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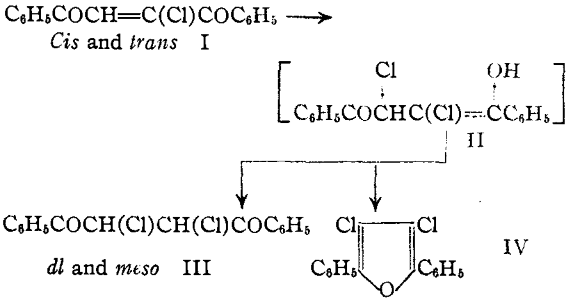
Evidence for the 1,4-Addition of Hydrogen Halides to α,β-Unsaturated Ketones. The Dibenzoylmonohalogenoethylenes

BY ROBERT E. LUTZ AND FRANK N. WILDER

Both the *cis* and *trans*-dibenzoylchloroethylenes I add hydrogen chloride in chloroform solution to give exclusively the *meso*-dibenzoyldichloroethane III. In ethereal solution, however, a mixture of the *dl* and *meso*-dibenzoyldichloroethanes is obtained, the *meso* form predominating, and the ratio of yields in both cases practically identical. In no case has the addition taken place in accordance with Markownikoff's rule. Stereochemically, from the point of view of 1,2 addition to the ethylene linkage, these facts are inconsistent, since one would expect to obtain different products or at least different mixtures from starting materials of opposite configurations. The fact that identical results are obtained regardless of the configurations of the starting materials, is evidence that addition does not take place directly at the ethylene linkage, but rather by a mechanism in which the stereoisomerism is destroyed in some intermediate step. The results are accounted for by the alternative 1,4 addition mechanism which leads to the formation of the intermediate enol II in which the double bond responsible for the stereoisomerism has been destroyed.

The addition of hydrogen chloride to the *cis* and *trans* isomers in 95% ethanol at 0° furnishes still more striking evidence. Mixtures of *meso*-dibenzoyldichloroethane III and diphenyldichlorofuran IV are obtained in both cases in a practically identical ratio of yields. The products expected of a 1,2 addition of hydrogen chloride directly to the ethylene linkage, namely, *dl* and *meso*-dibenzoyldichloroethanes, are stable under even more drastic conditions than those involved here and therefore cannot be intermediates in the formation of the furan (they are of course converted into the furan by such dehydrating agents as acetic anhydride and sulfuric acid). The possibility of a 1,2 addition followed by partial dehydration to the furan is thereby definitely excluded. Only 1,4 addition or its equivalent accounts for the formation of the furan and for the constant ratio of the products regardless of the configuration of the starting material.

The course of these reactions may be summarized as follows



There is no evidence either here or in the analogous cases given as evidence for the 1,6 addition of hydrogen to the unsaturated 1,4 diketones,[1] to show how the postulated intermediate enols or dienols of the type of II and HO—C=C—C=C—OH undergo loss of water with closure of the furan ring. It can only be said that these intermediates are particularly susceptible to the interaction of an enolic group with the γ-carbonyl or its enol to form furans, and are much more reactive in this sense than the difficultly enolizable saturated 1,4 diketones into which they are capable of being rearranged.

Experimental Part

The Dibenzoylhalogenoethylenes.—The *trans*-dibenzoylchloro and bromoethylenes have been made by the elimination of one molecule of hydrogen halide from either the *dl*- or *meso*-dibenzoyldihalogenoethanes III by heating with alcohol.[2] The *cis* isomers can best be obtained by the oxidation of the diphenylmonohalogenofurans with nitric and glacial acetic acids. The configurations of these compounds have been assigned on the basis of (a) the synthesis of the *cis* isomers from the furan (all four of these compounds, both *cis* and *trans*, are stable under the conditions of this oxidation),[3] and (b) the characteristic inversion of the *trans* isomers to the *cis* on exposure to the sunlight in the absence of a

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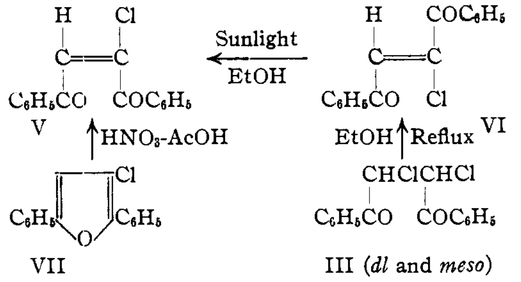
[1] Lutz, THIS JOURNAL, **51**, 3008 (1929); Lutz and Taylor, *ibid.*, **55**, 1595 (1933).

[2] Conant and Lutz, *ibid.*, **47**, 881 (1925). The *trans* dibenzoylchloroethylene was designated as the β-isomer, and the *cis* (obtained by adding hydrogen chloride to dibenzoylacetylene) as α. Only one dibenzoylbromoethylene (*trans*) was obtained by these methods.

[3] *Cf.* Lutz and Wilder, *ibid.*, **56**, 978 (1934).

catalyst.[4] These relationships are illustrated in the case of the chloro derivatives as follows



V VI VII III (*dl* and *meso*)

Acceptance of these configurations validates the hypothesis suggested in an earlier paper[2] that the addition of hydrogen chloride to dibenzoylacetylene takes place largely in a *cis* manner; on the same basis hydrogen bromide has added to give mainly the *trans* product.

Cis-Dibenzoylchloroethylene V is prepared in 80% yield by the nitric–glacial acetic acid oxidation at 50° of 2,5-diphenylchlorofuran according to the procedure described in a preceding paper.[3] It is prepared also by the action of sunlight (two days) on a 95% ethanol solution of the *trans* isomer; m. p. 70.5–71° (corr.).

Anal. Calcd. for $C_{16}H_{11}O_2Cl$: Cl, 13.3. Found: Cl, 13.3.

It gives a sharp mixed melting-point depression with the *trans* (β) isomer prepared by the elimination of hydrogen chloride from the *dl* and *meso*-dibenzoyldichloroethanes. The melting point is considerably higher than that given for the so-called α-isomer prepared by the addition of hydrogen chloride in alcohol to dibenzoylacetylene,[2] but it was found that the original sample[2] was impure; repeated recrystallization from ethanol raised its melting point to that given above. Mixed melting points showed the identity of the two samples. The original experiment[2] was repeated, using absolute ethanol containing 5% of hydrogen chloride, with similar results, the product being a mixture melting at 50–52° which consisted largely of the *cis* isomer, and probably contained some of the *trans* isomer which has very similar physical properties. The *trans*-dibenzoylchloroethylene and *dl* and *meso*-dibenzoyldichloroethanes were shown to be stable in 5% absolute alcoholic hydrogen chloride.

Exposure of both the *cis* and *trans* isomers in chloroform solution with a trace of iodine present as catalyst, to the action of sunlight for two days, gave largely in each case unchanged material with some resinous decomposition products. The experiments were repeated several times. The reported inversion of the α-isomer by this method[2] is therefore in error. Since the sample used in the original experiment was impure, it is evident that the rise in melting point was due really to purification. Examination of the original notes (Lutz, Ref. 2) on the experiment revealed the fact that a mixed melting point was not recorded, and if, contrary to the usual custom followed in all other cases, this check had been neglected, it would account for the error.

Both the *cis* and the *trans* isomers were recovered unchanged when treated with nitric and glacial acetic acids under the above conditions.

The Action of Alcoholic Hydrogen Chloride on the Dibenzoylchloroethylenes.—Both the *cis* and *trans* isomers (and also dibenzoylacetylene) in separate experiments on 0.2-g. samples, were suspended each in 3–4 cc. of 95% ethanol in a test-tube, cooled in an ice-bath and the solution saturated with hydrogen chloride. Within a few minutes the suspended solid dissolved and a granular precipitate of *meso*-dibenzoyldichloroethane began to appear, followed later by the formation of a mass of fine needle crystals of diphenyldichlorofuran. After standing for one hour the mixture of crystals was filtered off. This was digested with a little hot alcohol and was quickly filtered from the residue of the difficultly and slowly soluble *meso*-dibenzoyldichloroethane which was obtained thus nearly pure. On cooling the filtrate the much more soluble diphenyldichlorofuran crystallized nearly pure. In the case of *cis*-dibenzoylchloroethylene the yields of the two products were, respectively, 0.1 and 0.06 g., the rest of the material being accounted for as semi-solid residue from the alcoholic hydrogen chloride filtrates which probably contained more of these substances and possibly also small amounts of the *dl*-dibenzoyldichloroethane. The *trans*-dibenzoylchloroethylene and dibenzoylacetylene gave the same products in practically identical yields. The products in all cases were identified by mixed melting points.

A sample of *dl*-dibenzoyldichloroethane, dissolved in 95% ethanol, saturated with hydrogen chloride at 0°, and allowed to stand for two hours, was recovered unchanged on diluting with water. The *meso* isomer was likewise stable under these conditions.

2,5-Diphenyl-3-bromofuran,[5] $C_6H_5C{=}CHC(Br){=}C{-}C_6H_5$ (O).—Prepared by the action of acetic anhydride and a small amount of concd. sulfuric acid at room temperature in the usual way on dibenzoylbromoethane. It crystallized as fine needles from ethanol, m. p. 82–82.5° (corr.).

Anal. Calcd. for $C_{16}H_{11}OBr$: Br, 26.7. Found: Br, 27.0.

Cis-Dibenzoylbromoethylene, $C_6H_5COCH{=}C(Br)CO\text{-}C_6H_5$, was prepared by the nitric and glacial acetic acid oxidation of diphenylbromofuran at 50° (yield 60%); crystallized from ethanol; m. p. 66.5 (corr.).

Anal. Calcd. for $C_{16}H_{11}O_2Br$: Br, 25.4. Found: Br, 25.6.

Reduction with zinc and acetic acid (short heating) gave dibenzoylethane.

Both the *cis* and *trans* isomers were recovered unchanged when heated for one hour with the nitric–glacial acetic acid mixture at 50°.

Summary

The *cis*-dibenzoylchloro and bromoethylenes

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(4) Neither the *cis* nor the *trans* isomers are acted upon by sunlight in chloroform solution containing iodine as a catalyst, conditions which quickly bring about inversion of the various labile *cis* diaroylethylenes and diaroyldihalogenoethylenes into the corresponding *trans* isomers [Ref. 2, and Paal and Schulze, *Ber.*, **35**, 168 (1902); Conant and Lutz, This Journal, **45**, 1303 (1923); Lutz, *ibid.*, **52**, 3405 (1930)]. The supposed conversion of *cis* (α) dibenzoylchloroethylene into the *trans* (β) isomer by this method which was previously reported (Ref. 2) is erroneous.

(5) Pratt, Dissertation, Harvard University, 1927.

are obtained by the nitric and glacial acetic acid oxidation of diphenylhalogenofurans, and are assigned configurations on the basis of these syntheses.

The addition of hydrogen chloride to *cis* and *trans*-dibenzoylchloroethylenes under different conditions gives mixtures of *dl* and *meso*-dibenzoyldichloroethanes and diphenyldichlorofuran as independent end-products, the ratios of yields being independent of the configuration of the starting material. These facts are regarded as evidence for the 1,4 mechanism in the addition of halogen acids to α,β-unsaturated ketones.

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Effect of Inorganic Salts upon the Swelling and the Shrinking of Wood[2]

BY ALFRED J. STAMM

Wood, like all other fibrous materials, possesses the property of shrinking and swelling upon the loss or gain of moisture. The swelling, according to the classification of Katz,[3] is of the maximum swelling type. On drying green wood no shrinkage occurs until the moisture content is reduced below the fiber-saturation point (the moisture content below which the activity of the water becomes less than one). The shrinkage as manifested by the percentage change in external dimensions increases with an increase in the density of the wood. It is greatest in the tangential direction (tangent to the annual rings), varying from 6.0 to 12.0%. In the radial direction (from the center of the tree to the periphery) it varies from 3.0 to 7.0% and in the longitudinal direction (parallel to the fibers) it is only a small fraction of one per cent. The practically negligible longitudinal swelling and shrinking is accounted for on the basis of the swelling taking place only between the thread-like micelles which, in general, are oriented parallel to the length of the fibers. The greater shrinkage in the tangential direction than in the radial is accounted for on the basis of ray cells which have their longitudinal component in the radial direction of the wood, restraining the dimension changes in that direction.

x-Ray studies have shown that the swelling of a cellulosic fiber by water does not affect its crystal lattice.[3] The water must go between the constituent units of the structure rather than within these units (intermicellar swelling as contrasted to intramicellar swelling). Concentrated solutions of certain salts such as lithium thiocyanate, as well as of alkalies, however, change the crystal lattice,[4] showing that their action is intramicellar.

Unfortunately, it is extremely difficult to determine the total swelling of fibrous materials from the dimension changes. With wood, where the external dimension changes are easy to follow, it is extremely difficult to even approximate the internal changes that take place in the lumen of the fibers. In a homogeneous material free from stresses and strains the lumen would change in size on swelling and shrinking of the material, the same as the external dimensions of a piece of the material which would just fill the lumen. This, however, is not the case for wood or any other fibrous material. Because of these difficulties, swelling and shrinking measurements have, in general, been made in terms of weight change. This procedure may, however, be very misleading as swelling can only be proportional to the weight change over the sorption range. Absorption by the grosser capillary structure cannot cause swelling. Data for the absorption of salt solutions by wood, such as those of Schwalbe and Fischer,[5] are therefore hardly a measure of the swelling and further give no information as to whether the salts remain in solution in the water which becomes bound, or if they are merely dissolved in the free capillary water. There also seems to be a lack of information on the effect that these salts have upon the subsequent shrinkage of the fibrous materials.

Swelling Measurements

To avoid the foregoing difficulties as far as possible, measurements in the studies reported

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(1) Maintained at Madison, Wis., in coöperation with the University of Wisconsin.

(2) Presented before the Colloid Division, American Chemical Society, Chicago, Ill., September *11–15, 1933.*

(3) Katz, *Trans. Faraday Soc.*, **29**, 279 (1933).

(4) Katz and Derksen, *Rec. trav. chim.*, **50**, 149, 737, 746 (1931).

(5) Schwalbe and Fischer, *Kolloid Z.*, **57**, 338 (1931).