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FATTY ACIDS

VI. THE THIN-LAYER CHROMATOGRAPHIC BEHAVIOUR OF MERCURY ADDUCTS OF ACETYLENIC ESTERS AND A STUDY OF THE DEMERCURATED PRODUCTS

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SUMMARY

The thin-layer chromatographic behaviour of the intermediate mercury adduct of monoacetylenic, diacetylenic and enyoic esters is described. Treatment of the mercury intermediate with hydrochloric acid gave oxo-esters instead of regenerating the original acetylenic esters. Demercurated products were identified by chromatographic and spectroscopic methods.

INTRODUCTION

The chromatographic separation of a mixture of saturated and unsaturated fatty esters according to the degree of unsaturation is readily achieved by using silver nitrate-impregnated silica or Florisil as adsorbent[1–9] or by conversion of the unsaturated fatty esters into the corresponding methoxyacetoxymercuri adduct followed by column or thin-layer chromatographic (TLC) separation[10–13]. Treatment with dilute mineral acid of the isolated acetoxymercuri adduct after chromatographic separation regenerates the original ethylenic ester without isomerization or double-bond migration[14–16]. The comparatively low polarity of methoxyhalogenomercuri adducts of unsaturated fatty esters is an advantage over the corresponding acetoxymercuri adduct in the separation of polyunsaturated esters[17–19].

No similar work has yet been reported on the separation of acetylenic esters from either saturated or ethylenic esters as their mercury adducts. We have recently performed the oxymercuration–demercuration reactions of acetylenic esters using hydrochloric acid or sodium borohydride as demercuration agent[20]. In this paper, we report the TLC behaviour of the mercury intermediate of monoacetylenic, diacetylenic and enynoic esters, and demonstrate the failure to regenerate the original acetylenic esters by treatment of the TLC-isolated mercury intermediate with dilute hydrochloric acid.

EXPERIMENTAL

Unsaturated fatty esters

Methyl oleate was obtained from commercial sources. Methyl 5-, 9- and 10-undecynoates, octadec-*cis*-10-en-5-ynoate and 9,13-octadecadiynoate were synthesized[21-23].

Preparation of mercury adducts

Acetoxymercuri adduct. The unsaturated fatty ester (100 mg) was refluxed with excess of mercury(II) acetate (550 mg) in methanol (20 ml) for 1 h. Water (40 ml) was added and the reaction mixture extracted with chloroform (3 × 25 ml), dried over anhydrous sodium sulphate and the solvent evaporated under reduced pressure.

Bromomercuri adduct. Potassium bromide (180 mg) was added to the acetoxymercury–methanol mixture (prepared as above) and the mixture stirred for $\frac{1}{2}$ h. Water (40 ml) was added and the total reaction mixture stirred for a further $\frac{1}{2}$ h. The bromomercuri adduct was isolated with chloroform in the usual manner.

Thin-layer chromatography

The mercury adducts were spotted on to silica-coated TLC plates (layer thickness 0.3 mm) and developed with mixtures of dioxane–light petroleum (b.p. 60–80°)–acetic acid (Table I). Preparative TLC was effected on silica plates (20 × 20 cm, layer thickness 0.5 mm) and developed with dioxane–light petroleum (b.p. 60–80°)–diethyl ether (10:10:1) for acetoxymercuri adducts and with dioxane–light petroleum (b.p. 60–80°) (1:30) for bromomercuri adducts. The components were detected by spraying the developed TLC plates with a 1 % ethanolic solution of diphenylcarbazone[24].

Isolation of demercurated products

Silica bands containing the mercury adduct (made visible by spraying with ethanolic diphenylcarbazone solution) were scraped off the TLC plates and allowed to stand in hydrochloric acid–methanol (1:3) (20 ml) for $\frac{1}{2}$ h. Water (40 ml) was added and the ethereal extract was washed successively with water (3 × 30 ml), 1 % potassium hydroxide solution (30 ml) and saturated sodium chloride solution (2 × 50 ml).

Analysis of demercurated products

Gas–liquid chromatographic (GLC) analyses were carried out on a Pye 104 or Varian 940 FID chromatograph on 2-m long columns using 10% Silar 10C (195°) or 10% FFAP (210°) as stationary phases and nitrogen (flow-rate 40–50 ml/min) as the carrier gas.

Infrared (IR) spectra were recorded on neat liquid samples sandwiched between sodium chloride discs on a Perkin-Elmer 337 spectrometer.

Nuclear magnetic resonance (NMR) spectra were recorded on 20% solutions in deuterated chloroform using a Hitachi Perkin-Elmer 20A spectrometer (60 MHz). Chemical shifts were measured in parts per million downfield from the internal standard tetramethylsilane ($\tau = 10$).

Analytical TLC was carried out on silica plates (layer thickness 0.3 mm), light petroleum (b.p. 60–80°)–diethyl ether (1:1) being used for development. The components on the plates were made visible by spraying with either Brady's reagent (2,4-

dinitrophenylhydrazine) or 3'5'-dichloro(R)-fluoroscein (1 % solution in ethanol) or by exposing the plate to iodine vapour.

Mass spectrometry (MS) was carried out on a Hitachi RMS-4 mass spectrometer operated at 70 eV, with a source pressure of 10^{-6} torr at 180°. Samples were introduced by direct insertion.

A Cary 83 laser Raman spectrometer was used with a slit width of 2 cm^{-1}. The neat sample was irradiated in a 10-μl capillary cell.

RESULTS AND DISCUSSION

TLC behaviour of mercury adducts of acetylenic esters

The R_F value of the acetoxymercuri adduct of methyl oleate is much greater than those of the adducts of the acetylenic esters (Table I), as the methyl oleate adduct contains only one mole of mercury(II) per mole of oleate while the acetylenic esters seem to add more than one mole of mercury(II) acetate per mole, thus contributing to the higher polarity of the adducts formed. However, the polarity of the mercury adducts of the acetylenic esters did not seem to follow the pattern with the degree of unsaturation exhibited by mercurated polyenoates (Table I).

TABLE I

R_F VALUES OF ACETOXYMERCURI AND BROMOMERCURI ADDUCTS OF UNSATURATED FATTY ESTERS

Substrate ester	Acetoxymercuri adduct				Bromomercuri adduct	
	30:70:5*	40:60:5*	50:50:5*	60:40:5*	25:75**	40:60**
$C_{18:1(9c)}$	0.56	0.68	0.95	0.97	0.60	0.86
$C_{11:1(5c)}$	0.14	0.22	0.44	0.65	0.31	0.65
$C_{11:1(9c)}$	0.10	0.18	0.30	0.48	0.29	0.65
$C_{11:1(10a)}$	0.09	0.16	0.26	0.47	0.21	0.64
$C_{18:2(5c,10c)}$	0.15	0.28	0.51	0.84	0.37	0.66
$C_{18:2(9a,13a)}$	0.11	0.20	0.42	0.62	0.37	0.66

* Solvent: dioxane–light petroleum (b.p. 60–80°)–acetic acid.
** Solvent: dioxane–light petroleum (b.p. 60–80°).

The R_F value of the mercury adduct of methyl octadec-*cis*-10-en-5-ynoate is higher than that of methyl 5-undecynoate, the latter having an R_F value nearly identical with that of the mercury adduct of methyl octadecadiynoate. The mercury adducts of methyl 9- and 10-undecynoates are the most polar of the adducts of the acetylenic esters.

The bromomercuri adducts were comparatively less polar than the acetoxymercuri adducts (Table I). The R_F values of the bromomercuri adduct of methyl octadec-*cis*-10-en-5-ynoate and 9,13-octadecadiynoate are nearly identical with that of mercurated methyl 5-undecynoate.

The mechanism of the oxymercuration reaction of acetylenic esters is not known and no immediate explanation for the unusual TLC behaviour of the mercury adducts of the acetylenic esters can be offered. However, the fact that the R_F values of the

TABLE II

ANALYSIS OF THE DEMERCURATED ADDUCTS OF METHYL UNDECYNOATES

A. GLC and TLC

Substrate (ester)	Products	$ECL_{Silar\ 10C}$ (%)	R_F; light petroleum (b.p. 60–80°)–diethyl ether (1:1)
$C_{11:1(5a)}$	5-Oxo-	19.33 (50)	0.58
	6-Oxo-	19.33 (50)	0.58
$C_{11:2(9a)}$	9-Oxo-	20.25 (46)	0.58
	10-Oxo-	20.74 (54)	0.52
$C_{11:1(10a)}$	10-Oxo-	20.74 (100)	0.52

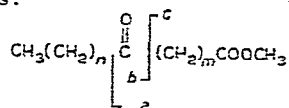B. IR spectral analysis
   1740 cm^{-1} (ester carbonyl stretching)
   1710 cm^{-1} (oxo carbonyl stretching)

C. NMR and MS

   (i) Methyl 5(6)-oxoundecanoate
       NMR signals: 9.1 (CH_3CH_2–), 8.5–8.8 (–$(CH_2)_n$–),
                    7.7 (–CH_2COOMe), 7.65 (–CH_2COCH_2–),
                    and 6.35 τ (–$COOCH_3$)
   MS major peaks:

$$CH_3(CH_2)_n \overset{O}{\underset{b}{\overset{\|}{C}}} \underset{a}{\overset{c}{|}} (CH_2)_m COOCH_3$$

   (a) m = 3, n = 5:
       214 (M, 5)*   183 (M − 31, 32)*   129 (a + 1, 100)
       127 (b + 14, 31)   113 (b, 47)*   112 (a + 14 − 31, 98)*
       101 (c, 77)

   (b) m = 4, n = 4:
       214 (M, 5)*   183 (M − 31, 32)*   144 (a + 1, 71)
       115 (c, 40)   113 (b + 14, 47)*   112 (a − 31, 98)*
       99 (b, 26)

   (ii) Methyl 9(10)-oxoundecanoate
       NMR signals: 8.71 (CH_3CHCO–), 8.91 (–$(CH_2)_n$–),
                    8.4 (–CH_2CH_2CO–), 7.9 (CH_3CO–),
                    7.72 (–CH_2CO–) and 6.35 τ (–$COOCH_3$).

   MS major peaks:
   (a) m = 7, n = 1:
       214 (M, 14)   199 (M − 15, 20)*   183 (M − 31, 100)*
       185 (a, 65)   157 (c, 57)*   154 (a − 31, 12)
       143 (c − 14, 99)   71 (b + 14, 34)   57 (b, 13)*
   (b) m = 8, n = 0
       214 (M, 14)   199 (a or M − 15, 20)*   183 (M − 31, 100)*
       171 (c, 78)   168 (a − 31, 6)   157 (c − 14, 57)*
       57 (b + 14, 13)*   43 (b, 55)

   (iii) Methyl 10-oxoundecanoate
       NMR signals: 8.71 (–$(CH_2)_n$–), 8.4 (–CH_2CH_2CO–)
                    7.9 (CH_3CO–), 7.72 (~4H. –CH_2CO–)
                    and 6.35 τ (–$COOCH_3$).

   MS major peaks (m = 8, n = 0):
                    214 (M, 20)   199 (a or M − 15, 20)   183 (M − 31, 58)
                    171 (c, 10)   168 (M − 31, 2)   157 (c − 14, 99)
                    125 (c − 14 − 32, 77)   57 (b + 14, 23)   43 (b, 100)

* Fragment arising from more than one component of the mixture.

bromomercuri adducts of the diacetylenic and enynoic esters were similar to those of the monoacetylenic mercury adducts suggests that only partial oxymercuration may have taken place.

Demercuration of adducts of acetylenic esters with hydrochloric acid

Reaction of hydrochloric acid–methanol with the acetoxy and bromomercuri adducts produced the same products, as shown by TLC and GLC analyses.

Methyl oleate. Methyl oleate (95%) was regenerated when the corresponding mercury adduct was treated with hydrochloric acid. GLC analysis on a Silar 10C column showed no isomerization of the double bond.

Methyl undecynoates. Treatment of the mercury adducts of methyl 5-, 9- and 10-undecynoate gave the corresponding methyl 5(6)-, 9(10)- and 10-oxoundecanoates, respectively, in good yields (95, 90 and 45%, respectively). Their structures were confirmed by a combination of TLC, GLC, IR, NMR and MS analyses (Table II).

Methyl octadec-cis-10-en-5-ynoate. Methyl 5(6)-oxooctadec-*cis*-10-enoate (50%) was obtained when the mercury adduct of methyl octadec-*cis*-10-en-5-ynoate was treated with hydrochloric acid. GLC, TLC and IR analyses of the product gave results similar to those found earlier[20]. [Equivalent chain length (ECL) on Silar 10C = 26.52: R_F (light petroleum–diethyl ether, 1:1) = 0.62; and IR, 1740 cm^{-1} (ester), 1700 cm^{-1} (oxo) carbonyl stretching].

Methyl 9,13-octadecadiynoate. On TLC analysis, the product of the demercurated methyl octadecadiynoate adduct gave (light petroleum–diethyl ether, 1:1) three yellow spots (R_F values 0.57, 0.51 and 0.38) when sprayed with Brady's reagent (indicating the presence of carbonyl compounds), these R_F values being lower than that of methyl 5(6)-oxoundecanoate (R_F = 0.68). Further exposure of the TLC plate to iodine vapour made three more spots visible with R_F values of 0.53, 0.46 and 0.32.

The IR analysis of the crude product confirmed the presence of ester (1740 cm^{-1}) and oxo (1710 cm^{-1}) carbonyl functions, while the NMR spectrum of the crude product showed signals arising from protons α- ($\sim$8 H, 7.5–7.8 τ) and β- ($\sim$4 H, 8.25–8.4 τ) to the C=O and/or C≡C system. No signals were observed at 6.5–7.0 τ or between 4.0–5.0 τ, thus precluding the presence of any methoxy or ethylenic protons.

GLC analysis of the products on FFAP stationary phase gave two major peaks with ECL values of 23.14 (51%, A1) and 24.06 (49%, A2). After hydrogenation, three peaks were found with ECL values of 22.18 (23%, B1), 22.56 (37%, B2) and 23.15 (40%, B3). From this analysis, it seems that component A1 is the same as B3, while A2 gave rise to B1 and B2 after hydrogenation, suggesting that A2 contained an acetylenic centre as the NMR spectrum excluded the possibility of the presence of any double-bond system. Calculation of the ECL value for methyl oxooctadecynoate based on the fractional chain length values of a triple bond and an oxo function gave a value of 24.04, which is close enough to the ECL value found for component A2.

Raman spectral analysis was attempted, but owing to the intense coloration of the sample (despite several attempts to decolorise the sample by silica column chromatography and the use of activated charcoal) no satisfactory spectrum could be obtained. During these operations, the sample was decomposed after irradiation for 2 h in the laser beam and no further analyses were possible.

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