Tetrahedron Letters, Vol.22, No.32, pp 3049 - 3052
Printed in Great Britain

0040-4039/81/323049-04$02.00/

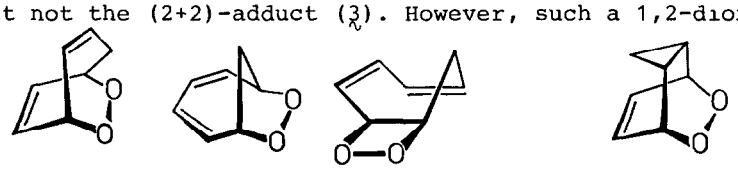
SINGLET OXYGENATION OF CYCLOHEPTATRIENE: ISOLATION AND CHARACTERIZATION OF THE 1,2-DIOXETANE

Waldemar Adam *[1] and Hector Rebollo[2]

[Institute of Organic Chemistry, University of Würzburg, Am Hubland, D-8700 Würzburg, West-Germany and Department of Chemistry, University of Puerto Rico, Rio Piedras, Puerto Rico 00931, USA]

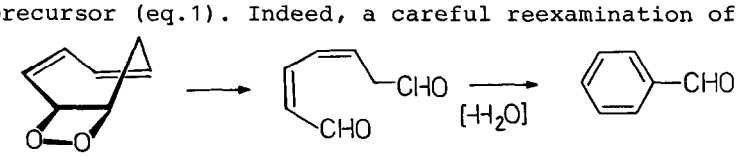
SUMMARY: Tetraphenylporphyrin-sensitized photooxygenation of cycloheptatriene afforded the 1,2-dioxetane (3a) in 9% yield, thus completing the set of possible cycloaddition products; the 1,2-dioxetane (3a) is the precursor to the benzaldehyde product, but not the (2+6)-cycloadduct (2a).

Of the four possible cycloadducts of 1,3,5-cycloheptatriene, the (2+4)- and (2+6)-adducts of the tropilidene valence isomer, respectively (1) and (2), and the (2+4)-adduct (4) of the norcaradiene isomer have recently been reported[3], but not the (2+2)-adduct (3). However, such a 1,2-dioxetane



(1) (2) (3) (4)

could be isolated from 7-methylcycloheptatriene, but in this case the corresponding (2+6)-cycloadduct was not observed.[4] We suspected that the thermally labile unsubstituted 1,2-dioxetane (3) rearranged into the more stable (2+6)-adduct (2), analogous to the formation of the (2+6)-cycloadduct between chlorosulfonyl isocyanate and cycloheptatriene via the intermediary (2+2)-cycloadduct.[5] Presumably for steric reasons the 7-methyl substituent blocked out the (3)→(2) rearrangement, which would account for the fact that no 1,2-dioxetane could be isolated from the unsubstituted cycloheptatriene and that no (2+6)-adduct could be isolated from the 7-methylcycloheptatriene. However, ca. 5% benzaldehyde was observed in the singlet oxygenation of the unsubstituted cycloheptatriene[3], for which the 1,2-dioxetane (3) is a likely precursor (eq.1). Indeed, a careful reexamination of the



(3a) (5a) (1)

TABLE I: Yields and NMR Spectral Data of the 1,2-Dioxetanes.

	Yield[a]	^{1}H NMR ($CDCl_3$)					^{13}C NMR ($CDCl_3$)		
	(%)	δ(ppm)	Type	No.H	Pattern	J(Hz)	δ(ppm)	Type	Pattern
		2.45-2.80	$H_{7,exo}$	1	m	$J_{1,2}$(7.10)	31.58	C_7	t
		3.10-3.50	$H_{7,endo}$	1	d of t	$J_{1,7}$(11.15)	81.96	C_1	d
3a (R=H)	9	5.18-5.45	H_1	1	ABC	$J_{1,8}$(13.36)	90.73	C_2	d
		5.70-6.10	$H_{3,4,5,6}$	4	m	$J_{7,6}$(13.00)	126.0	$C_{3,4,5,6}$	d
		6.15-6.35	H_2	1	d of d	$J_{8,6}$(13.70)	130.8		
		0.95-1.20	$R(CH_3)$	3	t	$J_{1,2}$(7.2)	11.80	$R(CH_3)$	q
		1.25-1.90	$R(CH_2)$	2	m	$J_{1,7}$(11.1)	21.90	$R(CH_2)$	t
		3.30-3.67	H_7	1	m		42.82	C_7	d
3c (R=Et)	15	4.93-5.15	H_1	1	d of d		81.83	C_1	d
		5.60-6.17	$H_{3,4,5,6}$	4	m		92.55	C_2	d
		6.20-6.34	H_2	1	d of d		124.33	$C_{3,4,5,6}$	d
							132.19		
		0.90-1.15	$R(CH_3)$	6	d of d	$J_{1,2}$(8.0)	17.45	$R(CH_3)$	q
		1.80-2.25	R(CH)	1	m	$J_{1,7}$(11.1)	20.82	$R(CH_3)$	q
		3.40-3.70	H_7	1	m	$J_{1,8}$(5.0)	25.60	R(CH)	d
3d (R=iPr)	11	5.25-5.50	H_1	1	d of d	$J_{1,6}$(12.0)	46.49	C_7	d
		5.70-6.15	$H_{3,4,5,6}$	4	m		81.70	C_1	d
		6.15-6.40	H_2	1	d		91.25	C_2	d
							125.79	$C_{3,4,5,6}$	d
		0.95-1.15	$R(CH_3)$	9	s		129.91		
3e (R=tBu)	7	3.2-3.4	H_7	1	m		b		
		5.7-6.4	H_{1-6}	6	m				

a. after chromatography. b. not enough material.

singlet oxygenation of cycloheptatriene at low temperature confirmed that the 1,2-dioxetane (3) is formed, thus completing the set of all possible cycloadducts of the tropilidene valence isomer of the unsubstituted cycloheptatriene.

The photo-oxygenation of cycloheptatriene was carried out at -40°C by irradiating a 0.3 M solution in CH_2Cl_2 containing tetraphenylporphyrin (TPP) as sensitizer (15mg/100 ml) and employing a 150-W sodium street lamp as light source. After complete consumption of the cycloheptatriene, as monitored by ^{1}H-NMR, the CH_2Cl_2 was carefully roto-evaporated (0°C and 20 torr) and the residual oil chromatographed on silica gel (activity grade III) at -30°C, eluting with 1:1 CH_2Cl_2-C_5H_{12} mixture. The chemiluminescent, peroxidic material was collected as a single fraction, affording the 1,2-dioxetane (3a) as colorless oil, 95% peroxide titer by iodometry and characterized by low temperature ^{1}H-NMR and ^{13}C-NMR (cf. Table I). Quite analogously the alkyl derivatives (3b-e), R=Me, Et, iPr and t-Bu, were prepared by low temperature singlet oxygenation of the corresponding 7-substituted 1,3,5-cycloheptatrienes (Table I).[6]

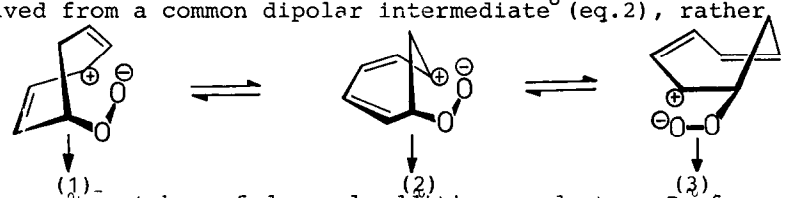
On warm-up to room temperature, all 1,2-dioxetanes (3a-e) exhibited direct chemiluminescence[4], affording the corresponding substituted benzaldehydes as major decomposition product. The thermal decomposition of the parent dioxetane (3a) was investigated in greater detail since only for the unsubstituted cycloheptatriene the (2+6)-cycloadduct (2a) is observed on singlet oxygenation.[7]

A sample of 1,2-dioxetane (3a), 95% by iodometry, was allowed to decompose directly in the ^{1}H-NMR spectrometer, while continuously monitoring the aldehyde and the (2+6)-cycloadduct (2a) regions, allowing the temperature to warm up slowly from -40°C to +40°C. The characteristic benzaldehydic proton at 9.7-10.0 ppm began to appear on warm-up, while the dioxetanyl protons at 5.1-5.4 and 6.0-6.2 ppm disappeared. Furthermore, an additional aldehydic proton resonance appeared at 9.4-9.7 and 10.2-10.4, presumably the initial cleavage product of (3a), i.e. the unsaturated dialdehyde (5a). Efforts to isolate this aldehyde by low temperature column chromatography failed. Neither was it possible to isolate the unsaturated dialdehyde (5a) when the 1,2-dioxetane (3a) was decomposed photolytically by irradiation at 300-400 nm (at -78°C). Thus, it appears that the dioxetane (3a) is the precursor to the benzaldehyde,

presumably via the dialdehyde (5a) as intermediate (eq.1); but considerable amounts of this intermediate are diverted into intractable polymeric product.

In regard to the mechanistic origin of the (2+6)-cycloadduct (2a), we can rigorously state that the 1,2-dioxetane (3a) is not the precursor. Control experiments confirmed that no endoperoxide (2a) was formed from dioxetane (3a) under any conditions. Even the possibility that the transformation (3a)→(2a) could be promoted by silica gel was excluded beyond any reasonable doubt.

We speculate that the tropilidene products (1) to (3) are derived from a common dipolar intermediate[8] (eq.2), rather



(2)

than represent bona fide cycloaddition products. In favor of this suggestion are the facts that the concerted (2+2)- and (2+6)-cycloaddition modes are thermally forbidden, while in the tropilidene valence tautomer of cycloheptatriene none of the double bonds possess a planar dienic conformation which is essential for the allowed (2+4)-cycloaddition mode.

ACKNOWLEDGEMENTS are made to the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, the NIH, NSF and PRF for financial support. We thank Dr. D. Scheutzow for the help with the NMR spectra.

REFERENCES:

1. Direct correspondence to the Würzburg address.
2. Graduate fellow in the Support for University Biomedical Education (SUBE) project sponsored by the NIH-MBS program. A travel grant from the Thyssen Stiftung is gratefully acknowledged.
3. W. Adam and M. Balci, J. Am. Chem. Soc., 101, 7537 (1979).
4. W. Adam, M. Balci, O. Cueto and B. Pietrzak, Tetrahedron Lett., 4137 (1979).
5. E. J. Moriconi and C. F. Hummel, J. Org. Chem., 41, 3583 (1976).
6. Also the 1,2-dioxetanes of the 7-methoxy- and 7-phenylcycloheptatriene have been observed; G. Pollak and H. Rebollo (unpublished results).
7. W. Adam, M. Balci, B. Pietrzak and H. Rebollo, Synthesis, 820 (1980).
8. W. Adam, J. del Fierro, F. Quiroz and F. Yany, J. Am. Chem. Soc., 102, 2127 (1980).

(Received in Germany 15 April 1981)