH_3SH	$(AcSCH_3)H^+$ (91)	$(AcSCH_3)Ac^+$ (133)	
	$(CH_3)_2O$	$AcO(CH_3)_2^+$ (89)		
	$(CH_3)_2S$	$AcS(CH_3)_2^+$ (105)		
	AcSAc			$(AcSAc)Ac^+$ (161)
$(CD_3CO_2CH_3)H^+$ (78)	$AcOCH{=}CH_2$		$(CD_3CO_2CH_3)Ac^+$ (120)	
$(CD_3CO_2CH_3)D^+$ (79)	AcOAc		$(CD_3CO_2CH_3)Ac^+$ (120)	
$C_2H_5COSH_2^+$ (91)	$(CH_3)_2O$	$(C_2H_5CO)O(CH_3)_2^+$ (103)		$(C_2H_5COSH)C_2H_5CO^+$ (147)

[a] Formed from AcX by proton transfer from acidic fragment ions, usually CH_3CO^+ m/z 43, abbreviated as Ac^+. [b] The precursors are listed to the left of the product ion listed along same row. [c] Protonated esters (methyl, ethyl, phenyl, allyl acetates, and thioacetates) are unreactive as acylating agents and do not react with RY. They react only to receive Ac^+ from reactive AcX neutrals. [d] Rate studies gave k_2 for methanolysis of acetic acid and vinyl acetate as 4.7×10^{-10} and 6.0×10^{-10} cm^3 s^{-1} $molecule^{-1}$, respectively. Methanthiolysis gave k_2 as 3.2×10^{-10} and 4.1×10^{-10} cm^3 s^{-1} $molecule^{-1}$, respectively. [e] m/z 89 is also formed from $AcXAc^+$ with CH_3OCH_3. [f] m/z 105 is also formed from $(CH_3)_2SH^+$ (m/z 63) and neutral AcX. [g] m/z 101 expected from route a (Scheme I) is a minor product ion but it arises by an entirely different reaction channel, as reported in a separate publication.

with mechanisms involving tetracovalent intermediates.[3d] The results we now report of the positive-ion–molecule chemistry of numerous acyl compounds with oxygen and sulfur nucleophiles indicate that acyl-transfer reactions under ICR conditions proceed more commonly by way of acylium ion complexes **2** than by tetrahedral intermediates **1**. In particular, we describe some unusual acylation reactions that strongly support acyl transfer as a direct displacement process.

To distinguish between acylation via **1** or **2**, we have studied the gaseous ion chemistry of compounds which are expected to react differently by way of **1** than by **2**. The logic is illustrated by the methanolysis of thioacetic acid (Scheme I, X = SH, Y = O). If **1** is an intermediate, it can partition along two routes to give **3** and H_2O (route a) and/or **4** and H_2S (route b). Assuming that the most exothermic route will prevail, **3** (m/z 91) is anticipated to be formed in preference to **4** (m/z 75).[5] In comparison, reaction via **2** will lead to **4** only. In fact, the major product ion in the ion chemistry of thioacetic acid and methanol is **4** (m/z 75), whereas **3** (m/z 91) is *not observed*. Likewise, with thioacetic acid and methanethiol (X = YH = SH), **1** should partition mainly along route a to give **3** (m/z 107) and H_2O, whereas **2** should lead to **4** (m/z 91) and H_2S only. Indeed, m/z 91 is the major product ion, and m/z 107 is *not formed*. Related reactions of protonated vinyl and isopropenyl acetates, acetic anhydride, and acetyl sulfide with methanol and methanethiol each gave product ions consistent with acyl transfer by way of **2**, as summarized in Table I.[6,7]

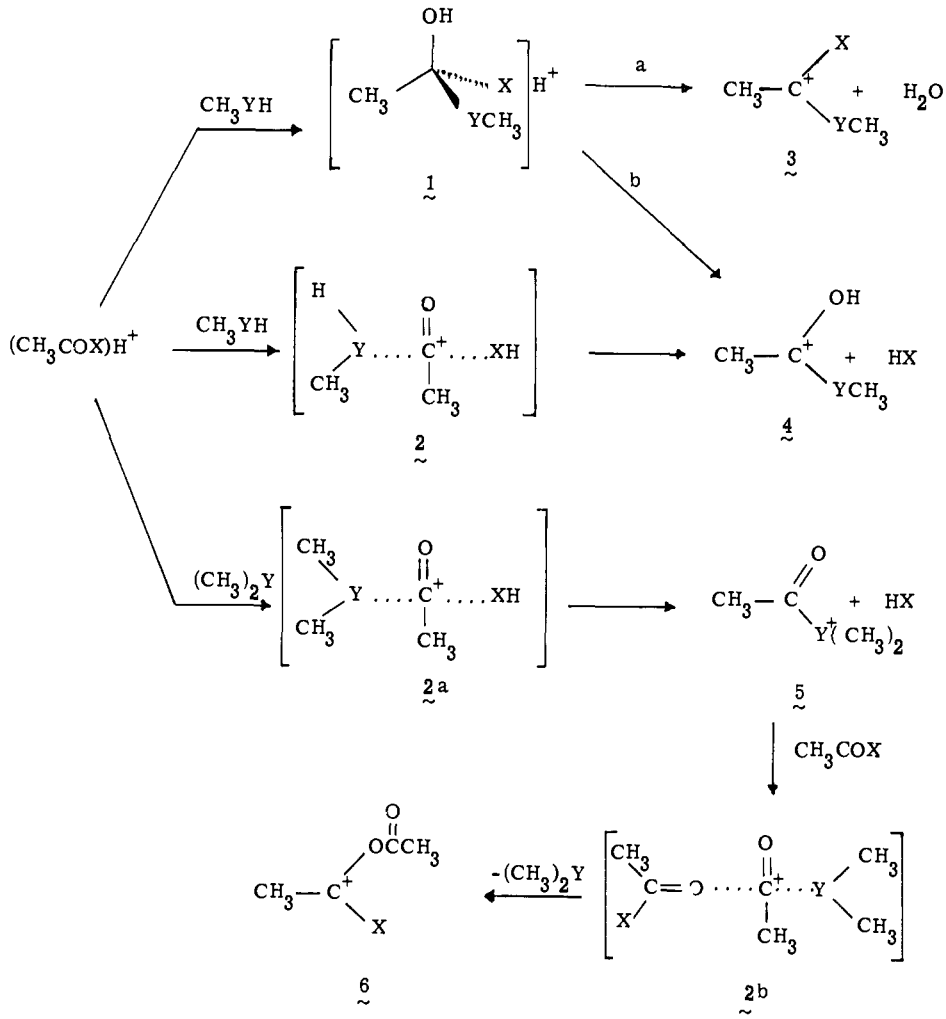
(3) (a) P. W. Tiedemann and J. M. Riveros, *J. Am. Chem. Soc.*, **96**, 185 (1974); (b) T. B. McMahon, *Can. J. Chem.*, **56**, 670 (1978); (c) J. L. Beauchamp, *NATO Adv. Study Inst. Ser., Ser. B*, *6*, 418–436 (1975). (d) J. K. Pau, J. K. Kim, and M. C. Caserio, *J. Am. Chem. Soc.*, **100**, 3831 (1978).

(4) For negative-ion chemistry of acyl compounds, see (a) E. K. Fukuda and R. T. McIver, Jr., *J. Am. Chem. Soc.*, **101**, 2498 (1979); (b) K. Takashima and J. M. Riveros, *ibid.*, **100**, 6128 (1978); (c) M. Comisarow, American Chemical Society/Chemical Society of Japan Chemical Congress, Organic Abstract 247, Honolulu, Hawaii, April 1979. (d) O. I. Asubiojo and J. I. Brauman, *J. Am. Chem. Soc.*, **101**, 3715 (1979); W. N. Olmstead and J. I. Brauman, *ibid.*, **99**, 4219 (1978); (e) J. H. Bowie and B. D. Williams, *Aust. J. Chem.*, **27**, 1923 (1974); J. H. Bowie, *Acc. Chem. Res.*, **13**, 76 (1980).

(5) The enthalpy of the reaction $R_1R_2C{=}O^+R + H_2S \rightarrow R_1R_2C{=}S^+R + H_2O$ corresponds to the enthalpy difference in routes a and b (Scheme I) and is estimated to be exothermic by 14 kcal mol^{-1} for $R_1 = R_2 = R = H$, 20 kcal/ mol^{-1} for $R_1 = R_2 = H$, $R = CH_3$, and 7 kcal mol^{-1} for $R_1 = R = CH_3$, $R_2 = OH$, on the basis of heats of formation of ions and neutrals.

(6) Pressure range is 10^{-6}–10^{-7} torr. Pulsed ICR techniques using a trapped-ion-analyzer cell were employed, as described by R. T. McIver, Jr., *Rev. Sci. Instrum.*, **49**, 111 (1977); **41**, 555 (1970). All reaction channels were established by double-resonance experiments and time–intensity plots.

Scheme I



Unexpectedly, we find that acylation of alkyl ethers and sulfides occurs with a variety of protonated acyl compounds (Table I). These reactions are unlikely to proceed through tetracovalent intermediates **1** because, in the absence of a labile proton on the attacking nucleophile, loss of HX from **1** is not possible without invoking internal proton transfers of high energy. However, facile acylation of $(CH_3)_2Y$ is entirely consistent with the intermediacy of **2a** (Scheme I). That the product ions **5** (m/z 89, Y = O) have the oxonium ion structure was established as follows. Ion **5** is a major product of reaction between methyl ether and protonated vinyl acetate, but **5** in turn acylates the neutral ester to give **6** (m/z 129), showing that acylation occurs in the absence of labile protons on either the ion or the neutral (Scheme I).[8] If **5** had the alternate structure $CH_3C^+(OCH_3)_2$, the formation and destruction of **5** would require unprecedented 1,3-methyl shifts.[9] We reasoned that 1,3-methyl shifts could be detected by using ^{18}O-labeled methyl ether. Rearrangement between oxonium and carbonium forms would render the oxygens of **5** indistinguishable and would subsequently lead to labeled and unlabeled **6**, m/z 131 and 129.

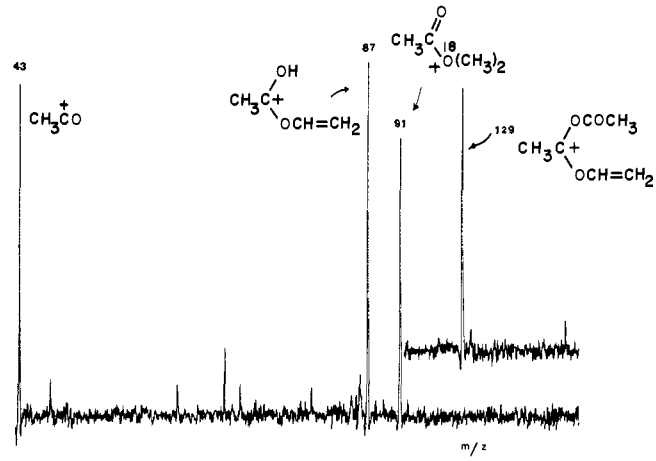


Figure 1. ICR mass spectrum of $CH_3CO_2CH{=}CH_2$ at 8×10^{-7} torr with $(CH_3)_2{}^{18}O$ at 9×10^{-7} torr after 85-ms reaction time. Double-resonance experiments establish the sequence of ion formation as 43 → 87 → 91 → 129 and 87 → 129.

But, as seen in Figure 1, methyl ether (98% enriched in ^{18}O)[3d] and vinyl acetate gave **5** (m/z 91) and **6** (m/z 129) *only*. Thus, rearrangement is not indicated. Moreover, ions of structure $CH_3C^+(OCH_3)_2$ were generated independently by two different routes, as shown in eq 1 and 2,[10] but, unlike **5** (m/z 89) produced

$$CH_3C(OCH_3)_3 \xrightarrow[-CH_3OH]{RH^+} CH_3C^+(OCH_3)_2\ (m/z\ 89) \quad (1)$$

$$CH_2 = C(OCH_3)_2 \xrightarrow{RH^+} CH_3C^+(OCH_3)_2\ (m/z\ 89) \quad (2)$$

(7) The reaction channel of route a was not observed. In those instances where ions corresponding to **3** were observed (X = $OCH{=}CH_2$, OAc, SAc), it was shown that different ion precursors were involved (see Table I).

(8) Ions **6** of m/z 129 are also formed by the reaction of eq 4a, X = $OCH{=}CH_2$.

(9) 1,3-shifts are unfavorable from orbital-symmetry considerations. Rapid equilibration of tautomers by concerted 1,3-proton shifts do not occur in the gas phase [J. L. Holmes and F. P. Lossing, *J. Am. Chem. Soc.*, **102**, 3732 (1980); J. D. Dill, F. W. McLafferty, *ibid.*, **101**, 6526 (1979)]. Nevertheless, ions of the type $CH_3C^+(OH)_2$ are calculated to be 27 kcal mol^{-1} more stable than the tautomer $CH_3C(O)O^+H_2$ [A. C. Hopkinson, K. Yates, and I. G. Csimadia, *J. Phys. Chem.*, **53**, 1784 (1970); G. I. Mackay, A. C. Hopkinson, and D. K. Bohme, *J. Am. Chem. Soc.*, **100**, 7460 (1978); F. M. Benoit and A. G. Harrison, *ibid.*, **99**, 3980 (1977)].

in the acetylation of methyl ether, ions of m/z 89 from reactions 1 and 2 were unreactive toward all nucleophiles added (AcOH, $AcOCH{=}CH_2$, Ac_2O, H_2O, CH_3OH).

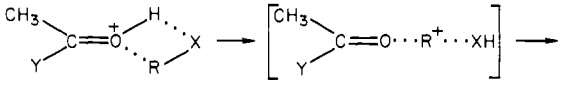
The acylation reactions described thus far can be expressed satisfactorily by the process of eq 3 where the acylium ion complex **2** is either an intermediate or a transition state. We also wish

$$RY + AcXH^+ \rightarrow [RY\cdots Ac^+\cdots XH] \rightarrow RYAc^+ + HX \quad (3)$$

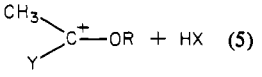
to report related reactions whereby acyl transfer occurs between the protonated parent of one acyl compound and the neutral form of another (eq 4). In the special case where AcX = AcY (eq 4a) the reaction is a self-acylation process that is mechanistically indistinguishable from reaction 3. However, when the acyl components are *different*, as in the reactions of protonated methyl acetate or thioacetate with neutral acyl derivatives, the roles of the reactants are reversed and the acyl group is transferred from the neutral to the ion rather than from the ion to the neutral (eq 4b and Table I). For example, protonated methyl acetate-d_3 and Ac_2O gave $(CD_3CO_2CH_3)Ac^+$ (m/z 120) as expected for acyl transfer from the neutral anhydride to the protonated ester. Also, sequential acyl transfers are evident in the reactions of methanol or methanethiol with acyl compounds, because the product ion of acyl transfer by reaction 3 (R = H) is the reactant ion for acyl transfer by eq 4b. These sequences are summarized in Table I. The key question is whether there is any mechanistic distinction between reactions 3 and 4. We wish to point out that reaction 4b is strikingly similar to gas-phase alkylation reactions of carbonyl compounds.[3d,11] Both reactions conform to the generalized concept of exothermic gas-phase nucleophilic displacement in which an endothermic proton transfer precedes or is concurrent with the displacement step formulated as cation transfer (eq 5, R is alkyl or acyl). Viewed in this way, any fundamental distinction between

$$AcX + AcXH^+ \rightarrow [AcX\cdots Ac^+\cdots XH] \rightarrow AcXAc^+ + HX \quad (4a)$$

$$AcYH^+ + AcX \rightarrow AcYAc^+ + HX \quad (4b)$$



R = alkyl, acyl



(5)

reactions 3-5 disappears, and there is no reason to invoke more complex acylation mechanisms of addition-elimination.

Historically, the concept of acyl transfer as a direct displacement was first described definitively by Day and Ingold[12] but has not been considered seriously since Bender demonstrated through ^{18}O-exchange experiments that tetracovalent intermediates are involved in acid- and base-catalyzed hydrolysis reactions.[13] Yet it is fair to say that the gas-phase results described here serve to emphasize the importance of environmental conditions on the course of ionic reactions. The question arises as to whether addition-elimination acyl-transfer mechanisms are quite as general in condensed phase as now supposed. This comment is especially pertinent to enzyme-catalyzed acyl-transfer reactions, because the hydrophobic reaction environment at the active site of an enzyme[14] means that ions nearby will be poorly solvated. Lacking hydroxylic solvation, reacting ions at the enzyme surface could very well exhibit reactions and reactivities comparable to gaseous ions. In view of this, the wider applicability of the gaseous process in condensed phase is worthy of consideration.

(10) RH^+ are acidic fragments and product ions resulting from electron impact of the neutral reactants.

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(12) J. N. E. Day and C. K. Ingold, *Trans. Faraday Soc.*, **37**, 686 (1941).

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Acknowledgment. We are indebted to the National Science Foundation and the donors of the Petroleum Research Foundation, administered by the American Chemical Society, for their support of this work through Grants NSF CHE 7807993 and ACS-PRF 11585-AC4.

Enantioselective Aldol Condensations. 2. Erythro-Selective Chiral Aldol Condensations via Boron Enolates[1]

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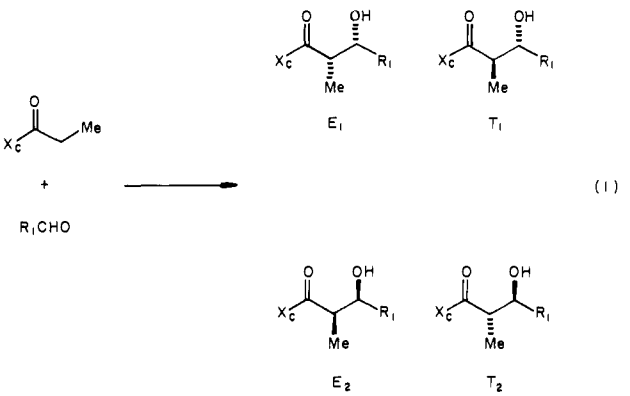
The development of chiral enolates which participate in highly stereoregulated aldol condensations has been a challenging undertaking.[2] The control of both reaction diastereoselection ($E_1 + E_2$ vs. $T_1 + T_2$) and enantioselection (E_1 vs. E_2 or T_1 vs. T_2) must be addressed in conjunction with this problem (eq 1). The



(1)

purpose of this communication is to report our observations on the utility of the chiral 2-oxazolidones **1a** and **2a** as recyclable chiral auxiliaries, X_c, for carboxylic acids in highly enantioselective aldol condensations via the boron enolates[2e,3,4] derived from the respective *N*-propionylimides **1b** and **2b**.

Oxazolidone **1a**, mp 71-72 °C, $[\alpha]_D$ +14.8° (*c* 7.0, $CHCl_3$), was prepared from (*S*)-valinol[5] and either phosgene or diethyl carbonate in high yield.[6] In a similar fashion, the commercially available (1*S*,2*R*)-norephedrine[7] was transformed into oxazolidone **2a**, mp 120-121 °C, $[\alpha]_D$ +163.7° (*c* 1.0, $CHCl_3$).[8] The *N*-propionyloxazolidones **1b** and **2b** were prepared in 80-90% yield by lithiation of **1a** or **1b** (*n*-BuLi, 0.3 M THF) and subsequent reaction with propionyl chloride (1.0 equiv, -78 °C). The non-

(1) Presented at the 12th International Symposium on the Chemistry of Natural Products, Tenerife, Canary Islands. Evans, D. A.; Takacs, J. M.; McGee, L. R.; Ennis, M. D.; Mathre, D. J.; Bartroli, J. *Pure Appl. Chem.* **1981**, in press.

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