

CONVERSION OF  $\gamma$ -NITROKETONES TO  $\gamma$ -DIKETONES BY THE NEF  
REACTION

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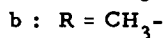
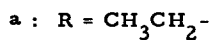
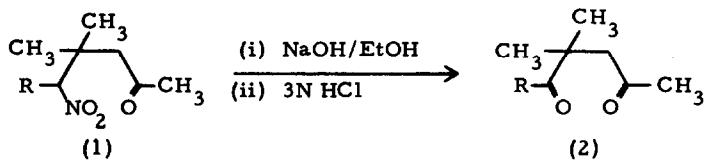
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Van Tamelen and Thiede<sup>1</sup> have suggested that the Nef reaction<sup>2,3</sup> is susceptible to steric inhibition, with respect to the attack of water at the carbon bearing the double bond in the intermediate nitronic acid derived from the initial nitro-compound. This suggestion was based at least in part on the failure<sup>1</sup> of 4,4-dimethyl-5-nitro-2-pentanone to undergo conversion to the corresponding aldehyde 2,2-dimethyl-4-oxopentanal. The supposed limitations of the Nef reaction have been mentioned subsequently by Noland<sup>3</sup> and very recently by McMurry and Melton<sup>4</sup>, who describe a useful, mild conversion of  $\gamma$ -nitroketones to  $\gamma$ -diketones using aqueous titanium (III) chloride.

This latter report<sup>4</sup> prompts the disclosure of the following results<sup>+</sup>. The  $\gamma$ -nitroketones 4,4-dimethyl-5-nitro-2-heptanone (1a)<sup>5</sup> and 4,4-dimethyl-5-nitro-2-hexanone (1b)<sup>5,6</sup> undergo conversion by the Nef reaction in 70% yield to the  $\gamma$ -diketones 4,4-dimethyl-2,5-heptandione (2a)<sup>7</sup> and 3,3-dimethyl-2,5-hexandione (2b)<sup>8</sup> respectively, provided that ethanolic sodium hydroxide is used. The nitroketones are only sparingly soluble in aqueous alkali and the reaction fails in water alone: this probably accounts for the observation of van Tamelen and Thiede<sup>1</sup>.

$\gamma$ -Nitroketones are readily available from the Michael addition of nitroalkane anions to  $\alpha,\beta$ -unsaturated ketones and consequently the related  $\gamma$ -diketones are now easily

attainable. This point has also been made by McMurry and Melton<sup>4</sup> and while their method is very mild, the Nef reaction described here would be economical and suitable for large-scale work.



+ Satisfactory i. r. and p. m. r. data were obtained for all compounds described.

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