the water phase was extracted once with ether and discarded. The ether layers were combined, washed with a little water, and dried with "Drierite." The solvent was removed leaving 1.20 g. (90%) of a clear, yellow oil which solidified completely when touched with a spatula, m.p. 97–98°. The crude material was recrystallized twice from hexane to obtain the analytical sample, m.p. 102.5–103.5°; $\lambda_{\max}^{\text{alc}}$ 281 mμ, ϵ 25,000; $[\alpha]_D^{25}$ −480° (2% chloroform). The infrared spectrum of this optically active ketone was identical with that of the racemic material first prepared by Woodward, *et al.*[8]

Anal. Calcd. for $C_{15}H_{18}O$: C, 84.06; H, 8.46. Found: C, 84.24; H, 8.74.

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(8) See footnote number 25 of the paper by R. B. Woodward, F. Sondheimer, D. Taub, K. Heusler, and W. M. McLamore, *J. Am. Chem. Soc.*, **74**, 4223 (1952).

Ozonization of Cyclooctatetraene

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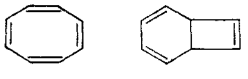
Previous ozonizations of cyclooctatetraene in non-hydroxylic solvents led to the conclusion that it reacts with ozone through the fused ring structure II.[2] Although no physical evidence indicated the presence of this structure in equilibrium with cyclooctatetraene I, studies in bromination of I have demonstrated that certain cationic additions may proceed through this form.[3–5] Furthermore, rearrangement reactions[6] of cyclooctatetraene have been considered as typical homoallylic rearrangements[7] and for this reason ozonization reactions of this cycloolefin, under certain conditions, may be expected to proceed abnormally. It is therefore possible that the extremely low yields (1 to 2%) of the ozonization products reported by Wibaut and Sixma may have been due to abnormal rearrangements and the conclusions drawn may not be entirely valid.



I II

Since we have already shown that abnormal ozonizations of allylic compounds proceed normally in hydroxylic solvents[8] to give high yields of normal products, we felt that the ozonization of cyclooctatetraene in these solvents may give results in accordance with its normal structure.

Accordingly, therefore, freshly purified cyclooctatetraene[9] was ozonized in methanol under various conditions and the peroxide intermediate formed in each case reduced with sodium bisulfite and immediately the 2,4-dinitrophenylhydrazone precipitated. The results of three independent experiments are recorded in Table I.

TABLE I

OZONIZATION OF CYCLOOCTATETRAENE

Temp., °C.	C.O.T., Mmoles	O_3 Added, Mmoles	O_2 Absorbed, Mmoles	Active (O), M Atoms	Glyoxal, Mmoles
−16.5	10.03	42.7	40.6	25.6	15.0
−20	10.00	80.0	—	49.0	22.0
−78	5.22	44.1	23.7	17.9	20.0

The rate with which cyclooctatetraene absorbed the first three moles of ozone was fairly constant, then the rate decreased and much of the ozone passed through unabsorbed during the addition of the last mole. Consequently the solution in the last two cases was overozonized purposely in order to insure complete reaction.

At the end of each experiment and after the dissolved ozone was removed by passing through the mixture dry nitrogen, the peroxide content of the solution was determined and the total active oxygen recorded in Table I, column five. At −20° the peroxide found was much more than the amount expected and the excess was attributed to methyl hydroperoxide and other peroxides[10] which form from methanol after the olefin is completely consumed. At −20° methanol absorbs ozone at the rate of 7.8 mmoles per hr. while at −78° the rate is negligible. However, the formation of peroxides from methanol does not affect our results since reduction of the pure ozonized methanol with aqueous sodium bisulfite gave no carbonyl compounds.

Finally, the results shown in Table I indicate that, under the conditions of our experiments, cyclooctatetraene ozonizes in accordance with structure I rather than II as previously proposed.

EXPERIMENTAL

In 80 cc. of methanol was dissolved 1.042 g. (0.01 mole) of freshly distilled cyclooctatetraene and the solution cooled to −20°. Ozone was then passed through the solution for two hr. at the rate of 0.04 mole per hr. Dry nitrogen was

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(1) From the Ph.D. Thesis of John T. Nolan, Jr., Massachusetts Institute of Technology, May, 1955.

(2) J. P. Wibaut and F. L. J. Sixma, *Rec. trav. chim.*, **73**, 797 (1954).

(3) S. L. Friess and V. Boekelheide, *J. Am. Chem. Soc.*, **71**, 4145 (1949).

(4) W. Reppe, O. Schlichting, K. Klager, and T. Toepel, *Ann.*, **560**, 1 (1948).

(5) K. Ziegler and H. Wilms, *Ann.*, **567**, 1 (1950).

(6) A. C. Cope, N. A. Nelson, and D. S. Smith, *J. Am. Chem. Soc.*, **76**, 1100 (1954).

(7) E. Vogel, Habilitationshrift, Karlsruhe, 1957.

(8) N. A. Milas and J. T. Nolan, Jr., Paper presented before the International Ozone Conference, Chicago, November 1956.

(9) We are indebted to Prof. A. C. Cope for the cyclooctatetraene used in this work.

(10) The structure of these peroxides is being investigated.

then allowed to pass through the solution until the exit gases gave no test for ozone. The peroxide content of the solution was then determined and found to consist of 40 mmoles of active oxygen.

For the determination of glyoxal the following procedure was used. To 1 cc. of the ozonized cycloöctatetraene solution (measured at room temp.) was added 10 cc. of water containing 1 g. of sodium bisulfite and the mixture was treated with excess 2,4-dinitrophenylhydrazine reagent and heated on the water bath for 0.5 hr. From this was obtained 0.1142 g. of glyoxal bis-2,4-dinitrophenylhydrazone, m.p. 316° (from pyridine) alone and when mixed with an authentic sample. Jacobs and Witcher[11] report m.p. 311–312° for this derivative. No other carbonyl products were isolated. Therefore the total yield of glyoxal from this experiment corresponds to 2.2 mmoles of glyoxal per mmole of cycloöctatetraene ozonized.

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[11] T. L. Jacobs and W. J. Witcher, *J. Am. Chem. Soc.*, **64**, 2635 (1942).

Polymethylol[1]

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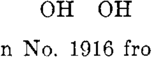
The preparation of vinylene carbonate has been described as well as its polymerization product.[2] This same reference describes a hydrolysis product of the polymer as being water-soluble, and the statement is made that it is "undoubtedly —(CH-OH)$_n$—".[3]

This solubility behavior is inconsistent with the behavior of other polymeric materials having a regularly repeating sequence of hydroxyl functions along a long carbon chain. Pure poly(vinyl alcohol) of reasonably high molecular weight, for instance, is not soluble in cold water but is soluble in hot water. The solution on cooling is metastable, tending to gel on prolonged standing.

We have hydrolyzed poly(vinylene carbonate) under alkaline conditions to give a product whose solubility behavior is in line with that predicted for a polymer having the structure given.



$$—(\underset{\displaystyle OH}{\underset{|}{CH}}—\underset{\displaystyle OH}{\underset{|}{CH}}—)_n$$

The carbonate was prepared by the method of Newman and Addor.[2] The monomer was polymerized in a sealed tube at 75°, with 0.5% of benzoyl peroxide as catalyst. The hard, clear polymer was dissolved in dimethylformamide and the solution poured into a large volume of distilled water. The white precipitate was washed with distilled water and dried at 50°. The inherent viscosity determined in dimethylformamide was 0.31. The poly(vinylene carbonate) was suspended in 1*N* sodium hydroxide solution at room temperature, the polymer soon going into solution, and the hydrolyzed product precipitating out as a white powder about a minute later. This was filtered off, washed well with water, and dried.

Anal. Calcd. for CH_2O:C, 40.0; H, 6.7. Found: C, 39.2; H, 7.2.

The filtrate obtained after hydrolysis on acidification generated carbon dioxide.

Polymethylol is insoluble in water up to 140° and in most organic solvents, swells in boiling dimethylformamide, and is soluble in hot dimethyl sulfoxide, precipitating from this hot solution on cooling. A number of derivatives could be prepared by reaction in hot dimethyl sulfoxide, including the acetate, cinnamate, and phenyl urethane.

A possible explanation for the inconsistence regarding solubility may be found in the fact that partially esterified poly(vinyl alcohol) and cellulose are water-soluble (or at least more hydrophilic), whereas the parent alcohols are insoluble in cold water. By analogy, it could be argued that the hydrolysis product obtained by Newman and Addor might have been an incompletely hydrolyzed poly(vinylene carbonate).

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[1] Communication No. 1916 from the Kodak Research Laboratories.

[2] M. S. Newman and R. W. Addor, *J. Am. Chem. Soc.*, **75**, 1263 (1953).

[3] Since the manuscript was submitted, a paper on the hydrolysis of polyvinylene carbonate, by K. Hayashi and G. Smets, has appeared in *J. Polymer Sci.*, **27**, 281 (1958).

A Convenient Synthesis of Glutaconic Ester

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Glutaconic ester has frequently been prepared[2–4] by procedures which employ acetonedicarboxylic ester, a compound which is cumbersome to prepare but which has recently become commercially available.[5] In the most recent procedure,[3] a good yield (67%) of glutaconic ester was reported. However, the yields were variable since the required high pressure catalytic hydrogenation of acetonedicarboxylic ester was difficult to reproduce; the hydrogenation was sensitive to the age of the catalyst and to its method of preparation.

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[5] Available from Chas. Pfizer Co., Brooklyn, N. Y.