

## Photochemical Ring Enlargement of $\alpha$ -Cyanocycloalkanones

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**Summary** Irradiation of two  $\alpha$ -cyanocycloalkanones gives the corresponding enals as major products, together with ring expanded products with incorporation of a nitrogen atom into the ring.

PHOTOCHEMICAL ring expansions of suitably substituted cyclic ketones leading to larger ring ketones and macrolides have gained recent attention.<sup>1</sup> We report on our studies of the cyclic  $\alpha$ -cyano-ketones (**1a**) and (**1b**) which undergo a novel ring enlargement with incorporation of a nitrogen atom into the ring on irradiation.

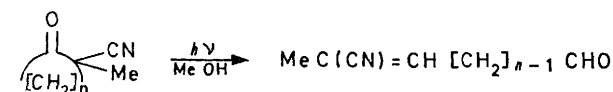
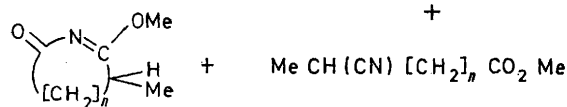
Photolysis (Hanovia 450 W Hg high pressure lamp) of a 1–2% degassed solution of (**1a**)<sup>2</sup> in methanol followed by preparative g.l.c. gave the *E*† aldehyde (**2a**) (30%) [ $\nu_{\max}$  CHCl<sub>3</sub> 2210(m), 1720 cm<sup>-1</sup> (s);  $\delta$  (CDCl<sub>3</sub>): 9.93 (1H, t, *J* ca. 1 Hz), 6.3 (1H, m), 2.6–1.5 (6H, m), 1.85 (3H, d, *J* ca. 1 Hz)] and the *Z*† aldehyde (**2a**) (61%) [ $\nu_{\max}$  CHCl<sub>3</sub> 2210(m), 1720 cm<sup>-1</sup> (s);  $\delta$  (CDCl<sub>3</sub>): 10.0 (1H, t, *J* ca. 1 Hz), 6.13 (1H,

m), 2.7–1.6 (6H, m), 1.92 (3H, d, *J* ca. 1 Hz)] as major products, distinguished by their <sup>1</sup>H n.m.r. spectra,<sup>3</sup> together with the ester (**3a**) (7%), identified by spectral comparison with an authentic sample obtained from the corresponding acid.<sup>4</sup> In addition, a very minor product (ca. 1%) was obtained and assigned structure (**4a**) on the basis of its i.r. [ $\nu_{\max}$  CHCl<sub>3</sub> 1690 (w), 1660 cm<sup>-1</sup> (s)] and n.m.r. spectra [ $\delta$  (CDCl<sub>3</sub>) 1.22 (3H, d, *J* 7 Hz), 1.5–2.6 (9H, two multiplets), 3.7 (3H, s)] and its alkaline hydrolysis into 2-methylheptanedioic acid, in turn converted into its dimethyl ester (spectral and g.l.c. comparisons with an authentic sample<sup>4</sup>).

Similar irradiation of (**1b**)† (obtained from 2-cyanocycloheptanone<sup>5</sup>) in methanol gave the *E*† aldehyde (**2b**) (8%) [ $\nu_{\max}$  CHCl<sub>3</sub> 2210 (m), 1720 cm<sup>-1</sup> (s);  $\delta$  (CDCl<sub>3</sub>) 9.93 (1H, t, *J* ca. 1 Hz), 6.35 (1H, m), 2.5–1.3 (8H, m), 1.87 (3H, d, *J* ca. 1 Hz)] and the *Z*† aldehyde (**2b**) (78%) [ $\nu_{\max}$  CHCl<sub>3</sub> 2210 (m), 1720 cm<sup>-1</sup> (s);  $\delta$  (CDCl<sub>3</sub>) 9.9 (1H, t, *J* ca. 1 Hz), 6.12 (1H, m), 2.6–1.2 (8H, m), 1.93 (3H, d, *J* ca. 1 Hz)] as major products, together with an oil (13%) assigned struc-

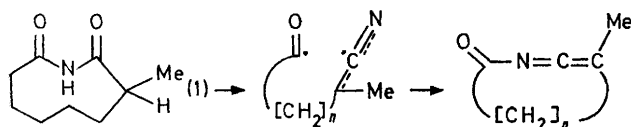
† Satisfactory elemental analysis was obtained on the 2,4-DNP derivative.

‡ Characterized by accurate mass measurement owing to difficulties in obtaining a pure 2,4-DNP derivative.

(1a)  $n = 4$ b  $n = 5$ 

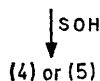
(4)

(3)



(5)

(6)



ture (4b) on the basis of mass measurement ( $M^+$  183.12575), and the close similarity of its i.r. [ $\nu_{\text{max}}$   $\text{CHCl}_3$  1690 (m), 1660  $\text{cm}^{-1}$  (s)] and n.m.r. spectra [ $\delta$  ( $\text{CDCl}_3$ ) 1.18 (3H, d,  $J$  7 Hz), 1.3–2.7 (11H, two multiplets), and 3.7 (3H, s)] to those of the material attributed structure (4a). Further support for this rearrangement (1)  $\rightarrow$  (4) is afforded by the isolation in 18% yield from the irradiation of (1b) in dioxan–water (50:50) of a crystalline compound, m.p. 138.5–139.5°, whose i.r. [ $\nu_{\text{max}}$   $\text{CHCl}_3$  3340 (w), 1690  $\text{cm}^{-1}$  (s)] and n.m.r. spectra [ $\delta$  ( $\text{CDCl}_3$ ) 1.23 (3H,  $J$  6 Hz), 1.7 (8H, broad), 2.83 (3H, m), and 8.27 (1H, broad, exchangeable with  $\text{D}_2\text{O}$ )] are consistent with its structure being the imide (5).

The formation of these ring-enlarged products may be rationalised in terms of a cleavage-recombination mechanism to give the intermediate cyclic ketenimine (6), which then undergoes addition of methanol to form (4) or addition of water to form (5).<sup>6</sup> The relative yields of (4a) and (4b) are consistent with the expected relative stabilities of the ketenimines (6a) and (6b).

The authors are grateful to the National Research Council of Canada for support of this work.

(Received, 4th June 1973; Com. 806.)

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