Photochemical Ring Enlargement of α-Cyanocycloalkanones

By Gerald K. Chip and Thomas R. Lynch*

(*Scarborough College and Department of Chemistry, University of Toronto, West Hill, Ontario, Canada* M1C 1A4)

Summary Irradiation of two α-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.[1] We report on our studies of the cyclic α-cyano-ketones (**1a**) and (**1b**) which undergo a novel ring enlargement with incorporation of a nitrogen atom into the ring on irradiation.

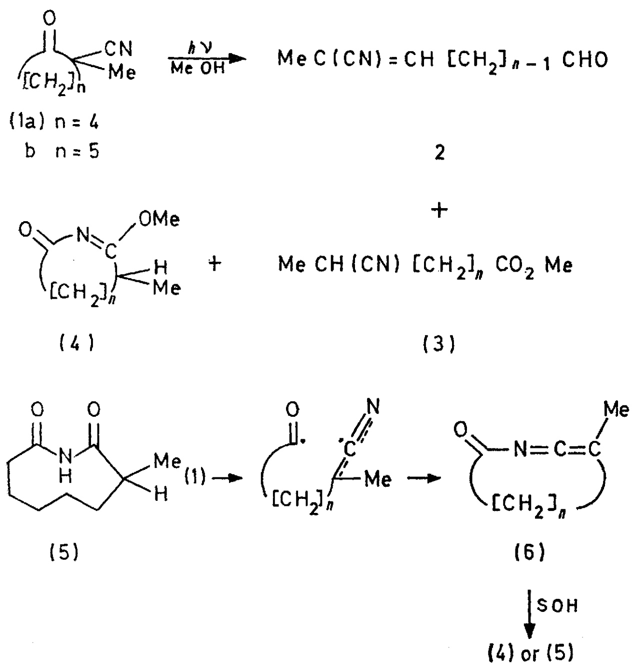
Photolysis (Hanovia 450 W Hg high pressure lamp) of a 1—2% degassed solution of (**1a**)[2] in methanol followed by preparative g.l.c. gave the *E*† aldehyde (**2a**) (30%) [ν_{max} $CHCl_3$ 2210(m), 1720 cm^{-1} (s); δ ($CDCl_3$): 9·93 (1H, t, *J ca.* 1 Hz), 6·3 (1H, m), 2·6—1·5 (6H, m), 1·85 (3H, d, *J ca.* 1 Hz)] and the *Z*† aldehyde (**2a**) (61%) [ν_{max} $CHCl_3$ 2210(m), 1720 cm^{-1} (s); δ ($CDCl_3$): 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 ^{1}H n.m.r. spectra,[3] together with the ester (**3a**) (7%), identified by spectral comparison with an authentic sample obtained from the corresponding acid.[4] In addition, a very minor product (*ca.* 1%) was obtained and assigned structure (**4a**) on the basis of its i.r. [ν_{max} $CHCl_3$ 1690 (w), 1660 cm^{-1} (s)] and n.m.r. spectra δ ($CDCl_3$) 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[4]).

Similar irradiation of (**1b**)† (obtained from 2-cyanocycloheptanone[5]) in methanol gave the *E*‡ aldehyde (**2b**) (8%) [ν_{max} $CHCl_3$ 2210 (m), 1720 cm^{-1} (s); δ ($CDCl_3$) 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%) [ν_{max} $CHCl_3$ 2210 (m), 1720 cm^{-1} (s); δ ($CDCl_3$) 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.



ture (**4b**) on the basis of mass measurement (M^+ 183·12575), and the close similarity of its i.r. [ν_{max} $CHCl_3$ 1690 (m), 1660 cm^{-1} (s)] and n.m.r. spectra [δ ($CDCl_3$) 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**) → (**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. [ν_{max} $CHCl_3$ 3340 (w), 1690 cm^{-1} (s)] and n.m.r. spectra [δ ($CDCl_3$) 1·23 (3H, *J* 6 Hz), 1·7 (8H, broad), 2·83 (3H, m), and 8·27 (1H, broad, exchangeable with D_2O)] 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**).[6] 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.)

---

[1] R. G. Carlson and D. E. Henton, *Chem. Comm.*, 1969, 674; R. G. Carlson and E. L. Biersmith, *ibid.*, 1969, 1049; R. G. Carlson, J. H.-A. Huber, and D. E. Henton, *ibid.*, 1973, 223.

[2] R. E. Meyer, *Helv. Chim. Acta.*, 1933, **16**, 1291.

[3] A. N. Kurtz, W. E. Billups, R. B. Greenlee, H. F. Hamil, and W. T. Pace, *J. Org. Chem.*, 1965, **30**, 3141.

[4] F. Minisci and A. Portolani, *Gazzetta*, 1959, **89**, 1941.

[5] C. Iwanoff, *Chem. Ber.*, 1954, **87**, 1600.

[6] G. R. Krow, *Angew. Chem. Internat. Edn.*, 1971, **10**, 435.