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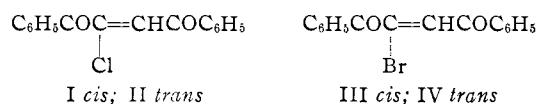
The Action of Alcoholic Hydrogen Halides on the Monohalo *cis*- and *trans*-Dibenzoylethylenes¹

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Both *cis*- and *trans*-chlorodibenzoylethylenes react irreversibly with 95% ethanolic hydrogen chloride to give *meso*-dibenzoylethylene dichloride and the corresponding furan. However, when absolute ethanol is used the sole product is the 2-ethoxy-3-furanone. The directive effect of 5% of water on the course of the reaction is interpreted in terms of prevention of build-up of an essential intermediate in which hydrolysis at the 3-position is the rate-controlling step in the formation of the 2-ethoxy-3-furanone. Several *cis*-addition furanizations, and a reductive furanization by ethanolic hydrogen bromide are reported.

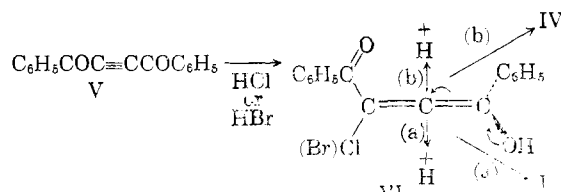
This investigation centers on the different courses of reaction of hydrogen chloride with *cis*- and *trans*-chlorodibenzoylethylenes (I-IV) in 95% ethanol to give identical ratios of *meso*-dibenzoylethylene dichloride (VIIIb) and 3,4-dichloro-2,5-diphenylfuran (IX),^{3,4} and in absolute ethanol to give exclusively 2-ethoxy-2,5-diphenylfuranone-3 (XIV).⁵⁻⁷ Its purpose was the corroboration of the determinative effect of the presence or absence of 5% of water on the course of such reactions and a consideration of the mechanistic questions involved.



Preparation of the Halodibenzoylethylenes.^{8,9}—*cis*-Chloro- and bromodibenzoylethylenes (I, III) were obtained by nitric-acetic acid oxidative cleavage of the 3-halofurans. The preparation of *trans*-chlorodibenzoylethylene (II) by dehydrohalogenation of the dibenzoylethylene dichlorides VIII has been improved greatly by avoidance of excess of the reagent, triethylamine, and minimizing the somewhat slower secondary dehydrohalogenation to dibenzoylacetylene (V).¹⁰ The action of one equivalent of triethylamine on the dibenzoylethylene dibromides XIa,b, however, gave unchanged material and dibenzoylacetylene instead of the desired *trans*-bromodibenzoylethylene IV, because here, as was demonstrated in separate experiments, the second dehydrohalogenation goes more rapidly than the first. Resort

was then made to addition of hydrogen bromide to dibenzoylacetylene⁹ which took place *trans* in contrast to hydrogen chloride addition which goes *cis*.⁹

The striking difference in the stereochemical mode of addition to dibenzoylacetylene, of hydrogen chloride in the *cis* manner and hydrogen bromide *trans*,⁹ is understandable in terms of Zimmerman's proposal,¹¹ assuming decreasing steric requirements of bromine, benzoyl and chlorine in the ketonization of the allenic enol produced as an intermediate in 1,4-addition, VI. In the case of the chloro compound the least hindered approach of the proton donor would be that represented by (a)→I, and for the bromo compound the opposite,



(b)→IV.¹¹ From plane scalar drawings^{12a} one might predict that *cis*-chlorodibenzoylethylene because of the small size of the chlorine atom (1.80 Å.) would be the higher-energy form like *cis*-dibenzoylethylene, whereas *trans*-bromodibenzoylethylene where bromine (1.95 Å.) is close in size to methyl (2.00 Å.) would be the higher-energy form like *trans*-methylidibenzoylethylene. However, earlier experiments indicate that actually both the chloro and bromo *cis* isomers are the labile forms.^{3,12b} This seeming steric anomaly might be accounted for by the opposite inductive effects of bromine and methyl on the resonance contribution of the furanoid form which is possible in the *cis* isomers.^{12b}

The Action of Hydrogen Halide in Ethanol Containing 5% of Water.—The earlier experiments on the *cis*- and *trans*-chlorodibenzoylethylenes using 95% ethanol saturated with hydrogen chloride at 0°, have been repeated with similar results; the reaction presumably proceeded through VII and X, and the *meso*-dichloride VIIIb was obtained predominantly over the dichlorofuran IX. The *rac*- and *meso*-dichlorides and the 2-ethoxy-

(11) This type of mechanism has been proposed by H. E. Zimmerman [J. Org. Chem., 20, 549 (1955)] and here receives direct experimental support.

(12) (a) L. P. Kuhn, R. E. Lutz and C. R. Bauer, THIS JOURNAL, 72, 5058 (1950); (b) cf. R. E. Lutz and C.-K. Dien, J. Org. Chem., in press.

(1) This work received some of its support from a contract with the Office of Ordnance Research, U. S. Army.

(2) Philip Francis du Pont Fellow, 1955-1956.

(3) R. E. Lutz and F. N. Wilder, THIS JOURNAL, 56, 1193 (1934).

(4) This reaction in 95% ethanol, and also the reactions with hydrogen chloride in chloroform to give the *meso*-dichloride, and the reaction in ether to give identical ratios of *rac*- and *meso*-dichlorides, have been cited as evidence for the reality of the "1,4-addition" mechanism. Initial *cis-trans* rearrangement or equilibration in these reactions might conceivably occur through reversible 1,4-addition enolization, but this does not invalidate the argument for the 1,4-addition mechanism.

(5) R. E. Lutz, F. N. Wilder and C. I. Parrish, THIS JOURNAL, 56, 1980 (1934). The compounds formulated in that paper as XV and XVI are in reality the 2-alkoxy-3-furanones⁸ and should be formulated like XIV above.

(6) R. E. Lutz and A. H. Stuart, *ibid.*, 58, 1885 (1936).

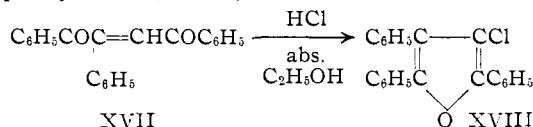
(7) Furanone formation under these conditions took place also with other compounds including methoxy- and ethoxydibenzoylethylenes,⁵ dibenzoylethylene oxide and chlorohydrin⁸ and dibenzoylacetylene.⁴

(8) R. E. Lutz and F. N. Wilder, *ibid.*, 56, 1987 (1934).

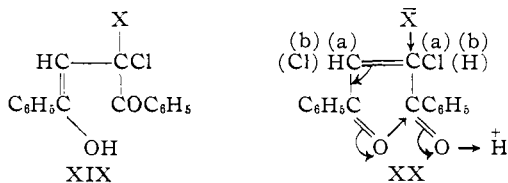
(9) J. B. Conant and R. E. Lutz, *ibid.*, 47, 881 (1925).

(10) R. E. Lutz and W. R. Smithy, Jr., J. Org. Chem., 16, 51 (1951).

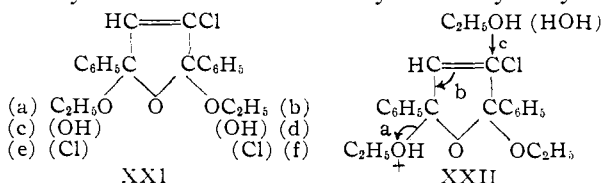
which could not produce a furanone analogous to XIV, failed to give the hoped for cyclic ketal²⁰ analogous to XXIab. Instead it underwent addition furanization exclusively to 3-chloro-2,4,5-triphenylfuran (XVIII).



Mechanistic Considerations.—Stereoisomerization obviously does not occur in the sulfuric acid-catalyzed acylations and ethanolyses of the halo-dibenzoyl ethylenes where only the *cis* isomers react, presumably by *cis*-addition cyclization through XX¹⁷ rather than simple 1,4-addition through VII or XIX. The hydrogen halide-ethanol reactions go with both *cis* and *trans* isomers; and, if stereoequilibrium is involved, they also may proceed by *cis*-addition cyclization *via* XXa or b.



A modified mechanism of 3-furanone formation can now be offered. The requirement of alcohol containing a minimal concentration of water suggests that there is involved build-up of a relatively persistent intermediate which is prevented or/and destroyed by water: namely, the cyclic ketal XXIab, analogs of which are actually isolated in the reactions with *cis*-dihalodibenzoyl ethylenes and which are easily hydrolyzed.²⁰ The rate-determining step is presumed to be the 3-hydrolytic or alcoholytic attack under 2,2,3,3-group oppositions, XXIIabc; and water required to complete hydrolysis at 3 is supplied by the alcoholysis I → XXIab. Weakly acidic hydroxylic



species such as the enol XIX and cyclic hemiketals XX, XXIad and XXIbc are doubtless formed but may be presumed to be too short-lived to stage the hydrolysis at 3. With as much as 5% of water to minimize cyclic ketal formation, the ready reversal of steps up to this point would allow addition contrary to Markovnikov's rule through VII and/or X (XXb) and irreversible ketonization and/or furanization, to become the main reaction path.

(20) R. E. Lutz and M. G. Reese, *THIS JOURNAL*, a paper following shortly.

Experimental

trans-Chlorodibenzoyl ethylene (II).⁹—A solution of 30 g. of VIIIb (or a) in 300 ml. of chloroform was treated dropwise with 10 g. of triethylamine in 100 ml. of chloroform and refluxed for 2 hours. After extraction with water, drying over sodium sulfate and evaporation, the residue was crystallized from ethanol, 22.9 g. (89%), m.p. 73.5–75° (it gave a mixture m.p. depression with I). *Anal.* Calcd. for C₁₆H₁₁O₂Cl: C, 70.99; H, 4.10. Found: C, 70.77; H, 3.83.

trans-Bromo-1,2-dibenzoyl ethylene (IV).⁹—In experiments on XIa and b identical with those on VIII, mixtures were obtained which could be separated by fractional crystallization from ethanol into starting material and dibenzoyl acetylene (V). Only from XIa was a small amount of IV isolated (ca. 5%). A similar experiment involving one equivalent each of XIb, IV and triethylamine gave largely unchanged XIb and dibenzoyl acetylene (V).

Action of Hydrogen Chloride in 95% Ethanol on *cis*- and *trans*-Chlorodibenzoyl ethylenes. (I, II).^{3,5}—(a) In repetition of earlier work³ suspensions of 1 g. each of I and II in 12 ml. of 95% ethanol at 0° were saturated with hydrogen chloride for 1 hr. and the crystalline precipitates were fractionally crystallized from ethanol; yields from I and II, ca. 40% of VIIIb and 18–19% of IX. The *meso*- and *rac*-dichlorides VIII were unchanged after subjection to the above conditions.

(b) A suspension of 2 g. of I (or II) in 50 ml. of 20–25% hydrogen chloride in 95% ethanol after standing for 24 hr. gave needles which were fractionally crystallized from ethanol; yields from I and II, 7 and 5% of VIIIb and 39 and 35% of IX, respectively.

Action of 20–25% hydrogen chloride in absolute ethanol on *cis*-²¹ and *trans*-chlorodibenzoyl ethylenes,⁵ as in (b) above (24 hr. at room temperature), gave 90% yields of the furanone XIV. Samples of VIIIb and X under these conditions were unchanged, and a sample of VIIIa (*rac*) gave a very low yield of XIV and non-crystalline product. **The use of concd. sulfuric acid** (25 ml. of sp. gr. 1.84) instead of hydrogen chloride in 100 ml. of absolute ethanol on 2-g. samples of I and II (as above) gave 82% of the furanone XIV from I and 73% of unchanged starting material from II.

Action of hydrogen chloride in absolute ethanol on *cis*- and *trans*-bromodibenzoyl ethylenes (III and IV), carried out like (a) above, gave 56% of the furanone XIV from I and 76% from II. **The action of ethanol-concd. sulfuric acid** (as above) gave 42% of unchanged material from III and 82% from IV; in neither case was the furanone XIV isolated. **Action of abs. ethanolic hydrogen chloride on *cis*-dibenzoylstyrene (XVII)** (as above) gave 64% of XVIII of m.p. 118–120° (identified).²²

Action of hydrogen bromide in 95% ethanol (saturated at 0°) on 1 g. each of III and IV (1 hr.) gave ca. 74% of crystalline 3,4-dibromo-2,5-diphenylfuran (XIII); recrystallized from ethanol, m.p. 88.5–89.5°.

Anal. Calcd. for C₁₆H₁₀Br₂O: C, 50.82; H, 2.67. Found: C, 50.68; H, 2.82.

After treatment as above a sample of VIIIb was recovered unchanged; the *rac* isomer VIIIa gave 35% of VIIIb and 26% of furan XIII.

Reductive Furanization of *cis*- and *trans*-Bromodibenzoyl ethylenes (III and IV).—Solutions of 3 g. of each in 25% hydrogen bromide in absolute ethanol after standing for 24 hr. at room temperature were evaporated under reduced pressure. Crystallizations from ethanol gave 3-bromo-2,5-diphenylfuran (XVI); yield from III, 29%; from IV, 49%; identified by mixture m.p. and analysis (Calcd. for C₁₆H₁₁BrO: C, 64.23; H, 3.71. Found: C, 63.97; H, 3.76). When subjected to the same conditions, the furanone XIV gave 56%, and VIIIb 45%, of unchanged material, and VIIIa gave resin.

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(21) R. E. Lutz and D. N. Wilder, *ibid.*, **56**, 978 (1934).

(22) F. R. Japp and F. Klingemann, *J. Chem. Soc.*, **57**, 602 (1890).