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(16) The effects of band overlap (usually with higher intensity, higher energy bands), of hidden underlying lower intensity bands, and of changing band shape with changing solvent, all of which we include in the term *spectral anomalies*, can cause shifts in ν_{max} of as much as 0.4–0.5 kK. We have attempted to minimize such complications by taking ν_{max} as the midpoint between the two positions on the spectrum where OD (optical density) = $0.90OD_{max}$. We consider that for "well behaved" spectra, combined uncertainties in ν_{max} due to *usual spectral anomalies* and experimental precision limits in determining the spectra are about 0.10 kK.
(17) In type-A hydrogen bonding the solvent acts as proton donor and the solute as proton acceptor; the converse applies in type-B bonding.[24]
(18) It was later decided that weak type-A hydrogen bonding by HBD solvents to the nitro oxygens might slightly influence the spectrum of **5**; for this reason and because of the low *s* value, which would increase the consequence of such an effect on π_1^*, the results for **5** were not included in determining the π^* values for the amphiprotic solvents.
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(22) This emphasis reflects the NSWC's interest in properties and spectra of *nitro compounds*.
(23) As examples of the latter type, primary solvents of the initial set whose π^* values were changed when π_1^* results for at least 20 indicators were averaged were: CCl_4, 0.317 → 0.294; $ClCH_2CH_2Cl$, 0.783 → 0.807.
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(38) Reference 31, pp 242 ff.
(39) We shall give evidence in this regard in terms of ϵ/ϵ_0 values as functions of solvent polarity and solvent HBA basicity in future papers. As a preliminary example, ϵ(**15**)/ϵ(**14**) = 0.315, θ(**15**) = 56° in Me_2SO; ϵ(**15**)/ϵ(**14**) = 0.166, θ(**15**) = 66° in CCl_4.
(40) Additional $E_T(30)$ values were taken from Fowler, Katritzky, and Rutherford's collection,[11] and converted to ν(**46**)$_{max}$ values. Acetonitrile and nitromethane were treated as HBA-D solvents.
(41) We have pointed out in an earlier paper[4] that type-A hydrogen bonding effects strongly influence the $E_T(30)$ values of HBA-D solvents.
(42) Dioxane is one of several common solvents with zero dipole moment which show SPP effects significantly higher than their dielectric constant or refractive index would suggest.
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(44) The *d* term is estimated through the equation, $d = 2\Delta XYZ/[s(al) + s(ar)]$, where ΔXYZ is the difference between values calculated through the aliphatic and aromatic solvent regression equations at $\pi^* = 0.7$, and s(al) and s(ar) are the slopes of those regression equations.
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A 1,3-Hydride Shift in the Rearrangement of (1-Phenylallyl)oxyacetic Acid to 2-Ethyl-2-phenyl-1,3-dioxolan-4-one[1]

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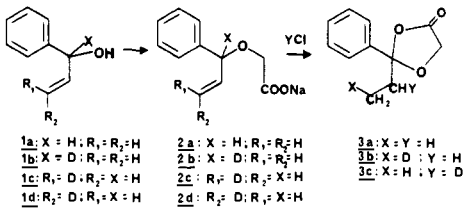
Abstract: Condensation of the sodium salt of α-ethenylbenzenemethanol (**1a**) with sodium chloroacetate in DMF gave **2a** which upon treatment with 2 N HCl solution in the presence of ether gave 2-ethyl-2-phenyl-1,3-dioxolan-2-one (**3a**). When the same sequence of reactions was carried out starting with the deuterated allyl alcohols **1b**, **1c**, or **1d** the rearrangement gave in each case the monodeuterated product **3b**. When **2a** was treated with DCl another monodeuterated compound **3c** was isolated. From a 1:1 mixture of **1b** and **1c** only **3b** was obtained. These results are consistent with a 1,3-hydride shift in an open-chain system (**2a**) with formation of **3a**. A chiral product (+)-**3a** was isolated starting with chiral alcohol (+)-**1a** consistent with a concerted mechanism for the rearrangement.

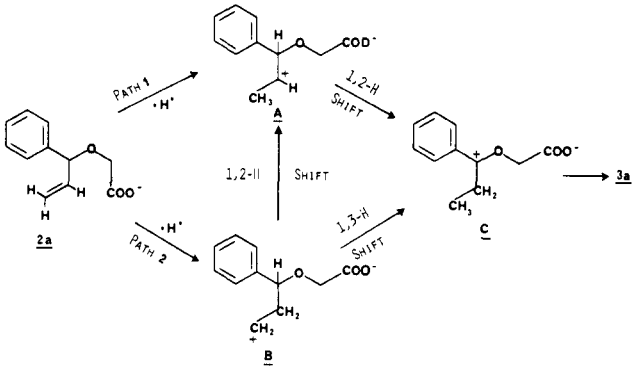
The 1,3-hydride shifts seem to play only a minor role in organic chemistry. They are observed in bicyclic systems, e.g., norbornyl[2] cations, where they can compete with Wagner–Meerwein rearrangements and where two consecutive 1,2-hydride shifts would require the intermediacy of a bridgehead carbonium ion. The same may be said about the reported 1,3-hydride shifts observed in adamantane.[3] In open-chain systems, 1,3-hydride shifts do not compete favorably with 1,2-hydride shifts under thermodynamic control,[4] but can account for 15–30% of the substitution products under kinetically controlled conditions.[5] In this paper we report some of our observations regarding 1,3-hydride shifts under hydrolytic conditions.

In the course of our investigation[6] of the 2,3-sigmatropic rearrangement of allyloxy acetic acids to 2-oxy-5-pentenoic acids[1] we wanted to prepare (1-phenylallyl)oxyacetic acid starting with the sodium salt of the known 1-phenylallyl alcohol[7] (**1a**) and the sodium salt of chloroacetic acid in absolute DMF. Upon acidification of the crude condensation product with dilute (2 N) hydrochloric acid in a two-phase system we isolated a neutral compound $C_{11}H_{12}O_3$ in good yield which we assigned structure **3a**. The NMR spectrum of this novel

Scheme I



Scheme II



compound clearly revealed the presence of an ethyl group. The diastereotopic protons of the dioxolanone gave rise to a two-hydrogen quartet at δ 4.23 ppm. Also the observed carbonyl absorption at 1810 cm^{-1} in the infrared spectrum of **3a** is in good agreement with values[8] reported for similar compounds. For structure proof compound **3a** was hydrolyzed to propiophenone in 80% aqueous acetic acid.

The net result of this multistep sequence (alkylation-acidification-hydrolysis) consists in the transformation of 1-phenyl-2-propen-1-ol (**1a**) into propiophenone with the aid of glycolic acid or the equivalent thereof. This transformation was previously[9] accomplished in 2% yield by heating the allyl alcohol **1a** to reflux for 4 h in 10% aqueous KOH in ethanol and in quantitative yield in the presence of 2 equiv of *n*-butyllithium.[10] Our rearrangement complements the known transformation of the phenylallyl alcohol **1a** to cinnamyl alcohol[11] by the action of dilute acid.

About the Mechanism of the Rearrangement. Barring any deep-seated rearrangement of the carbon skeleton during the acidification of the salt **2a**, we see essentially two pathways (1 and 2; see Scheme II) leading from **2a** to **3a**. Protonation of the double bond in **2a** could lead either to a primary carbonium ion B or a secondary carbonium ion A. The latter could give the product **3a** by a 1,2-hydride shift of the benzylic proton followed by the capture of the internal nucleophile by the rearranged carbonium ion C. As an alternate pathway, the secondary carbonium ion A could deprotonate to form an enol ether which through reprotonization also would lead to C. Reprotonization could take place from the solvent with possible exchange of the original benzylic proton or from within a cage which, in the final analysis, would be equivalent to a 1,2-hydride shift from the secondary carbonium ion A.

On the other hand, the primary carbonium ion B could be transformed into a methyl group via a 1,3-hydride shift of the benzylic proton to give C followed by lactonization as described above. Product formation from the primary carbonium ion via two consecutive 1,2-hydride shifts (B → A → C) would also lead to the product **3a**. It should be emphasized that we do not intend to differentiate between nonclassical and classical carbonium ions.

In order to differentiate between these possibilities, we prepared 1-phenyl-2-propen-1-ol-*1*-d_1[10] (**1b**) from deuteriobenzaldehyde[12] and vinyl bromide via the Grignard reagent. Condensation of **1b** with sodium chloroacetate under the same conditions as employed above gave **2b** which was then treated with dilute hydrochloric acid to give the lactone **3b**. That the deuterium had migrated to the methyl group was confirmed by mass spectral data and NMR data as well. The mass spectrum shows the molecular ion of *m/e* 193, an indication that no deuterium has been lost during the rearrangement. The next lower fragment corresponds to the mass unit *m/e* 177, which is consistent with the loss of a monodeuterated methyl group. The base peak of the spectrum, *m/e* 163, corresponds to the loss of a monodeuterated ethyl group. These observations are in full agreement with the results of the NMR spectrum obtained for **3b**. In place of the *three*-proton triplet (δ 0.94 ppm) for **3a** the deuterated compound **3b** exhibited a *two*-proton triplet and in place of the two-proton *quartet* (δ 2.08 ppm) observed for **3a** the deuterated compound **3b** now featured a two-proton *triplet*. Both triplets observed in the spectrum of the deuterated compound **3b** are complex as might be expected for two sets of diastereotopic protons for the two nonequivalent methylene groups. The ring methylene group gave rise to the same quartet that was also observed in the nondeuterated compound **3a**.

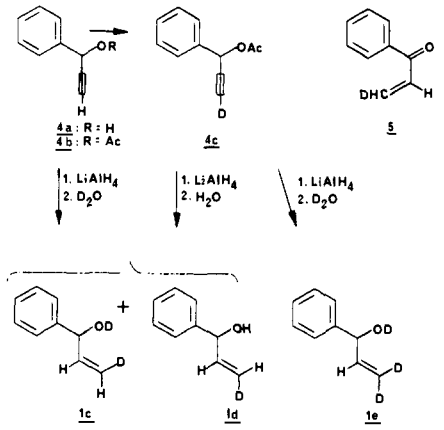
In another experiment, we treated the sodium salt **2a** with diluted DCl, prepared from D_2O and HCl. The NMR spectrum of the compound thus obtained (**3c**) showed in place of the three-proton *triplet* a three-proton *doublet* (δ 0.93 ppm) and in place of the *two*-proton quartet a *one*-proton quartet (2.08 ppm). These findings are consistent with the observations described above: The double bond in **2a,b** is protonated (deuterated) in an anti-Markownikoff fashion to form the primary carbonium ion. A 1,3-hydride (deuteride) shift generates a benzylic cation which then undergoes intramolecular cyclization with formation of the product **3a,b**. The preparation of **3c** results in the formation of a second chiral center with the possibility of forming two diastereomers. Since we observed the presence of a reasonably well-resolved doublet in the NMR spectrum of **3c** we conclude that the addition followed by the rearrangement takes place in a stereospecific manner, but additional work will be required to elaborate this point further. The stereoselectivity of bromine addition to chiral allyl alcohols has been reported[13] in the literature.

From these experiments it becomes evident that the secondary carbonium ion A cannot play a role in the rearrangement of **2a** to **3a**, thus eliminating the protonation via path 1 as well as the two 1,2-hydride shifts indicated in Scheme II. There arises the question why the protonation of the double bond of **2a** takes place in an anti-Markownikoff fashion according to path 2.

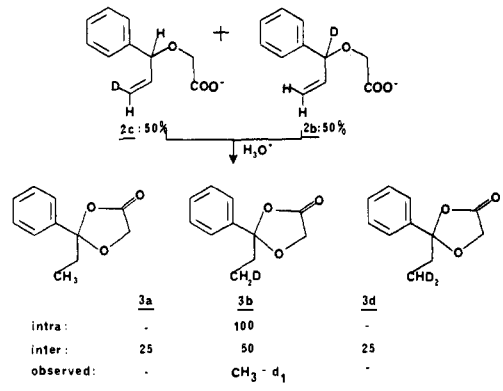
The data discussed so far represent only indirect evidence for an *intramolecular* hydride shift. In the case of an *intermolecular* hydride shift, one might argue that the carbonium ion B (Scheme II) could add a hydroxide from the reaction medium, a possibility which we have not observed so far. But first we searched for some evidence that the carbon skeleton itself was unchanged in the course of the rearrangement. This was accomplished by starting with the deuterated allyl alcohols **1c** and **1d**. Both were converted to their respective allyloxyacetic acid salts and both gave the previously prepared deuterated product **3b**.

For the preparation of the starting materials. advantage was taken of the known reduction of 1-phenylpropargyl alcohol (**4a**) in the presence of lithium aluminum hydride to give **1a** in excellent yield.[7d] When the reduction was carried out followed by the addition of D_2O to hydrolyze[14] the aluminum complex, we obtained a 60:40 mixture of **1c** and **1d**. Excess *E* isomer was available via the reduction of the deuterated propargyl acetate **4c** followed by the decomposition with water. To ascertain the required regiospecificity of these reductions,

Scheme III



Scheme IV



the intermediate from **4c** was also decomposed with D_2O to yield the bisdeuterated compound **1e** as the only product. Of the original three vinyl protons in **1a** only the low-field proton, α to the benzylic carbon, was retained in **1e** as evidenced by comparison of the NMR spectra of these compounds.

The presence of two stereoisomers, **1c** and **1d**, was verified by NMR spectroscopy using shift reagent [Eu(fod)$_3$]. The largest shift was observed for the benzylic proton (d, J = 6 Hz), the smallest shift for the E proton of **1c** (d, J = 10 Hz), and an intermediary shift for the Z proton of **1d** (d, J = 17 Hz). Integration of the shifted spectra gave the ratios of the isomers. Both allylic alcohols enriched in **1c** and **1d** were oxidized to the phenyl vinyl ketones **5**. In the NMR spectra of the products two upfield doublets, equivalent to *one* proton could be observed with J values of 10 and 17 Hz, respectively, in agreement with the regiospecificity and the ratios deduced above.

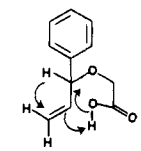
While in general propargyl alcohols are converted into trans-hydrogenated allyl alcohols by reaction with lithium aluminum hydride and subsequent hydrolysis (see ref 14), 1-phenylpropargyl alcohol undergoes this transformation in a regio- but not stereospecific (though stereoselective) manner.

Having prepared the various deuterated starting materials, we determined whether the rearrangement described above was of first order (*intramolecular*) or of second or higher order (*intermolecular*). When a mixture consisting of 50% **1b** and 50% **1c** was carried through to the final product, no crossover of the deuterium label was observed. The NMR spectrum of the product **3b** from this experiment was identical with the spectra of **3b** obtained from either **1b**, **1c**, or **1d**. This then established the *intramolecular* mode of our hydride shift, since both compounds **1b** and **1c** should give one and the same product **3b**. Since the yields for the preparations of **3b** remain about the same for all three pathways, it may be concluded that a possible isotope effect seems to pose no problem for the isolation of **3b**.

In the case of a bimolecular reaction, three different products might have been expected: nondeuterated **3a**, monodeuterated **3b**, and bisdeuterated **3d** in a ratio of 1:2:1, assuming that the isotope effect $k_H/k_D = 1$. Taking into account an isotope effect[12] $k_H/k_D > 1$, products **3a** and **3d** would each be subject to a single isotope effect and their ratio would remain 1:1. Part of **3b** would be subject to no isotope effect while the remaining part of **3b** would be subject to a double isotope effect (see Scheme IV). Nevertheless, compounds **3a** and **3d** should be detectable in a mixture with **3b**, since in the NMR spectrum the methylene groups of the ethyl side chains of **3a** and **3d** would give rise to a quartet and a doublet, respectively, at 2 ppm.

Two derivatives of phenylvinylcarbinol (**1a**) are described in the literature. They are the half ester of phthalic acid[15] and the acetate.[9] According to the literature, both of these can be hydrolyzed under basic conditions to give back the carbinol **1a**. But more importantly, the hydrogen phthalate of **1a** does not undergo a rearrangement when treated[15] with dilute hydrochloric acid. From this observation we conclude that in our case the protonation of the double bond of **2a** might take place via an intramolecular mechanism, a route less likely in the case of the hydrogen phthalate due to a medium-ring transition state. The dissimilarity of the mechanisms involving the rearrangement of **1a** to propiophenone in the presence of base[10,11] on the one hand and our rearrangement of **2a,b** to **3a,b** on the other hand is further manifested in the reported inertness of **1b** in the presence of 2 equiv of *n*-butyllithium.[10]

A concerted mechanism D for the rearrangement to **3** is



D

supported by our observation that a chiral product (+)-**3a** was isolated when the sequence of reactions was carried out starting from the known[15-17] chiral allyl alcohol (+)-**1a**. We are not in a position to make a judgment about the enantiomeric excess in (+)-**3a**, since the chiral shift reagent Eu(TFC)$_3$ (tris[3-(trifluoromethylhydroxymethylene)-*d*-camphorato]europium(III)) did not allow a separation of the signals in the case of the racemic **3a**, which might have been attributed to diastereomeric complexes.

Model considerations seem to favor an antarafacial (trans) addition over a suprafacial (cis) addition to the double bond. In light of orbital symmetry conservation[18] it would be desirable to follow the chirality of the benzylic carbon (inversion or retention) during the rearrangement.

Experimental Section

Proton magnetic resonance spectra were obtained on a Varian Associates A-60 spectrometer and are recorded in hertz or δ values (parts per million) relative to Me_4Si (tetramethylsilane) as internal standard. Infrared spectra were recorded on a Perkin-Elmer spectrophotometer, Model 457. Thin layer chromatography (TLC) was carried out on glass plates coated with silica gel HF-254, E. Merck AG. Mass spectra were measured on a LKB 9000 mass spectrometer.

α-Ethenyl-α-*d*-benzenemethanol (1b).[10] The Grignard reagent was prepared from 3.6 g (0.15 mol) of Mg and 21.0 g (0.20 mol) of vinyl bromide in a total of 200 mL of dry THF. After 2 h at room temperature the solution of 11.5 g (0.11 mol) of benzaldehyde-*1*-d_1[12] in 80 mL of THF was added slowly. The mixture was kept at room temperature overnight, poured on saturated NaCl solution, worked up with ether in the usual way, and dried over Na_2SO_4 and the product

was distilled: bp 60–75 °C (0.3mm); yield 11.0 g (76%); *m/e* 135 (M^+); NMR ($CDCl_3$) δ 2.2 (s, 1, exchangeable with D_2O, OH) 5.0–5.4 (m, 2, $=CH_2$), 5.7–6.4 (m, 1, =CHCO), 7.2–7.4 (m, 5, C_6H_5); IR (film) 3360 cm^{-1} (OH).

(*Z*)-α-(Ethen-2-*d*-yl)-benzenemethanol-*O*-*d* (1c). A solution of 15.0 g (0.114 mol) of commercial α-ethynylbenzenemethanol in 200 mL of ether was added slowly to a suspension of 7.2 g (0.189 mol) of $LiAlH_4$ in 200 mL of ether.[7d] The mixture was heated to reflux for 4 h. Then 20 mL of D_2O was added slowly and the mixture was kept at room temperature overnight. The ether was filtered off and evaporated to give the crude product which was distilled: bp 51–52 °C (0.3 mm); yield 14.0 g (91%); NMR ($CDCl_3$) δ 5.0–5.4 (m, 2, benzylic H + =CHD), 5.7–6.3 (m, 1, =CHCO), 7.2–7.4 (m, 5, C_6H_5). This material contains approximately 40% of **1d**.

(*E*)-α-(Ethen-2-*d*-yl)-benzenemethanol (1d). This isomer was prepared from 2.0 g (0.011 mol) of **4c** and 1.5 g (0.04 mol) of $LiAlH_4$ as described above. The complex was decomposed with 10 mL of water: yield 1.2 g (78%): NMR ($CDCl_3$) δ 3.0 (s, 1, exchangeable with D_2O, OH), 4.9–5.4 (m, 2, benzylic H+ =CHD), 5.7–6.2 (m, 1, =CHCO), 7.2–7.4 (m, 5, C_6H_5). This material contains approximately 40% of **1c**.

α-(Ethen-2,2-d_2-yl)-benzenemethanol-*O*-*d* (1e). A solution of 2.0 g (0.011 mol) of **4c** in 100 mL of ether was added slowly to a suspension of 1.5 g (0.04 mol) of $LiAlH_4$ in 100 mL of ether. After 5 h at reflux, the complex was decomposed by slowly adding 10 mL of D_2O. The solids were filtered off, and the organic layer was dried (Na_2SO_4) and evaporated to give the crude product which was distilled in a Kugelrohr: yield 1.3 g (83%); NMR ($CDCl_3$) δ 5.06 (d, 1, J = 6 Hz, benzylic H), 5.8–6.2 (broad, 1, =CHCO), 7.2–7.4 (m, 5, C_6H_5).

2-Ethyl-2-phenyl-1,3-dioxolan-4-one (3a). To the suspension of 3.5 g (0.15 mol) of NaH in 100 mL of absolute DMF there was slowly added 18.0 g (0.13 mol) of 1-phenyl-2-propen-1-ol[7] (**1a**) in 100 mL of DMF. After the mixture was kept at room temperature for 3 h, there was added 16.6 g (0.14 mol) of sodium chloroacetate. This mixture was stirred at room temperature overnight. The solvent was evaporated under reduced pressure. The residue was dissolved in water and acidified with 2 N HCl in the presence of ether. The organic layer was separated and dried over Na_2SO_4. This left 19.2 g (75%) of crude **3a** which was distilled: bp 97–104 °C (0.4 mm) (8.1 g); GLC one component: *m/e* 163 ($M^+ - 29$); NMR ($CDCl_3$) δ 0.92 (t, 3, J = 7.5 Hz, CH_3), 2.08 (q, 2, J = 7.5 Hz, CH_2CH_3), 4.23 (q, 2, J = 15 Hz, $\Delta\nu$ = 16.1 Hz, OCH_2), 7.2–7.6 (m, 5, C_6H_5); IR (film) 1810 cm^{-1} (C=O).

Anal. Calcd for $C_{11}H_{12}O_3$ (192.2): C, 68.7; H, 6.3. Found: C, 69.0; H, 6.5.

A solution of 0.5 g (0.003 mol) of **3a** in 15 mL of 90% aqueous acetic acid was stirred at room temperature overnight. The solvent was evaporated and the residue worked up in ether and washed with 2 N Na_2CO_3 to give propiophenone found to be identical with an authentic sample.

(+)-2-Ethyl-2-phenyl-1,3-dioxolan-4-one (3a). To the suspension of 0.5 g (0.021 mol) of NaH in 25 mL of absolute DMF there was added slowly 2.0 g (0.015 mol) of (+)-α-ethenyl-α-benzenemethanol (**1a**), α_D +7.0 (CS_2) (lit.[15,17] α_D +12.1 (CS_2)), in 25 mL of absolute DMF. After 1.5 h at room temperature there was added 1.9 g (0.016 mol) of solid sodium chloroacetate. The mixture was kept at room temperature overnight. The solvent was removed under high vacuum at 50 °C. The residue was dissolved in water in the presence of ether. The organic phase was discarded. The aqueous phase was acidified with 2 N HCl in the presence of fresh ether and extracted. The organic phase was dried (Na_2SO_4) and evaporated to give the crude (+)-**3a** which was distilled in a Kugelrohr to give 1.4 g (49%) of product: α_D +7.4 (CS_2); NMR [$CDCl_3$ + Eu(TFC)$_3$] δ 0.93 (t, 3, J = 7.5 Hz, CH_3), 2.08 (q, 2, J = 7.5 Hz, CH_2CH_3), 4.25 (q, 2, J = 15 Hz, $\Delta\nu$ = 16.1 Hz, OCH_2), 7.2–7.6 (m, 5, C_6H_5).

2-(Ethyl-2-*d*)-2-phenyl-1,3-dioxolan-4-one (3b). A. From α-Ethenyl-α-*d*-benzenemethanol (1b). To the suspension of 1.2 g (0.05 mol) of NaH in 40 mL of absolute DMF there was added slowly a solution of 5.5 g (0.04 mol) of 1-phenyl-2-propen-1-ol-1-d_1 (1b). After 1.5 h at room temperature 4.7 g (0.04 mol) of sodium chloroacetate was added. The mixture was stirred at room temperature overnight. The solvent was evaporated under reduced pressure. The residue was dissolved in water and extracted with ether. The aqueous layer was acidified with 2 N HCl in the presence of ether. The organic layer was separated and dried over Na_2SO_4. Evaporation of the solvent gave 6.8 g (88%) of crude **3b**. The product was distilled twice: yield 2.2 g (29%); bp 90–93 °C (0.8 mm); GLC one component; *m/e* 193 (M^+), 177 ($M^+ - 16$), 163 ($M^+ - 30$), 148; NMR ($CDCl_3$) δ 0.92 (t, 2, J = 7.5 Hz, CH_2CH_2D), 2.08 (t, 2, J = 7.5 Hz, CH_2CH_2D), 4.24 (q, 2, J = 15 Hz, $\Delta\nu$ = 16.1 Hz, OCH_2), 7.2–7.6 (m, 5, C_6H_5); IR (film) 1810 cm^{-1} (C=O).

B. From (*Z*)-α-(Ethen-2-*d*-yl)benzenemethanol-*O*-*d* (1c). Starting with 1.35 g (0.056 mol) of NaH and 6.0 g (0.044 mol) of **1c** followed by the addition of 5.3 g (0.046 mol) of sodium chloroacetate there was obtained 3.3 g (39%) of **3b** after distillation, bp 64–75 °C (0.3 mm); NMR ($CDCl_3$) identical with NMR from A.

C. From (*E*)-α-(Ethen-2-*d*-yl)-benzenemethanol (1d). Starting with 0.15 g (0.006 mol) of NaH and 0.6 g (0.004 mol) of **1d** followed by the addition of 0.52 g (0.004 mol) of sodium chloroacetate there was obtained 0.3 g (35%) of **3b** after distillation in a Kugelrohr, NMR ($CDCl_3$) δ 2.08 (t, 2, J = 7.5 Hz, CH_2CH_2D).

D. From a 1:1 Mixture of 1b and 1c. To a suspension of 1.75 g (0.073 mol) of NaH in 75 mL of absolute DMF a mixture of 4.015 g (0.03 mol) of **1b** and 4.020 g (0.03 mol) of **1c** in 75 mL of DMF was added slowly. After 3 h at room temperature there was added 7.0 g (0.06 mol) of sodium chloroacetate and stirring was continued overnight. The solvent was evaporated under reduced pressure and acidified with 2 N HCl solution in the presence of ether. The organic layer was dried over Na_2SO_4 and evaporated to give 5.2 g of crude product. This was distilled to give 3.6 g (31%) of **3b**: bp 64–70 °C (0.2 mm); NMR ($CDCl_3$) δ 0.93 (t, 2, J = 7.5 Hz, CH_2D), 2.07 (t, 2, J = 7.5 Hz, CH_2CH_2D), 4.20 (q, 2, J = 15 Hz, $\Delta\nu$ = 14.7 Hz, OCH_2), 7.2–7.6 (m, 5, C_6H_5).

2-(Ethyl-1-d_1)-2-phenyl-1,3-dioxolan-4-one (3c). The sodium salt of **2a** was prepared starting with 1.03 g (0.04 mol) of NaH, 5.5 g (0.04 mol) of 1-phenyl-2-propen-1-ol[7] (**1a**), and 4.7 g (0.04 mol) of sodium chloroacetate. After the DMF was evaporated the residue was covered with ether and treated with a solution of 2 g of dry HCl gas in 50 mL of D_2O. The organic layer was washed with 2 N Na_2CO_3 solution and was worked up as done for preparation of **3a** to give 1.5 g of product which was distilled: bp 67–68 °C (0.07 mm); *m/e* 193 (M^+), 163 ($M^+ - 30$); NMR ($CDCl_3$) δ 0.93 (d, 3, J = 8 Hz, $CHDCH_3$), 2.08 (q, 1, J = 8 Hz, $CHDCH_3$), 4.24 (q, 2, J = 15 Hz, $\Delta\nu$ = 16.1 Hz, OCH_2), 7.2–7.6 (m, 5, C_6H_5); IR (film) 1800 cm^{-1} (C=O).

α-(Ethyn-2-*d*-yl)benzenemethanol Acetate (4c). A solution of 4.7 g (0.027 mol) of the known[16] **4b** in 50 mL of ether was added to a suspension of 0.7 g (0.029 mol) of NaH in 50 mL of ether. After 4 h at room temperature 10 mL of D_2O was added slowly, and the organic phase was filtered off and dried (Na_2SO_4) to give the crude product which was distilled in a Kugelrohr: yield 4.4 g (94%); NMR ($CDCl_3$) δ 2.07 (s, 3, CH_3), 6.44 (s, 1, CHO), 7.2–7.7 (m, 5, C_6H_5).

1-Phenylpropen-3-*d*-1-one (5). A solution of 1 g (0.007 mol) of **1c** or **1d** was treated with 2 mL of Jones reagent. After 10 min at room temperature the mixture was worked up in ether and the crude product was distilled in a Kugelrohr: NMR[19] ($CDCl_3$) δ 5.83 (d, J = 10 Hz, *E*-vinyl H), 6.35 (d, J = 17 Hz, *Z*-vinyl H), total 1 H, 7.0–7.8 (m, 4, 1 vinyl + C_6H_3), 7.8–8.2 (m, 2, C_6H_2).

Acknowledgment. We would like to express our thanks to Dr. W. J. Houlihan for his interest and encouragement, Dr. Renate Coombs for providing the mass spectral data, and Dr. S. Barcza and his co-workers for recording the IR and NMR spectra and for helpful discussions. Stimulating discussions with Professor J. Hendrickson are gratefully acknowledged.

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Reactions of CH_3^+ (CD_3^+) with C_3H_6O Isomers

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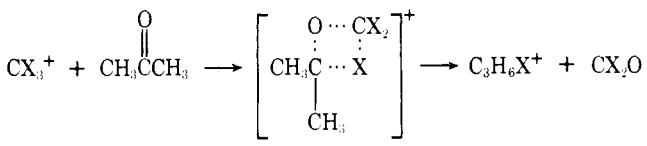
Abstract: Product distributions for the near thermal translational energy (≤0.1 eV) reactions of CH_3^+ and CD_3^+ with propionaldehyde, propylene oxide, trimethylene oxide, and allyl alcohol are reported and compared to previous results for acetone. With the exception of allyl alcohol, each of the C_3H_6O isomers exhibits a reaction pathway with CD_3^+ leading to formation of a $CD_3OCH_2^+$ ionic product. Other ionic reaction products include $C_2H_5^+$, CH_3O^+, $C_3H_5^+$, $C_3H_7^+$, CH_3CO^+, $C_3H_5O^+$, and $C_3H_6O^+$. The results are generally consistent with CH_3^+ attack at the oxygen atom and formation of a short-lived intermediate adduct in approximately 80% of the reactive collisions; less important reaction channels include charge exchange, hydride transfer, and attack at sites other than oxygen.

A recent study by Smith, Herold, Elwood, and Futrell[1] of ion–molecule reactions of CH_3^+ (CD_3^+) with acetone (and acetone-d_6) demonstrated that no less than ten primary bimolecular reactions occur. The remarkably rich chemistry indicated by this work contrasts sharply with recent studies[2,3] of halomethyl ion (CF_3^+, CF_2Cl^+, etc.) reactions with acetone. In these cases Ausloos et al.[3] found $C_3H_6X^+$ (X = F or Cl) to be the dominant reaction product. This reaction presumably occurs via a four-center mechanism;[3]



(1)

For the most exothermic reactions involving the CF_3^+ reactant ion a $C_3H_5^+$ product, corresponding to HX elimination from the highly excited $C_3H_6X^+$ ion generated in reaction 1, was also observed.

Corresponding products ($C_3H_7^+$ and $C_3H_5^+$) were observed in the tandem Dempster–ion cyclotron resonance (ICR) study of CH_3^+ (CD_3^+) reactions with acetone; however, the analogous product from reaction 1 ($C_3H_7^+$) accounts for only 12% of the total products. A moderate amount of $C_3H_5^+$ was also observed (8%) but was attributed to

$$CD_3^+ + CH_3COCH_3 \rightarrow C_3H_5^+ + CD_3OH + 1.7\ eV \quad (2)$$

since H, D isotopic scrambling (which is known to occur in deuterium labeled propyl cations *prior* to H_2 or HD elimination[4]) was not observed.

An unexpected reaction of CD_3^+ (CH_3^+) with acetone results in elimination of an ethylene molecule from an intermediate adduct as follows:

$$CD_3^+ + CH_3COCH_3 \rightarrow CD_3OCH_2^+ + C_2H_4 \quad (3)$$

Remarkably, while this reaction requires extensive rearrangement of the intermediate it accounts for 11% of all reaction products and occurs totally *without* H, D isotopic scrambling.[1]

To elucidate the mechanism of this reaction it was considered desirable to examine reactions of CH_3^+ (CD_3^+) with other C_3H_6O isomers, on the assumption that the relative ease with which the intermediate was formed in reaction 3 might provide information concerning its structure. In this work we present branching ratios obtained for CH_3^+ (CD_3^+) reactions with propionaldehyde, trimethylene oxide, propylene oxide, and allyl alcohol. It will be shown that the several reactions can be partitioned into those occurring via direct reaction channels (proton transfer, charge transfer, and possibly hydride ion abstraction) and those involving an intermediate adduct, which can be rationalized on the basis of plausible structures of the respective reaction intermediates. Although several of the reaction products can be rationalized in terms of an intermediate resulting from attack at the oxygen atom, in several cases attack at other sites must also be considered.

Experimental Section

In this work we have utilized a tandem Dempster–ICR mass spectrometer, described elsewhere,[5] to study the near thermal energy (≤0.1 eV average translational energy—laboratory frame) reactions of mass-selected CH_3^+ and CD_3^+ ions. Such studies, under single collision conditions, avoid mass discrimination effects present in most tandem instruments, the integrations required in crossed-beam experiments, and the artifacts common to more conventional ICR–double resonance studies.

The mass-selected CH_3^+ (CD_3^+) ions are decelerated to ≤0.1 eV and injected into an ICR cell where reaction occurs with the C_3H_6O isomer (typically at a pressure of 10^{-6} Torr). Ions are detected using a variable frequency marginal oscillator calibrated for each ion frequency.[5] Total absolute CH_3^+ (CD_3^+) rate constants were not determined; however, all were fast, on the order of 10^{-9} cm^3 molecule^{-1} s^{-1}, consistent with previous studies of CF_3^+ reactions with acetone.[2,3]

CH_3^+ (CD_3^+) reactant ions were prepared by 25-eV electron impact on CH_4 (CD_4). The ions are probably internally excited, although recent work[6] indicates that electronic excitation is unlikely on the present reaction time scale (10^{-3} s). While CH_3^+ vibrational energy may affect the branching ratios, preliminary results for reactions with a number of molecules show that it is rather unusual for nominally endothermic CH_3^+ reactions to account for more than 10–15% of the

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