

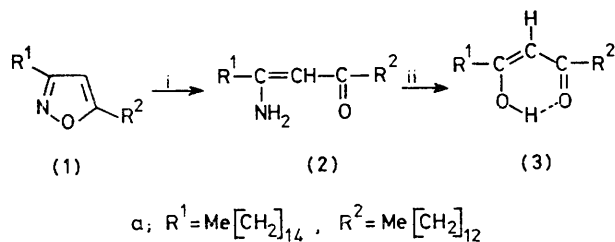
## Synthesis of Hentriacontane-14,16-dione, a $\beta$ -Diketone Found in Plant Waxes

By GIORGIO BIANCHI\* and MARCO DE AMICI

*(Institute of Organic Chemistry, The University, Viale Taramelli 10, 27100 Pavia, Italy)*

**Summary** Hentriacontane-14,16-dione (**3a**), a  $\beta$ -diketone of biological interest, has been synthesized starting from the isoxazole (**1a**). CATALYTIC hydrogenation (step i) under mild conditions of isoxazoles (**1**) with the formation of enamino-ketones (**2**) which are readily converted into the corresponding  $\beta$ -

diketones (3) by acid hydrolysis (step ii) should provide a good route for the synthesis of naturally occurring long chain  $\beta$ -diketones and hydroxy  $\beta$ -diketones.<sup>1</sup>



Current interest in epicuticular waxes of higher plants, several species of which produce large amounts of  $\beta$ -dicarbonyl compounds, prompts us to report the preliminary synthesis of hentriacontane-14,16-dione (3a) which is a major component of wheat, barley, and other plants' waxes.<sup>2</sup>

When 1-nitrohexadecane† was heated under reflux in benzene solution for 7 h with a slight excess of pentadec-1-yne<sup>3</sup> and phenyl isocyanate in the presence of catalytic

amounts of triethylamine, the corresponding isoxazole was obtained, which may be isolated as a colourless crystalline compound, m.p. 56.5 °C, in 35% yield by column chromatography.‡ Some unchanged nitroalkane and alkyne were recovered. No furoxane (the cyclic dimer of the nitrile oxide) was formed under these conditions.

Hydrogenation in ethanol on Raney Nickel at room temperature and pressure gave the enamino-ketone (2a) which by subsequent acid hydrolysis ( $\text{H}_2\text{SO}_4$ , 1:1) afforded a 75% overall yield of the  $\beta$ -diketone (3a) identical by t.l.c., i.r. and u.v. spectral data with the naturally occurring hentriacontane-14,16-dione.<sup>4</sup>

We are unaware of any previous report of long chain  $\beta$ -diketone synthesis in which the carbonyl groups are located on even positions. We are also unaware of examples of 1,3-dipolar cycloadditions involving aliphatic nitrile oxides and alkynes with chain lengths longer than 5 and 10 carbon atoms, respectively.

We thank C.N.R. (Rome) for financial support.

(Received, 14th August 1978, Com. 889.)

† The 1-nitrohexadecane (m.p. 29.5–31.5 °C, leaflets from light petroleum) was prepared essentially by the method described for the synthesis of 1-nitro-octane in *Org. Synth.* 1963, Coll. vol. IV, 724. In *Angew. Chem.*, 1943, 56, 161, Ch. Grundmann reported the formation of nitrohexadecane by direct nitration of hexadecane with  $\text{HNO}_3$ .

‡ Satisfactory analytical results were obtained for all the new compounds.

<sup>1</sup> A. Quilico, in 'Five- and Six-Membered Compounds with Nitrogen and Oxygen,' Interscience, New York, 1962, p. 42.

<sup>2</sup> A. P. Tulloch in, 'Chemistry and Biochemistry of Natural Waxes,' ed. P. E. Kolattukudy, Elsevier, Amsterdam, 1976, p. 235.

<sup>3</sup> B. B. Elsner and P. F. M. Paul, *J. Chem. Soc.*, 1951, 893.

<sup>4</sup> G. Bianchi and M. Corbellini, *Phytochemistry*, 1977, 16, 943.