Nucleophilic Attack at αβ-Unsaturated Carbonyl Systems. The Reactions of Acrolein and Methyl Acrylate with CF₃O⁻, [F⁻ ··· HOMe], RO⁻, and [RO⁻ ··· HOR]. An *ab initio* and Ion Cyclotron Resonance Study

Gunter Klass, John C. Sheldon, and John H. Bowie *
*Departments of Chemistry, University of Adelaide, South Australia 5001, Australia*

Ab initio calculations suggest that the fluoride negative ion should react with acrolein to form a number of potentially stable [M + F⁻] ions. These include a number of ' solvated ' ions together with those formed by conjugate addition, and addition to the carbonyl centre. The energies of many of these species relative to reactants are low and comparable (-130 to -180 kJ mol⁻¹) and it is likely that they will be in equilibrium unless collisional deactivation removes the excessive energy of the system. Acrolein reacts with the fluoride ion donors CF₃O⁻ and [F⁻ ··· HOMe] to give detectable [M + F⁻] ions, and with MeO⁻ and [MeO⁻ ··· HOMe] to yield [M + MeO⁻] species. There is no experimental evidence available to suggest structures for these species. The methoxide negative ion deprotonates acrolein and methyl acrylate to produce allenic ions [CH₂=C=C(R)(O⁻)] (not the corresponding species [CH₂=C̄–COR]) and these ions undergo a number of complex reactions with the neutral substrate. The CD₃O⁻ negative ion reacts with methyl acrylate [α-²H₁] (CH₂=CD–CO₂Me) to yield both stable and decomposing [M + CD₃O⁻] species. The decomposing adduct yields both [CH₂=C=C(OMe)(O⁻)] and [CH₂=C=C(OCD₃)(O⁻)] by a reaction sequence which must involve the intermediacy of the tetrahedral species (CH₂=CH)(MeO)(CD₃O)C–O⁻

In previous papers we have described i.c.r. studies of the reactions between nucleophiles and carbonyl-containing substrates.[1] Alkoxide ions (RO⁻) and alkanol alkoxides [RO⁻ ··· HOR] may react with various esters to form decomposing species of tetrahedral geometry,[1-3] but it is not clear in many cases whether the tetrahedral species is a transition state or a reactive intermediate. Brauman[4,5] on the basis of kinetic data has suggested in the particular case of the reaction between halide negative ions and acyl halides that the tetrahedral species is a transition state. This proposal has been used to rationalise results from other systems.[6,7] In contrast, many stable adducts [M + Nu⁻] formed between nucleophiles (Nu⁻) and carbonyl-containing substrates (M) do not have tetrahedral structures, and are known to correspond to hydrogen-bonded ' solvated ' negative ions of various types.[8-11] In the particular case of the reaction of [RO⁻ ··· HOR] with carbonyl systems >CH–CO⁻, the formation of the [M + RO⁻] ion involves the equilibration of the ' central ' hydrogen of the nucleophile with that of >CH–CO⁻. The reaction pathway (to form *c*) is complex but the ' equilibration ' step is thought to proceed by the sequence *a* ⟶ *b*.[11]

In this paper we report the reactions of CF₃O⁻, [F⁻ ··· HOMe], MeO⁻, and [MeO⁻ ··· HOMe] with several αβ-unsaturated carbonyl systems. A nucleophile can, in principle, attack *e.g.* acrolein at the carbonyl carbon, at the β-carbon, or at a hydrogen substituent. In solution reactions, most nucleophiles attack unsaturated carbonyl compounds at the carbonyl group, *e.g.* hydroxide ion[12] and alkoxide ion[13] react with alkyl acrylates to give ester hydrolysis and ester exchange respectively. For αβ-unsaturated ketones and aldehydes, nucleophilic attack at the carbonyl centre is often reversible leading to attack at the β-carbon. This results in a slower but thermodynamically more favourable reaction (*e.g.* Michael addition, retro-aldol reaction). MO calculations have been used to rationalise such reactivity.[14,15]

Several recent studies have reported the reaction of gas-phase nucleophiles to αβ-unsaturated systems. The cyclopentadienyl anion is thought to undergo conjugate addition to acrylonitrile to yield C₅H₅CH₂CHCN;[16] reaction of MeO⁻ with acrolein yields an [M − H]⁻ ion whereas a similar reaction with [MeO⁻ ··· HOMe] produces a stable [M + MeO⁻] negative ion.[17]

Our aim in the present study was to use *ab initio* calculations
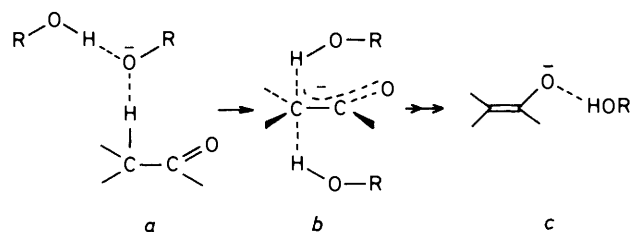
of a model system (F⁻–acrolein) in order to predict the reactions that should occur in this and analogous systems, and then to devise suitable reactions in an attempt to substantiate the predictions. We were particularly interested in the possibility of nucleophilic attack at the carbonyl centre in such systems.

Results and Discussion

Ion cyclotron resonance spectra were determined as described in the Experimental section. The F⁻–acrolein system was used as a model and the species shown in Figure 1 have been characterised by SCF LCGO MO calculations. The number of species in the system has obliged us to work at the 4-31G level of atomic bases.† The geometry and energy of each species we propose have been optimised to standard criteria by the force-minimization routine of GAUSSIAN 80.[20]

(A) *The Reaction of Fluoride Negative Ion Donors with Acrolein and Methyl Acrylate.*—In Figure 1 we consider the possibility of F⁻ either deprotonating acrolein or of adding to the substrate to form any one of a number of [M + F⁻] negative ions. Deprotonation at any centre is seen to be endothermic; the only deprotonation reaction which could occur with F⁻ under these conditions would be the formation of the allenic ion CH₂=C=C(H)O⁻. It appears that F⁻ should add to
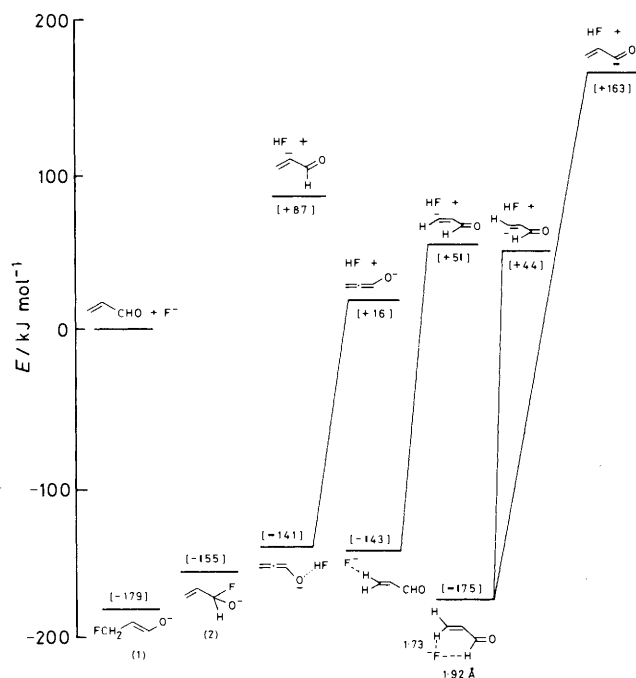

Figure 1. *Ab initio* calculations for the F$^-$-acrolein system. Energies of possible products (in kJ mol^{-1}) calculated at the 4-31G level.

The solvated species [diagram] does not form a discrete intermediate

acrolein to form any one of a number of stable adducts, provided that there is some way to dissipate the energy of formation of each adduct. ' Stable ' [M + F$^-$] ions include the ' Michael addition ' product (1), the tetrahedral species (2), and several ' solvated ' species. As the energies of many of these species are low and comparable (*e.g.* the five species with energies below −141 kJ mol^{-1}), we expect equilibration between them. The barriers for any interconversion are arguably less than 50 kJ mol^{-1}.

We have reported the application of both CF$_3$O$^-$ and [F$^-$ ··· HOMe] (prepared by a Riveros-type reaction [21-23] from CF$_3$O$^-$ and HCO$_2$Me) as fluoride negative ion donors to simple carbonyl systems.[24] The energies of CF$_3$O$^-$ and [F$^-$ ··· HOMe] (relative to CF$_2$O + F$^-$ and HOMe + F$^-$) are −142 [9] and −185 kJ mol^{-1}.[24] Comparing these energies with those of species shown in Figure 1, it is clear that neither ion should deprotonate acrolein, but that both could react with acrolein to yield stable [M + F$^-$] species. Experimentally, neither CF$_3$O$^-$ nor [F$^-$ ··· HOMe] deprotonate either acrolein or methyl acrylate, but both yield fluoride ion adducts with both substrates [see equations (1) and (2) for the acrolein case]. Fluoride ion attachment is more pronounced from [F$^-$ ··· HOMe] than from CF$_3$O$^-$. Both reagents react with methyl acrylate [by an S_N2 reaction, see equation (3)] to yield the acrylate negative ion.*

(B) *The Reaction of* [MeO$^-$] *and* [MeO$^-$ ··· HOMe] *with Acrolein.*—The methoxide negative ion reacts with acrolein to

Eliminations of H$_2$O and CH$_3$· from the [(M − H) + M]$^-$ ion from acrolein

| Nucleophile	Neutral	Adduct				
		H$_2$O	HOD	D$_2$O	CH$_3$·	CH$_2$D·
[structure]	[structure] D / CHO	80	20		75	25
[structure]	[structure] CDO	75	18	7	65	35

produce an [M − H]$^-$ species, and it has been suggested [17] that this ion is produced by reaction (4). We have investigated the reactions of MeO$^-$ and CD$_3$O$^-$ with acrolein, CH$_2$=CH−CDO and CH$_2$=CD−CHO and we confirm that it is the hydrogen attached to the α carbon which is specifically removed. However Figure 1 suggests that reaction (4) may be endothermic and we have confirmed this by *ab initio* calculations. Reaction (4) is endothermic (+52 kJ mol^{-1}), whereas reaction (5) is exothermic (−20 kJ mol^{-1}). Thus we propose that the [M − H]$^-$ ion corresponds to the allenic ion shown in equation (5).

The [M − H]$^-$ ion reacts with acrolein to form an adduct at *m/z* 111, the decomposing form of which eliminates carbon monoxide, water, and a methyl radical.† The adduct could be produced by nucleophilic addition to the carbonyl centre or by conjugate addition. Any such adduct requires extensive rearrangement(s) to accommodate the eliminations of H$_2$O and CH$_3$·. The data in the Table show that the losses mainly involve the hydrogens attached to the β-carbons. Both eliminations are either preceded (or accompanied by) partial hydrogen scrambling, or are produced by a number of discrete processes. Reactions of this type are rare in negative ion chemistry; we do not wish to speculate on possible mechanisms.
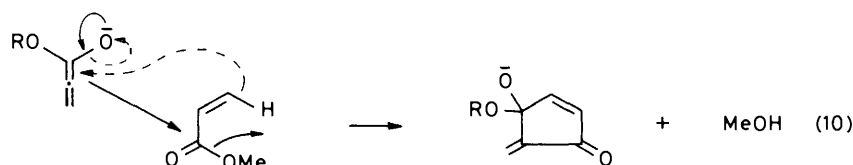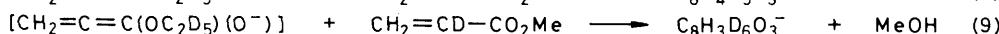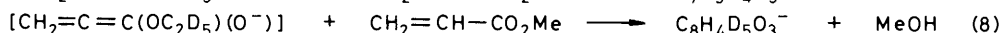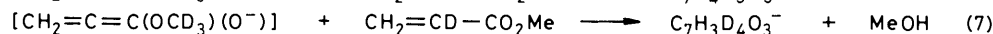
The reaction between acrolein and [MeO$^-$ ··· D−OMe] (from MeO$^-$ and DCO$_2$Me [21]) gives an i.c.r. spectrum very similar to that of the MeO$^-$-acrolein system. The only difference is that the species [M + MeO$^-$] produces a peak approximately ten times more abundant than that from the MeO$^-$-acrolein system. The formation of the [M + MeO$^-$] species does not involve any equilibration of the ' central ' hydrogen (deuterium) of the nucleophile with a substrate hydrogen [compare the corresponding reaction *a* ⟶ *b* (see Introduction) for simple carbonyl compounds [11]).

(C) *The Reaction of* RO$^-$ *Negative Ions with Methyl Acrylate.*—Although the formation of a stable tetrahedral structure (2) is predicted on energetic grounds (see Figure 1), we have been unable to confirm this experimentally. The formation of the corresponding tetrahedral species [M + RO$^-$]

---

* I.c.r. spectrum of negative ions from the system CF$_3$OF–methyl acrylate (partial pressures of CF$_3$OF and methyl acrylate 5 × 10^{-6} and 1 × 10^{-5} Torr respectively, other reaction conditions see Experimental section): percentage figures refer to relative power absorptions, *m/z* 19 (0.3%) [F$^-$], 71 (16%) [CH$_2$=CH−CO$_2^-$], 85 (100%), [CF$_3$O$^-$], 105 (7%) [M + F$^-$].

† I.c.r. spectrum of negative ions for the system CD$_3$ONO–acrolein (partial pressure of CD$_3$ONO and methyl acrylate 5 × 10^{-6} and 1 × 10^{-5} Torr, respectively, other reaction conditions see Experimental section): percentage figures refer to relative power absorptions, *m/z* 32 (10%) [DNO$^-$], 34 (40%) [CD$_3$O$^-$], 46 (8%) [NO$_2^-$], 55 (78%) [CH=C=CHO$^-$], 58 (10%) [A], 62 (6%) [$^-$CD$_2$-ONO], 83 (85%) [(M + 55)$^-$ − CO], 90 (11%) [M + CD$_3$O$^-$], 93 (18%) [(M + 55)$^-$ − H$_2$O], 96 (28%) [(M + 55)$^-$ − CH$_3$·], 111 (100%) [M + 55]$^-$.

DNO$^{-•}$ + CH$_2$=CH−CHO ⟶ CH$_2$D−ĊH−CHO [A] + NO$^•$ (i)
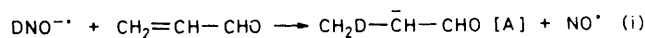
[A] is formed by reaction (i) (not that suggested by Bartmess [17]).

$$CF_3O^- + CH_2{=}CH{-}CHO \longrightarrow [CH_2{=}CH{\cdot}CHO + F^-] + CF_2O \quad (1)$$

$$[F^-{\cdots}HOMe] + CH_2{=}CH{-}CHO \longrightarrow [CH_2{=}CH{\cdot}CHO + F^-] + MeOH \quad (2)$$

$$CF_3O^- + CH_2{=}CH{-}CO_2Me \longrightarrow CH_2{=}CH{-}CO_2^- + (MeF + CF_2O) \quad (3)$$

$$MeO^- + CH_2{=}CH{-}CHO \longrightarrow CH_2{=}\bar{C}{-}CHO + MeOH \quad (4)$$

$$MeO^- + CH_2{=}CH{-}CHO \longrightarrow [CH_2{=}C{=}C(H)(O^-)] + MeOH \quad (5)$$

Figure 2. I.c.r. spectrum of negative ions for the system MeONO–methyl acrylate. Partial pressure of MeONO and methyl acrylate 5×10^{-6} and 1×10^{-5} Torr respectively. [B] and [C] are formed by the reactions:

$$HNO^{-{\cdot}} + CH_2{=}CH{-}CO_2Me \longrightarrow Me{-}\bar{C}H{-}CO_2Me \text{ [B]} + NO^{\cdot} \quad (cf.\ ref.\ 25)$$

$$Me{-}\bar{C}H{-}CO_2Me \text{ [B]} + MeONO \longrightarrow \underset{MeO_2C}{\overset{Me}{>}}{=}NO^- \text{ [C]} + MeOH \quad (cf.\ refs.\ 26{-}28)$$

Figure 3. I.c.r. spectrum of negative ions for the system CD_3ONO– methyl acrylate. Partial pressure of CD_3ONO and methyl acrylate 5×10^{-6} and 1×10^{-5} Torr, respectively. [D] and [E] are formed by the respective reactions:

$$DNO^{-{\cdot}} + CH_2{=}CH{-}CO_2Me \longrightarrow CH_2D{-}\bar{C}H{-}CO_2Me \text{ [D]} + NO^{\cdot}$$

$$CH_2D{-}CH{-}CO_2Me \text{ [D]} + MeONO \longrightarrow \underset{MeO_2C}{\overset{CH_2D}{>}}{=}NO^- \text{ [E]} + MeOH$$

$$[CH_2{=}C{=}C(OCD_3)(O^-)] \quad + \quad CH_2{=}CH{-}CO_2Me \quad \longrightarrow \quad C_7H_4D_3O_3^- \quad + \quad MeOH \quad (6)$$

$$[CH_2{=}C{=}C(OCD_3)(O^-)] \quad + \quad CH_2{=}CD{-}CO_2Me \quad \longrightarrow \quad C_7H_3D_4O_3^- \quad + \quad MeOH \quad (7)$$

$$[CH_2{=}C{=}C(OC_2D_5)(O^-)] \quad + \quad CH_2{=}CH{-}CO_2Me \quad \longrightarrow \quad C_8H_4D_5O_3^- \quad + \quad MeOH \quad (8)$$

$$[CH_2{=}C{=}C(OC_2D_5)(O^-)] \quad + \quad CH_2{=}CD{-}CO_2Me \quad \longrightarrow \quad C_8H_3D_6O_3^- \quad + \quad MeOH \quad (9)$$

from RO^- and methyl acrylate could be inferred if a suitable transesterification product could be detected. Thus we studied the reactions between methyl acrylate and MeO^-, CD_3O^-, EtO^-, and $C_2D_5O^-$ and of $CH_2{=}CHDCO_2Me$ with CD_3O^- and $C_2D_5O^-$. The i.c.r. spectra of these systems are complex and show peaks which are produced by a variety of ion–molecule reactions. The spectra of MeO^-–methyl acrylate and CD_3O^-–methyl acrylate are shown for comparison purposes in Figures 2 and 3.

All acrylate spectra show small peaks corresponding to $[M + RO^-]$ species, and an abundant peak is always observed at m/z 71 due to the acrylate anion. Figure 2 shows the presence of an abundant $[M - H]^-$ species and the spectrum of MeO^-–$CH_2{=}CD^-CO_2Me$ shows exclusive loss of the α-deuterium to form the allenyl negative ion $[CH_2{=}C{=}C(OMe)-(O^-)]$ (by analogy with the acrolein reaction; see above and also Figure 4). The spectra produced by the reactions of CD_3O^-, EtO^-, and $C_2D_5O^-$ with methyl acrylate show the ' M – H ' process to be complex; for example Figure 3 contains peaks from ions e and f ($ca.$ 3 : 1), whereas that of C_2D_5-O^-–methyl acrylate shows the corresponding species e: $[CH_2{=}C{=}C(OC_2D_5)(O^-)]$ (4 : 1). The observation that the two peaks are always detected in unequal amounts suggests that there are (at least) two mechanisms involved in the formation of the ions, $viz.$ [considering the CD_3O^-–methyl acrylate system (Figure 3)], (i) formation of both e and f through tetrahedral species d (Scheme),* and (ii) ' direct ' deprotonation by CD_3O^-.

The $[M - H]^-$ ions react with neutral methyl acrylate to form both detectable and decomposing adducts (see Figures 2 and 3). The decomposing adduct eliminates methanol, and the results of labelling experiments [see equations (6)—(9)] show that the elimination involves the methoxy and a terminal hydrogen from that part of the adduct which originates from the neutral methyl acrylate. We suggest that adduct formation results from reaction at the carbonyl centre and that the decomposition may be rationalised by sequence (10).

(D) *Reactions of* $[RO^- \cdots HOR]$ *Negative Ions with Methyl Acrylate.*—The i.c.r. spectra of $[MeO^- \cdots D{-}OMe]$–methyl acrylate and $[CD_3O^- \cdots HOCD_3]$–methyl acrylate show $[M + RO^-]$ peaks which are $ca.$ 30 times more abundant than those formed directly from MeO^- and methyl acrylate. No H–D equilibration accompanies the formation of

$[M + MeO^-]$ from $[MeO^- \cdots D{-}OMe]$–methyl acrylate. In the $[CD_3O^- \cdots HOCD_3]$–methyl acrylate case, ions e and f are coupled only to CD_3O^-. The relative abundances of those peaks are the same as those observed for the CD_3O^-–methyl acrylate system (Figure 3). Thus the decomposing adduct d (Scheme) is produced solely from CD_3O^-, whereas the stable adduct $[M + CD_3O^-]$ is produced almost exclusively from $[CD_3O^- \cdots HOCD_3]$.

These observations are in accord with *ab initio* calculations for the model system MeO^-–acrolein (Figure 4). Formation of the deprotonated allenyl ion through the tetrahedral intermediate (see the dotted lines in Figure 4) is exothermic (-20 kJ mol^{-1}) for the MeO^-–acrolein system. In contrast, the reaction of $[MeO^- \cdots HOMe]$ and acrolein giving the allenyl ion ($CH_2{=}C{=}CHO^-$) and methanol, is strongly endothermic ($+115$ kJ mol^{-1}).
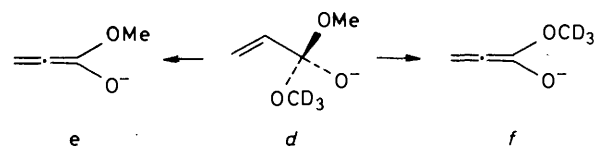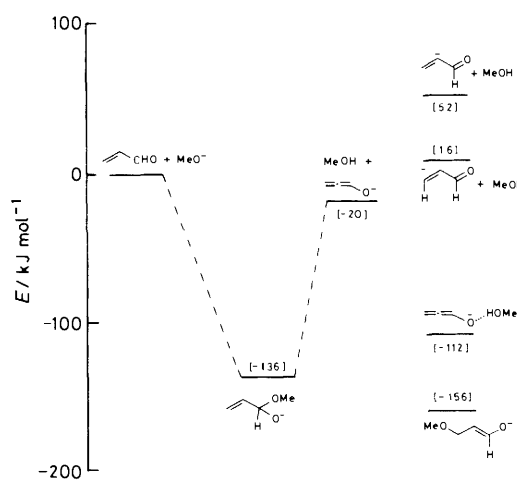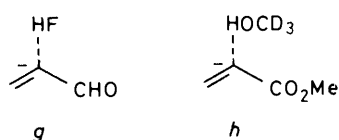
Scheme.

Figure 4. *Ab initio* calculations for the MeO^-–acrolein system. Energies of possible products calculated at the 4-31G level

Conclusion

Ab initio calculations suggest that the reaction between F^- and acrolein should produce an equilibrium mixture of a number of stable $[M + F^-]$ ions. Stable $[M + F^-]$ and $[M + RO^-]$ species are observed for the systems studied. In

---

* Species g is not a reactive intermediate in the F^-–acrolein sequence; however it is possible that the analogous species h could be a transition state in reaction $d \longrightarrow e$.

the case of methyl acrylate, the decomposing $[M + RO^-]$ negative ion must pass through a tetrahedral species [see e.g. d (Scheme)] on the way to products.

Experimental

I.c.r. spectra were measured with a Dynaspec ICR 9 spectrometer. Spectra can either be obtained in the 0—5 eV range (primary ions formed by dissociative thermal electron capture) or in the range 40—80 eV (primary negative ions formed by dissociative secondary electron capture). The latter range gives the better sensitivity, hence spectra were obtained routinely at a nominal 70 eV. Other reaction conditions: $\omega_c/2\pi$ 125.0 kHz, RONO (or CF_3OF) pressure 5×10^{-6} Torr, pressure of carbonyl compound 1×10^{-5} Torr. In the case of $[RO^- \cdots HOR]$ experiments, HCO_2R was also added at a partial pressure of 5×10^{-6} Torr. The ion current was in the 10^{-10} A range, emission current 0.2 μA, and ion transit time 1×10^{-3} s. Precursor ions in reaction sequences were determined by the cyclotron ejection technique.

Alkyl nitrites were prepared on the day of the i.c.r. experiment. Methyl nitrite, [$^2H_3$]methyl nitrite, ethyl nitrite, and [$^2H_5$]ethyl nitrite were prepared by a reported method from the appropriate alcohol and sodium nitrite.[29] Methyl [^2H]-formate was prepared by a standard procedure.[30] Trifluoromethyl hypofluorite was a commercial sample.

Labelled Carbonyl Compounds (*Deuterium Incorporation Calculated from the Appropriate Molecular Cation*).—[1-^2H]-*Acrolein*. Treatment [31,32] of methyl 9,10-ethanoanthracene-11-carboxylate [31] with lithium aluminium deuteride gave [12-$^2H_2$]-9,10-ethanoanthracen-11-ylmethanol, needles, m.p. 109—111 °C, yield 68%; $^2H_1 = 5$, $^2H_2 = 95\%$,[32] which was oxidised [31] (using silver carbonate on Celite [33]) to [12-$^2H_2$]-9,10-ethanoanthracene-11-carbaldehyde, needles, m.p. 95—97 °C; yield 45%; $^2H_1$ 5%, $^2H_2$ 95%. Thermolysis [31] of this species gave a quantitative yield of [1-^2H]acrolein, $^2H_0$ 4%, $^2H_1$ 96%.

[2-^2H]*Acrolein*. To a stirred, cooled (-78 °C) solution of di-isopropylamine (3.0 g, 0.030 mol) in anhydrous tetrahydrofuran (150 cm³) was added (under nitrogen) n-butyl-lithium in hexane (20 cm³, 1.4M, 0.028 mol). After stirring at -78 °C for 10 min, methyl 9,10-ethanoanthracene-11-carboxylate (6.0 g, 0.023 mol) in anhydrous tetrahydrofuran (100 cm³) was added dropwise over 30 min, and stirred (-78 °C) for a further 30 min. Deuterium oxide (3.0 g, 0.15 mol) was added dropwise, the mixture allowed to warm to 20 °C, and filtered. The filtrate was dried (anhydrous $MgSO_4$), concentrated *in vacuo* and the product crystallized from diethyl ether–light petroleum (b.p. 60—70 °C) (1 : 1) to yield methyl [11-^2H]-9,10-ethanoanthracene-11-carboxyla te (4.6 g, 76%), rhombic crystals, m.p. 115—117 °C; $^2H_0$ 7%, $^2H_1$ 93%.

This compound was converted into [2-^2H]acrolein, $^2H_0$ 7%, $^2H_1$ 93%, by the same sequence of reactions as described above for [1-^2H]acrolein except that (i) lithium aluminium hydride replaces lithium aluminium deuteride, and (ii) the reduction [31] was worked up with NaOD and D_2O to avoid loss of the label.

Methyl [2-^2H]*acrylate*. Methyl [11-^2H]-9,10-ethanoanthracene-11-carboxylate, $^2H_0$ 7%, $^2H_1$ 93%, was thermolysed [31] to yield methyl [2-^2H]acrylate, $^2H_0$ 7%, $^2H_1$ 93%.

References

1 J. H. Bowie, *Acc. Chem. Res.*, 1980, **13**, 76.
2 G. Klass, D. J. Underwood, and J. H. Bowie, *Aust. J. Chem.*, 1981, **34**, 507.
3 M. F. Dottore and J. H. Bowie, *J. Chem. Soc., Perkin Trans. 2*, 1982, 283.
4 O. I. Asubiojo and J. I. Brauman, *J. Am. Chem. Soc.*, 1979, **101**, 2715.
5 J. I. Brauman and M. J. Pellerite, *J. Am. Chem. Soc.*, 1980, **102**, 5993.
6 J. E. Bartmess, R. L. Hays, and G. Caldwell, *J. Am. Chem. Soc.*, 1981, **103**, 1338.
7 J. E. Bartmess, R. L. Hays, H. N. Khatri, R. N. Misra, and S. R. Wilson, *J. Am. Chem. Soc.*, 1981, **103**, 4746.
8 C. E. Melton, G. A. Ropp, and T. W. Martin, *J. Phys. Chem.*, 1960, **64**, 1577.
9 R. L. Clair and T. B. McMahon, *Can. J. Chem.*, 1979, **57**, 307.
10 R. L. Clair and T. B. McMahon, *Can. J. Chem.*, 1979, **57**, 474.
11 G. Klass, J. C. Sheldon, and J. H. Bowie, *Aust. J. Chem.*, 1982, **35**, 2471.
12 W. C. Mast and C. H. Fisher, *Ind. Eng. Chem.*, 1949, **41**, 790.
13 P. L. de Benneville, L. S. Luskin, and H. J. Sims, *J. Org. Chem.*, 1958, **23**, 1355.
14 D. Eisenstein, J.-M. Lefour, C. Minot, N. T. Anh, and G. Soussan, *Compt. rend.*, 1972, **264C**, 1310.
15 K. N. Houk and R. W. Strozier, *J. Am. Chem. Soc.*, 1973, **95** 4094.
16 R. N. McDonald, A. K. Chowdbury, and D. W. Setzer, *J. Am. Chem. Soc.*, 1980, **102**, 6491.
17 J. E. Bartmess, *J. Am. Chem. Soc.*, 1980, **102**, 2483.
18. L. Radom, *Modern Theor. Chem.*, 1977, **4**, 333.
19 J. Chandrasekar, J. G. Andrade, and P. von Rague Schleyer, *J. Am. Chem. Soc.*, 1981, **103**, 5609.
20 J. S. Binkley, R. A. Whitehead, R. Seeger, D. J. DeFrees, H. B. Schlegel, S. Topiol, L. R. Kahn, and J. A. Pople, GAUSSIAN 80, Department of Chemistry, Carnegie-Mellon University, 1980.
21 L. K. Blair, P. C. Isolani, and J. M. Riveros, *J. Am. Chem. Soc.*, 1973, **95**, 1057.
22 P. C. Isolani and J. M. Riveros, *Chem. Phys. Lett.*, 1975, **33**, 362.
23 J. F. G. Faigle, P. C. Isolani, and J. M. Riveros, *J. Am. Chem. Soc.*, 1976, **88**, 2049.
24 J. H. Bowie and J. C. Sheldon, *Aust. J. Chem.*, 1983, **36**, 289.
25 C. H. DePuy, V. M. Bierbaum, R. J. Schmitt, and R. H. Shapiro, *J. Am. Chem. Soc.*, 1978, **100**, 2920.
26 G. Klass and J. H. Bowie, *Aust. J. Chem.*, 1980, **33**, 2271.
27 J. H. J. Dawson and N. M. M. Nibbering, *Int. J. Mass Spectrom. Ion Phys.*, 1980, **33**, 3.
28 G. K. King, M. M. Maricq, V. M. Bierbaum, and C. H. DePuy, *J. Am. Chem. Soc.*, 1981, **103**, 7133.
29 W. A. Noyes, *Org. Synth.*, 1936, **16**, 108.
30 W. Stephens and A. Van Es, *Recl. Trav. Chim. Pays-Bas*, 1964, **83**, 1287.
31 L. E. Friedrich and G. B. Schuster, *J. Am. Chem. Soc.*, 1972, **94**, 1193.
32 P. D. Bartlett and F. A. Tate, *J. Am. Chem. Soc.*, 1953, **75**, 91.
33. A. McKillop and D. W. Young, *Synthesis*, 1979, 401.