The Structure of Cycloöctatetraene Oxide

By Owen H. Wheeler

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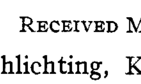
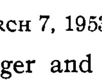
Reppe, Schlichting, Klager and Toepel[1] found that cycloöctatetraene, on treatment with perbenzoic acid in chloroform, forms a monoxide for which they proposed the structure I. Friess and Boekelheide,[2] however, suggested that cycloöctatetraene oxide has the structure II, by analogy with the proven structure of cycloöctatetraene dibromide (IV).[1] Recently, Cope and Tiffany[3] prepared the oxide with peracetic acid and, on chemical evidence, favor the structure I.

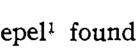
I



II



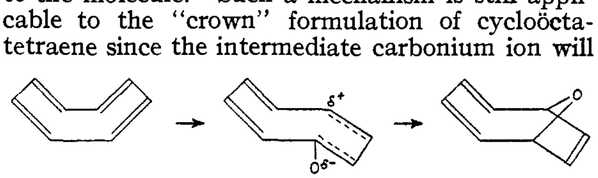
III



IV

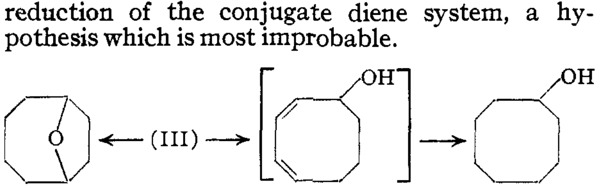
The light absorption ($\lambda_{\max}^{m\mu}$ 240, ϵ 4,000[2,3]) is not in accord with either of these structures. Structure I would be expected to exhibit absorption similar to cycloöcta-1,3,5-triene ($\lambda_{\max}^{m\mu}$ 265, ϵ 3,600[4]) with the wave length slightly increased and the intensity decreased due to the additional strain in the molecule. Cycloöctatetraene dichloride (IV, R = Cl) and dibromide (IV, R = Br) have light absorption $\lambda_{\max}^{m\mu}$ 270, ϵ 5,640 and 3,640, respectively,[5] whilst 0,2,4-bicycloöctadiene (IV, R = H) has absorption $\lambda_{\max}^{m\mu}$ 274, ϵ 3,340.[4] Thus the mutual steric repulsion of the halogen atoms leads to an increase in the angle α with attendant decrease in the angle β and decreased strain in the cyclohexadiene ring, giving a shift in wave length toward that of cyclohexadiene itself ($\lambda_{\max}^{m\mu}$ 256, ϵ 7,940).[6] Hence the oxide ring in structure II would lead to a decrease in angle α with subsequent increase in angle β and decreased strain in the cyclohexadiene ring, and such a compound would be expected to have $\lambda_{\max}^{m\mu}$ *ca.* 270, ϵ *ca.* 3,000.

The mode of formation of structure I involves 1,2-addition, whereas structure II necessitates internal addition in the intermediate carbonium ion to give a bridged ring structure (*cf.* Friess and Boekelheide[2] for the mechanism of the formation of the dibromide). An alternative reaction involves attack of the reagent, formation of a 4-carbon mesomeric ion and addition of the oxonium ion to the end of this system, that is, 1,4-addition to the molecule. Such a mechanism is still applicable to the "crown" formulation of cycloöctatetraene since the intermediate carbonium ion will be planar (see Person, Pimentel and Pitzer[7] for discussion of the steric structure of cycloöctatetraene). Such 1,4-addition has not been previously reported, and in this case may be due to the peculiar geometry of the cycloöctatetraene molecule. Butadiene has been shown to undergo normal 1,2-addition,[8] and cyclohexa-1,3-diene gives a mono- and di-oxide of unproven structure.[9] 1,4-Peroxides are known, *e.g.*, ergosterol peroxide,[10] and ascaridole formed by 1,4-oxidation of α-terpinene.[11]



The structure that is suggested for cycloöctatetraene oxide is, therefore, the internal oxide III, the illustrated "chair" configuration being less strained than the alternative "tub" form. This structure involves fused 5 and 7 member rings, and the absorption of the diene system would be comparable to that of cycloheptadiene ($\lambda_{\max}^{m\mu}$ 248, ϵ 7,400[12]), with the lowering of intensity due to the rigidly held configuration.

This internal oxide structure III seems to be in better accord with the chemical evidence than the other two proposed structures. Reppe, *et al.*,[1] found that hydrogenation, with cooling, led to uptake of 4 moles of hydrogen with the formation of cycloöctanol. This supports either structure I or III and, as noted by Cope and Tiffany,[3] precludes structure II, since the bridge ring would not be expected to open under the conditions used (reduction over palladium–calcium carbonate in methanol at 0°) and the fused ring dibromide IV gives 0,2,4-dicycloöctane on reduction.[1] Reppe, *et al.*,[1] also observed that hydrogenation without cooling resulted in exothermic absorption of 3 moles of hydrogen giving a saturated compound containing a non-reacted oxygen function. This evidence, which was not discussed by later workers, is in accord with structure III, the compound formed still possessing an internal oxide link, whereas the oxide rings in structures I and II might be expected to be reduced under the conditions used. Friess and Boekelheide[2] found that partial reduction of cycloöctatetraene oxide gave a mixture of products, having infrared absorption characteristic of a carbinol grouping, as well as absorption $\lambda_{\max}^{m\mu}$ 230, ϵ 620, suggesting the presence of some cycloöctadiene derivative (cycloöctadiene, $\lambda_{\max}^{m\mu}$ 230, ϵ 6,000[13]). This is interpreted by these workers on their structure II as involving splitting of the oxide and opening of the fused ring, before reduction of the conjugate diene system, a hypothesis which is most improbable.



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Thus, whilst the available chemical evidence does not definitely differentiate between structures I and III, the light absorption suggests that cyclooctatetraene oxide is cycloöcta-2,5,7-triene-1,4-oxide (III).

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Sodium Salts of Alkyl α-Sulfopalmitates and Stearates[1,2]

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Salts of sulfonated esters of the higher saturated fat acids have been shown to be surface active agents,[3,4] but their preparation in a state of purity has not been adequately described. The reaction of liquid sulfur trioxide with palmitic or stearic acid results in α-sulfonation,[5] and we have now prepared from the diacid ($R'CH(SO_3H)CO_2H$, method D) or the monosodium salt ($R'CH(SO_3Na)CO_2H$, method M) 24 esters of the general formula $R'CH(SO_3Na)CO_2R$, where R′ is $C_{14}H_{29}$ (palmitate series) or $C_{16}H_{33}$ (stearate series). In 22 cases R was a normal alkyl group of 1 to 18 carbon atoms. Two esters of secondary alcohols were included. Tables I and II give the melting points, methods of preparation, and elemental analyses.

The elemental analyses agreed with the theoretical values, the maximum deviation in the value for percentage of carbon being 0.47 and the average deviation 0.21.

The sodium salts of the α-sulfonated esters were white hygroscopic solids, readily soluble in water, the solubility decreasing with increase in molecular weight. They were unexpectedly resistant to hydrolysis, especially in acid solutions, presumably because the sulfonate group retards hydrolysis at the ester linkage through steric hindrance. Since saponification of the esters may be incomplete even after a four-hour reflux period with excess alcoholic potassium hydroxide, saponification equivalent values are not useful indications of purity.

The melting points of the methyl esters were considerably higher than those of the next four homologs. Beginning with the hexyl esters, the compounds became transparent solids at the temperatures noted in parentheses, before melting some 10 to 30° higher, usually with decomposition. Esters of secondary alcohols had higher melting points than esters of corresponding primary alcohols.

TABLE I, $C_{14}H_{29}CH(SO_3Na)CO_2R$

R	Melting point, °C.	Method	Elemental analyses found, % C	H	S	Na
CH_3	180.9–182.8	D	54.41	8.63	8.62	6.20
C_2H_5	95.2–96.7	D	55.95	8.96	8.42	5.91
C_3H_7	63.3–65.1	M	56.74	9.13	8.01	5.66
C_4H_9	59.7–60.6	M	57.94	9.33	7.78	5.47
C_5H_{11}	60.8–61.6	M	58.46	9.50	7.63	5.29
C_6H_{13}	(177–179) 189–190	M	59.63	9.69	7.14	5.08
C_8H_{17}	(187–189) 202–203	D	61.10	10.06	6.85	4.78
$C_{10}H_{21}$	(191–193) 206–206.5 d.	D	62.22	10.21	6.32	4.59
$C_{12}H_{25}$	(157–158) 168–168.8	D	63.69	10.74	5.93	4.36
$C_{16}H_{33}$	(188–189) 219–221 d.	D	66.26	10.59	5.53	3.91
$C_{18}H_{37}$	(195–196) 217–219 d.	D	66.60	10.88	5.17	3.66
$CH_3CH_2CHCH_3$	113.5–114.2	D	58.13	9.55	7.75	5.56

TABLE II, $C_{16}H_{33}CH(SO_3Na)CO_2R$

R	Melting point, °C.	Method	Elemental analysis found, % C	H	S	Na
CH_3	179.8–180.0	M	56.85	9.15	8.04	5.70
C_2H_5	97.4–99.2	D	57.58	9.35	7.93	5.55
C_3H_7	72.3–73.6	M	58.48	9.64	7.52	5.26
C_4H_9	66.5–67.6	M	59.64	10.01	7.28	5.30
C_5H_{11}	64.8–65.6	M	60.02	9.97	7.15	5.01
C_6H_{13}	(167–169) 186.2–187.4	M	61.20	9.61	7.07	4.89
C_8H_{17}	(170–172) 193–195 d.	D	62.68	10.09	6.85	4.53
$C_{10}H_{21}$	(191–193) 215–216 d.	D	63.53	10.34	6.24	4.24
$C_{12}H_{25}$	(194–196) 208–210 d.	D	64.74	10.72	5.85	4.17
$C_{16}H_{33}$	(193–194) 218–220 d.	D	67.10	10.90	5.23	3.76
$C_{18}H_{37}$	(209–210) 221–223 d.	D	67.58	11.03	5.07	3.66
$(CH_3)_2CH$	75.8–77.2	D	59.11	9.72	7.57	5.22

Definite relatively low melting points have seldom been reported for alkali metal salts of organic acids. Analogous compounds of low molecular weight, potassium ethyl sulfoacetate and potassium ethyl

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(1) This paper was presented at the Fall Meeting of the American Chemical Society, Chicago, Ill., September 7–11, 1953.

(2) The palmitate esters, for example, may also be named as 2-sulfohexadecanoic acid, 1-alkyl ester, 2-sodium salt or alkyl 2-sulfohexadecanoate, 2-sodium salt.

(3) F. Guenther, J. Conrad and K. Saftien, U. S. Patent 2,043,476 (June 9, 1936).

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