Tetrahedron Letters No.1, pp. 37-39, 1965. Pergamon Press Ltd.
Printed in Great Britain.

PHOTO-ISOMERIZATION OF 2,2,5,5-TETRAMETHYL-1,3-CYCLOHEXANEDIONE

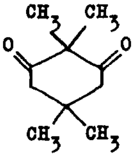
H. Nozaki, Z. Yamaguti and R. Noyori
Department of Industrial Chemistry
Kyôto University, Kyôto, Japan

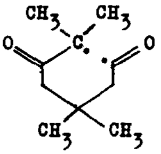
(Received 16 November 1964)

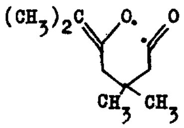
The recent report by Hikino and de Mayo[1] on the photochemical addition of olefins on dimedone has prompted us to record the photo-induced rearrangement of dimethyldimedone or 2,2,5,5-tetramethyl-1,3-cyclohexanedione (I).[2]

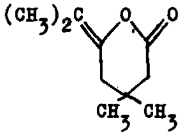
A solution of I (3.0 g.) (λ_{max} 292 mμ ($\varepsilon = 46$) in *n*-heptane[3]) in benzene (400 ml.) was irradiated with high-pressure mercury arc (250W with no filter) at room temperature under the atmosphere of nitrogen. After 2 hrs. irradiation a photostationary state was attained and a mixture (85% recovery) of 3.6% of unchanged I, 92% of an enol lactone with exocyclic double bond (II), and 1.3% of the isomeric enol lactone with endocyclic double bond (III) was obtained. The analysis was carried out by gas chromatography on a high-vacuum silicone grease column and the relative retention times were 1.00 (I), 1.66 (II) and 0.85 (III), respectively. Each component was isolated pure by preparative gas chromatography on the same column. The novel enol lactone (II), 5-hydroxy-3,3,6-trimethyl-5-heptenoic acid δ-lactone, formed an oil, b.p. 67-68°/2.5 mm., n_D^{20} 1.4725. This was characterised by IR spectrum (neat; 1760, 1692, and 1217 cm.$^{-1}$), by NMR spectrum (CCl_4 soln. with $Si(CH_3)_4$ internal ref., δ 2.26 p.p.m., weight 4, methylene protons; δ 1.71 and 1.63

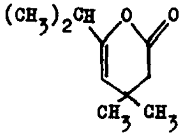
p.p.m., weight 3, respectively, isopropylidene methyl protons; δ 1.02 p.p.m., weight 6, gem-methyl protons) and by elemental analyses. Hydrolysis of II with potassium hydroxide in aqueous ethanol gave 3,3,6-trimethyl-5-ketoheptanoic acid (IV) in 60% yield, whose semicarbazone melted at 154-155° (dec.) (lit.[2] 155° (dec.)).

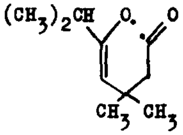

I


V


VI


II


III


VII

$(CH_3)_2CH\text{-}CO\text{-}CH_2\text{-}C(CH_3)_2CH_2COOH$ IV

The isomeric enol lactone III has previously [2] been obtained by cyclizing the keto acid IV with acetyl chloride. Reexamination of this cyclization product by gas chromatography indicated the presence of 38% of II besides 62% of III.[4]

A pure sample of III isolated by preparative gas chromatography had b.p. 102-103°/19 mm. and n_D^{20} 1.4540 and showed IR absorptions (neat) at 1770, 1683, 1240 and 1212 cm.$^{-1}$ (enol ester) besides an unidentified absorption at 1060 cm.$^{-1}$

Irradiation of a benzene solution of the lactone III with endocyclic double bond for 10 hrs. gave no evidence for the formation of even a trace of the isomeric lactone II with exocyclic double bond, but an unidentified product with much shorter retention time was produced. In contrast, however, similar irradiation of II in benzene for 10 hrs. afforded a mixture of 3.2% of the dimedone I and 1.6% of the isomeric lactone III along with 95% of the unchanged lactone II. Practically no thermal exchange of II to III could be observed on refluxing a benzene solution of II for 24 hrs. and on heating the neat lactone II for 3 hrs. at 195°.

These results may be explained by assuming the photolytic fission of the C_1-C_2 bond of I and CO-O bond of II followed by odd electron migration and isomerization to afford biradicals V, VI and VII, which are the precursors of I, II and III, respectively.

Acknowledgment

The authors are indebted to Dr. S. Yuguti and his associates at Central Research Institute of Toyo Rayon Co. for NMR spectra and to the people at Elemental Analyses Center of Kyôto University for analyses.

References

(1) H. Hikino and P. de Mayo, J. Amer. Chem. Soc. **86**, 3583 (1964).

(2) B. Eistert and W. Reiss, Chem. Ber. **87**, 92 (1954).

(3) R. D. Desai, J. Chem. Soc. **1932**, 1079.

(4) For analogous cyclizations, see R. B. Woodward, F. Sondheimer, D. Taub, K. Heusler and W. M. McLamore, J. Amer. Chem. Soc. **74**, 4223 (1952); D. Rosenthal, P. Grabowich, E. F. Sabo and J. Fried, J. Amer. Chem. Soc. **85**, 3971 (1963).