nos. 8–11 mentioned above, but calculation showed that the values of $\Delta(1/k)/\Delta(1/[Cl^-])$ varied and were lower than above. This is probably due to the fact that k increases more than predicted from equation (8) owing to the chloride ion catalysis as stated above. As to experiments 1–3 and 12–14, in which acid is present more than the equivalent of DMA, the activity coefficient of acid–anion and oxonium-ion will decrease with acid concentration while that of undissociated acid will increase and, consequently, the third term in equation (8) will increase. This deduction agrees with the experimental data, which show that the higher acid concentration corresponds to the lower reaction rate.

Summary

The hydrochloric- or sulfuric-acid-catalyzed condensation of dimethylaniline with formaldehyde into *p,p'*-tetramethyldiaminodiphenylmethane was kinetically studied by the estimation of the consumed amount of formaldehyde (sulfite method), and following was recognized. 1. Formation of *p*-dimethylaminobenzyl alcohol (or benzylcarbonium ion) is rate-determining. 2. The rate is proportional to the product of the concentration of dimethylaniline and formaldehyde present. 3. The reaction is very slow in the absence of acid, but the excess acid again reduces the rate. 4. The addition of inorganic salt (*e. g.*, sodium chloride) increases the rate. The probable mechanism was postulated and the rate equation derived from it provided a satisfactory explanation for the obtained data.

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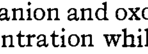
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

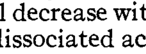
The Structure of Diketene and Butylketene Dimer

BY CHARLES D. HURD AND CATHERINE ANNE BLANCHARD

In 1936 Hurd and Williams proposed[1] as the structure for diketene an equilibrium mixture of 2-butenoic β-lactone (I) and acetylketene, CH_3-CO—CH=C=O, the most critical evidence in its favor being the formation of a phenylhydrazine derivative of m. p. 144–145° from the products of ozonolysis of diketene. This was interpreted as representing pyruvaldehyde bisphenylhydrazone. Values reported in the literature[2] for this compound are 145, 147–148, 148, 154°.



I



II

A. L. Wilson proposed[3] for diketene structure II, or 3-butenoic β-lactone. On ozonolysis, a compound of this structure should yield formaldehyde and malonic acid. Since formaldehyde phenylhydrazone[4] melts at 145°, it is apparent that this could have been the phenylhydrazine derivative obtained by Hurd and Williams.

Recent work[5] from various approaches has produced new evidence which is more readily explained by II than I, hence the ozonolysis of diketene has been reinvestigated. If formaldehyde and malonic acid were both characterized and if pyruvaldehyde was absent, this would become additional evidence in favor of II. Such, indeed, proved to be the findings.

To gain experience, styrene and benzylideneacetone were ozonized and the ozonide hydrolyzed in the presence of zinc dust. Formaldehyde was formed in 57% yield (as the methone derivative) from the former and pyruvaldehyde in 37% yield (as the bisphenylhydrazone) from the latter. These yields of aldehydes are of the same order as those obtained by Church, Whitmore and McGrew[6] when hydrolyzing various ozonides under like conditions: formaldehyde, 6–35%; acetaldehyde, 38%; butyraldehyde, 27%; valeraldehyde, 38%.

Since malonic acid as such was not found in the earlier work,[1] attention was directed to more delicate methods of characterization. It was found that small quantities of this acid could be identified as cinnamylidenemalonic acid.

Purified diketene was then subjected to ozonolysis. Formaldehyde was characterized not only as the methone derivative in 30% yield but also as the 2,4-dinitrophenylhydrazone. No evidence for pyruvaldehyde could be found. Malonic acid, as cinnamylidenemalonic acid, was established as a product of the ozonolysis. This evidence, therefore, supports 3-butenoic β-lactone as the structure of diketene.

It should be pointed out that the above evidence does not prove that diketene is homogeneously represented by structure II. Any acetylketene present, however, must be trivial since its quantity must be too small to give rise to recognizable quantities of pyruvaldehyde on ozonolysis. 2-Bu-

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[1] Hurd and Williams, THIS JOURNAL, **58**, 962 (1936).

[2] von Pechmann, *Ber.*, **20**, 2453 (1887); Dieckmann and Platz, *ibid.*, **38**, 2990 (1905); Pinkus, *ibid.*, **31**, 36 (1898); Nef, *Ann.*, **335**, 255 (1904).

[3] See Boese, *Ind. Eng. Chem.*, **32**, 16 (1940).

[4] Shriner and Fuson, "Identification of Organic Compounds," John Wiley and Sons, New York, N. Y., 2nd ed., 1940 p. 188.

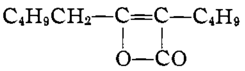
[5] Taufen and Murray, THIS JOURNAL, **67**, 754 (1945); Whiffen and Thompson, *J. Chem. Soc.*, 1005 (1946); Wassermann, *ibid.*, 1323 (1948); Blomquist and Baldwin, THIS JOURNAL, **70**, 29 (1948); Miller and Koch, *ibid.*, **70**, 1890 (1948).

[6] Church, Whitmore and McGrew, *ibid.*, **56**, 176 (1934).

tenoic β-lactone (I) also might be present. If so, it would account for acetic acid formed during ozonolysis,[1] but since acetic acid could originate also from II *via* malonic acid, this evidence is not of a critical nature.

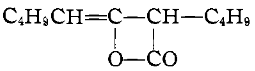
Alkylketene dimers may be prepared[7] by dehydrohalogenation of acyl halides with triethylamine. Roberts and co-workers[8] have demonstrated that these dimers cannot have the 1,3-cyclobutanedione structure but otherwise no critical evidence regarding the structure of these compounds is reported. Hence, our studies were extended to include ozonolysis of butylketene dimer.

Structure III would be analogous to I, IV to II and V to the acetylketene structure for diketene. Of these three structures only IV should yield an aldehyde on ozonolysis, namely, valeraldehyde. Actually, on treating butylketene dimer with ozone and hydrolyzing the ozonide in the presence of zinc dust, valeraldehyde was obtained and characterized in 42% yield as the 2,4-dinitrophenylhydrazone. 2-Butyl-3-octenoic β-lactone (IV), therefore, appears to represent the structure of this dimer.



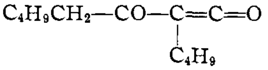
$$\begin{array}{l} C_4H_9CH_2-C=C-C_4H_9 \\ \qquad\qquad\ \ |\quad\ \ | \\ \qquad\qquad\ O-CO \end{array}$$

III



$$\begin{array}{l} C_4H_9CH=C-CH-C_4H_9 \\ \qquad\qquad\ \ |\quad\ \ | \\ \qquad\qquad\ O-CO \end{array}$$

IV



$$\begin{array}{l} C_4H_9CH_2-CO-C=C=O \\ \qquad\qquad\qquad\quad\ | \\ \qquad\qquad\qquad\ C_4H_9 \end{array}$$

V

Experimental

Diketene.—Diketene was prepared by the method of Williams and Krynitsky.[9] It was distilled under diminished pressure through a carefully dried apparatus, equipped with a Davis column. About 15 ml. of diketene was collected at 66–67° (90 mm.). When frozen, it melted at −8 to −7°. Another test of its purity was the reaction of 0.47 g. of it with aniline (in water), to give an isolated yield of 0.88 g. (89%) of acetoacetanilide, m. p. 84–86°.

2-Butyl-3-octenoic β-Lactone.—This dimer of butylketene was prepared by adding 20 g. of triethylamine dropwise into 28 g. of caproyl chloride, b. p. 54–55° (33 mm.), following directions of Hanford and Sauer.[7] A 29% yield of product (5.8 g.) was collected at 139–140° (26 mm.).

Valeraldehyde.—*n*-Pentyl alcohol was dehydrogenated over brass turnings at 375°. The aldehyde thus obtained was converted into valeraldehyde 2,4-dinitrophenylhydrazone, m. p. 96°. This was used below for mixed melting point determinations.

Ozonolysis of Diketene.—A 5.7% ozone stream was passed for twelve hours into a solution of 7 ml. of diketene and 100 ml. of carbon tetrachloride. Then 90 g. of water and 15 g. of zinc dust was added and the mixture was shaken vigorously for fifteen minutes. Considerable heat was liberated. The aqueous layer was filtered. Acetaldehyde was absent by the sodium nitroprusside test.

A solution of 2,4-dinitrophenylhydrazine was added to one-tenth of the solution. The precipitate of formaldehyde 2,4-di-nitrophenylhydrazone which formed immediately melted at 165° after three crystallizations.

One-half of the aldehyde solution was treated with methone. The precipitate which gradually accumulated weighed 3.15 g. After three recrystallizations from alcohol, a sample melted at 187°. When this was mixed with authentic formaldehyde dimethone of m. p. 187°, the m. p. was not depressed. The m. p. of formaldehyde dimethone is given as 189°, acetaldehyde dimethone as 134°, and pyruvaldehyde dimethone as 164°.

In another comparable run, 3.3 g. of the methone derivative was obtained from 3 ml. of diketene, or 30%.

One-third of the original aldehyde solution was oxidized using 75 ml. of 3% hydrogen peroxide, neutralized with sodium hydroxide and the salts evaporated to dryness. The salts were then treated with dilute hydrochloric acid and extracted with ether. The ether was removed by distillation. Two ml. of an acid solution remained in the distilling flask.

A few drops of this acid were made alkaline with sodium carbonate. This solution decolorized a cold potassium permanganate solution. A brown precipitate of the oxide was formed. This is characteristic of formic acid and different from acetic, malonic or oxalic acids.

One ml. of the acid solution was taken for conversion to cinnamylidenemalonic acid in order to get a quantitative idea of the amount of malonic acid present. The weight of the derivative was 0.26 g., a yield of 8%. The m. p. of a sample of recrystallized material was 197°. Cinnamylidenemalonic acid melts at 205°. A mixed melting point determination was 197–198°. When this derivative was prepared from 0.1 g. of malonic acid, 0.16 g. of cinnamylidenemalonic acid was obtained, which represents a 71% yield. From this, it was calculated that the yield of malonic acid obtained on oxidation was about 15%.

Styrene and Benzylideneacetone.—Ozonolysis of 10 ml. of styrene following directions similar to those outlined above for diketene yielded formaldehyde which was isolated as the methone derivative, m. p. 180°, in 57% yield. Benzylideneacetone (1.5 g.), similarly ozonized and processed, gave rise to pyruvaldehyde bisphenylhydrazone, m. p. 138–140°, in 37% yield. Two crystallizations from alcohol brought up the m. p. to 143°. A mixed m. p. determination of this product with benzaldehyde phenylhydrazone was 115–125°.

Ozonization of Butylketene Dimer.—An ozone stream was passed through 75 ml. of dry carbon tetrachloride containing 3 g. of butylketene dimer for four hours. The ozonide was hydrolyzed with 75 ml. of water in the presence of 10 g. of zinc dust.

The carbon tetrachloride layer was extracted with a slight excess of 5% sodium bisulfite solution and the aqueous layer was acidified with dilute hydrochloric acid and then treated with 2,4-dinitrophenylhydrazine reagent. Immediately a yellow precipitate formed. After allowing time for the product to settle, the precipitate was filtered and recrystallized from dilute alcohol; m. p. 98°. The yield was 42% (0.96 g.). A mixture of the product and of the known derivative of valeraldehyde melted at 96–97°. No search was made for butylmalonic acid among the products of ozonolysis.

Summary

Ozonolysis of diketene gives rise to formaldehyde and malonic acid. Ozonolysis of butylketene dimer yields valeraldehyde. These data strongly support 3-butenoic β-lactone as the structure for diketene and 2-butyl-3-octenoic β-lactone for butylketene dimer.

EVANSTON, ILLINOIS RECEIVED AUGUST 8, 1949

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[7] Wedekind, *Ber.*, **34**, 2070 (1901); **41**, 2297 (1908); *Ann.*, **323**, 246 (1902); **378**, 261 (1910); Hanford and Sauer, "Organic Reactions," Vol. III, John Wiley and Sons, New York, 1946, p. 140; Sauer, THIS JOURNAL, **69**, 2444 (1947).

[8] Roberts, Armstrong, Trimble and Burg, THIS JOURNAL, **71**, 843 (1949).

[9] Williams and Krynitsky, "Organic Syntheses," **21**, 64 (1941).