Tetrahedron Letters No.7, pp. 653-656, 1971. Pergamon Press. Printed in Great Britain.

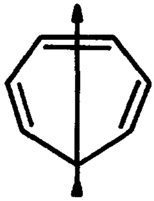
THE PHOTOCHEMISTRY OF CYCLOHEPTATRIENES - DIRECTIVE EFFECT ON RING CLOSURE OF A 1-ELECTRON WITHDRAWING SUBSTITUENT

A.R. Bremher, A.A. Gorman and J.B. Sheridan

Department of Chemistry, University of Manchester, Manchester M13 9PL.

(Received in UK 21 December 1970; accepted for publication 19 January 1971)

The light induced ring closure of cycloheptatrienes to bicyclo-[3,2,0]-hepta-2,6-dienes is generally directionally specific in those cases where theoretically two bicyclic products may be formed (1). We have recently rationalised this fact in terms of the effect of substituents on the direction of polarisation in the excited state (1), which according to our analysis must be as shown in 1 for cycloheptatriene itself.



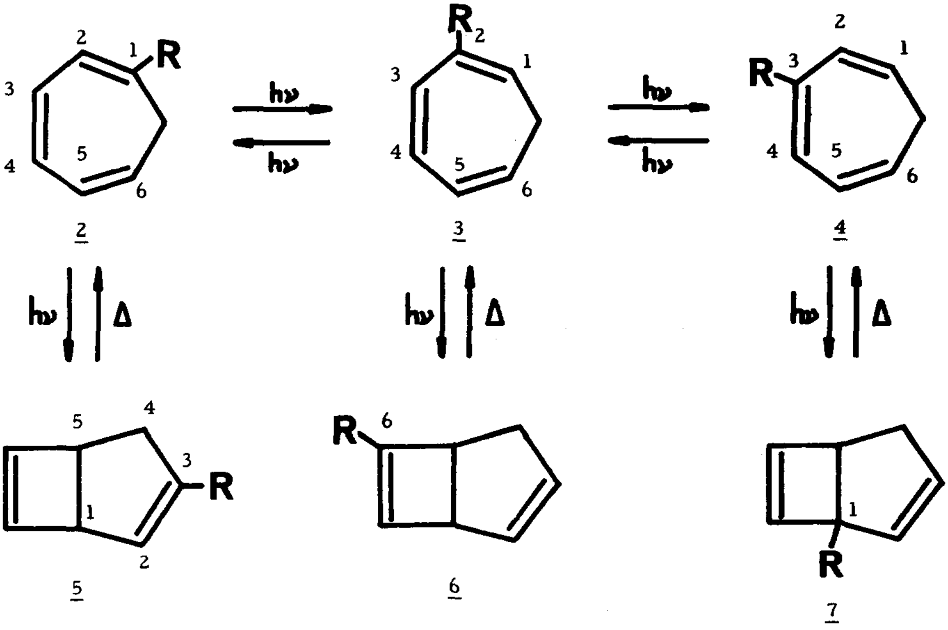
1

The rules for ring closure of monosubstituted compounds are summarised in the following table. One or more examples of the ring closure of the cycloheptatriene types starred in the table have been observed (1-7) and in all cases the reaction proceeds in the predicted direction.

electron donating substituent		electron withdrawing substituent	
position	ring closure	position	ring closure
1*	1,4	1	3,6
2*	3,6	2*	1,4
3*	1,4	3*	3,6
* observed experimentally			

We wish to report here the first example of the electrocyclic ring closure of a cycloheptatriene carrying a 1-electron withdrawing substituent and that ring closure does in fact proceed in the manner predicted by our rules.

The irradiation of a 0.012M solution of 1-carboethoxy-cycloheptatriene (2) in benzene (Hanovia medium pressure mercury arc; pyrex) was monitored by glc.[1] After 100 hr. the reaction mixture consisted of three products which were photostable in pyrex, namely 3-carboethoxy-bicyclo-[3,2,0]-hepta-2,6-diene (5, 4%), 6-carboethoxy-bicyclo-[3,2,0]-hepta-2,6-diene (6, 76%) and 1-carboethoxy-bicyclo-[3,2,0]-hepta-2,6-diene (7, 19%) and the 2- and 3-carboethoxy-cycloheptatrienes (3 and 4, total 1%). 6 and 7 must be the consequences of direct ring closure of 3 and 4 respectively, which together constitute 91% of the total photoproduct after 35 min. Irradiation of a mixture of 3 and 4 (3:4 = 4:1) gave a similar final product distribution; 5 (2%), 6 (70%) and 7 (26%)[2]. This showed that the light induced conversion of 2 to 3 is reversible. Apart from those mentioned

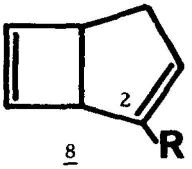


R = -CO_2Et

---

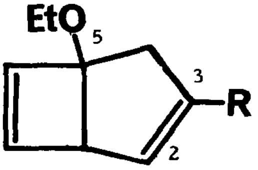
[1] A small amount of ethyl phenylacetate present in the starting material was unchanged throughout the reaction.

[2] The remaining material (2%) consisted of 3 and 4.



8

R = $-CO_2Et$



9

no other products could be detected and no material was lost due to polymerisation. The three bicyclic dienes 5, 6 and 7 were isolated by preparative glc.

G. Linstrumelle (7) has previously reported the quantitative photochemical conversion of 2 (Hanovia high pressure mercury arc; benzene solution in pyrex) to 3, which underwent further reaction to give 4[3], 6 and 7[4]. The production of a bicyclic product directly from 2 was not reported.

The NMR. spectrum of 3-carboethoxy-bicyclo-[3,2,0]-hepta-2,6-diene (5) showed signals due to a carboethoxy function, an allylic methylene group (7.46τ), two ring junction protons (6.22 and 6.61τ) and three olefinic protons. Two of the latter gave rise to a pair of doublets (J = 3 cps) at 3.92 and 3.72τ, typical of two cyclobutene vinyl protons in the bicyclo-[3,2,0]-hepta-2,6-diene system (9). The remaining olefinic signal, a quartet (J = 2 cps) at 3.20τ, must therefore have been due to the β-proton of the αβ-unsaturated ester function in 5 or 8. That this signal was virtually identical in shape and chemical shift (3.25τ) to that arising from the C(2)-proton in 9 (10) strongly suggested that the ester function was at C(3) as in 5. This was confirmed as follows.

a) The ratio of 6:5 in the irradiation mixture varied from 2:1 (15 min.) to 19:1 as the reaction proceeded. The alternative structure 8 would have arisen via ring closure of 2-carboethoxy-cycloheptatriene (3) as did 6. Their relative amounts would therefore have remained constant under conditions where neither is photoreactive. Since this was not the case structure 8 could be excluded.

---

[3] It was shown that the conversion of 3 to 4 is reversible.

[4] The light induced rearrangements of 6 and 7 in quartz have previously been described by us (8).

b) As expected the carboethoxy-cycloheptatrienes can be thermally interconverted via 1,5 hydrogen shifts (7, 11). We have however been able to thermally ring open each of the bicyclic dienes 5, 6 and 7 to give their " parent" cycloheptatrienes under conditions which do not lead to significant thermal isomerisation of the latter. As anticipated the product thought to be 3-carboethoxy-bicyclo-[3, 2, 0]-hepta-2, 6-diene (5) gave predominantly the 1-carboethoxy-cycloheptatriene (2) thus confirming its structure.

The light induced photoisomerisations of two other cycloheptatrienes which possess electron withdrawing substituents at C(1), namely 1-cyano- (4) and 1-benzoyl-cycloheptatriene (12),have previously been described. In both cases only formation of the corresponding 2-substituted cycloheptatriene was observed.

ARB and JBS thank the Science Research Council for financial support.

References

1. A.R. Brember, A.A. Gorman, R.L. Leyland and J.B. Sheridan, *Tetrahedron Letters*, 1970, 2511.
2. O.L. Chapman and S.L. Smith, *J. Org. Chem.*, 27, 2291, (1962).
3. A.P. ter Borg, E. Razenberg and H. Kloosterziel, *Chem. Comm.*, 1210, (1967).
4. W.G. Borden, O.L. Chapman, R. Swindell and T. Tezuka, *J. Am. Chem. Soc.*, 89, 2979, (1967).
5. L.B. Jones and V.K. Jones, *J. Am. Chem. Soc.*, 89, 1880, (1967); *ibid.*, 90, 1540, (1968); *J. Org. Chem.*, 34, 1298, (1969).
6. T. Toda, M. Nitta and T. Mukai, *Tetrahedron Letters*, 1969, 4401.
7. G. Linstrumelle, *Tetrahedron Letters*, 1970, 85.
8. A.A. Gorman and J.B. Sheridan, *Tetrahedron Letters*, 1969, 2569.
9. W.G. Dauben and R.L. Cargill, *Tetrahedron*, 12, 186, (1961).
10. A.R. Brember, M.Sc. Thesis, Manchester, 1970.
11. A.A. Gorman and J.B. Sheridan, to be published.
12. J.A. Blair and C.J. Tate, *Chem. Comm.*, 1319, (1970).