Summary

Evidence has been presented to show that vinyl polymers formed by the action of catalysts such as peroxides and boron fluoride or by photochemical activation have the same arrangement of monomeric units in the polymer chain. The nature of the monomer unit determines whether the polymer is of the "head to tail" or "head to head, tail to tail" variety.

Vinyl acetate loses acetic acid when polymerized by the action of boron fluoride complexes and the polymer is intractable.

Polyvinyl bromide loses hydrogen bromide as well as bromine when heated with zinc and hence this reaction is not useful for determining structure in this case.

URBANA, ILLINOIS RECEIVED JULY 12, 1940

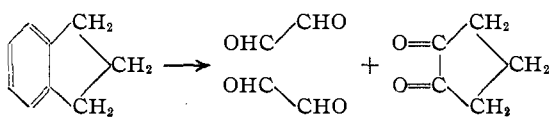
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Ozonization of Hydrindene

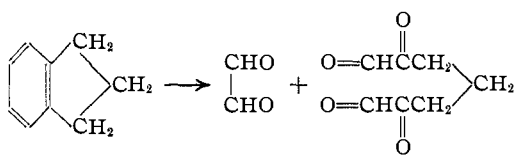
BY LOUIS LONG, JR.,[1] AND LOUIS F. FIESER

While Lothrop[2] has shown that bond fixation comparable to that associated with the unique chemical characteristics of naphthalene derivatives[3] does not exist in the hydrindene series, recent studies of competition reactions[4] and of relative reactivities[5] indicate that there is a certain qualitative differentiation, with respect to stability or abundance, between the two Kekulé forms and that this is in the direction predicted by Mills and Nixon.[6] The use of derivatives of a hydrocarbon for the investigation of bond structure of course introduces some element of uncertainty because of the possibility that the substituent may stabilize one of the Kekulé forms.[7] In the case of hydrindene, where any differentiation is likely to be a subtle one, this consideration may be of some importance.

The method of ozonization, first applied to the problem of bond structure by Levine and Cole,[8] has been investigated as a possible means of gaining information concerning the hydrocarbon itself. Levine and Cole obtained from *o*-xylene fragments establishing the presence in the starting material of both possible Kekulé forms. Hydrindene would likewise be expected to give rise to products characteristic of the arrangement of the double bonds. As the primary products, the preferred structure I (in terms of the Mills–Nixon hypothesis) should yield two moles of glyoxal and one of cyclopentanedione-1,2, while the alternate structure II should yield glyoxal and α,α'-diketopimelic dialdehyde.



I



II

The ozonization of hydrindene proceeded satisfactorily in ethyl chloride at −30° or in acetic acid at room temperature, and the proportion of ozone unabsorbed was comparable with that observed with benzene and naphthalene.[9] The ozonide showed a tendency to decompose explosively only when produced in ethyl acetate or acetic anhydride solution. Of the various methods tried for decomposing the ozonide the catalytic hydrogenation process of F. G. Fischer[10] seemed by far the most satisfactory. The solution resulting from ozonization in acetic acid could be submitted directly to hydrogenation, and on employing ethyl chloride this solvent could be distilled without difficulty, after removal of traces of free ozone, and replaced by alcohol for the hydrogenation. The reaction mixtures were processed by distillation, crystallization, and the formation of carbonyl derivatives.

(1) Present address: Cobb Chemical Laboratory, University, Virginia.

(2) Lothrop, THIS JOURNAL, **62**, 132 (1940).

(3) Fieser and Lothrop, *ibid.*, **57**, 1459 (1935).

(4) Lindner and co-workers, *Monatsh.*, **72**, 354, 355, 361 (1939).

(5) Baker, *J. Chem. Soc.*, 476 (1937); McLeish and Campbell, *ibid.*, 1103 (1937); Sandin and Evans, THIS JOURNAL, **61**, 2916 (1939).

(6) Mills and Nixon, *J. Chem. Soc.*, 2510 (1930).

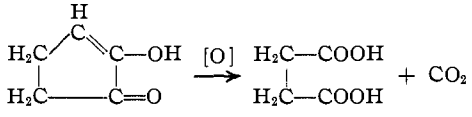
(7) Fieser and Seligman, THIS JOURNAL, **60**, 173, note 18 (1938).

(8) Levine and Cole, *ibid.*, **54**, 338 (1932).

(9) Brus and Peyresblanques, *Compt. rend.*, **190**, 501, 685 (1930).

(10) F. G. Fischer, Düll and Ertel, *Ber.*, **65**, 1468 (1932).

Unfortunately the diagnostic reaction involving cleavage of the aromatic double bonds was found to be obscured by a side reaction resulting in the formation of α-hydrindone. This oxidation reaction is similar to that observed by Durland and Adkins[11] on ozonization of various hydrophenanthrenes. The yield of α-hydrindone in one instance was as high as 60%, and a certain amount of this interfering ketonic substance was invariably encountered. This made it difficult to isolate other reaction products and the amounts obtained were small. Positive identification, however, was made of glyoxal and succinic acid. The succinic acid could hardly have arisen from II through α,α′-diketopimelic dialdehyde, for Blaise and Gault[12] have shown that α,α′-diketopimelic acid yields glutaric acid on oxidation. The more likely precursor is cyclopentanedione-1,2, since Dieckmann[13] has shown that this compound is largely enolic and affords succinic acid on oxidation with permanganate. That such a reaction



can occur in the reaction with ozone is indicated by the observation that the ozonization of pulegone yields β-methyladipic acid instead of methylcyclohexanedione.[14] As a test of the hypothesis cyclopentanedione-1,2 was prepared by Dieckmann's synthesis,[15] and less satisfactorily by selenium dioxide oxidation of cyclopentanone,[16] and ozonized in acetic acid solution. The ozonide was decomposed by catalytic hydrogenation as before and succinic acid was isolated in 62.5% yield.

There is thus little doubt that the succinic acid obtained on ozonization of hydrindene arises from the structure I. The acid was isolated in as much as 11.4% yield and therefore accounts for at least a significant amount of the hydrocarbon not converted into α-hydrindone. Glyoxal, which could arise from both structures I and II, was isolated as the *p*-nitrophenyl osazone or as glyoxime in maximum yield amounting to only 1.4% of that calculated for the more favorable case (I). Although the instability of the dialdehyde doubtless militates against its isolation in quantity, there is at least no indication here that bond cleavage occurred to a considerable extent in a direction other than that affording succinic acid. The reaction mixtures throughout were examined carefully for the presence of α,α′-diketopimelic dialdehyde, the diketo acid, and glutaric acid, but these substances were not detected. Although this negative evidence cannot be regarded as entirely conclusive, it is perhaps significant that glutaric acid is the most likely degradation product of II and that, with the isolation procedure employed, this substance would have accompanied the lower homolog found.

The results thus indicate that hydrindene behaves differently from *o*-xylene in giving ozonization products derived from only one of the two Kekulé forms. Since there is little reason to expect a difference in reactivity between the two forms, at least in the initiating attack by the first mole of ozone, the evidence points to the predominance of the Mills–Nixon structure I. Since such a favoring of one form would by no means preclude a perhaps facile rearrangement to the alternate structure, the conclusion accords with that reached from studies of derivatives indicating that although there is no rigid fixation of bonds in the hydrindene system, a definite preference exists for one structure, as postulated by Mills and Nixon.

Experimental Part

The ozonizer employed yielded 6.5% of ozone when dry oxygen was supplied at a rate of 10 liters per hour. The gas flow was measured by a flow meter of the type described by Church, Whitmore and McGrew[17] and the ozone content was determined both before and after passage through the reaction tube by potassium iodide analysis according to Smith.[18] The hydrindene was from a lot carefully purified by Dr. T. L. Gresham, b. p. 79.0° (no range) at 29 mm., $n^{20.7}$D 1.5382. As anticipated from observations of others,[9] the ozone absorption was initially only 75–90% in the best cases and gradually decreased during the reaction, and hence the total amount of ozone absorbed could be estimated only approximately.

In preliminary experiments the ozonization was conducted at room temperature in glacial acetic acid and the ozonide decomposed with zinc dust according to Harries[19] or by the modified procedure of Noller and Adams,[20] but the results were unpromising and no satisfactory derivatives could be isolated following interaction with *o*-phenylenediamine. On trying ethyl chloride as solvent at −30° a rapid decomposition approaching an explosion resulted in one instance on removal of the solvent at the water pump

(11) Durland and Adkins, THIS JOURNAL, **61**, 429 (1939).
(12) Blaise and Gault, *Bull. soc. chim.*, [4] **1**, 75 (1907).
(13) Dieckmann, *Ber.*, **35**, 3201 (1902).
(14) H. Neresheimer, Inaugural Dissertation, Kiel, 1907.
(15) Dieckmann, *Ber.*, **30**, 1470 (1897).
(16) Riley, Morley and Friend, *J. Chem. Soc.*, 1875 (1932).
(17) Church, Whitmore and McGrew, THIS JOURNAL, **56**, 176 (1934).
(18) L. I. Smith, *ibid.*, **47**, 1844 (1925).
(19) Harries and Haarmann, *Ber.*, **48**, 32, 231 (1915).
(20) Noller and Adams, THIS JOURNAL, **48**, 1074 (1926).

vacuum and room temperature. This difficulty was obviated later by removing the residual ozone with a stream of dry nitrogen prior to evaporation. Decomposition of the ozonide produced in ethyl chloride was tried using zinc dust with a trace of silver nitrate and hydroquinone,[17] and with potassium iodide, sulfuric acid and ethanol,[21] in the latter case with somewhat promising indications. All of the above methods of decomposition, however, were abandoned as much less satisfactory than the process of catalytic hydrogenation.[10] Ethyl alcohol proved to be a suitable solvent for the hydrogenation, while ethyl acetate was tried without success. The following experiments are typical of the best procedures developed.

Ozonization in Ethyl Chloride.—A solution of 0.408 mole of hydrindene in 25 cc. of ethyl chloride was treated with 6.6% ozone flowing at 9.8 liters per hour for twenty hours at a temperature of −30° maintained by a bath of ice and ethanol to which was added the requisite amount of solid carbon dioxide. An all-glass reaction vessel was used, and in order to prevent evaporation of ethyl chloride the emergent gas stream was passed through a Vigreux column surrounded by solid carbon dioxide. Within a short time a white solid began to separate and this eventually filled the solution. The total ozone absorption was 129% of that calculated for addition to three double bonds. At the end of the period indicated the dissolved ozone was removed by passing a slow stream of dry nitrogen through the apparatus for one and one-half hours, keeping the suspension at −30° but allowing the ethyl chloride to evaporate. To the residual white solid material 20 cc. of absolute alcohol, pre-cooled to −60°, was added and the suspension was allowed to come slowly to room temperature in the course of forty-eight hours in order to effect complete solution. The clear, light yellow solution of the ozonide was treated with 0.5 g. of palladium–calcium carbonate catalyst[10] and shaken with hydrogen. The reaction proceeded slowly and came to a stop after about twelve hours, when 480 cc. of hydrogen had been absorbed.

The resulting solution was filtered and distilled at 1 mm., using a gas trap cooled with dry-ice–alcohol and placed in the vacuum line before the oil pump. About 2 cc. of liquid giving a Schiff test collected in the trap, and after warming this with dilute hydrochloric acid to hydrolyze any acetal, treatment with an alcoholic solution of *p*-nitrophenylhydrazine gave 82 mg. of brick-red, crystalline **glyoxal *p*-nitrophenylosazone**, m. p. 303–304°, corr. The substance was extracted with alcohol in a Soxhlet apparatus, and on repeating the operation using acetone it was obtained as red needles of the above m. p. and giving a characteristic blue solution in alcoholic potassium hydroxide.

Anal. Calcd. for $C_{14}H_{12}O_4N_6$: C, 51.21; H, 3.69; N, 25.63. Found: C, 51.10; H, 3.59; N, 25.85.

On cooling the main distillate to about −72° it slowly afforded a mass of colorless crystals suspended in a red-yellow oil, and by centrifugation at 0° 0.19 g. of yellowish plates, m. p. 31–32°, was collected. After two crystallizations from petroleum ether (b. p. 35°) with the aid of solid carbon dioxide, and subsequent vacuum distillation, the substance was obtained as colorless tablets, m. p. 37–39°. This was found to be nearly pure α-hydrindone (m. p. 41–42°).

(21) Jacobs, THIS JOURNAL, **58**, 2272 (1936).

Anal. Calcd. for C_9H_8O: C, 81.75; H, 6.10. Found: C, 81.12; H, 6.00.

The remaining oil (2.89 g.) on treatment with petroleum ether yielded 70 mg. of colorless crystals, m. p. 95–100°. After recrystallization from petroleum ether and vacuum sublimation, well-formed rhombic needles were obtained, m. p. 114–116°. The substance did not react with semicarbazide and was identified as **succinic anhydride.** The residual oil was then distilled at 1 mm. through a simplified Podbielniak column[21] and separated into two fractions: 0.53 g., b. p. 80–82°; 0.40 g., b. p. 83–100°. The residue was a dark red oil (1.28 g.) which gave no semicarbazone derivative and which was examined for the presence of α,α′-diketopimelic acid with negative results. Both of the above fractions seemed to consist largely of α-hydrindone, for when cooled with solid carbon dioxide they solidified to give a mass of yellowish white crystals which when recrystallized twice melted at 32–35°. The material from the first fraction on reaction with semicarbazide and crystallization of the product from absolute alcohol afforded α-hydrindone semicarbazone, m. p. 227–229° (compare 233°, dec.[22]).

Anal. Calcd. for $C_{10}H_{11}ON_3$: C, 63.46; H, 5.86; N, 22.22. Found: C, 63.84; H, 5.82; N, 22.32.

The ozonization in ethyl chloride was repeated with twice the above amounts, and in working up the mixture after hydrogenation the solution was transferred under a pressure of dry nitrogen, with exclusion of air and moisture, to an all-glass fractionating still for use with a mercury vapor pump. The significant results were a recovery of about 27% of the starting material and the conversion of about 60% of the hydrindene consumed into α-hydrindone.

Ozonization in Acetic Acid.—A solution of 0.816 mole of hydrindene in 25 cc. of purified glacial acetic acid was ozonized with 6.8% ozone flowing at 6.18 l. per hour for forty-eight hours at 20–22°. About half of the liquid had been lost by entrainment. The clear, light yellow solution was transferred to a flask containing 0.5 g. of palladium–calcium carbonate catalyst and shaken with hydrogen, with the addition of eight 0.25-g. portions of catalyst as required. After eighty hours 1056 cc. of hydrogen had been absorbed. The solution was filtered and the solvent removed by distillation through a Podbielniak column at 2 mm. under nitrogen. The residue deposited crystals on standing, and separation by centrifugation gave 9.2 g. of red oil and 0.61 g. of white crystals of crude **succinic acid,** m. p. 155–165°. On two recrystallizations from methanol–chloroform the substance melted at 183–184° and did not depress the m. p. of a comparison sample.

The red oil was distributed between the water and ether and the layers were separated and each treated with a solution of semicarbazide in methanol. From the ether layer there was obtained 1.4 g. of α-hydrindone semicarbazone, m. p. 225–228°. Two crystallizations from methanol (Norit) gave colorless material, m. p. 224.6–225.6°, corr. (found: C, 63.56; H, 5.58; N, 22.30). The aqueous layer deposited 0.29 g. of almost white micro crystals, m. p. 245°, dec., corresponding to the m. p. of cyclopentanedione-1,2-disemicarbazone.[16] Attempts to obtain a pure sample by crystallization from methanol or acetic acid were unsuc-

(22) von Auwers and Auffenberg, *Ber.*, **52**, 106 (1919).

cessful and the identity of the substance was not established.

Another ozonization was conducted in acetic acid as above and the carbonyl compounds were isolated as the oximes. Succinic acid, glyoxime and α-hydrindone oxime were identified, but in total amount equal to only 13.8% of the hydrindene used. An additional product was obtained by fractional sublimation and crystallization of the oxime from the aqueous layer. This melted with gas evolution at 210°, corr., which is not far from the m. p. of cyclopentanedione-1,2 dioxime, but analyses indicated a wholly different composition (found: C, 17.12; H, 5.05; N, 13.83).

Other Solvents.—In trial ozonizations conducted in other solvents or without solvent, all of the previously mentioned products were again detected but cyclopentanedione-1,2 could not be identified. It was observed that the ozonide prepared with purified ethyl acetate or acetic anhydride as solvent was of an explosive nature; at about room temperature a rapid and spontaneous evolution of heat occurs. Although it decomposed readily on moderate heating, the ozonide was resistant to catalytic hydrogenation at room temperature at atmospheric pressure. Hydrogenation occurred rapidly at room temperature, however, at a pressure of 1000 lb. (67 atm.).

Cyclopentanedione-1,2.—The diketone was prepared most conveniently by Dieckmann's synthesis,[15] the over-all yield from ethyl glutarate being 38%. One distillation in vacuum gave a colorless, crystalline product, m. p. 44–54°.

Some trial was made of the method of Riley, Morley and Friend,[16] who obtained the crude diketone as a yellow oil, which failed to solidify, in 5% yield by the oxidation of cyclopentanone in alcohol with selenium dioxide. Glacial acetic acid was tried as solvent, as reported by Dane, Schmitt and Rautenstrauch[23] for the oxidation of methylcyclopentenone, but cyclopentanone proved to be much more reactive than this substance and in one experiment conducted in a sealed tube a violent explosion occurred at a temperature of about 54°. Methanol seemed more satisfactory than ethanol, and some improvement over the procedure reported[16] was made by adding the dioxide (55.6 g.) in water (120 cc.) to a stirred solution of cyclopentanone (42 g.) in methanol (150 cc.) and stirring the mixture at room temperature for six hours. The filtered solution was evaporated in vacuum and the product was dried in ether and distilled through a Podbielniak column (extraction from ether with alkali,[16] even at 0°, resulted in deep-seated decomposition). There was obtained 2.23 g. of material which solidified to colorless needles on standing at 0°. The dioxime[16] formed colorless needles from water; this melted with decomposition at about 190°.

Anal. Calcd. for $C_5H_8O_2N_2$: N, 21.88. Found: N, 21.91.

For **ozonization,** a solution of 1 g. of crystalline cyclopentanedione-1,2 in 25 cc. of acetic acid was treated for sixteen hours with 6% ozone at a rate of 4.5 liters per hour. As some heat was generated at the beginning of the reaction, the ozonization tube was initially cooled in a bath at 0°. The originally slightly yellow solution became colorless as the reaction progressed and a small amount of white powder separated. The resulting mixture was treated with 0.5 g. of palladium–calcium carbonate catalyst and hydrogenated for three hours, when 62 cc. of hydrogen (23% of theoretical) had been absorbed. After filtration from the catalyst the solvent was removed in vacuum, leaving a crystalline residue. When washed with ether, this afforded 0.75 g. (62.5%) of colorless succinic acid. A recrystallized sample melted at 181.5–183.5° and did not depress the m. p. of a known sample.

(23) Dane, Schmitt and Rautenstrauch, *Ann.*, **532**, 29 (1937).

Summary

On ozonization of hydrindene, followed by catalytic hydrogenolysis of the ozonide, a considerable amount of the hydrocarbon is merely oxidized to α-hydrindone. The only cleavage fragments detected are glyoxal and succinic acid, and it is shown that the latter arises from cyclopentanedione-1,2. The results indicate that hydrindene exists preponderantly in the Kekulé form postulated by Mills and Nixon to have preferential stability.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASSACHUSETTS RECEIVED JULY 11, 1940