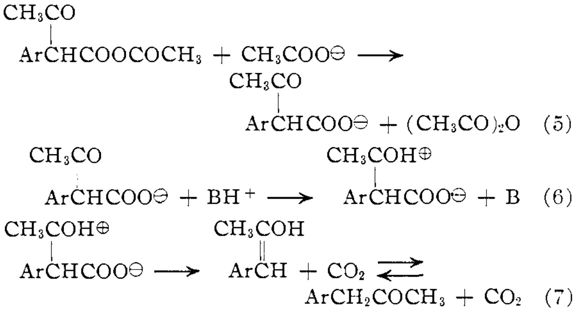


$$\overset{CH_3CO}{\overset{|}{ArCHCOOCOCH_3}} + CH_3COO^{\ominus} \longrightarrow \overset{CH_3CO}{\overset{|}{ArCHCOO^{\ominus}}} + (CH_3CO)_2O \quad (5)$$

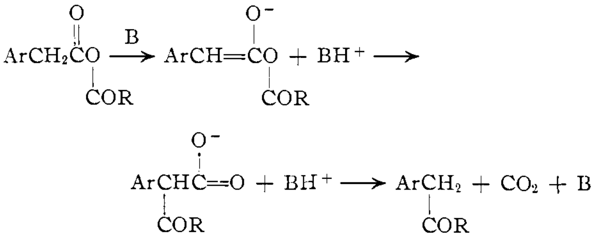
$$\overset{CH_3CO}{\overset{|}{ArCHCOO^{\ominus}}} + BH^+ \longrightarrow \overset{CH_3COH^{\oplus}}{\overset{|}{ArCHCOO^{\ominus}}} + B \quad (6)$$

$$\overset{CH_3COH^{\oplus}}{\overset{|}{ArCHCOO^{\ominus}}} \longrightarrow \overset{CH_3COH}{\overset{\|}{ArCH}} + CO_2 \rightleftarrows ArCH_2COCH_3 + CO_2 \quad (7)$$

In this mechanism, anhydrides are the reactants and step 4, involving carbon–oxygen bond rupture, is the rate-determining step. The mechanism satisfies the requirements that the reaction be first order with respect to the active methylene component and that the effect of moisture is as described earlier. Step 5 contributes as a driving force because the anion of the strong β-keto acid will form rapidly in the presence of salts of weaker acids. Excess anhydride ensures anhydrous conditions and maintains a supply of reactants, and decarboxylation may act as a secondary driving force by removing some of the acid produced during the reaction. The decarboxylation of a β-keto acid was suggested early by Fittig[50]; King and McMillan[52] agree with Rondestvedt, *et al.*,[4c] on this point for the decarboxylation of acylated oxazolones. Based on a review by Brown[53] on the decarboxylation of β-keto acids in the presence of bases, the decarboxylation of β-keto acid zwitterion is proposed in step 7.

**O to C Migration.**—A number of O to C migrations have been described in the literature to explain the formation of C-acylated compounds. One of the early examples[54] described the formation of acetone from a sodium acetate–acetic anhydride complex. Fried[55] has pictured the C-acylation of β-arylglutamic anhydride with acetyl chloride and pyridine to proceed through an O-acyl derivative followed by an O to C migration. Such a reaction path is difficult to apply to the acylation of oxazolones resulting from amino acids with only one α-hydrogen although they are readily acylated in base.

A slightly modified O to C migration was proposed by Buchanan and McArdle[23a] for the acylative decarboxylation of arylacetic acids. This



$$ArCH_2\underset{\underset{COR}{|}}{\overset{\overset{O}{\|}}{C}}O \xrightarrow{B} ArCH{=}\underset{\underset{COR}{|}}{\overset{\overset{O^-}{|}}{C}}O + BH^+ \longrightarrow$$

$$\underset{\underset{COR}{|}}{ArCH}\overset{\overset{O^-}{|}}{C}{=}O + BH^+ \longrightarrow \underset{\underset{COR}{|}}{ArCH_2} + CO_2 + B$$

mechanism was essentially presented by Levene and Steiger[56] earlier for the acylative decarboxylation of amino acids.

Many reactions are in accord with this mechanism such as the reaction of oxazolones with acetic acid in pyridine[13] and the numerous examples of intramolecular ring closure under the influence of acetic anhydride and base[57,58] though they might logically be described as proceeding by an aldol-type mechanism. An intramolecular O to C migration is in general agreement with the experimental evidence cited in this paper (first-order kinetics, proposed carbon–oxygen bond rupture as rate-determining).

**Acknowledgments.**—The authors wish to acknowledge a grant-in-aid from Research Corporation which supported this work. D. M. F. gratefully acknowledges a research fellowship from the National Science Foundation.

PULLMAN, WASH.

---

[52] J. A. King and F. H. McMillan, Abstract of Papers, 12th International Congress of Pure and Applied Chemistry, New York, N. Y., September, 1951, p. 381.

[53] B. R. Brown, *Quart. Rev. Chem. Soc. (London)*, **5**, 131 (1951).

[54] W. H. Perkin, *J. Chem. Soc.*, **49**, 317 (1886).

[55] J. Fried, in R. C. Elderfield, Ed., "Heterocyclic Compounds," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1950, p. 359.

[56] P. A. Levene and R. E. Steiger, *J. Biol. Chem.*, **79**, 95 (1928).

[57] W. H. Perkin, Jr., *J. Chem. Soc.*, **85**, 416 (1904).

[58] H. Waldmann and G. Pitschak, *Ann.*, **527**, 183 (1937).

---

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

# Cyclic Diketals of 1,2-Disubstituted *cis*-1,2-Dibenzoylethylenes[1]

BY ROBERT E. LUTZ AND MILLARD G. REESE[2]

RECEIVED JULY 18, 1958

Easily hydrolyzable cyclic diketals (2,5-dialkoxy-2,5-dihydrofurans) are produced by acid-catalyzed alcoholysis of *cis* but not *trans* disubstituted dibenzoylethylenes. Metathetical reactions at the 2- and 2,5-positions are described. Structural proof, mechanism of formation and facility of the *cis* cyclization reactions are considered. With absolute ethanolic hydrogen chloride *cis*- but not *trans*-dibromodibenzoylethylene underwent halogen displacement and cyclization to the 4-chloro-2-ethoxy-3-furanone. With acetic anhydride and sulfuric acid it gave the 4-bromo-2-acetoxy-3-furanone.

As a part of the study of *cis* addition cyclizations of unsaturated 1,4-diketones, this paper deals with the conversion of 1,2-disubstituted dibenzoylethylenes into 2,5-dialkoxy-2,5-dihydrofurans of the type IV which are cyclic diketals. The work stems from earlier studies[3] in which it had been shown that absolute ethanolic hydrogen chloride converts both *cis*- and *trans*-monochloro-

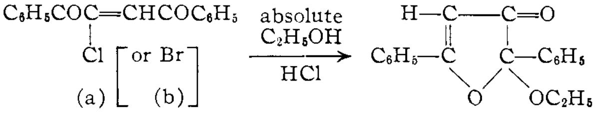
---

[1] During the earlier stages this work received some of its support from a contract with the Office of Ordnance Research, U. S. Army.

[2] (a) National Science Foundation Postgraduate Fellow, 1956–(1957). (b) Some of the experiments reported here were carried out by Grover C. Helsley.

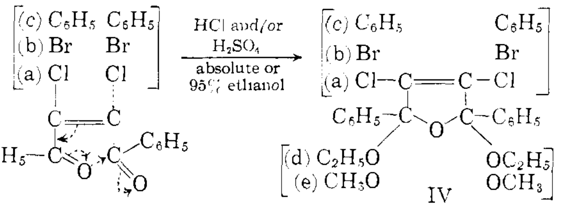
[3] R. E. Lutz and M. G. Reese, THIS JOURNAL, **81**, 127 (1959); *cf.* also references cited therein.

dibenzoylethylenes (I) into 2,5-diphenyl-2-ethoxy-3-furanone (II), and that the presence of 5% of water leads instead to the 1,2-dichloro saturated 1,4-diketone and the 3,4-dichlorofuran (V).



I, *cis* or *trans* II

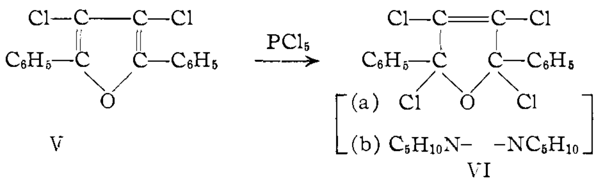
In the extension of these studies to the dichlorodibenzoylethylenes where addition–furanization is precluded, significantly different results were obtained. Only the *cis* isomer IIIa, and not the *trans* isomer, reacted with hydrogen chloride, in either absolute or 95%[2b] ethanol, but instead of giving the expected chlorofuranone (XV) it gave the two stereoisomeric cyclic diketals IVad-A and B. The other cyclic diketals (IVae, bd and cd) were obtained similarly, but each only in one and presumably the *trans* form.



III IV

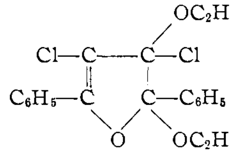
isomer A, m.p. 125.5° (*trans*?)
isomer B, m.p. 65.5° (*cis*?)

Several non-phenylated analogs of the cyclic diketals IV have been made previously but in a different way through reactions involving essentially 1,4-additions to furans,[4] for example, diethoxylation of furan itself by the action of halogen in alcohol.[5] In the 2,5-diphenylfuran series the transitory formation of 2,5-addition compounds has been assumed in *cis* oxidative cleavages by nitric–acetic acid mixture,[6] hydrogen peroxide,[7] lead tetraacetate[8] and phosphorus pentachloride.[9] In the latter reaction (through V) the product was shown to contain the 2,5-dichloride VI$\alpha$(or a phosphorus-containing complex) by hydrolysis which gave the *cis* unsaturated 1,4-diketone IIIa.[9] Consistent with this view of the nature of the intermediate VI$\alpha$ we now find that ethanolysis of the reaction mixture gives the cyclic diketal IVad, and that treatment with piperidine gives the dipiperidyl analog VIb.[2b] These two products, IVad and VIb, were assigned 2,5-structures of the type IV, and the alternative 2,3-structures of type VII were excluded, on the basis of the absence in

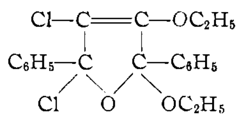


V VI

four cases (IVad-A, B, IVbd and VIb) of significant styrene-type ultraviolet absorptivity in the 240–250 m$\mu$ region. The structural distinction from the 2,3-type VII and the still less likely structure VIII, is further supported by this evidence: the facile hydrolysis of the compounds by alcohol–water–hydrochloric acid mixture to the corresponding *cis* unsaturated 1,4-diketones III; a typical transetherification (IVad $\leftrightarrows$ IVae); and the inactivity and retention of the 3,4-chlorine atoms of IVad-A and B, during 2,5-hydrolysis to III$\alpha$, and under treatment with boiling alcoholic silver nitrate, amines and sodium methoxide.

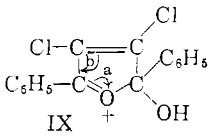


VII



VIII

It is significant that *trans*-dichlorodibenzoylethylene (IIIa) failed to react with hydrogen chloride in either absolute or 95% ethanol under the conditions which are effective with the *cis* isomer. The formation of the cyclic diketals from IIIa and b therefore appears to be typical *cis* addition cyclization[10] occurring through a protonated cyclic intermediate, *e.g.*, IX, where the cyclization step is markedly favored both by configuration and by the steric effects of the two ethylenic substituents. Hydrolytic attack at the 3-carbon of IX to generate the 3-furanone carbonyl (of XV) evidently takes place with considerable reluctance, thus allowing the cyclic diketal IVad to form and to persist. This resistance toward hydrolysis at position 3 and preference for attack at 5 may be explained in part in terms of the considerable steric oppositions of the 2,2,3,3,4-groups which would be involved in a 5-membered ring intermediate such as VII (*cf.* ref. 3).



IX

In the foregoing discussion of facile cyclization reactions of *cis* unsaturated 1,4-diketones under conditions not affecting the *trans* isomers, the term "*cis* addition cyclization" has been used to indicate the apparent mechanistic stereochemical requirement for the first steps of such reactions.[11] Obviously this is not related to the consistent and respective stereochemical follow-throughs to different diastereoisomeric products which are often

---

[4] A. P. Dunlop and F. N. Peters, "The Furans," Reinhold Publishing Corp., New York, N. Y., 1953, p. 51.

[5] (a) N. Clauson-Kaas, *Kgl. Danske Videnskab Selskab, Mat.-fys. Medd.*, **24**, No. 6, 18 (1947), [*C. A.*, **42**, 1930 (1948)]; (b) J. Fakstorp, D. Raleigh and L. E. Schniepp, THIS JOURNAL, **72**, 869 (1950); (c) N. Clauson-Kaas, *Acta Chem. Scand.*, 1, 379 (1947), [*C. A.*, **44**, 8375 (1950)].

[6] (a) B. T. Freure and J. R. Johnson, THIS JOURNAL, **53**, 1142 (1931); (b) A. F. Shepard and J. R. Johnson, *ibid.*, **54**, 4385 (1932); (c) R. E. Lutz and F. N. Wilder, *ibid.*, **56**, 978 (1934).

[7] R. E. Lutz and C-K. Dien, *J. Org. Chem.*, **23**, 1861 (1958).

[8] C-K. Dien and R. E. Lutz, *ibid.*, **22**, 1355 (1957).

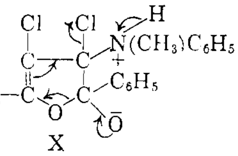
[9] R. E. Lutz and F. N. Wilder, THIS JOURNAL, **56**, 2145 (1934); (b) R. E. Lutz, F. N. Wilder, A. H. Stuart and W. C. Connor, *ibid.*, **59**, 2314 (1937).

[10] C-K. Dien and R. E. Lutz, *J. Org. Chem.*, **21**, 1492 (1956).

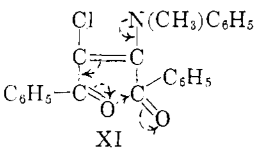
[11] (a) R. E. Lutz, T. Amacker, S. M. King and N. H. Shearer, *ibid.*, **15**, 195 (1950); (b) R. E. Lutz and S. M. King, *ibid.*, **17**, 1519 (1952).

observed in simple additions to suitably substituted *cis*- and *trans*-ethylenic pairs.

Another related category of *cis* reactions is illustrated by the displacement of one halogen by ammonia or an amine, easily in *cis*, but with difficulty in *trans*-dihalodibenzoylethylenes (*e.g.*, IIIa).[11] To the list of examples we now add the reaction of IIIa (the *trans* isomer did not react) with methylaniline to give the monosubstitution product which is presumed to be *cis*- XI, both on steric and resonance grounds,[11] and because of the probable mechanism of amine attack at an electrophilic $\alpha$-carbon of IIIa, passage through cyclic intermediate phases, e.g. X, with generation of a necessarily *cis* double bond.

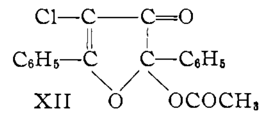


X



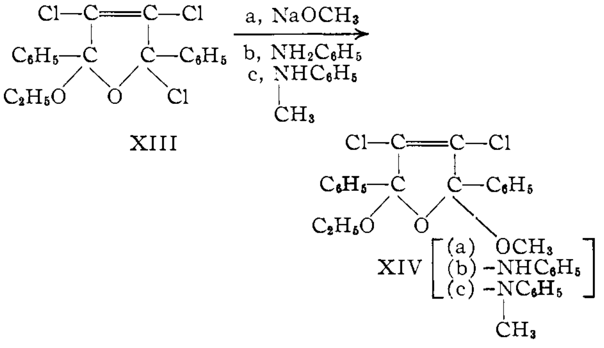
XI

Attempts to obtain a 2,5-diacetoxy analog of the cyclic diketals IV have consistently failed. With acetic anhydride and sulfuric acid, the *cis*- but not the *trans*-dichlorodibenzoylethylene, and also the cyclic diketal IVad, were converted into the 2-acetoxy-4-chloro-3-furanone (XII). Probably the 2,5-diacetoxy compound is actually formed but is relatively unstable and easily hydrolyzed at the 3-position because of the greater electron attraction of acetoxyl as compared with ethoxyl. Presumably the reaction proceeds through a cyclic cation analogous to IX.



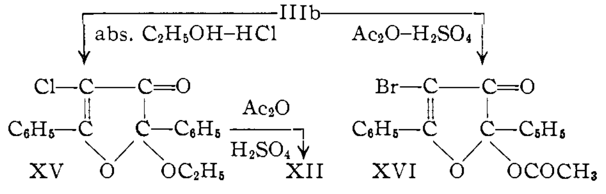
XII

The two stereoisomeric cyclic diketals of *cis*-dichlorodibenzoylethylene (IVad) were treated with thionyl chloride in the hope of obtaining the 2,5-dichloro compound VIa. However, the resulting non-crystalline product was shown by its reactions to contain the reactive monochloro compound XIII in which the electron-attracting 2-chlorine atom tends to stabilize the remaining 5-ethoxyl against similar hydrochlorolysis. The 2-chloro compound underwent metathetical displacement reactions with alcohols to give IVae and IVad, with sodium methoxide to give XIVa, and with aniline and N-methylaniline to give XIVb and c, respectively. The structures of the latter two compounds were shown by their aniline-type ultraviolet absorptivities and absence of the added absorptivity which would be contributed by a styryl group such as must exist in a structure of type VII.



***cis*-Dibromodibenzoylethylene (IIIb)** was converted into its cyclic diketal IVbd in absolute ethanol by the use of sulfuric acid as catalyst rather than hydrogen chloride. The *trans* unsaturated diketone failed to react under these conditions. The structure IVbd was established by the absence of styrene-type ultraviolet absorptivity, the failure to react with alcoholic silver nitrate, and the ready acetic acid hydrolysis to IIIb.

Unexpectedly *cis* - dibromodibenzoylethylene (IIIb) reacted differently with absolute ethanol containing hydrogen chloride rather than sulfuric acid as the catalyst. Instead of giving the cyclic diketal it underwent displacement of one bromine by a chlorine atom and gave the new 4-chloro-2-ethoxy-3-furanone (XV). The *trans* isomer did not react under these conditions. The chlorofuranone was characterized by analysis, by its doubly-peaked 3-furanone ultraviolet absorption spectrum, and by acetic anhydride–sulfuric acid conversion into the known chloroacetoxyfuranone XII.



The action of a mixture of acetic anhydride and sulfuric acid on *cis*- but not on *trans*-dibromodibenzoylethylene gave the known 2-acetoxy-4-bromo-3-furanone (XVI), another example of *cis* addition cyclization. A 2,5-diacetoxy-2,5-dihydrofuran was not isolated.

***cis*-Diphenyldibenzoylethylene (IIIc)**, which cannot by addition give either a furan or a furanone, reacted with absolute ethanolic hydrogen chloride to give the cyclic diketal IVcd which could be readily acid-hydrolyzed back to IIIc. The large *cis*-stilbene-type ultraviolet absorptivity of the cyclic diketal at 260 m$\mu$ is not distinctive; however, the 2,5-structure IVcd rather than the 2,3 is assigned on the basis of steric considerations and by analogy.

**Acknowledgment.**—Some of the experiments necessary to check and complete this investigation were carried out by Grover C. Helsley.

## Experimental[12]

**Action of 25% hydrogen chloride in absolute ethanol on *trans*-IIIa** (1 g. in 25 ml.) at room temperature for 24 hours (solution was not quite complete), evaporation under reduced pressure and crystallization from ethanol, gave 95% recovery of *trans*-IIIa. A similar experiment on *trans*-IIIb (27 hr.) gave 97% recovery. In another experiment (like b below), for 3 days, little evidence of solution of *trans*-IIIa was noted and recovery was 93%. The action of 50 ml. of propyl or isopropyl alcohols containing 4 ml. of concd. sulfuric acid on *cis*-IIIa at room temperature for 24 hr. gave

---

[12] Ultraviolet absorptions were determined in 0.00005 *M* absolute ethanol solutions, using a Beckman DU spectrophotometer.

oils, but in the case of isopropyl alcohol 37% of starting material was recovered.

**The action of saturated hydrogen chloride in 95% ethanol** on *trans*-IIIa (1 g. in 12 ml.) at 0° for 2 hr., followed by evaporation under reduced pressure and crystallization from ethanol, gave 93% recovery of *trans*-IIIa. Similarly *cis*-IIIa gave 55% recovery, but 12% of *trans*-IIIa was also obtained and identified.

These experiments indicate that *trans*-IIIa is actually the stable isomer (like *trans*-IIIc[13]), and that it is formed slowly under these conditions while the more reactive *cis* isomer in part is held as or is converted into cyclic products, *e.g.*, IVad. In the *cis* isomer the resonance contribution of the furanoid form (indicated in IIIa), under the favorable steric influence of the two ethylenic substituents, should be appreciable but would be opposed by the electron attraction of these substituents, but it would appear that this effect is insufficient to render the *cis* isomer the stable form.

**3,4-Dichloro-2,5-diethoxy-2,5-diphenyl-2,5-dihydrofuran (IVad)**.—(a) A suspension of 20 g. of *cis*-IIIa in 300 ml. of 25% absolute ethanolic hydrogen chloride was allowed to stand for 24 hr. Solution occurred within a short time. The crystalline precipitate which appeared after cooling was recrystallized from absolute ethanol; 8 g. (34%) of isomer-A, presumably *trans*, m.p. 125–125.5°. Concentration of the first filtrate (above) and crystallization of the product from absolute ethanol gave 6.4 g. (24%) of isomer-B, presumably *cis*, m.p. 67.5–68.5°.

(b) In an experiment like (a) using 95% ethanol, solution was complete within 30 min. and a precipitate began to form. After standing for 3 days, cooling and filtering, the filtrate by ultraviolet absorptivity analysis was shown to contain practically no IIIa; crude yield 92%, m.p. 100–110°; after one crystallization from 95% ethanol, m.p. 122–125° (73%).

(c) Repetition of (b) using IVae; yield of IVad-A, crude 80%, purified 62%.

(d) Three grams of *cis*-IIIa in 75 ml. of absolute ethanol and 5 ml. of concd. sulfuric acid after 24 hr. at room temperature, deposited a crystalline precipitate which was crystallized from absolute ethanol; 1.29 g. (32%) of isomer-A. From the filtrate upon addition of water, extracting with ether, drying, evaporating, and crystallizing the residue, 1.15 g. (29%) of isomer-B was isolated. In boiling ethanolic silver nitrate neither isomer gave a precipitate. Neither showed significant ultraviolet absorptivity in the 240 mμ region.

*Anal.* Calcd. for $C_{20}H_{20}Cl_2O_3$: C, 63.33; H, 5.32. Found: Isomer-A: C, 63.19; H, 5.27. Isomer-B: C, 62.96; H, 5.24.

**Hydrolysis** of isomer-A (1 g.) suspended in 50 ml. of 75% ethanol containing 10 ml. of concd. hydrochloric acid, refluxing for 3 hr., pouring the mixture into ice, extraction with ether, drying with sodium sulfate, evaporating, and crystallization of the residue from absolute ethanol, gave 0.58 g. (72%) of *cis*-IIIa (identified by mixture m.p.). Isomer-B reacted similarly.

**Reductions** of isomers-A and -B by zinc dust and boiling acetic acid (2 min.) gave dibenzoylethane (71,84%); V is stable under these conditions. Hydrolysis must have occurred first. A sample of isomer-A was recovered after treatment with zinc dust in absolute ethanol (3 hr. refluxing, 88%), and with lithium aluminum hydride in ether (3 hr., 87%).

The action of 25–2 ml. of **acetic anhydride–concd. sulfuric acid** on 1 g. of isomer-A (room temperature, 24 hr.), hydrolysis and crystallization from absolute ethanol, gave 0.57 g. (68%) of XII (see below). Isomer-B reacted similarly.

Refluxing **methanolic triethylamine** (1 hr.) on isomers-A and B was without effect (recovery 90 and 85%). Transetherification did not occur. Refluxing methanolic **sodium methoxide** (excess) for 30 min. also was without effect on isomer-A (recovery 90%).

Action of thionyl chloride, refluxing for 1 hr., addition of petroleum ether and evaporation to dryness under reduced pressure gave an oil believed to be XIII (see use in experiments below). Processing after treatment of this oil with a mixture of acetic acid, acetic anhydride and potassium acetate gave only *cis*-IIIa (42%).

Treatment with phosphorus pentachloride-oxychloride mixture (reflux, 15 min.), vac. evaporation (to VI), treatment with phosphorus trichloride under reflux for 15 min., and hydrolysis and crystallization from ethanol, gave 38% of *cis*-IIIa and no furan V. In still another experiment extraction of the residue VI with petroleum hexane and treatment with methylaniline gave only *cis*-IIIa (35%).

**3,4-Dichloro-2,5-dimethoxy-2,5-diphenyl-2,5-dihydrofuran (IVae)**.—Treatment of V with phosphorus pentachloride and oxychloride by the earlier method[8] (1 g., 10 g. and 20 ml., respectively), refluxing gently for 15 min., vac. evaporation, extraction with two 50-ml. portions of petroleum hexane, evaporation, and treatment with 50 ml. of methanol (reflux 30 min.), gave 0.58 g. (48%) of IVae m.p. 95.5-97°. In a similar experiment starting with IVad, yield 50%, m.p. 96-97°.

*Anal.* Calcd. for $C_{18}H_{16}Cl_2O_3$: C, 61.55; H, 4.59. Found: C, 61.32; H, 4.47; ultraviolet absorption in the 240 mμ region, none.

**3,4-Dichloro-2-ethoxy-5-methoxy-2,5-diphenyl-2,5-dihydrofuran (XIVa)**.—A solution of 1 g. of IVad-A in 16 ml. of thionyl chloride was refluxed for 1 hr. and evaporated to dryness under reduced pressure. The residual oil (XIII) was treated with 50 ml. of methanol containing 0.4 g. of sodium methoxide, refluxing for 30 min. Vacuum evaporation to *ca.* 20 ml., cooling and filtering from a small amount of sludge, and further cooling, gave 0.42 g. (43%) of crude XIVa; recrystallized from methanol, m.p. 105–107°.

*Anal.* Calcd. for $C_{19}H_{18}Cl_2O_3$: C, 62.47; H, 4.97. Found: C, 62.67; H, 5.05.

**3,4-Dichloro-2-ethoxy-5-anilino-2,5-diphenyl-2,5-dihydrofuran (XIVb)**.—Crude XIII from 1 g. of IVad-A (above) was treated with 1 g. of aniline in 10 ml. of dry ether, and the resulting aniline hydrochloride was filtered off. Evaporation to dryness gave an oil which crystallized from dilute ethanol and from ligroin; yield 0.3 g. (27%), m.p. 101-102°.

*Anal.* Calcd. for $C_{24}H_{21}Cl_2NO_2$: C, 67.61; H, 4.97. Found: C, 67.78; H, 5.28.

**3,4-Dichloro-2-ethoxy-5-(N-methylanilino)-2,5-diphenyl-2,5-dihydrofuran (XIVc)**, prepared from IVad-A or B as above, using methylaniline, recrystallized from petroleum pentane; yield *ca.* 26%, m.p. 154–155°.

*Anal.* Calcd. for $C_{25}H_{23}Cl_2NO_2$: C, 68.18; H, 5.26; $OC_2H_5$, 10.23. Found: C, 68.11; H, 5.21; $OC_2H_5$, 10.10.

**3,4-Dibromo-2,5-diethoxy-2,5-diphenyl-2,5-dihydrofuran (IVbd)**.—A solution of 6 g. of *cis*-IIIb in 100 ml. of absolute ethanol and 10 ml. of concd. sulfuric acid was allowed to stand for 24 hr. at room temperature. Cooling and addition of a small amount of water precipitated 2.95 g. (41%) of IVbd; recrystallized from absolute ethanol, m.p. 94.5–16.5°; ultraviolet absorption: none in the 240 mμ region.

*Anal.* Calcd. for $C_{20}H_{20}Br_2O_3$: C, 51.30; H, 4.31. Found: C, 51.07; H, 4.47.

Doubling the concentration of sulfuric acid in the above experiment gave the same product in lowered yield (23%).

**Hydrolysis** of 1 g. by bringing a 10-ml. concd. acetic acid solution just to boiling, gave *cis*-IIIb (59%).

**4-Chloro-2-ethoxy-2,5-diphenyl-3-furanone (XV)**.—A solution of 5 g. of *cis*-dibromodibenzoylethylene (IIIb) in 100 ml. of 25% absolute ethanolic hydrogen chloride was allowed to stand at room temperature for 24 hr. and was vac. evaporated. Crystallization from absolute ethanol gave 3.3 g. of XV (83%); further crystallization brought the m.p. to 89-91°; ultraviolet absorption: $\lambda_{max}$ 252.5, 327 mμ; $\epsilon$ 9,340, 15,620.

*Anal.* Calcd. for $C_{18}H_{15}ClO_3$: C, 68.68; H, 4.80; $OC_2H_5$, 14.31. Found: C, 68.50; H, 4.65; $OC_2H_5$, 13.97.

It was converted by acetic anhydride and a small amount of concd. sulfuric acid (24 hr. at room temperature) in 29% yield into XII (see below) (identified).

**4-Chloro-2-acetoxy-2,5-diphenyl-3-furanone (XII)**.—A solution of 2 g. of IIIa in 50 ml. of acetic anhydride and 4 ml. of concd. sulfuric acid, after standing for 16 hr. at room temperature, and cooling, deposited crystals which were filtered and washed with cold acetic anhydride (1.36 g.). Hydrolysis of the filtrate gave 0.3 g.; total yield 76%; recrystallized from absolute ethanol, m.p. 174.5-176.5°; ultraviolet absorption: $\lambda_{max}$ 250, 322.5 mμ; $\epsilon$ 7,850, 15,950.

*Anal.* Calcd. for $C_{18}H_{13}ClO_4$: C, 65.76; H, 3.98. Found: C, 65.86; H, 3.87.

---

[13] N. Zinin, *Jahresber. Fort. Chem.*, 409 (1875).

In an attempt to prepare XII from *trans*-IIIa by the action of 50–4 ml. acetic anhydride–concd. sulfuric acid mixture at room temperature for 16 hr., 82% of starting material was recovered.

**4-Bromo-2-acetoxy-2,5-diphenyl-3-furanone** (XVI).—A solution of 1.5 g. of IIIb in 35 ml. of acetic anhydride and 3 ml. of concd. sulfuric acid, after standing for 24 hr. at room temperature and cooling, deposited crystals; recrystallized from absolute ethanol, 0.61 g. (43%), m.p. 185.5–187.5°; ultraviolet absorption, $\lambda_{max}$ 250, 322 m$\mu$; $\epsilon$ 8,080, 15,030.

*Anal.* Calcd. for $C_{18}H_{13}BrO_4$: C, 57.93: H, 3.51. Found: C, 57.96; H, 3.48.

**2,5-Diethoxy-2,3,4,5-tetraphenyl-2,5-dihydrofuran** (IVcd) was prepared like IVad; crystallized from absolute ethanol, 5.6 g. (47%), m.p. 156.5–157.5°; ultraviolet absorption $\lambda_{max}$ 260 m$\mu$, $\epsilon$ 15,520.

*Anal.* Calcd. for $C_{32}H_{30}O_3$: C, 83.08; H, 6.54. Found: C, 82.95; H, 6.30.

**Hydrolysis** of 0.5 g. by 60 ml. of 80% ethanol and 5 ml. of concd. hydrochloric acid, refluxing for 6 hr., processing as with IVad, gave 0.2 g. (48%) of IIIc. **Reductive conditions,** zinc dust and boiling acetic acid for 2 min., converted IVcd to tetraphenylfuran (62%); IIIc under these conditions also gave tetraphenylfuran (75%). Acetic acid, boiling for 2 min., converted IVcd to IIIc (95%).

**Treatment of** *cis*-**dibenzoylstilbene (IIIc) with acetic anhydride concd. sulfuric acid mixture** (25–1 ml.) for 24 hr. at room temperature, followed by hydrolysis and processing, gave 87% of starting material.

**1-Chloro-2-(N-methylanilino)-1,2-dibenzoylethylene (XI).**—A solution of 2 g. of *cis*-IIIa and 2.8 g. of methylaniline in 50 ml. of dry ether reacted over 24 hr. at room temperature with deposition of methylaniline hydrochloride (filtered). After washing with water, drying over sodium sulfate and vac. evaporating, the resulting oil was crystallized from absolute ethanol; yield 0.88 g. (36%), orange crystals, m.p. 137–138°.

*Anal.* Calcd. for $C_{23}H_{18}ClNO_2$: C, 73.50; H, 4.83. Found: C, 73.65; H, 5.13.

*trans*-IIIa did not react under the above conditions, recovery 84%.

CHARLOTTESVILLE, VA.

---

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING, UNIVERSITY OF OSAKA PREFECTURE, JAPAN]

# The Reaction of Olefins with Aromatic Substances in the Presence of Mercury Salts and Catalyst. III. Reaction of Various Olefins with Anisole

BY KATSUHIKO ICHIKAWA,[1] SUSUMU FUKUSHIMA, HAJIME OUCHI AND MINORU TSUCHIDA

RECEIVED AUGUST 4, 1958

The formation of $\beta$-arylethyl acetates and/or diarylethanes by the action of ethylenemercury salt addition compounds on aromatics in the presence of alkylating catalysts has been extended successfully to other olefins, *i.e.*, propylene, 2-butene and styrene. Structural determination of intermediate mercurials and final products shows that this reaction is of the $S_N2$ type. Cyclohexene, a typical cycloölefin unlike other olefins reacts slowly with anisole to give methoxyphenylcyclohexene and not the expected *p*-methoxyphenylcyclohexyl acetate.

A new method of synthesis of $\beta$-arylethyl acetates and *sym*-diarylethanes by reaction of ethylene with aromatic compounds in the presence of mercury salts and catalyst was reported recently.[2]

It was established that this reaction proceeds through the intermediate mercurial $ArCH_2CH_2HgZ$ (Z = acid radical) which is formed by the reaction of an ethylene–mercury salt complex compound with the aromatic.

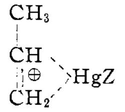
Several features of the mechanism, however, remained unsettled and required further investigation.[3] For example, it was not determined whether the reaction of this complex with aromatics is a carbonium ion reaction or whether the aromatic participates directly in an $S_N2$ type displacement on the complex.

This paper reports results of the application of this reaction to other olefins such as propylene, 2-butene, styrene and cyclohexene and discusses further, by bringing new experimental evidence to bear, the question of the mechanism mentioned above.

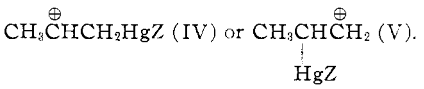
The results obtained are summarized in Table I.

The reaction of the propylene–mercuric acetate addition compound with anisole gives 1-(*p*-methoxyphenyl)-2-propyl acetate (I) in yields of up to 67%.

If we assume that the reaction proceeds through a free carbonium ion, *i.e.*, the complex dissociates into ions before it reacts with the aromatic compound, then the complex



may give either of two carbonium ions



$$\overset{\oplus}{C}H_3CHCH_2HgZ\ (IV)\ \text{or}\ CH_3CH\overset{\oplus}{C}H_2\ (V).$$
$$\qquad\qquad\qquad\qquad\qquad\quad |\ HgZ$$

The secondary carbonium ion IV, much more stable than the primary ion V, will be formed preferentially and the reaction should result in the formation of 2-(*p*-methoxyphenyl)-1-propyl acetate (VI). The acetate actually obtained, however, proved to be I exclusively (demonstrated by hydrolysis to the alcohol and subsequent conversion to the *p*-toluenesulfonate). This eliminates reaction by the carbonium ion and makes the direct participation of anisole in an $S_N2$ type reaction on the complex the more reasonable mechanism. Anisole can combine with either the central carbon atom of propylene to form VI or with the terminal carbon atom to form I through the intermediate VII or

---

[1] Institute for Chemical Research, Kyoto University, Yoshida, Kyoto, Japan.

(2) K. Ichikawa, S. Fukushima, H. Ouchi and M. Tsuchida, THIS JOURNAL, **80**, 6005 (1958).

(3) Prof. G. F. Wright, University of Toronto, does not agree with our proposed mechanism of the reaction of $ArCH_2CH_2HgZ$ to form $ArCH_2CH_2Z$ and metallic mercury in the preceding paper II.[2] He suggested a radical reaction of $RHgZ + HgZ_2 \rightarrow RZ + Hg_2Z_2$ and a subsequent reaction of $Hg_2Z_2 \rightleftarrows HgZ_2 + Hg$ (private communication); see also D. A. Shearer and G. E. Wright, *Can. J. Chem.*, **33**, 1002 (1955).