

## Anomalous Nitrations of $\alpha,\beta$ -Unsaturated Esters: a Role for $\alpha$ -Carbonyl Cations?

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Reaction of  $\alpha,\beta$ -unsaturated esters with nitronium tetrafluoroborate at  $-16\text{ }^\circ\text{C}$  affords products which suggest the intermediacy of highly reactive  $\alpha$ -carbonyl cations.

Nitration has a long-established place in the literature of organic chemistry. The various oxides of nitrogen provide a bewildering array of potential nitration mechanisms.<sup>1</sup> We were intrigued by reports<sup>2</sup> of nitric acid-induced nitration of  $\alpha,\beta$ -unsaturated esters, leading to  $\beta$ -nitro- $\alpha$ -hydroxy products. Although the authors chose not to comment on the possible origin of these compounds, the unusual regiochemistry suggested to us the possibility of formation of  $\alpha$ -carbonyl cations.  $\alpha$ -Carbonyl cations are expected to be rather unstable. Nevertheless they are documented, and the rare chemistry of cations adjacent to electron-withdrawing groups has recently been reviewed.<sup>3</sup>

Several alternative mechanisms could account for the formation of the observed products (see Scheme 1). One features a concerted addition of a nitronium donor and water to the double bond; this mechanism would not require localisation of extensive positive charge adjacent to the carbonyl group, but would involve the organisation of three separate molecules in the transition state.

A second mechanism which would not demand significant charge build-up could involve a thermal  $[2 + 2]$  cycloaddition reaction. Such concerted addition has previously been proposed<sup>4</sup> for the nitration of cyclohexene by nitronium ion. The adduct with the regiochemistry represented in Scheme 1 would afford the observed products following hydrolysis.

A third mechanism which might account for the observed regiochemistry would involve radical addition of  $\cdot\text{NO}_2$ , followed by trapping to form an  $\alpha$ -nitro- $\beta$ -nitro ester; in this case, hydrolysis of the nitrite would be required to afford the observed product. Nitro-nitrite adducts have been seen in reactions of alkenes with  $\text{NO}_2\text{-N}_2\text{O}_4$ ,<sup>5</sup> and complex equilibria

between oxides of nitrogen can exist in solutions of nitric acid.

However, each of these proposed mechanisms caused us concern, and so we resolved to obtain further information about the nature of the reactive intermediates in nitrations of alkenes. To probe the possible accumulation of positive charge adjacent to the carbonyl group, we selected substituted acrylate esters and nitronium tetrafluoroborate in dry acetonitrile for our studies. Our first experiment employing methyl methacrylate **1** (Scheme 2) afforded two products, the allylic nitro compound **2** (40%) and the addition product **3** (8%). Notably, the regiochemistry of the adduct in **3** was consistent with the  $\alpha$ -carbonyl cation hypothesis; the appearance of allylic nitration was not surprising.<sup>4,6</sup>

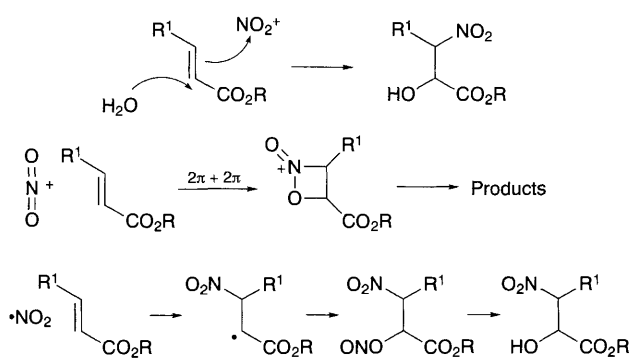
We reasoned that if addition reactions such as that observed did not involve significant charge on the  $\alpha$ -carbon, then changing the substitution pattern on the  $\beta$ -carbon should not dramatically affect the nature of the reaction. However, if there were considerable build-up of positive charge on the  $\alpha$ -carbon, then a more substituted  $\beta$ -carbon might induce cationic rearrangements. To investigate this, we employed the ethacrylate ester **4**. Although this substrate did not provide a shift of either hydride or carbon to the  $\alpha$ -centre, it nevertheless gave resounding evidence of the high positive charge density formed at this carbon. The products were the cyclopropane **6** (21%) and the allylic nitration product **5** (29%). Formation of cyclopropanes is known to occur from propyl cations under a number of different synthetic reaction conditions, and is postulated to proceed *via* a protonated cyclopropane.<sup>7</sup> The observed yield for cyclopropane formation here would be among the highest recorded for a cyclopropane formation from a propyl cation.<sup>8</sup>

To confirm this special result, the corresponding *n*-butyl ester **7** was also subjected to the reaction, and afforded the allylic nitro product **8** (28%) and the corresponding cyclopropane **9** (22%). The identity of this cyclopropane was confirmed by independent synthesis.

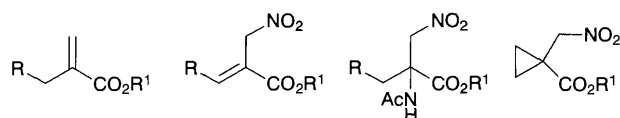
These experiments demonstrate that the reactive intermediates formed in nitration reactions of  $\alpha,\beta$ -unsaturated esters with nitronium tetrafluoroborates behave as would be expected for highly reactive  $\alpha$ -carbonyl cations.

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Scheme 1



1 R = H, R<sup>1</sup> = Me    2 R = H, R<sup>1</sup> = Me    3 R = H, R<sup>1</sup> = Me    6 R<sup>1</sup> = Et  
4 R = Me, R<sup>1</sup> = Et    5 R = Me, R<sup>1</sup> = Et    9 R<sup>1</sup> = Bu  
7 R = Me, R<sup>1</sup> = Bu    8 R = Me, R<sup>1</sup> = Bu

Scheme 2

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