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.

Acknowledgment. We are indebted to Lucidol Division of Wallace and Tiernan, Inc., for financial support of this investigation and to Miss Rachel H. Keto for the determination of the rate of ozone absorption by pure methanol at −20°.

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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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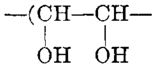
Received September 6, 1957

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.



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

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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Received September 11, 1957

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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[1] Present address: Stanford Research Institute, Menlo Park, Calif.

[2] H. v. Peckmann and K. Jenisch, *Ber.*, **24**, 3250 (1891).

[3] H. L. Lochte and P. L. Pickard, *J. Am. Chem. Soc.*, **68**, 721 (1946).

[4] C. Grundmann and H. Paul, *Chem. Ber.*, **86**, 186 (1953).

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

We have now developed a convenient three-step synthesis of glutaconic ester with an over-all yield of 63–75% by the following procedure. The commercially available diethyl ethoxymethylenemalonate[6] was condensed with malonic ester. The resulting tetraester was hydrolyzed and decarboxylated with dilute hydrochloric acid, and the crude glutaconic acid which resulted was esterified by the usual procedure.

EXPERIMENTAL

Diethyl glutaconate. To a solution of 23.0 g. (1.00 mole) of sodium in 300 ml. of absolute ethanol was added 160 g. (1.00 mole) of diethyl malonate, followed by 216 g. (1.00 mole) of diethyl ethoxymethylenemalonate.[6] After the mildly exothermic reaction[7a] was complete, the reaction mixture was allowed to stand at room temperature for 24 hr. during which time the red solution solidified. A mixture of acetic acid (150 ml.), concentrated hydrochloric acid (100 ml.), and water (1 l.) was added, and the solution was extracted with benzene. The benzene was removed from the extract *in vacuo*,[7b] and the liquid residue was refluxed with dilute (1:2) hydrochloric acid (300 ml.) for 24 hours. The water and other volatile materials were removed *in vacuo*;[7b] the residue was dissolved in absolute ethanol, dried with magnesium sulfate, filtered, and again concentrated *in vacuo*.[7b] The residue was dissolved in absolute ethanol (300 ml.); 6 ml. of concentrated sulfuric acid was added, and the solution was refluxed overnight. The reaction mixture was processed in the usual manner and gave 117 g. (63.0%) of diethyl glutaconate[3]; b.p., 84–87°/0.5 mm., n_D^{20} 1.4448, The diester was hydrolyzed to give glutaconic acid,[8,9] m.p. 136–137°; neut. equiv., 65.0 (calcd. 65.1).

From a second preparation a 75% yield of diethyl glutaconate was obtained.

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(6) Available from Kay-Fries Chemicals, Inc., New York, N. Y.

(7) (a) L. Claisen, *Ann.*, **297**, 1 (1897). (b) The pressure was not measured but it was obtained with the aid of a water pump.

(8) E. Buchner, *Ber.*, **27**, 881 (1894).

(9) B. M. Iselin and K. Hoffmann, *J. Am. Chem. Soc.*, **76**, 3220 (1954).

(10) This work was supported by funds from Mead Johnson and Co., Evansville, Ind.

Stereochemistry of the Cyclopentadiene-Itaconic Anhydride Adduct

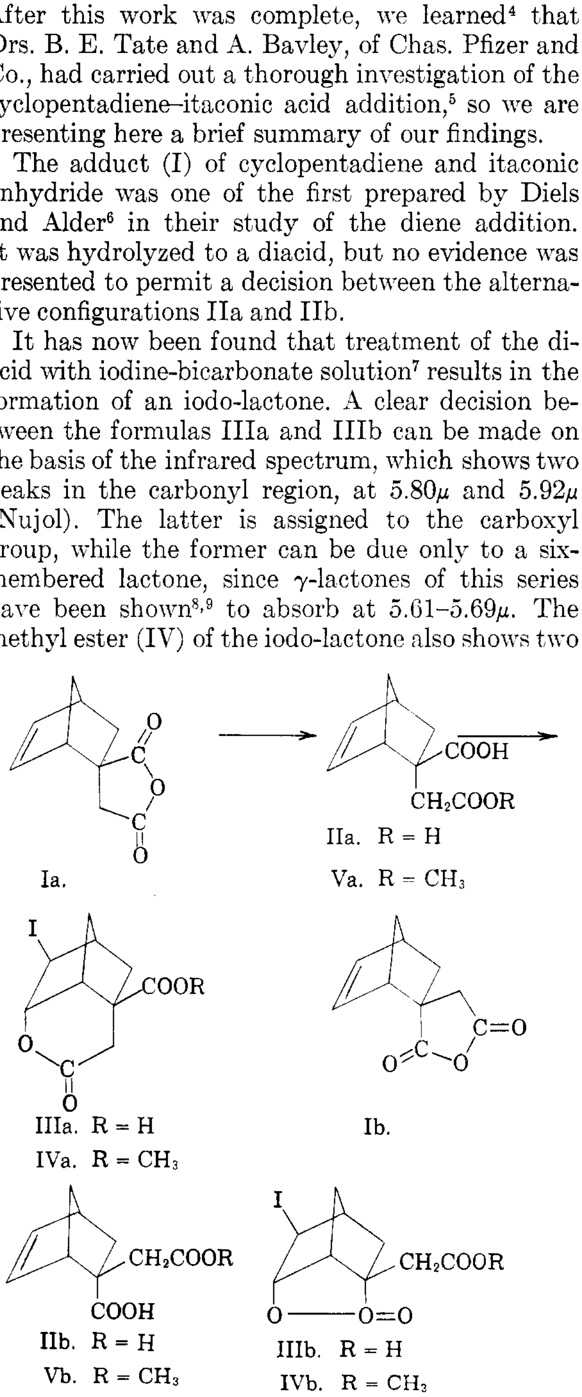
Richard K. Hill and Thomas V. van Auken[1]

Received September 20, 1957

It has recently been reported[2] that the Diels-Alder addition of methacrylic acid to cyclopentadiene yields a mixture of isomeric products, in which the aduct with the *exo*-carboxyl predominates in violation of the rule[3] of maximum overlap of unsaturation. We wish to report that an even more striking violation of this principle occurs in the addition of cyclopentadiene to itaconic anhydride. After this work was complete, we learned[4] that Drs. B. E. Tate and A. Bavley, of Chas. Pfizer and Co., had carried out a thorough investigation of the cyclopentadiene–itaconic acid addition,[5] so we are presenting here a brief summary of our findings.

The adduct (I) of cyclopentadiene and itaconic anhydride was one of the first prepared by Diels and Alder[6] in their study of the diene addition. It was hydrolyzed to a diacid, but no evidence was presented to permit a decision between the alternative configurations IIa and IIb.

It has now been found that treatment of the diacid with iodine-bicarbonate solution[7] results in the formation of an iodo-lactone. A clear decision between the formulas IIIa and IIIb can be made on the basis of the infrared spectrum, which shows two peaks in the carbonyl region, at 5.80μ and 5.92μ (Nujol). The latter is assigned to the carboxyl group, while the former can be due only to a six-membered lactone, since γ-lactones of this series have been shown[8,9] to absorb at 5.61–5.69μ. The methyl ester (IV) of the iodo-lactone also shows two



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(1) Taken from a thesis presented by T.V.A. to the Department of Chemistry, Princeton University, 1957, in partial fulfillment of the requirements for the B.A. degree.

(2) J. S. Meek and W. B. Trapp, *J. Am. Chem. Soc.*, **79**, 3909 (1957).

(3) K. Alder and G. Stein, *Ann.*, **514**, 1, 197 (1934).

(4) Private communication from Dr. B. E. Tate.

(5) B. E. Tate and A. Bavley, Abstracts of Papers, 132nd Meeting of the American Chemical Society, New York, September, 1957, 40P; *J. Am. Chem. Soc.*, **79**, 6519 (1957).

(6) O. Diels and K. Alder, *Ann.*, **460**, 98 (1928).

(7) A method first used in the bicyclic series by C. S. Rondestvedt, Jr., and C. D. Ver Nooy, *J. Am. Chem. Soc.*, **77**, 3583, 4878 (1955).

(8) J. A. Berson, *J. Am. Chem. Soc.*, **76**, 4975 (1954).