[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

## The Action of Alcoholic Hydrogen Halides on the Monohalo cis- and trans-Dibenzoylethylenes<sup>1</sup>

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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),<sup>8.4</sup> and in absolute ethanol to give exclusively 2 - ethoxy - 2,5 - diphenylfuranone - 3 (XIV).<sup>5-7</sup> 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.

C6H5COC==CHCOC6H5	$C_6H_5COC == CHCOC_6H_5$
	Br
CI	DI
I cis: II trans	III cis: IV trans

**Preparation of the Halodibenzoylethylenes**.<sup>8,9</sup> *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).<sup>10</sup> The action of one equivalent of triethylamine on the dibenzoylethylene dibromides XIab, 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

(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-furanones<sup>6</sup> 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,<sup>§</sup> dibenzoylethylene oxide and chlorohydrin<sup>§</sup> and dibenzoylacetylene.<sup>§</sup>

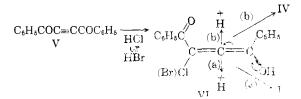
(8) R. E. Lutz and F. N. Wilder, *ibid.*, 56, 1987 (1934).

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

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

was then made to addition of hydrogen bromide to dibenzoylacetylene<sup>9</sup> 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*,<sup>9</sup> is understandable in terms of Zimmerman's proposal,<sup>11</sup> 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) $\rightarrow$ I, and for the bromo compound the opposite,



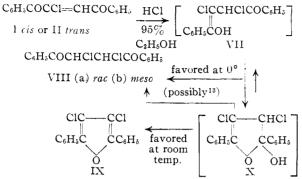
(b) $\rightarrow$ IV.<sup>11</sup> From plane scalar drawings<sup>12a</sup> one might predict that *cis*-chlorodibenzoylethylene because of the small size of the chlorine atom (1.80 Å.) would be the higher-energy form like *cis*-dibenzoylethylene, whereas *trans*-bromodibenzoylethylene where bromine (1.95 Å.) is close in size to methyl (2.00 Å.) would be the higher-energy form like *trans*-methyldibenzoylethylene. However, earlier experiments indicate that actually both the chloro and bromo *cis* isomers are the labile forms.<sup>3,12b</sup> 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.<sup>12b</sup>

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-

(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.

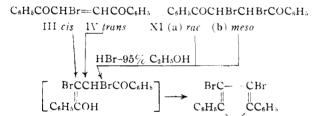
<sup>(11)</sup> This type of mechanism has been proposed by H. E. Zimmerman [J. Org. Chem., 20, 549 (1955)] and here receives direct experimental support.

furanone (XIV) are not furanized under these conditions and could not have been intermediates, and the reactions presumably proceeded through the enol of 1,4-addition VII followed by competing ketonization and furanization.<sup>13</sup>



For purposes of more rigorous comparison with the reactions that had been carried out in absolute ethanol, the above experiments in 95% ethanol were repeated at room temperature using 20-25%hydrogen chloride. Again the products were the dichlorofuran and *meso*-dibenzoylethylene dichloride, but in this case the dichlorofuran predominated. Temperature appears to have affected drastically the relative rates of ketonization and furanization of the intermediates VII and X.

The action of hydrogen bromide on the *cis*- and *trans*-bromodibenzoylethylenes III and IV in 95% ethanol differs from the above-described action of hydrogen chloride on I and II in giving only the furan XIII and neither dibromide XI. Presum-



XHI

ХĦ

ably the steric and electronic effects of the bromine atoms make the enol of 1,4-addition XII relatively persistent and easily cyclized, although furanization might conceivably be occurring through addition furanization of the *cis* isomer maintained in mobile acid-catalyzed stereoequilibrium (III  $\rightleftharpoons$ IV). Neither dibromide XI can be principal intermediates because they behave differently in separate experiments under the same reaction conditions; the *meso*-dibromide is stable whereas the *racemic* isomer is converted into a mixture of *meso*-dibromide and furan XIII.<sup>14</sup>

Action of Absolute Alcoholic Hydrogen Chloride.—In repetition of the earlier experiments *cis*and *trans*-chlorodibenzoylethylenes (I, II) and now also *cis*- and *trans*-bromodibenzoylethylenes (III,

(13) It is conceivable that  $\mathbf{X}$  could undergo a concerted ketonization ring opening by loss of the proton of the 1-hydroxyl and gain of a proton at the 4-carbon.

(14) This furanization is empirically comparable with the ready furanization of the *rac* but not the *meso* isomer by acetic anhydride and sulfuric acid where, however, epimerization does not occur.<sup>15</sup>

IV), reacted with 25% hydrogen chloride in absolute ethanol at room temperature, in accord with Markovnikov's rule, to give exclusively the 2-CeHCOC=CHCOCeH absolute HC= C=0

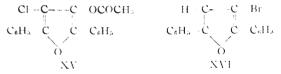
$$\begin{array}{c} \text{Cl (or Br)} \\ \text{I, II, III, IV} \end{array} \xrightarrow{25\% \text{ HCl}} C_6H_2C \xrightarrow{\text{CC}_6H_3} C_6H_4C \\ \end{array}$$

ethoxyfuranone XIV. Addition of hydrogen chloride to the chlorodibenzoylethylenes could not first have given the *rac-* or *meso-*dichlorides VIII or the furan IX because two of these compounds, VIIIb and IX, are stable under reaction conditions, and VIIIa gives largely oil and only a very little furanone XIV.

When the above acid-catalyzed ethanolyses were attempted using concentrated sulfuric acid instead of hydrogen chloride, the *trans* isomers II and IV were not affected, whereas the *cis* isomers I and III were converted into the furanone XIV. Under these conditions it would appear that typical *cis* addition cyclizations<sup>16,17</sup> have occurred.

The essentially irreversible formation of the furanone XIV is shown by its resistance to attack by hydrogen chloride in 95% ethanol. Reversal of this cyclization step presumably would have led back through chlorodibenzoylethylene to a mixture of the *meso*-dichloride VIIIb and the furan IX which are stable under these conditions. Actually such a reversal, to the furan, has been accomplished but by the much more drastic reagent phosphorus pentachloride<sup>18</sup> (presumably through an intermediate such as XXIef).

The action of acetic anhydride and sulfuric acid<sup>19</sup> on the chlorodibenzoylethylenes (I, II) could proceed in two ways, to give either the 2-acetoxy-3-furanone (analogous to XIV) or the 4-chloro-3-acetoxyfuran XV. Experiment<sup>19</sup> showed that the *trans* isomer was stable under these conditions whereas the *cis* isomer gave the chloroacetoxyfuran XV by *cis*-addition furanization.



Reductive Furanization by Absolute Ethanolic Hydrogen Bromide.—The action of this reagent on *cis*- and *trans*-bromodibenzoylethylenes (III, IV) to give the 3-bromofuran XVI brought about in one process both reduction and furanization. Neither *rac*- nor *meso*-dibromodibenzoylethanes nor the 2ethoxyfuranone are involved because in separate experiments under the same conditions these compounds gave only unchanged material and resins and did not give the easily isolable 3-bromofuran XVI. This furanization must involve reductive abstraction of a bromine atom by the solvent at some intermediate stage among the several that are possible (*e.g.*, bromo analogs of XIX-XXI<sup>17</sup>).

The reaction between absolute ethanolic hydrogen chloride and *cis*-dibenzoylstyrene (XVII),

(16) R. E. Lutz and C. R. Bauer, J. Org. Chem., 19, 324 (1954).

(17) C. K. Dien and R. E. Lutz, *ibid.*, **21**, 1496 (1955).

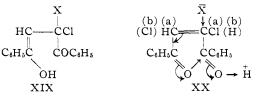
(18) R. E. Lutz and F. N. Wilder, THIS JOURNAL, 56, 2145 (1934).
(19) R. E. Lutz, F. N. Wilder, A. H. Stuart and W. C. Connor, *ibid.*, 59, 2414 (1937).

<sup>(15)</sup> R. E. Lutz, T'HIS JOURNAL, 48, 2916 (1926).

which could not produce a furanone analogous to XIV, failed to give the hoped for cyclic ketal<sup>20</sup> analogous to XXIab. Instead it underwent addition furanization exclusively to 3-chloro-2,4,5-triphenylfuran (XVIII).

$$\begin{array}{ccc} C_{6}H_{5}COC == CHCOC_{6}H_{5} & \xrightarrow{HCl} & C_{6}H_{5}C & \_CCl \\ \hline C_{6}H_{5} & C_{2}H_{5}OH & C_{6}H_{5}C & \_CC_{6}H_{5} \\ \hline XVII & O & XVIII \end{array}$$

**Mechanistic Considerations.**—Stereoisomerization obviously does not occur in the sulfuric acidcatalyzed acylations and ethanolyses of the halodibenzoylethylenes where only the *cis* isomers react, presumably by *cis*-addition cyclization through XX<sup>17</sup> rather than simple 1,4-addition through VII or XIX. The hydrogen halide–ethanol reactions go with both *cis* and *trans* isomers; and, if stereoequilibration 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*-dihalodibenzoylethylenes and which are easily hydrolyzed.20 The ratedetermining 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  $I \rightarrow XXIab$ . Weakly acidic hydroxylic HC==CC1  $C_2H_5OH(HOH)$ 

 $\begin{array}{c|c} & & & & & & & \\ C_{6}H_{5}C & CC_{6}H_{5} & & & HC \xrightarrow{c} CCl \\ \hline (a) & C_{2}H_{5}O & O & C_{2}H_{5} & (b) & C_{6}H_{5}C & CC_{6}H_{5} \\ (c) & (OH) & (OH) & (d) & a & \\ (e) & (Cl) & (Cl) & (f) & C_{2}H_{5}OH & O & OC_{2}H_{5} \\ \hline XX1 & & XXII \end{array}$ 

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-Chlorodibenzoylethylene (II).<sup>9</sup>—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 1). Anal. Calcd. for C<sub>16</sub>H<sub>11</sub>-O<sub>2</sub>Cl: C, 70.99; H, 4.10. Found: C, 70.77; H, 3.83. trans-Bromo-1,2-dibenzoylethylene (IV).<sup>9</sup>—In experi-

trans-Bromo-1,2-dibenzoylethylene (IV).<sup>9</sup>—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 dibenzoylacetylene (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 dibenzoylacetylene (V).

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(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.

and; yields from 1 and 11, 7 and 0.6 of 1110 and 00 and

Action of hydrogen chloride in absolute ethanol on *cis*and *trans*-bromodibenzoylethylenes (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).<sup>22</sup> Action of hydrogen hydrogen (caturated at

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.  $88.5-89.5^\circ$ .

Anal. Calcd. for C<sub>16</sub>H<sub>10</sub>Br<sub>2</sub>O: 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-Bromodibenzoylethylenes (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 C<sub>16</sub>H<sub>11</sub>-BrO: 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).