

ments performed in the dark. The fact that increasingly efficient degassing of the solvent prior to dissolution of ethane leads to progressive diminution of the conductivity of solutions prepared and measured in the dark suggests production of an electrolyte by reaction with a gaseous impurity. This reagent has been identified by exposing a solution in degassed sulfur dioxide to a large excess of oxygen in the dark and observing a hundredfold increase in conductivity to a level somewhat greater than the highest comparable values obtained without degassing of the solvent. The conductivity of the resulting solution does not change upon irradiation whereas that of solutions in degassed sulfur dioxide increases.

Table I summarizes some of the relevant data.

TABLE I<sup>a</sup>

Dilution l./mole of C <sub>2</sub> Ph <sub>6</sub>	Conductivity, <sup>b</sup> mho cm. <sup>-1</sup> × 10 <sup>6</sup>	Purity of solute <sup>c</sup>	Treatment of solvent
208.1	70.4	95.5	No degassing
216.0	58.2	97	No degassing
276.9	141.1	97	No degassing
219.2	9.86	94	Pumped 1 hr.
236.3	2.67	94	Pumped 4 hr.
226.2	0.95	97	Pumped 3 hr., redistilled from hexaphenylethane
111.7	3.77	97	Pumped 2 hr.
111.7	362.1	97	Above solution after treatment with oxygen
250	206	97	Above solution, diluted

<sup>a</sup> Data with light excluded. <sup>b</sup> Corrected for solvent conductivity which varied from  $0.15 \times 10^{-6}$  to  $0.3 \times 10^{-6}$  mho cm.<sup>-1</sup>. <sup>c</sup> By quantitative oxygenation.<sup>5</sup>

We wish to express our appreciation for support by the Research Corporation which made this work possible.

DEPARTMENT OF CHEMISTRY  
BOSTON UNIVERSITY  
BOSTON, MASSACHUSETTS

HARRY P. LEFTIN  
NORMAN N. LICHTIN

RECEIVED MARCH 29, 1954

#### PHOTOCHEMICAL REACTIONS OF METHYL DIAZOACETATE WITH POLYHALOMETHANES

Sir:

Preliminary studies indicate that the photochemical reactions of methyl diazoacetate with polyhalomethanes are typical free radical chain reactions and that methyl polyhalopropionates are formed which suffer dehydrohalogenation during the reaction and isolation to give methyl polyhaloacrylates. The unexpected identities of the acrylates obtained suggest a 1,2-shift of a halogen atom in an intermediate free radical as postulated in previous work (see equation 4 below).<sup>1</sup>

A solution of methyl diazoacetate (12 g., 0.12 mole) in chloroform (248 g., 2.08 moles) was irradiated by a quartz mercury discharge tube immersed in it. Nitrogen (2.64 l. at S.C., 97%) was evolved

(1) W. H. Urry and J. R. Eiszner, *THIS JOURNAL*, **74**, 5822 (1952).

over a period of eight hours. Products identified after distillation were methyl chloroacetate (5.55 g., 0.051 mole, b.p. 47–52° at 18 mm.,  $n_D^{20}$  1.4660, mol. wt. Rast, 106, gave N-phenylglycine, m.p. 127° when treated by the method of Koelsch<sup>8</sup> in an attempt to form the anilide), and presumed methyl  $\alpha,\beta,\beta$ -trichloropropionate (2.35 g., 0.02 mole, b.p. 85–90° at 18 mm.,  $n_D^{20}$  1.4626, mol. wt. Rast, 198). Treatment of the latter product with ammonium hydroxide gave  $\alpha,\beta$ -dichloroacrylamide<sup>4</sup> (m.p. 134.5–136°).

*Anal.* Calcd. for C<sub>3</sub>H<sub>3</sub>ONCl<sub>2</sub>: Cl, 50.7. Found: Cl, 52.1.

Its saponification gave  $\alpha,\beta$ -dichloroacrylic acid<sup>5</sup> (m.p. 84–85°) which was converted to its silver salt.

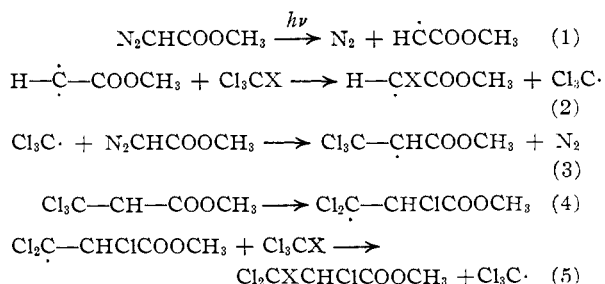
*Anal.* Calcd. for C<sub>3</sub>HO<sub>2</sub>Cl<sub>2</sub>Ag: Ag, 43.52. Found: Ag, 43.43.

In a similar experiment, the irradiation of methyl diazoacetate (15 g., 0.15 mole, b.p. 27–28° at 4 mm.,  $n_D^{20}$  1.4703) in bromotrichloromethane (208 g., 1.05 mole) gave nitrogen (3.20 l. at S.C., 96%) over a period of sixteen hours. Hexachloroethane (0.7 g., m.p. 183–184°, m.p. of mixture with authentic sample 183–184°) was identified as a product, and a series of fractions shown to be mixtures of methyl  $\beta$ -bromo- $\alpha,\beta,\beta$ -trichloropropionate and methyl  $\alpha,\beta,\beta$ -trichloroacrylate (9.1 g., b.p. 90–115° at 5 mm., average mol. wt. Rast, 237) were obtained. Saponification of this mixture gave a quantitative yield of  $\alpha,\beta,\beta$ -trichloroacrylic acid<sup>6</sup> (m.p. 71–73°, m.p. of mixture with authentic sample 72°), and its reaction with ammonium hydroxide gave  $\alpha,\beta,\beta$ -trichloroacrylamide<sup>7</sup> (m.p. 97–98°, m.p. of mixture with authentic sample 97–98°).

*Anal.* Calcd. for C<sub>3</sub>H<sub>2</sub>ONCl<sub>3</sub>: Cl, 61.00. Found: Cl, 60.84.

The same  $\alpha,\beta,\beta$ -trichloroacrylic acid and amide were obtained as derivatives of the product obtained in a similar reaction of methyl diazoacetate with carbon tetrachloride.

The structures of the acrylates identified suggest the following reaction sequence (where X = H in the chloroform reaction, X = Cl in carbon tetrachloride and X = Br in bromotrichloromethane).



(2) P. Walden, *Z. physik. Chem.*, **10**, 639 (1892).

(3) C. F. Koelsch and D. Tenenbaum, *THIS JOURNAL*, **55**, 3049 (1933).

(4) H. J. Prins, *J. prakt. Chem.*, **89**, 420 (1914).

(5) A. L. Koblansky, A. S. Wolkenstein and A. Orłowa, *ibid.*, **145**, 12 (1936).

(6) J. Böeseken and J. F. Garriere, *Rec. trav. chim.*, **34**, 179 (1915).

(7) G. Gilta, *Bull. soc. chim. Belg.*, **39**, 587 (1930).

A thorough study of this reaction and its scope is continuing.

GEORGE HERBERT JONES LABORATORY  
UNIVERSITY OF CHICAGO  
CHICAGO 37, ILLINOIS

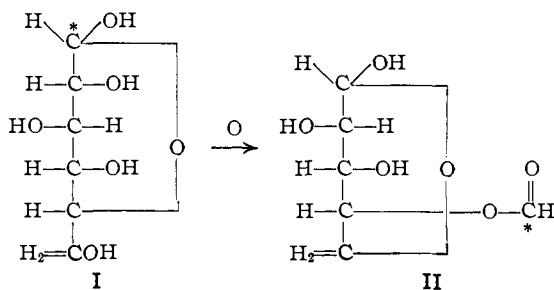
W. H. URRY  
J. W. WILT

RECEIVED MARCH 29, 1954

### SHORTENING THE CARBON CHAIN OF SUGARS<sup>1</sup>

Sir:

Several methods have been described for preparing sugars with fewer carbons than the starting compound by degradation of the appropriate higher-numbered family member. A critical evaluation of the various methods has been presented by Pigman and Goepf.<sup>2</sup> The author has now found that a reasonably selective degradation also may be achieved by direct oxidation of reducing sugars with lead tetraacetate or sodium bismuthate. The reaction appears to be controlled partly by the relative ease with which the oxidant cleaves hemiacetal-glycol groups,<sup>3,4</sup> *i.e.*, the diol of carbons 1 and 2 in the cyclic form of the reducing sugar (I), and also by the consequent formation of a stable formyl ester (II) which prevents attack of the lower portion of the molecule. Thus D-arabinose is easily prepared in at least 35% yield by oxidation of D-mannose in acetic acid with 1.5 moles of lead tetraacetate. The glycol cleavage is not, however, confined exclusively to carbons 1 and 2 for still lower members, such as D-erythrose, are also produced and indeed become the major products when a larger proportion of oxidant is used. The reaction has also been used to prepare D-arabinose from D-glucose, and D-lyxose from D-galactose, and appears to be applicable to reducing sugars generally.



In addition to its use as a preparative method the reaction is well suited to the stepwise degradation of sugars containing radioactive carbon. For example, the possibility of radioactive-carbon transfer during an experiment with a sugar labeled in carbon atom 1 may be examined conveniently on the micro scale. Thus 0.5 mg. of glucose-1-C<sup>14</sup> (I) (diluted with 1.5 mg. of glucose) was oxidized in 97% acetic acid with lead tetraacetate equivalent to 1-1.5 moles per mole and, after precipitation of lead, the formyl esters were gently hydrolyzed. The products were separated on the paper chro-

(1) Issued as N. R. C. No. 3277.

(2) W. W. Pigman and R. M. Goepf, Jr., "Chemistry of the Carbohydrates," Academic Press, Inc., New York, N. Y., 1948.

(3) R. Criegee, *Ber.*, **65**, 1770 (1932).

(4) R. C. Hockett and W. S. McClenahan, *THIS JOURNAL*, **61**, 1667 (1939).

matogram and radioactive areas were located by radioautography and by scanning with an end-window counter. The oxidation products, arabinose and erythrose, were non-radioactive while the unoxidized glucose retained its activity. It was evident, therefore, that the radioactivity resided entirely in carbon atom 1 of the glucose, in agreement with the expected result. A chromatogram of the oxidation products prior to hydrolysis contained radioactive spots, one of which gave the characteristic pentose color. These compounds were undoubtedly the expected intermediate formates esterified with the radioactive formic acid derived from carbon atom 1 (*e.g.*, II) since after hydrolysis they were replaced on the chromatogram by the free, non-radioactive, pentose and tetrose.

It is seen also that the radioactivity of carbons 1 and 2, and possibly of other carbon atoms, in samples of glucose of unknown labeling may be assayed by difference, by determining the specific activities of the individual sugars in the oxidation mixture after elution from the chromatogram.

The work will be described in detail elsewhere.

The kind assistance of Dr. D. C. Mortimer, Dr. P. R. Gorham and of Mr. J. Giroux is gratefully acknowledged.

DIVISION OF APPLIED BIOLOGY  
NATIONAL RESEARCH LABORATORIES  
OTTAWA, CANADA

A. S. PERLIN

RECEIVED MARCH 1, 1954

### THE SYNTHESIS OF $\beta$ -HYDROXY- $\beta$ -METHYLGLUTARIC ACID IN RAT LIVER HOMOGENATES<sup>1</sup>

Sir:

$\beta$ , $\beta$ -Dimethylacrylic acid has been postulated as a precursor of the isoprene-like unit which is thought to polymerize to rubber<sup>2</sup> in plants and to cholesterol in animal tissues.<sup>3</sup> It has been found recently that the rat liver homogenate preparation of Bucher<sup>4</sup> could synthesize  $\beta$ -DMA from acetic acid.<sup>5</sup> Thus incubation with C<sup>14</sup>H<sub>3</sub>COOH gave  $\beta$ -DMA labeled chiefly in carbons 2, 4 and 4' and little or no labeling in carbons 1 and 3. These results show that  $\beta$ -DMA, a branched chain fatty acid, is synthesized in animal tissues from small units and suggest that this compound may be a precursor of cholesterol since the pattern of labeling is similar to that postulated for the isoprenoid precursors of cholesterol by Würsch, *et al.*<sup>3</sup>

The fact that carboxyl labeled acetoacetate appears to be incorporated into cholesterol<sup>6</sup> without prior cleavage into C<sub>2</sub> units, seems to rule out the

(1) The following abbreviations are used:  $\beta$ -DMA =  $\beta$ , $\beta$ -dimethylacrylic acid;  $\beta$ -HMG =  $\beta$ -hydroxy- $\beta$ -methylglutaric acid; ATP = adenosine triphosphate; DPN = diphosphopyridine nucleotide; s.a. = specific activity; CoA = Coenzyme A. This investigation was supported by research grants from the Life Insurance Medical Research Fund and the Elisabeth Severance Prentiss Fund of Western Reserve University.

(2) B. Arreguin, J. Bonner and B. F. Wood, *Arch. Biochem.*, **21**, 104 (1949).

(3) J. Würsch, R. L. Huang and K. Bloch, *J. Biol. Chem.*, **195**, 439 (1952).

(4) N. L. R. Bucher, *THIS JOURNAL*, **75**, 498 (1953).

(5) H. Rudney, *Fed. Proc.*, **13**, 236 (1954).

(6) R. O. Brady and S. Gurin, *J. Biol. Chem.*, **189**, 371 (1951).