

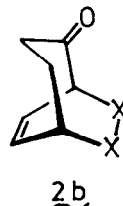
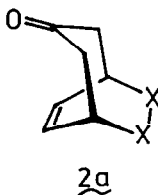
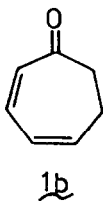
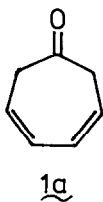
DIENIC REACTIVITY OF 3,5-CYCLOHEPTADIENONE:
REACTION WITH SINGLET OXYGEN.¹

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Summary: Photo-sensitized singlet oxygenation of 3,5-cycloheptadienone affords the corresponding endoperoxide and its diimide reduction, thermal isomerization and triphenylphosphine deoxygenation was studied.

The lack of dienic reactivity of 3,5-cycloheptadienone (1a) toward N-phenylmaleimide was ascribed³ to the twisted non-planar conformation of the diene moiety as a result of ring strain. Under more drastic conditions the 3,5-cyclo-diene 1a afforded, instead of the expected 3,5-cycloadduct 2a, the 2,4-cycloadduct 2b via the isomerized 2,4-cyclodiene 1b. Consequently, it came as a surprise



to us when we observed that photo-oxygenation of 3,5-cycloheptadienone proceeded smoothly to afford the 3,5-cycloadduct with singlet oxygen. Herewith we describe the isolation, characterization, and chemical transformations of the unprecedented

3,5-cycloadduct $2a$ ($X = O$) of singlet oxygen.

Tetraphenylporphyrin (TPP) photo-sensitized oxygenation of a 0.2 M CCl_4 solution of 3,5-cyclodiene $1a$ at $40^\circ C$ ⁴ afforded the 3,5-cycloadduct $2a$ ($X = O$) in 67% yield. The compound was characterized on the basis of the spectral data summarized in the table. Additional chemical evidence for the structural assignment of the 3,5-cycloadduct $2a$ ($X = O$) was provided by diimide reduction⁴ to the saturated endoperoxide 3 , photochemical rearrangement into the disepoxide 4 , and triphenylphosphine deoxygenation to the epoxyenone 5 . The results of these transformations are detailed below.

Reduction of $2a$ ($X = O$) with a five-fold excess of diimide, generated from the potassium azodicarboxylate⁴, in MeOH at $15-20^\circ C$ afforded the saturated endoperoxide in 92% yield. Its physical and spectral data is given in the table. Photolysis of $2a$ ($X = O$) in $CDCl_3$ at 300 nm led to the new disepoxide 4 in 80% yield, whose characterization is based on the physical and spectral evidence given in the table. Finally, deoxygenation of $2a$ ($X = O$) with triphenylphosphine in CH_2Cl_2 at $0^\circ C$ afforded the labile epoxyenone 5 in 78% yield (cf. Table). On heating the epoxyenone 5 in CCl_4 at $80^\circ C$ was converted into the enedione 6 in 83% yield. The spectral data in the table confirm its structure. The formation of 6 from 5 is rationalized by opening of the epoxy oxygen-carbon C_4 bond and migration of the H_d hydrogen to carbon C_4 .

It is of interest to mention that attempted silica gel chromatography of $2a$ at room temperature afforded a high yield of salicylaldehyde. This interesting silica gel-catalyzed rearrangement is postulated to occur as shown below. Although we have no direct chemical evidence for the rearrangement $2a \rightarrow 7$, similar silica gel-catalyzed endoperoxide-dioxetane transformations are known.⁶

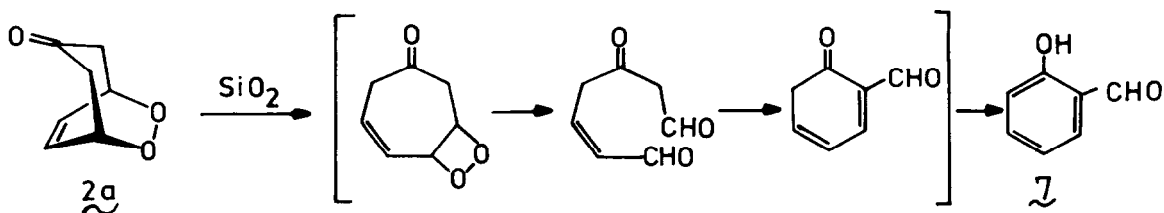
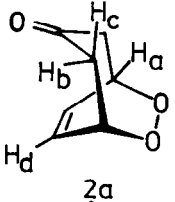
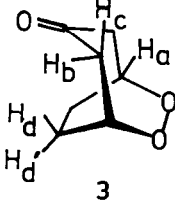
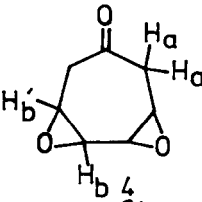
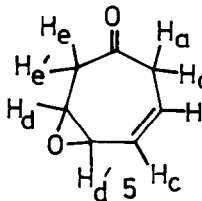
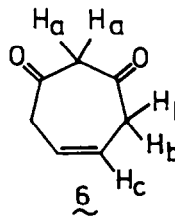


TABLE: YIELDS, PHYSICAL CONSTANTS, AND SPECTRAL DATA

Structure	Yield (%)	mp (°C) bp (°C/torr) n_D^{20}	Type	No. H	$^1\text{H-NMR}$ δ (ppm)	Pattern	IR ν (cm $^{-1}$)	MS (70 eV) m/e
	67	80-82 ^a CH ₂ Cl ₂ /MeOH (1:4)	H _a H _{b,c} H _d	2 4 2	4.69 2.85 6.38	AB ^b m m	3015 2960 1710	140
	92	89-90 ^a CH ₂ Cl ₂ /MeOH (1:4)	H _a H _{b,c} H _{d,d'}	2 4 4	4.45 3.30 1.50-2.00	m m m	2950 1705	142
	80	80/0.5 ^a 1.5560	H _{a,a'} H _{b,b'}	8	2.60-3.60	m	2985 1715	140
	78	30/0.01 ^c 1.5248	H _{a,a'} H _{d,d'} H _{e,e'} H _{b,b'}	6 2	2.50-3.60 5.70-6.10	m m	3030 2960 1710 1665	124
	83	60/0.1 ^a 1.5042	H _a H _b H _c	2 4 2	3.46 3.12 5.60	s m m	3020 2920 1730 1710 1660	124

a. Elemental analysis⁵ was within acceptable limits of 0.3% for C and 0.2% for H.

b. $J_{b(c),a} = 3.30$ Hz; $J_{b,c} = 17.50$ Hz.

c. Too unstable for analysis.

The dienic reactivity of the 3,5-cycloheptadienone (1a) towards singlet oxygenation is clearly established on the basis of the spectral and chemical evidence presented. In view of the synthetic utility of the dienic reactivity of 1a, we are exploring its chemistry in further detail.

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