The Photochemistry of 2-Hydroxyiminocyclododecanone

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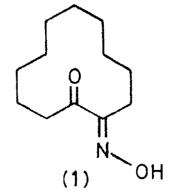
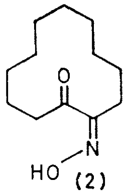
Summary Irradiation of (*E*)-2-hydroxyiminocyclododecanone (**1**) in methanolic solution through quartz with a medium-pressure mercury lamp gives (*Z*)-2-hydroxyiminocyclododecanone (**2**), 1-hydroxy-12-hydroxyiminobicyclo[8 2 0]dodecane (**3**), (2-oxocyclodecane)acetonitrile (**6**), and methyl undec-10-enoate (**7**), compounds (**3**), (**6**), and (**7**) are considered to be formed *via* Norrish type II processes

Stojiljković and Tasovac[1] have reported that the irradiation of (*E*)-2-hydroxyiminocyclododecanone (**1**) in methanolic solution through quartz with a low-pressure mercury Hanau lamp NK6/20 gives, after 45 h, a mixture of the starting material and compounds (**2**)—(**5**) Their report of the formation of (**4**) is of particular interest in that this would provide a route for the conversion of even- into odd-numbered cycloalkanones

We have examined the photochemistry of (**1**) in methanolic solution in quartz with a Hanovia 450 W medium-pressure mercury lamp and have obtained results that



(1)



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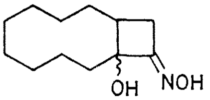

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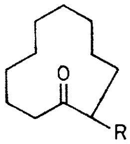


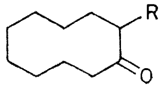
(4) R = CN
(9) R = CO_2H

$NC[CH_2]_{10}CO_2H$

(5)

$CH_2{=}CH[CH_2]_8CO_2Me$

(7)



(6) R = CH_2CN
(8) R = CO_2Me
(10) R = CH_2CO_2H

differ in some respects from those previously reported. Irradiation for 4—12 h gave compounds to which we assign the structures (**2**), (**3**), (**6**), and (**7**).

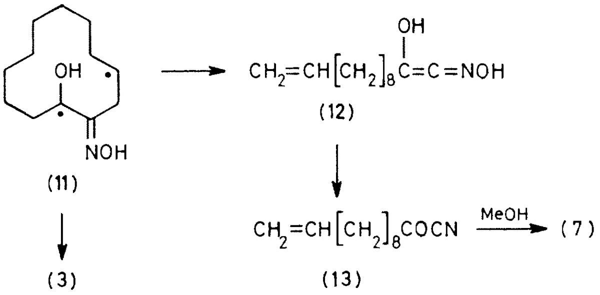
The initially formed product (**2**) was previously assigned[1] the (*Z*) configuration and we concur with this on the basis of a comparison of the chemical shifts of the C-3 carbons in the ^{13}C n.m.r. spectra of (**1**) (δ 26·1 p.p.m.) and (**2**) (δ 30·6 p.p.m.)[2] and the observation that (**2**) reverts to (**1**) on heating or standing at room temperature.

Compound (**3**), m.p. 121—123 °C (lit.,[1] 120—122 °C) was isolated in 40% yield after irradiation of (**1**) for 6 h. We have confirmed the earlier structural assignment[1] by ^{13}C n.m.r. spectroscopy (δ 83·4 and 164·2 p.p.m.) and consider it to be the *cis*-fused isomer, analogous to the corresponding product formed on irradiation of 2-methylenecyclododecanone.[3]

Compound (**6**)† was isolated in 5% yield as a colourless, viscous oil after irradiation of (**1**) for 12 h. Its structure was assigned on the basis of spectroscopic data [i.r. ν 2247 (w) and 1706 cm^{-1}; ^{1}H n.m.r. δ 2·3—2·6 (m, 3H) and 2·8—3·2 (m, 2H); ^{13}C n.m.r. δ 39·9, 48·2, 118·6, and 212·1 p.p.m.] and its independent synthesis by alkylation of 2-methoxycarbonylcyclodecanone (**8**) with chloroacetonitrile followed by demethoxycarbonylation. Compound (**6**) was also obtained in 57% yield by treatment of (**3**) with pyridine and acetic anhydride. A similar second-order Beckmann fragmentation, to give (**6**), occurred with long exposure of (**3**) to silica gel or on irradiation of (**3**) under the conditions of the original irradiation of (**1**).[4] Thus its formation during the latter irradiation can be ascribed to a secondary photolysis of the initially formed (**3**).

We obtained no evidence for the formation of a second nitrile corresponding to (**4**). It is perhaps significant that Stojiljković and Tasovac[1] hydrolysed the product that they considered to be (**4**) and obtained a product considered to be the β-keto acid (**9**), but did not note that it readily underwent decarboxylation. We have hydrolysed (**6**) in boiling 10% ethanolic potassium hydroxide to give (**10**), m.p. 73—74 °C [i.r. ν 3330—2900 and 1712 cm^{-1}; ^{1}H n.m.r. δ 2·2—3·0 (m, 5H) and 9·5 (br s, 1H); ^{13}C n.m.r. δ 36·2, 40·3, 47·8, 178·6, and 215·1 p.p.m.], whose structure was confirmed by its independent synthesis by the alkylation of (**8**) with methyl bromoacetate followed by hydrolysis and monodecarboxylation. As expected for a γ-keto acid, (**10**) does not readily undergo decarboxylation. Although our photolysis conditions were different from those of the earlier workers,[1] it seems not unlikely that the nitrile obtained by them was, in fact, (**6**).

Compound (**7**) was isolated in 13% yield as a colourless, viscous oil after irradiation of (**1**) for 12 h. Its structure was assigned on the basis of spectroscopic data [i.r. ν 1742, 1656 (w), 995 (m), and 913 (m) cm^{-1}; ^{1}H n.m.r. δ 3·67 (s, 3H), 4·8—5·1 (m, 2H), and 5·5—6·0 (m, 1H)] and comparison with an authentic sample.



The formation of (**3**) can readily be interpreted in terms of a Norrish type II process involving the carbonyl-group.[5] We proposed that the formation of (**7**) also involves such a process, with the diradical intermediate (**11**) undergoing fragmentation to (**12**)[6] followed by dehydration to (**13**). Methanolysis of (**13**) could then lead to (**7**).[7] Another pathway involving photocleavage of the four-membered ring of (**3**) is excluded by the observation that (**7**) is not formed on irradiation of (**3**) under the conditions of the irradiation of (**1**). Since we have established that (**6**) is formed in a secondary reaction from (**3**), the photochemistry of (**1**) was observed to be dominated by *syn-anti* photoisomerization of the oxime group[8] and Norrish type II processes involving the carbonyl-group.

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† Satisfactory elemental analytical data were obtained for all new compounds.

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