Technical

Synthesis of *GEM*-Dibromocyclopropanoid Fatty Esters Using Phenyl (Tribromomethyl) Mercury[1]

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ABSTRACT

The *gem*-dibromocyclopropanation of naturally occurring unsaturated hydroxy fatty esters, methyl ricinoleate (I) and methyl isoricinoleate (II), has been undertaken to provide compounds which might have potential utility. Phenyl(tribromomethyl)mercury reacts only with the carbon-carbon double bond of each substrate, leaving the OH group intact. The product, methyl 9,10-dibromomethylene-12-hydroxyoctadecanoate (III) and methyl 12,13-dibromomethylene-9-hydroxyoctadecanoate (IV), obtained from I and II, respectively, were characterized by elemental, infrared (IR) and nuclear magnetic resonance (NMR) analyses.

INTRODUCTION

Dihalocarbenes can be inserted into the OH group of carboxylic acids to give dihalomethyl esters (1). With alcohols the dihalomethyl ethers formed react further to give halide and ester. With allyl alcohol attack occurs at the O—H bond (2), but with 3-cycloalkenols attack occurs on the double bond (3). In continuation of our earlier work (4) related with the synthesis of fatty acid derivatives, containing photo or thermally activatable groups and exhibiting possible insecticidal or fungicidal activity (5), we carried out the reaction of phenyl(tribromomethyl)mercury with methyl 12-hydroxy-*cis*-9-octadecenoate (I) and methyl 9-hydroxy-*cis*-12-octadecenoate (II). It was observed that both I and II reacted with $PhHgCBr_3$ to add $:CBr_2$ across the C=C bond only, giving methyl 9,10-dibromomethylene-12-hydroxyoctadecanoate (III) and methyl 12,13-dibromomethylene-9-hydroxyoctadecanoate (IV) as the respective products.

EXPERIMENTAL PROCEDURES

The melting points were taken on Kofler Block and are uncorrected. IR spectra were obtained with a Pye Unicam model 3-200 spectrophotometer. ^{1}H-NMR spectra were run in $CDCl_3$ on a Varian A-60D with trimethylsilyl (TMS) as the internal standard. The 9- and 12-hydroxyolefinic fatty acids were isolated from the seed oils of *Ricinus communis* (Euphorbiaceae) and *Wrightia tinctoria* (Apocynaceae), respectively, following the Gunstone procedure (6). These acids were methylated by refluxing them separately with 5% methanolic sulfuric acid.

Reaction of Methyl 12-hydroxy-*cis*-9-octadecenoate (I) With Phenyl (Tribromomethyl) Mercury

In a three-necked round bottomed flask, a mixture of 1.56 g (5 mmol) of methyl 12-hydroxy-*cis*-9-octadecenoate (I) and 2.64 g (5 mmol) of $PhHgCBr_3$ (7) in 60 ml of dry benzene was heated with stirring at 60 C for 5-6 hr under nitrogen. The resulting dark yellow mixture on filtration yielded 1.33 g of crude phenylmercuric bromide, m.p. 265-268 C. The filtrate on rotary evaporation gave 0.70 g of a dark yellow liquid. Chromatographic purification of this crude material on silica gel (15 g) column using the eluent light petroleum-ether (92:8) gave 0.62 g of III; (Found: C, 49.79; H, 7.51; Br, 32.83; Calcd. for $C_{20}H_{36}O_3Br_2$: C, 49.75; H, 7.46; Br, 32.78%); IR (CCl_4): 3440 (OH), 3020 (cyclopropane C—H absorption), 1740 ($COOCH_3$) and 840, 685 (CBr_2 stretching) cm^{-1}. NMR ($CDCl_3$): ∂0.92 3H, distorted t, terminal $C\underline{H}_3$), 1.35 (br, s, chain $C\underline{H}_2$), 1.71 (2H, m, $\underset{CBr_2}{\underset{\diagdown\ \ \diagup}{C\underline{H}\text{——}C\underline{H}}}$), 2.22 (2H, m, $C\underline{H}_2CO_2CH_3$), 2.54 (1H, s, D_2O exchangeable, $O\underline{H}$), 3.60 (1H, m, $C\underline{H}OH$) and 3.67 (3H, s, $CO_2C\underline{H}_3$).

Reaction of Methyl 9-hydroxy-*cis*-12-octadecenoate (II) With Phenyl (Tribromomethyl) Mercury

The reaction was carried out similarly with 1.56 g (5 mmol) of II and 2.64 g (5 mmol) of $PhHgCBr_3$ in 60 ml of benzene at 60 C for 6 hr. The usual workup gave 1.35 g of PhHgBr and 0.75 g of a crude product. Its chromatographic purification using light petroleum-ether (90:10) as eluent furnished 0.69 g of IV; (Found: C, 49.77; H, 7.49; Br, 32.82; Calcd. for $C_{20}H_{36}O_3Br_2$: C, 49.75; H, 7.46; Br, 32.78%); IR (CCl_4): 3440 (OH), 3020 (cyclopropane C—H absorption), 1740 ($COOCH_3$) and 840, 680 (CBr_2 stretching) cm^{-1}. NMR ($CDCl_3$): ∂0.93, 1.36, 1.68 (2H, m, $\underset{CBr_2}{\underset{\diagdown\ \ \diagup}{C\underline{H}\text{——}C\underline{H}}}$), 2.3, 2.63 (1H, s, D_2O exchangeable, OH), 3.62 (1H, m, $C\underline{H}OH$) and 3.69.

RESULTS AND DISCUSSION

When an equimolar mixture of phenyl(tribromomethyl)-mercury (7) and methyl 12-hydroxy-*cis*-9-octadecenoate (I) was heated with stirring at 60 C, under an atmosphere of prepurified nitrogen, it took 5-6 hr for complete decomposition of $PhHgCBr_3$, as indicated by thin layer chromatography (TLC). Workup and chromatographic purification afforded a single TLC homogenous compound, which on the basis of its NMR and IR spectra, was established as 9,10-dibromomethylene-12-hydroxyoctadecanoate (III). Similarly, product obtained from the reaction of $PhHgCBr_3$ with methyl 9-hydroxy-*cis*-12-octadecenoate (II), was characterized as methyl 12,13-dibromomethylene-9-hydroxyoctadecanoate (IV).

With both substrates (I and II) the addition reaction is in agreement with the literature report (3). Studies on the evaluation of insecticidal properties of the compounds III and IV are in progress.

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