♣Oxymercuration-Demercuration of Hydroxy Acetylenic Acids

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ABSTRACT

Oxymercuration-demercuration of methyl 9-hydroxyoctadec-12-ynoate (I) and methyl 12-hydroxyoctadec-9-ynoate (II) gave 9-hydroxy-12-oxooctadecanoate (III) and 12-hydroxy-9-oxooctadecanoate (IV) in ca. 80% yields. Jones's oxidation of III and IV afforded a quantitative yield of 1,4-dioxooctadecanoate (V).

INTRODUCTION

The potential utility of diketo fatty acids (1,2) as synthetic intermediates for the synthesis of variety of heterocycles such as pyrroles, thiophenes, Jasmones and so forth, have created interest for the synthesis of these diketo acids. Earlier, Lie Ken Jie et al. (3a) prepared 1,4-, 1,5- and 1,6-diketo acids by oxymercuration and demercuration of synthetic diacetylenic esters. We have succeeded in the preparation of 1,4-diketo acids from naturally occurring β- and γ-hydroxy olefinic acids (ricinoleic and isoricinoleic). These acids were isolated from the seed oils of *Ricinus communis* and *Wrightia tinctoria* (3b) using Gunstone's partition procedure (3c). Acetylenic acids prepared from these hydroxy olefinic acids on oxymercuration-demercuration followed by Jones's oxidation yielded the desired 1,4-diketo acids.

EXPERIMENTAL PROCEDURES

Preparation of β- and γ-Hydroxyacetylenic Fatty Acids

β- and γ-Hydroxyolefinic acids were first converted to their acetate derivatives using acetic anhydride and pyridine (1:3) and then brominated in CCl_4 at 0 C. The resulting dibromide was then refluxed in a 20% aqueous ethanolic solution of KOH for 8 hr. The bulk of the solvent was removed under reduced pressure. The products were then worked up with diethyl ether after acidification. The product, on column chromatographic purification, yielded ca. 80% of β- and γ-hydroxyacetylenic acids. Methyl esters were prepared by *MeOH/H*$^+$ and were characterized as methyl 9-hydroxyoctadec-12-ynoate (I) and methyl 12-hydroxyoctadec-9-ynoate (II).

IR (cm^{-1}): 3480-3380, 1740, 1210, 1170, 1010.
NMR [Varian A 60, (δ ppm)]: 3.6s (-COOC$\underline{H}_3$), 3.8 m $(\text{-}\underset{\underset{\text{OH}}{|}}{\text{C}}\underline{\text{H}}\text{-})$,
2.2 m ($\underline{H}_2$C-COOCH$_3$: -$\underline{H}_2$C-C=C-CH$_2$-), 3.6 m $(\text{-}\underset{\underset{\text{O}\underline{\text{H}}}{|}}{\text{C}}\text{H-})$, 1.3 br,s
(chain-C$\underline{H}_2$-) and 0.9 t (terminal methyl)

Oxymercuration-Demercuration of I and II

Oxymercuration-demercuration of I and II were made using the procedure of Hudrlik (4). In separate experiments, the methyl esters of I and II (2 g, 0.00646 mol) in 20 mL tetrahydrofuran (THF) were added to the stirred solution of mercuric acetate (5 g, 0.01572 mol) in 20 mL of water at room temperature. The mixtures were further stirred for 2 hr to complete the mercuration. Examination of thin layer chromatography (TLC) confirms the mercuration (5), sodium borohydride (0.5M, 20 mL). NaOH (3 m, 30 mL) was added and the mixture was acidified with hydrochloric acid at 0 C to complete the demercuration. The reaction mixture was worked up with diethyl ether and dried over anhydrous sodium sulphate. Evaporation of ether and crystallization with petroleum benzene gave solid products III and IV (mp 52-54 C) in ca. 80% yield.

IR (cm^{-1}): 3440-3330, 1740, 1690, 1160, 1110, 1060 and 1035
NMR (δ ppm): 3.74s (COOC$\underline{H}_3$), 4.0 m $(\text{-}\underset{\underset{\text{OH}}{|}}{\text{C}}\underline{\text{H}}\text{-})$,
2.3 br,m ($\underline{H}_2$C-COOCH$_3$: H$_2$C-$\overset{\overset{\text{O}}{\|}}{\text{C}}$-C$\underline{H}_2$) and
2.5 m (O$\underline{H}$, D$_2$O exchangeable)
confirm the structures, III and IV, (Scheme 1).

Jones's oxidation (6) of III and IV gave 9,12-dioxooctadecanoate (V) as solid, mp 50-51 C (uncorrected, Kofler).

IR (cm^{-1}): 1740, 1690, 1170, 1060
NMR (δ ppm): 2.67s $(\text{-}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{-C}\underline{\text{H}}_2\text{-C}\underline{\text{H}}_2\text{-}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{-})$,
2.5-2.4 m $(\text{C}\underline{\text{H}}_2\text{-}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{, C}\underline{\text{H}}_2\text{-}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{, }\underline{\text{H}}_2\text{C-COOCH}_3)$
Mass [(JEOL JMS-D 300), m/z] 326, 294, 256,
241, 185, 184, 169, 127 and 113 (Scheme 2)

Treatment of V with a catalytic amount of p-toluenesulphonic acid in benzene gave furanoid esters (VI) (3). Spectral properties of these furanoid esters were the same as those reported in the literature (7).

RESULTS AND DISCUSSION

Neighboring group participation of hydroxyl with the double bond during bromination of hydroxyolefinic acid resulted in the formation of side products along with dibromide (8). Dehydrobromination of dibromides with alcoholic KOH (9) gave a low yield of the corresponding acetylene.

To overcome this difficulty, the hydroxyl groups of β- and γ-hydroxyolefinic acids were first converted into their corresponding acetate derivatives. These, on bromination and dehydrobromination, gave ca. 80% hydroxyacetylenic fatty acids (Ia and IIa). The acetylenic products as their methyl esters (I, II) showed characteristic signals in nuclear magnetic resonance (NMR) at δ 2.2 m ($\underline{H}_2$C-C≡C-C$\underline{H}_2$). The oxymercuration and demercuration of I and II successfully gave keto-hydroxy acids, III and IV. These, on Jones's oxidation, gave 9,12-diketo fatty acid (V) in quantitative yield. The IR of V gave bands at 1690 for the diketo grouping and its NMR spectrum gave characteristic signals at

2.67s $(\text{-}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{-C}\underline{\text{H}}_2\text{-C}\underline{\text{H}}_2\text{-}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{-})$ and 2.5-2.4 $(\underline{\text{H}}_2\text{C-C, }\underline{\text{H}}_2\text{C-}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{, }\underline{\text{H}}_2\text{C-}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{OOCH}_3)$.

Mass spectrum provided conclusive evidence for the formation of 1,4-diketo ester. It gave no information for formation of 9,13-diketo ester from the γ-hydroxyacetylene. The absence of signal at δ 4.57s completely ruled out the formation of 10,12-diketo ester. Nonformation of 9,13- and

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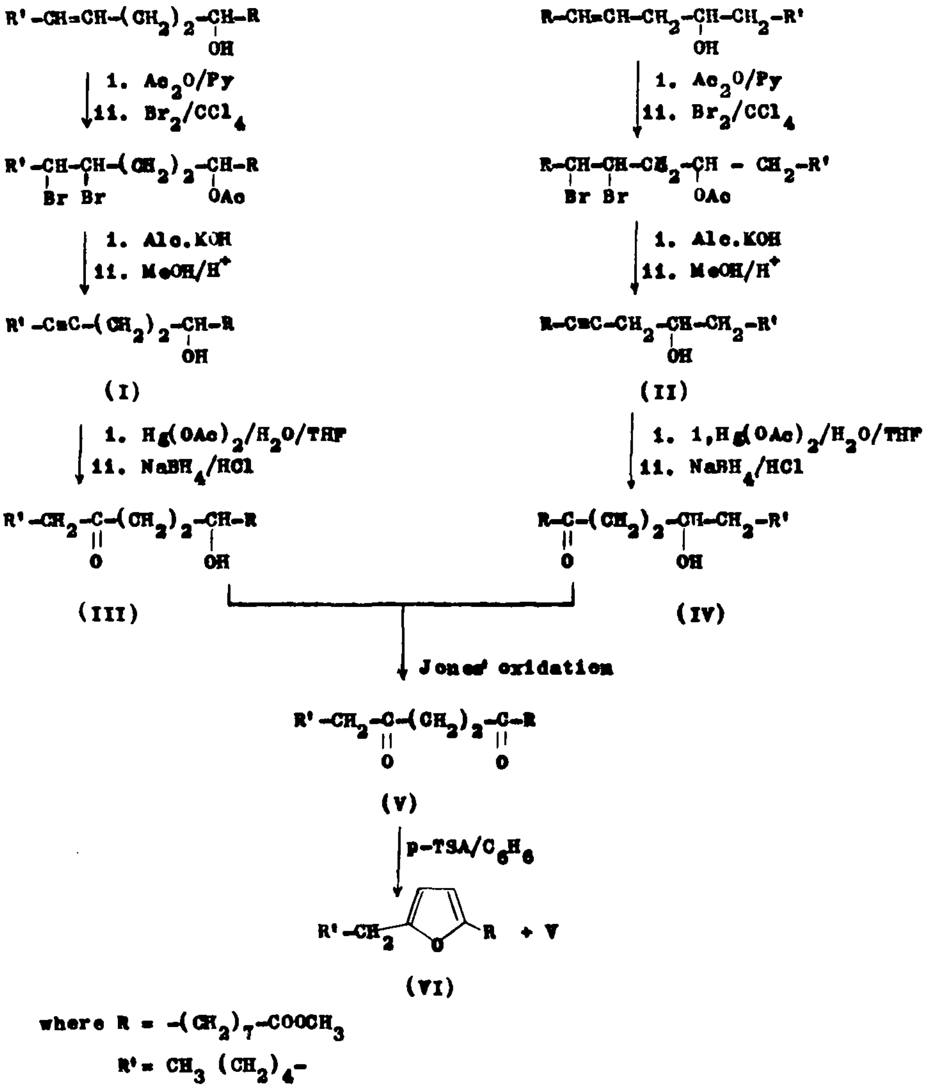
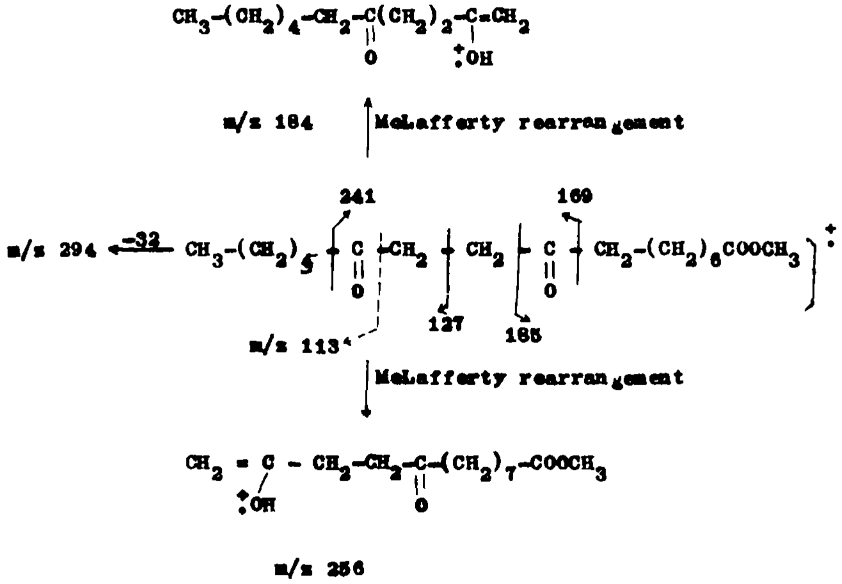


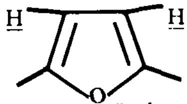
Scheme I



Scheme II

10,12-diketo esters had gained support on the basis of the Stork rule (2).

The reaction of V with a catalytic amount of p-toluenesulphonic acid in benzene yielded ca. 60% methyl 9,12-epoxyoctadec-9,11-dienoate (VI). NMR gave the characteristic signal at 5.7s for



The formation of VI gave proof that oxymercuration-demercuration, followed by Jones's oxidation, of β- and γ-hydroxyacetylene, led to formation of the 1,4-diketo acids.

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REFERENCES

1. Lie Ken Jie, M.S.F., S. Sinha and F. Ahmad, JAOCS 60:1777 (1983).
2. Stork, G., and R. Borch, JAOCS 86:935 (1964).
3a. Lie Ken Jie, M.S.F., and C.H. Lam, Chem. Phys. Lipids 19: 275 (1977).
3b. Ansari, F.H., G.A. Qazi, S.M. Osman and M.R. Subbaram, Ind. J. Appl. Chem. 34:157 (1971).
3c. Gunston, F.D., J. Chem. Soc. 1611 (1954).
4. Hudrlik, P.F., and A.M. Hudrlik, J. Org. Chem. 38:4254 (1973).
5. Feigl, F., Inorganic spot test analysis, translated by Ralph. E. Oesper, Elsevier Publishing Co. Amsterdam, 1958 p. 64.
6. Bowden, K., I.M. Heilbron, E.R.H. Jones and B.C.L. Weedon, J. Chem. Soc. 39 (1946).
7. Lie Ken Jie, M.S.F., and C.H. Lam, Chem. Phys. Lipids 21: 275 (1978).
8. Gunstone, F.D., and B.S. Perera, Ibid. 11:43 (1973).
9. Gunstone, F.D., and G.M. Hornby, Ibid. 3:91 (1969).

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Comparison of Homogeneous and Heterogeneous Palladium Hydrogenation Catalysts

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ABSTRACT

Mechanistic and kinetic studies of Pd-catalyzed hydrogenation at atmospheric pressure and 30-100 C were carried out with methyl sorbate, methyl linoleate and conjugated linoleate. Homogeneous Pd catalysts and particularly Pd-acetylacetonate [Pd(acac)$_2$] were significantly more selective than Pd/C in the hydrogenation of sorbate to hexenoates, mainly *trans*-2-hexenoate. Relative rate constants for the different parallel and consecutive reactions, determined by computer simulation, indicated that the low diene selectivity of Pd/C can be attributed to a significant direct reduction of sorbate to hexanoate. The similar behavior of PdCl$_2$ to that of Pd/C suggests that Pd(II) was initially reduced to Pd(O). Valence stabilization of PdCl$_2$ by adding DMF or a mixture of Ph$_3$P and SnCl$_2$ increased the diene selectivity but decreased the activity. Stabilization of Pd(acac)$_2$ with triethylaluminum (Ziegler catalyst) resulted in increased activity but decreased selectivity. The kinetics of methyl linoleate hydrogenation showed that although Pd(acac)$_2$ was only half as active as Pd/C, their respective diene selectivity was similar (10.4 and 9.6). The much greater reactivity of conjugated compared with unconjugated linoleate toward Pd(acac)$_2$ suggests the possible formation of conjugated dienes as intermediates that are rapidly reduced and not detected in the liquid phase during hydrogenation.

INTRODUCTION

Homogeneous Pd complexes have been tried as catalysts to a very limited extent for the partial hydrogenation of unsaturated fatty esters and oils. The mixture of PdCl$_2$ (PPh$_3$)$_3$ and SnCl$_2$ has been used as a homogeneous catalyst for hydrogenation of simple alkenes (1) and soybean methyl esters (2). In the latter study, no significant formation of stearate was observed. When Pd(acac)$_2$ was used as catalyst for the continuous hydrogenation of soybean oil (3), relatively low triene (triene to diene) selectivity (max. 2.9) was obtained. In batch hydrogenation of soybean oil, the same Pd-complex produced a triene selectivity of ca. 4 (4). This selectivity is significantly higher than that of heterogeneous Pd catalysts. The latter normally ranges between 2 and 2.5 (5).

PdCl$_2$ has been used as precursor for the preparation of both homogeneous and heterogenized homogeneous catalysts. PdCl$_2$ alone, without any valence stabilization agent, is reduced rapidly in hydrogen atmosphere to metallic Pd. On the other hand, together with a conjugated diene and DMF, PdCl$_2$ forms complexes that prevent reduction of Pd(II) to Pd(O) (6,7). Similar valence stabilization has been obtained by adding metal ions to PdCl$_2$ (8). The dienes in the Pd-complex formed are reduced selectively to monoenes. When all dienes are hydrogenated, then Pd(II) is reduced to Pd(O), which catalyzes the hydrogenation and isomerization of monoenes (7).

In the present work, different homogeneous Pd-complexes have been used as catalysts for the hydrogenation of methyl sorbate, methyl linoleate and conjugated methyl linoleate. The results are compared with hydrogenations with a heterogeneous Pd/C catalyst.

EXPERIMENTAL

All hydrogenations were performed at 1 atm H$_2$ pressure,

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