

A ONE-STEP ESTER TO HYDROCARBON REDUCTION

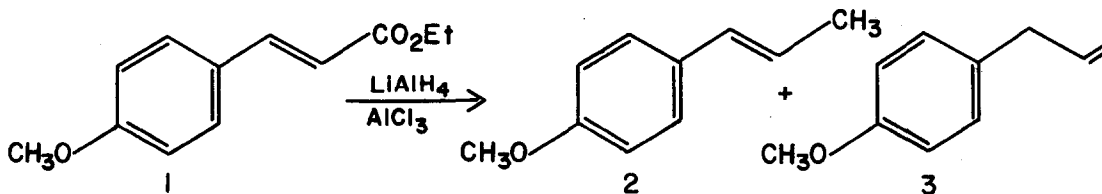
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Oxidation and reduction constitute an important part of organic chemistry, and such reactions of oxygenated functional groups occupy a central place in this area, with many reactions having been developed to transform one functionality into another of differing oxidation level. The reduction of a Group III oxidation level<sup>1</sup> functional group (e.g. -COOR) to a Group 0 functional group (-CH<sub>3</sub>) is, however, a transformation for which there is no general one-step reaction<sup>2</sup>. Indeed, even the number of specific one-step transformations of this type that have been reported is rather small, the examples being apparently restricted to catalytic hydrogenation of certain substrates under vigorous conditions<sup>3</sup>.

In view of the dearth of such reactions, we wish to report a reaction that we have discovered in the course of other work. Ethyl *p*-methoxycinnamate 1, on reduction with LiAlH<sub>4</sub>-AlCl<sub>3</sub> in ether, gives not the expected *p*-methoxycinnamyl alcohol, but a quantitative



yield of the two isomers anethole 2 and *p*-allylanisole (estragole) 3 in a 2:1 ratio (glc ratio 66 : 34). The identity of these compounds was established chromatographically using

authentic samples (6 foot, 5% QF-1 on Chromosorb G column at 140<sup>0</sup>, anethole retention time 10.5 min., *p*-allylanisole retention time 4.7 min.) followed by preparative glc (QF-1) purification and demonstration of identity of spectral properties with those of authentic samples (anethole:  $\nu_{\max}^{\text{film}}$  1605, 1500, 1220, and 968 cm<sup>-1</sup>;  $\lambda_{\max}^{\text{EtOH}}$  259 nm (log  $\epsilon$  4.29) (lit.  $\lambda_{\max}^{\text{EtOH}}$  258 nm (log  $\epsilon$  4.31)<sup>4</sup> and  $\lambda_{\max}^{\text{EtOH}}$  260 nm (log  $\epsilon$  4.26)<sup>5</sup>);  $\delta$  1.78 (3H,d,J=5Hz,CH<sub>3</sub>), 3.67 (3H,s,OCH<sub>3</sub>), 5.7-6.3 (2H,m,vinyl H), and 6.6-7.4 ppm (4H,q,aromatic H); *p*-allylanisole:  $\nu_{\max}^{\text{film}}$  1605, 1500, 1220, and 915 cm<sup>-1</sup>;  $\lambda_{\max}^{\text{EtOH}}$  229 (log  $\epsilon$  4.26), 281 (log  $\epsilon$  3.60) and 287 nm (log  $\epsilon$  3.52) (lit.  $\lambda_{\max}$  279 nm (log  $\epsilon$  3.60)<sup>6</sup>);  $\delta$  3.25 (2H,d,J=6Hz,Ar-CH<sub>2</sub>), 3.67 (3H,s,OCH<sub>3</sub>), 4.7-5.2 (2H,m) and 5.6-6.2 (1H,m) (vinyl H), and 6.6-7.2 ppm (4H,q,aromatic H)).

This reaction is, thus, an extremely rare instance of a one-step reduction of an ester to the corresponding hydrocarbon initiated by a metal hydride reagent<sup>7</sup>. That it is by no means general, however, is immediately clear from the reduction of the closely related ethyl cinnamate, which has been reported to reduce normally to the primary alcohol under apparently identical conditions to ours<sup>8</sup>. To ensure that this abrupt difference in reaction was due to the methoxyl substituent and was not an artifact of the comparison of results from different laboratories, ethylcinnamate was reduced, giving no hydrocarbon and producing cinnamyl alcohol in 95% yield, confirming the result of Jorgenson<sup>8</sup>. Although at first sight the effect of methoxyl might be surprising since hydride reductions of ketones are known to show positive  $\rho$  values<sup>9,10,11</sup> presumably the reduction to the hydrocarbon involves Lewis acid-catalyzed<sup>12</sup> carbonium ion formation with a substantial negative  $\rho$  value.

In a search of the literature to find closely related reactions we have found reports of certain alcohols being reduced to hydrocarbons under LiAlH<sub>4</sub>-AlCl<sub>3</sub> conditions<sup>13,14</sup>, and in a particularly relevant paper, the reductions of *p*-amino- and *p*-methoxybenzaldehydes to the corresponding toluenes, the electron donating substituents being essential for reduction to the hydrocarbon<sup>15</sup>. Thus although the reaction at hand may at present be almost unique, its existence might not have been entirely unpredictable, the possibly surprising feature being the quantitative ester reduction accompanied by no detectable double bond reduction.

In order to explore the limited generality of the reaction, reduction of the corresponding aldehyde and alcohol were also studied. *p*-Methoxycinnamyl alcohol, produced by LiAlH<sub>4</sub> reduction of methyl *p*-methoxycinnamate<sup>16</sup>, also was reduced by LiAlH<sub>4</sub>-AlCl<sub>3</sub> giving a quantitative

yield of the anethole-estragole mixture in essentially the same proportions (64:36). *p*-Methoxycinnamaldehyde, produced by  $MnO_2$  oxidation of *p*-methoxycinnamyl alcohol<sup>16</sup>, was also reduced quantitatively to give the same hydrocarbon mixture (anethole:estragole 67:33). Reduction of ethyl *o*-methoxycinnamate also gave quantitative reduction to hydrocarbon, the proportion of double bond isomers, however, being slightly different (*o*-anethole:  $\lambda_{\max}^{EtOH}$  250 nm ( $\log \epsilon$  4.03) (lit.  $\lambda_{\max}^{EtOH}$  248 nm ( $\log \epsilon$  4.03))<sup>6</sup>;  $\delta$  1.90 (3H,d,J=6Hz,CH<sub>3</sub>), 3.42 (3H,s,OCH<sub>3</sub>), 6.0-6.5 (2H,m,vinyl H), and 6.6-7.5 ppm (4H,m,aromatic H), 56%. *o*-Estragole:  $\lambda_{\max}^{EtOH}$  272 nm ( $\log \epsilon$  3.36) (lit.  $\lambda_{\max}^{EtOH}$  273 nm ( $\log \epsilon$  3.38))<sup>6</sup>;  $\delta$  3.38 (2H,d,J=7Hz, Ar-CH<sub>2</sub>), 3.80 (3H,s,OCH<sub>3</sub>), 4.8-5.2 (2H,m) and 5.6-6.3 (1H,m) (vinyl H), and 6.8-7.3 ppm (4H,m,aromatic H), 44%).

The reduction in a system with an amino activating group rather than methoxyl was also attempted. Reduction of ethyl *p*-aminocinnamate under the same conditions gave a complex mixture of products, from which the corresponding hydrocarbons *p*-allylaniline and *p*-propenylaniline<sup>17</sup> could be extracted only with tedious purification and in 18% yield.

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#### References and Footnotes

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