Tetrahedron Letters Vol. 21, pp 2501-2504
©Pergamon Press Ltd. 1980. Printed in Great Britain

0040-4039/80/0622-2501$02.00/0

PHOTOOXYGENATION OF BICYCLOPROPYLIDENE [++]

Ihsan Erden and Armin de Meijere [+]
Institut für Organische Chemie und Biochemie der Universität Hamburg
Martin-Luther-King-Platz 6, D-2000 Hamburg 13, West Germany

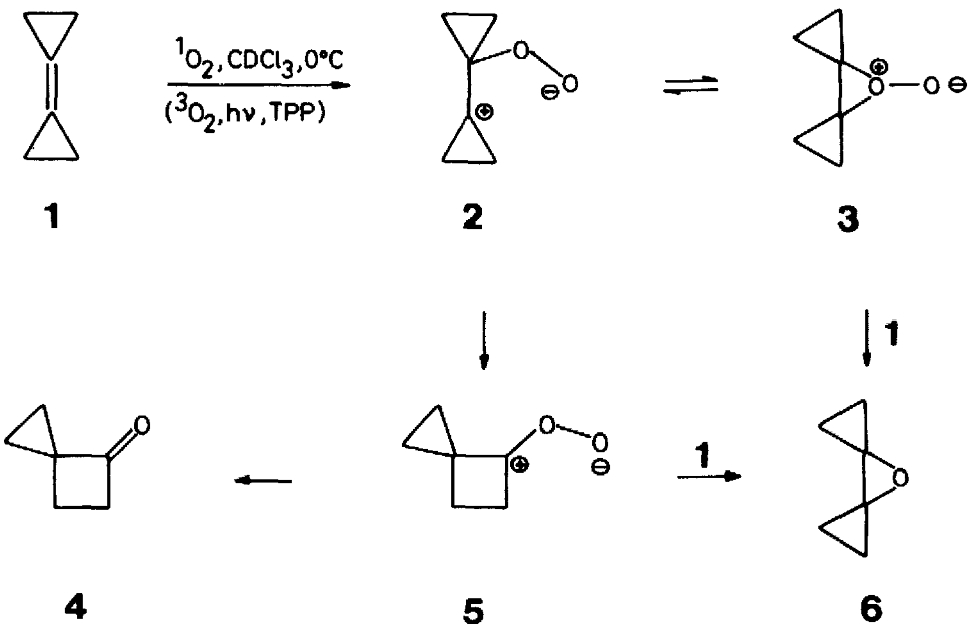
Gérard Rousseau and Jean Marie Conia [+]
Laboratoire des Carbocycles, Universite de Paris-Sud
Batiment 420, F-91405 Orsay, France

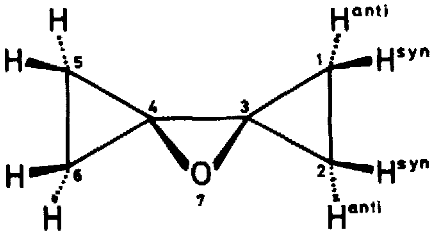
Summary: Upon photooxidation bicyclopropylidene (1) yields spiro[2.3]hexan-4-one (4) and 7-oxatrispiro[2.0.2.1]heptane (6). The formation of these is rationalized. Authentic 6 was prepared by epoxidation of 1, and 4 by isomerization of 6.

Recently, it has been reported that certain substituted methylenecyclopropanes are virtually inert towards singlet oxygen and others react with an extremely slow rate [1]. In accordance with this epoxidation of methylenecyclopropane has been found to proceed 74 times more slowly than that of methylenecyclopentane [2]. Our long standing interests in the photooxygenation of methylenecyclopropanes [3] and the cycloadditions of bicyclopropylidene (1) in general [4] have prompted us to study the reaction of this unique cumulene like olefin with singlet oxygen ($^1O_2$).

A solution of 1 (200 mg) in deuterochloroform (5 ml) was oxygenated at 30-35 °C under irradiation with a 250 W sodium lamp using tetraphenylporphyrin (TPP) as a sensitizer. Monitoring the reaction by ^{1}H-NMR spectroscopy indicated that 1 had disappeared completely after 6 hrs. The solution of the products was separated from the sensitizer by trap to trap distillation at 0 °C (0.1 torr), the two new components were identified as spiro[2.3]hexan-4-one (4) and 7-oxatrispiro[2.0.2.1]heptane (6) (ratio 6 : 10) on the basis of their spectroscopic data. Methylenecyclopropane did not react with $^1O_2$ under these conditions, and 1 showed no reaction in the absence of TPP or in the presence of the $^1O_2$ quencher diazabicyclooctane (DABCO).

An authentic sample of the yet unknown 6[5] was prepared by epoxidation of bicyclopropylidene (1) with m-chloroperbenzoic acid in the presence of sodium carbonate. In contrast to methylenecyclopropane, 1 in dichlormethane solution reacted spontaneously even at 0 °C, the reaction mixture was filtered after 5 min and the solvent evaporated under reduced pressure at -10 °C to yield an almost pure compound, as evidenced by its thin layer chromatogram (96% yield). Its ^{1}H-NMR spectrum (270 MHz, $CDCl_3$, TMS) showed two groups of signals centered at δ = 1.00 (AA'part of an AA'BB' system, 1(2,5,6)-H^{anti}) and 1.31 (BB'part, 1(2,5,6)-H^{syn}) in full accord with the structure 6.





6

The epoxide 6 is remarkably more stable towards lithium iodide than other oxaspiropentanes[6]. 6 rearranged with a reasonable rate only when heated to 75 °C ($CDCl_3$ solution, sealed ampoule), the sole product was the known spiro[2.3]hexan-4-one (4)[7], identified by its ^{1}H-NMR spectrum[8].

These results give a clue to the mechanism of the photooxidation of 1. Under the conditions employed, 4 would not be formed by rearrangment of 6. Most probably singlet oxygen attacks 1 in a similar way as 4-phenyl-1,2,4-triazolin-3,5-dione[4b] to initially form the intermediate 1,4-zwitterion 2, which undergoes a cyclopropylcarbinyl to cyclobutyl cation ring enlargement. The resulting zwitterion 5 can act as an epoxidizing agent on 1 to give 6 and 4. The observation of 6 being the predominant product may indicate that 2 is in an equilibrium with the perepoxide 3[9], which also epoxidizes 1 to simultaneously yield two molecules of 6.

Although 1 is remarkably reactive towards singlet oxygen[10], it does not, as with other electrophilic cyclophiles[4b], undergo a normal 1,2-cycloaddition, at least not under the conditions employed here.

References and Footnotes:

[+] Authors to whom correspondence should be addressed.

[++] This work was supported by the Deutsche Forschungsgemeinschaft (Project Me 405/11), the Fonds der Chemischen Industrie and the Centre National de la Recherche Scientifique.

[1] A.A. Frimer, T. Farkash, M. Sprecher, J. Org. Chem., 44, 989 (1979).

[2] D.H. Aue, M.J. Meshishnek, D.F. Shellhamer, Tetrahedron Lett. 1973, 4799.

[3] G. Rousseau, P. LePerchec, J.M. Conia, Tetrahedron 32, 2533 (1976); 34, 3475 (1978).

[4] a) D. Kaufmann, A. de Meijere, Angew. Chem. 85, 151 (1973); Angew. Chem. Int. Ed. Engl. 12, 159 (1973);
b) W. Weber, I. Erden, A. de Meijere, Angew. Chem. 92, in press (1980); Angew. Chem. Int. Ed. Engl. 19, in press (1980).

[5] 6 had only been suggested as a possible intermediate in the solvolytic rearrangement of 1,1'-bis-(trimethylsiloxy)-bicyclopropyl to 4 : J.M. Denis, J.M. Conia, Tetrahedron Lett. 1972, 4593.

[6] Cf. J.R. Salaün, J.M. Conia, Chem. Commun. 1971, 1579; J.R. Salaün, J. Champion, J.M. Conia, Org. Synthesis 57, 36 (1977) and ref. [2].

[7] This is in agreement with the preferred mode of rearrangement of other oxaspiropentanes [6], it contrasts the behaviour of the 2,2,5,5- and 2,2,6,6-tetramethyl derivatives of 6 [2].

[8] J.M. Denis, P. LePerchec, J.M. Conia, Tetrahedron 33, 399 (1977) and earlier papers cited therein.

[9] Although there is good evidence for perepoxides as intermediates in 1,2-additions of singlet oxygen to certain olefins, none has ever been proved unequivocally. See the discussion in A.P. Schaap, K.A. Zaklika, p. 174 - 242 in Singlet Oxygen, H.H. Wassermann, R.W. Murray ed., Academic Press. New York, 1979.

[10] This corresponds to the observed ionization potential of 1 (8.93 eV, cf. R. Gleiter, R. Haider, J.M. Conia, J.P. Barnier, A. de Meijere, W. Weber, J.C.S. Chem. Commun. 1979, 130), which is significantly lower than that of methylenecyclopropane (Ip = 9.52 eV, cf. ref. [2]).

(Received in Germany 17 April 1980)