SECTION C, PHYSICAL SCIENCES

A Study of the Autooxidation of Cyclohexene in the Presence of Benzoic Acid and Benzoic Anhydride

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In the course of an investigation on the decomposition of silver benzoate in cyclohexene (**I**), 2-cyclohexen-l-yl benzoate (**II**) was obtained as a product (Berlin and Gibbs, 1964). Since benzoic anhydride (**III**) was formed in the thermal decomposition of silver benzoate (Smith, 1957; Kaneskaya and Shemyakin, 1963), it might be an intermediate (Berlin and Gibbs, 1964) in formation of the ester **II**. Franzen and Edens (1961) found 2-cyclohexen-l-yl acetate as a major product when a mixture of lead tetraacetate and **I** were photolyzed. Benzoyl peroxide and **I** also give **II** by a radical mechanism (Kharasch and Sosnovsky, 1958; Doering *et al.*, 1960). A close analogy to the present work is revealed in the data of Shine and Snyder (1958) who observed that oxidation of **I** in acetic anhydride gave cyclohexyl acetate and two other products but the presence of **II** was not rigorously established.

Reagent-grade **III**, 2 parts, which was contaminated with 1 part of benzoic acid (**IV**), dissolved in 12 parts of **I** and heated at reflux in air for 39 hr gave **II** in 77% yield (by gas-liquid chromatographic [g.l.c.] analysis). Very pure **III** (prepared according to "Organic Syntheses", purity >99% by g.l.c.) in **I** was essentially unchanged when: (a) heated at reflux in air or nitrogen for 39 hr; (b) heated at reflux in air for 3.5 hr with AIBN catalyst; and (c) heated at reflux for 420 hr in air (or pure oxygen) while being irradiated with ultraviolet light. Hawkins (1961) has summarized the information available on the autooxidation of **I**, the conversion of which to cyclohexyl hydroperoxide (**V**) is known to be low (30-40%) (Farmer and Sundralingam, 1942).

Shine and Snyder (1958) postulated a radical mechanism for the formation of cyclohexyl acetate and suggested that the possible absence of **II** may be the result of further oxidation of this ester. In the present study the stability of **II** in a stream of oxygen (unless a metal catalyst was present) has been substantiated (Azanovskaya and Ablava, 1960). An important factor to consider in analyzing the reaction pathway must include the observation of Bateman and Hughes (1952) who found that **V** decomposed slowly at 80° and gave chiefly 2-cyclohexen-l-ol (**VI**). A solution of **IV** in **I** gave a trace of **II** after 55 hr at reflux. When a solution of the acid **IV** and the hydroperoxide **V** in **I** in (molar ratio of 3:1) was heated at reflux for 13 hr, a nearly quantitative yield (based on hydroperoxide) of **II** resulted. When **III** was added to a solution of **IV** in **I** containing the hydroperoxide **V** (ratio of **I**:**III**:**IV**:**V** was 2.6:1.5:4.9:1), **II** was again obtained in very high yield. Of significance was the isolation of additional benzoic acid above the quantity originally employed.

In an overall evaluation of the reactions involved, it appears, in view of the work of Bateman and Hughes (1952), that **V** probably decomposes to **VI** in our experiments also. Reaction of the alkoxy radical **VII** with **I** or **IV** would furnish the cyclohexenyl radical **VIII** (or perhaps the benzoyloxy radical), as shown in scheme A, Fig. 1. Certainly the alkoxy radical **VII**

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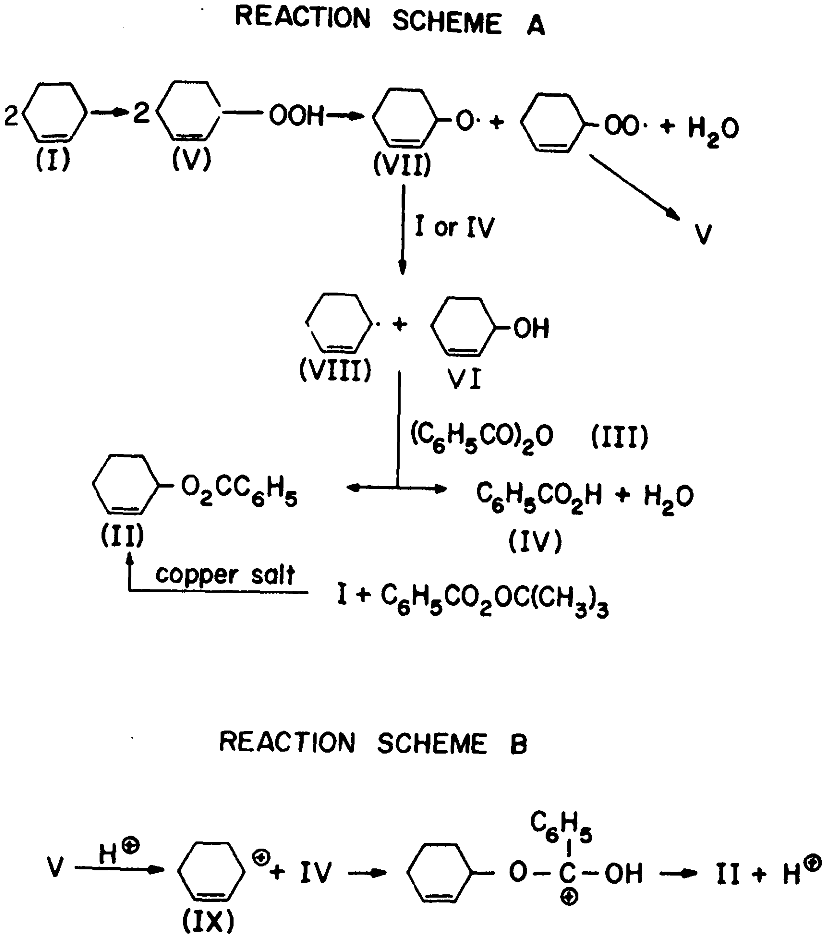

Fig. 1. Reaction Schemes.

(or another radical produced) could abstract hydrogen from the carboxyl group of benzoic acid. It would be expected that competition between **IV** and **I** as hydrogen sources would be important and somewhat product-controlling in the conversion of **VII** to **VI**. The structure of **II** was verified by independent synthesis *via* the sequence of Milas and Surgenor (1946) who condensed *t*-butyl perbenzoate and **I** in the presence of a copper salt. The method has been found very reliable by others also (Barnard and Yang, 1961).

Benzoylation of **VI** by **III** is a well known reaction; the acid **IV** would e formed in addition to **II**, which would explain the high yield of **II** when he mixture of **III** and **IV** was heated with **I**. Moreover, the increased quan- ty of **IV** is thus understandable. The relative stability of **III** in the pres- nce of **V** is somewhat surprising although **III** was not the solvent in our xperiments as was acetic anhydride in the work of Shine and Snyder 1958). Also **V** was in low concentration and is known to decompose owly to **VI** (Bateman and Hughes, 1952) and consequently the esterifica- on to give **II** would be slow. An auxiliary pathway for the decomposition of **V** in the presence of **IV** is certainly suggested from the short reaction time required to give a high yield of ester **II**. It is conceivable that the carbonium ion **IX** could form and in the presence of excess benzoic acid could give **II** also (Scheme B, Fig. 1).

Treatment of hydroperoxides with acids in the presence of certain nucleophiles was investigated by Davies, Foster, and Nery (1954) and is a close analogy. Commercial samples of allyl alcohol and **VI** were treated with an excess of **IV** in boiling cyclohexene for more than a day. The corresponding allylic esters were obtained which lends support to the postulate concerning formation of the ester **II** in the reaction of **IV** with the hydroperoxide. The mode of participation of **III** in the reaction of **IV** and **V** in **I** cannot be decided from the evidence available, but reaction of **VI** with **III** to give **II** is reasonable.

Experimental

All materials were obtained commercially or prepared by methods from the literature as cited in the text. All reaction mixtures were analyzed by gas chromatography using a Wilkens Hy Fi A-550 unit with hydrogen flame cell. Silicone rubber and SE-30 on Chromosorb W proved to be superior columns. All infrared data were recorded on a Beckman IR-5 on sodium chloride plates. All reactions were performed in standard ground glass equipment. Commercial nitrogen was further deoxygenated by the method of Arthur (1964).

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