Tetrahedron Letters,Vol.24,No.18,pp 1949-1950,1983 0040-4039/83/181949-02$03.00/0
Printed in Great Britain

PHOTOCYCLOADDITION OF ETHYL 2,3-DIOXOPYRROLIDINE-4-CARBOXYLATES TO ALKENES; THE SYNTHESIS OF ETHYL 2,3-DIOXOHEXAHYDROAZEPINE-6-CARBOXYLATES.[1]

Stewart T. Reid* and Dishna De Silva,
The Chemical Laboratory,
The University, Canterbury, Kent. CT2 7NH.

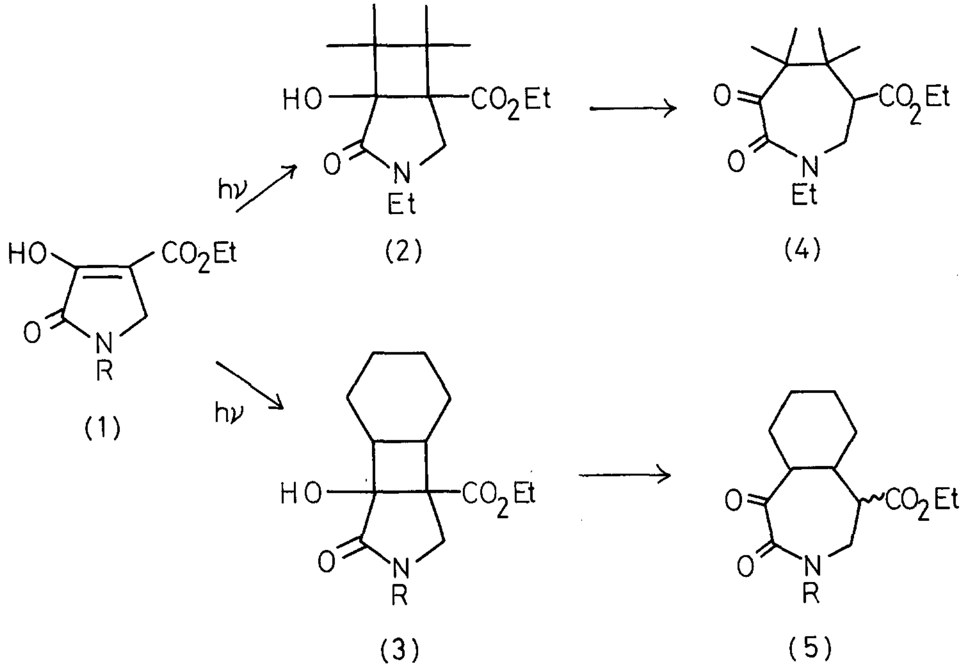
Cyclobutane derivatives, formed by $[_{\pi}2 + {}_{\pi}2]$ photoaddition of ethyl 1-benzyl- and 1-ethyl-2,3-dioxopyrrolidine-4-carboxylates to alkenes, undergo base-catalysed retro-aldol cleavage to yield novel 2,3-dioxohexahydroazepine-6-carboxylates.

αβ-Unsaturated carbonyl compounds readily undergo photochemically induced $[_{\pi}2 + {}_{\pi}2]$ cycloaddition to alkenes to yield cyclobutane derivatives. The addition of enolised β-dicarbonyl compounds has proved to be of particular synthetic value; cyclic β-diketones, for example, are converted in this way into 2-acylcyclobutan-1-ols which undergo facile base-catalysed retro-aldol cleavage leading to ring-expanded products.[2] Application of this reaction sequence to heterocyclic β-dicarbonyl compounds has been restricted to 4-hydroxycoumarin,[3] 4-hydroxyquinol-2(1*H*)-ones,[4,5] and the analogous β-keto sulphone derivative 3-acetoxybenzo[*b*]thiophen 1,1-dioxide.[6] No examples of photoaddition to enolised heterocyclic β-dicarbonyl compounds in which one of the carbonyl groups is exocyclic have been reported; heterocyclic β-keto esters fulfill this structural requirement and are readily available. We report successful additions of ethyl 1-benzyl- and 1-ethyl-2,3-dioxopyrrolidine-4-carboxylates to alkenes; base-catalysed ring expansion of these adducts affords novel 2,3-dioxohexahydroazepine-6-carboxylates.

Ethyl 1-ethyl-2,3-dioxopyrrolidine-4-carboxylate[7] (1; R = Et) was shown to exist as the enol tautomer in solution rather than as the dioxo form on the basis of the following spectroscopic evidence; ν_{max} (CH_2Cl_2) 3400, 1700, 1680 and 1635 cm^{-1}, $\delta_H(CDCl_3)$ 1.24 (3H,t), 1.36 (3H,t), 3.56 (2H,q), 4.00 (2H,s), 4.30 (2H,q) and 8.9 (1H, broad s) ppm. A 0.1M solution of the pyrrolidine in ethanol-2,3-dimethylbut-2-ene (1:1) was irradiated through Pyrex with a 450 w medium-pressure mercury arc until the infrared absorption at 1635 cm^{-1} was no longer present. During the irradiation, a crystalline precipitate was obtained and was recrystallised from ethanol and identified as a $[_{\pi}2 + {}_{\pi}2]$ photodimer.[8] Distillation of the solvent gave an orange-coloured oil which crystallised from cyclohexane to give in 21% yield a cycloadduct with m.p. 79-80°C, $\nu_{max}(CH_2Cl_2)$ 3440 and 1680 cm^{-1}, $\delta_H(CDCl_3)$ 1.02 (3H,s), 1.06 (3H,s), 1.10 (3H,s), 1.20 (6H,s and t), 1.32 (3H,t), 3.1-3.7 (4H,m), 4.22 (2H,q) and 4.6 (1H,br) and $\delta_C(CDCl_3)$ 12.3, 14.2, 19.5, 20.3, 20.7, 21.9, 37.1, 39.9, 45.7, 47.9, 53.1, 61.1, 78.2, 171.8 and 173.6 ppm. The adduct was assigned the structure (2).[9]

An analogous photoadduct (3; R = Et), m.p. 133-136°C, was obtained in 31% yield on irradiation of the same pyrrolidine in cyclohexene, and ethyl 1-benzyl-2,3-dioxopyrrolidine-4-carboxylate[7] (1; R = CH_2Ph) underwent a similar photocycloaddition to cyclohexene to give the cyclobutane (3; R = $\mathrm{CH_2Ph}$), m.p. 130-132°C. Crystalline photodimer was obtained in all photoreactions.

Ring expansion of these cyclobutanols to the corresponding azepines was achieved by heating with 0.1% sodium bicarbonate in ethanol. In this way, the adduct (2) was converted into the azepinedione (4) in 60% yield; m.p. 55-57°C, ν_{max} 1720, 1710 and 1650 cm^{-1}, $\delta_{H}(\mathrm{CDCl_3})$ 1.04 (6H,s), 1.16 (3H,s), 1.10 (3H,t), 1.28 (3H,s), 1.30 (3H,t), 2.9-3.7 (5H,m) and 4.14 (2H,q), and $\delta_{C}(\mathrm{CDCl_3})$ 12.8, 14.2, 17.1, 18.8, 19.3, 22.7, 41.5, 41.6, 45.4, 50.9, 51.7, 60.9, 167.8, 172.6 and 202.9 ppm. Crystalline azepines (5; R = Et or $\mathrm{CH_2Ph}$) were similarly obtained from the cyclohexene adducts (3; R = Et or $\mathrm{CH_2Ph}$); detailed assignments of structure were complicated, however, by the presence of three chiral centres and the precise stereochemistry of these products is at present uncertain.



References

1. Photochemical Transformations Part 14. For Part 13, see M.A.A.M. El Tabei, N.V. Kirby and S.T. Reid, Tetrahedron Lett., 1980, 565
2. P. de Mayo, Accounts Chem. Research, 1971, 4, 41; S.W. Baldwin, Organic Photochemistry, 1981, 5, 123
3. D.J. Haywood, R.G. Hunt, C.J. Potter and S.T. Reid, J.Chem.Soc., Perkin Trans. 1, 1977, 2458
4. R.G. Hunt, C.J. Potter, S.T. Reid and M.L. Roantree, Tetrahedron Lett., 1975, 2327
5. T. Naito and C. Kaneko, Chem. Pharm. Bull., 1980, 28, 3150
6. N.V. Kirby and S.T. Reid, J.Chem.Soc., Chem.Commun., 1980, 150
7. P.L. Southwick, E.P. Previc, J. Casanova and E.H. Carlson, J.Org.Chem., 1956, 21, 1087
8. The same dimer was obtained directly by irradiation of (1) in ethanol
9. Satisfactory analytical and spectroscopic data have been obtained for all new compounds

(Received in UK 10 February 1983)