[Contribution from the Havemeyer Chemical Laboratory of New York University]

STUDIES ON UNSATURATED 1,4-DIKETONES
II. FORMATION OF CERTAIN DERIVATIVES OF FURANE

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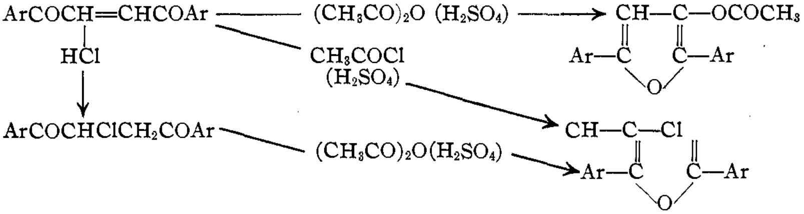
Unsaturated 1,4-diketones are of interest because they contain the same active, doubly conjugated system that is characteristic of *p*-quinones. Addition of such reagents as hydrogen chloride and aniline to dibenzoyl-ethylene[1] resembles in many respects the addition reactions of quinone,[2] *p*-quinones yield derivatives of hydroquinone, whereas unsaturated 1,4-diketones, if one assume 1,4 addition, give an intermediate unstable enol which either rearranges to a derivative of the saturated 1,4-diketone, or loses water to form a derivative of furane. Acetic anhydride and sulfuric acid react with both types, with dibenzoyl-styrene to give triphenyl-furanol-acetate, and with quinone to give hydroquinone triacetate.[3] A few similar experiments were made in this research on dibenzoyl- and ditoluyl-ethylene.[4]

Dibenzoyl-ethylene, when treated with acetic anhydride and a small amount of concd. sulfuric acid (a general standard procedure followed in this research), reacted rapidly to form 1,4-diphenylfuranol-acetate. Ditoluyl-ethylene reacted similarly to give 1,4-ditolylfuranol-acetate. It was found that under similar conditions dibenzoyl-chloro-ethylene (beta) and dibenzoyl-acetylene failed to react in this manner to give furanes.

When dibenzoyl- and ditoluyl-ethylenes in a similar series of experiments were treated with acetyl chloride instead of, or in the presence of, acetic anhydride, immediate reaction took place upon the addition of small amounts of concd. sulfuric acid with the formation of 1,4-diphenyl- and 1,4-ditolyl-2-chlorofurane.



Although dibenzoyl-chloro-ethylene and dibenzoyl-acetylene failed to react appreciably under these conditions, the 1,4-diphenyl-2,3-dichloro-

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[1] Paal and Schulze, *Ber.*, **33**, 3800 (1900); **35**, 168 (1902).

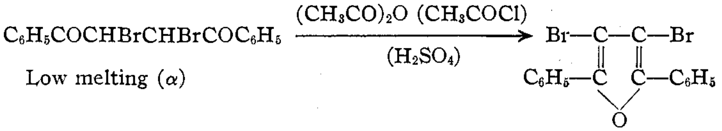
[2] (a) Hollander, *Chem. Weekblad*, **16**, 1063 (1919). (b) Eckert and Endler, *J. prakt. Chem.*, **104**, 81 (1922). (c) Hinsberg, *Ber.*, **27**, 3259 (1894). (d) Wichelhaus, *Ber.*, **5**, 851 (1872).

[3] Thiele, *Ber.*, **31**, 1247 (1898).

[4] Conant and Lutz, This Journal, **45**, 1303 (1923).

furane has been obtained[5] by the addition of hydrogen chloride followed either in the same reaction or in a second by dehydration.[6]

While the saturated 1,4-diketones are in many cases easily converted into furanes, an interesting resistance to this dehydration of one of two diastereo-isomers has been observed. Both diastereo-isomeric dibenzoyl-dichloro-ethanes have been shown to form furanes readily.[5] In the case of the two stereo-isomeric dibromides,[7] however, when treated in the usual manner with acetic anhydride and sulfuric acid, the alpha form reacted partially to give a low yield of the diphenyl-dibromofurane, whereas the beta isomer, though brought completely into solution by heating, failed to react appreciably. The configuration possessed by the alpha group of isomers then, seems to be the more favorable for ring closure of this type.



It has been suggested that the action of acetic anhydride and acetyl chloride on unsaturated 1,4-diketones involves addition of acetic acid as the first step.[3] This mechanism seems inconsistent with the following facts: acetyl chloride and acetic anhydride alone do not react appreciably with dibenzoylethylene, but react rapidly upon the addition of traces of concd. sulfuric acid; the concentrations of acetyl chloride and acetic anhydride are great and those of hydrogen chloride and acetic acid initially are very small; dibenzoyl-chloro-ethylene and dibenzoyl-acetylene will add hydrogen chloride with subsequent dehydration to the dichlorofurane, but will not react appreciably with acetyl chloride and sulfuric acid. A mechanism, involving the 1,4 addition of the solvent, acetic anhydride or acetyl chloride, and loss of acetic acid from the intermediate enol (or acetic anhydride from an acetylated di-enol), is suggested as being more consistent with these facts.

The action of acetyl chloride[8] and acetic anhydride[3] on quinone to form chloro- and dichloro-hydroquinone diacetate, and hydroquinone triacetate, may be interpreted in a like manner by 1,4 addition of acetyl chloride or acetic anhydride and enolization, but followed by acetylation of the hydroxyl groups.

It is interesting to note that reduction has been interpreted by a similar mechanism.[9] Quinone on reduction yields hydroquinone, a stable di-enol,

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[5] Conant and Lutz, This Journal, **47**, 881 (1925).

[6] See also the action of hydrogen chloride on dibenzoyl-styrene to give triphenylchlorofurane. Japp and Klingemann, *J. Chem. Soc.*, **57**, 674 (1890).

[7] Lutz, This Journal, **48**, 2905 (1926).

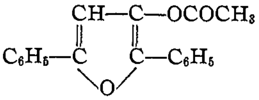
[8] Schulz, *Ber.*, **15**, 652 (1882).

[9] (a) Conant and Lutz, This Journal, **45**, 1047 (1923); (b) **46**, 1254 (1924); (c) Thiele, *Ann.*, **306**, 142 (1899).

but dibenzoyl-stilbene[10] on reduction with zinc and acetic acid yields a mixture of dibenzoyl-diphenylethane and tetraphenylfurane,[11] indicating a similar mechanism but involving simultaneously the rearrangement and dehydration of a hypothetical intermediate di-enol.

Further studies are now being made of addition reactions of unsaturated 1,4-diketones.

Experimental Part

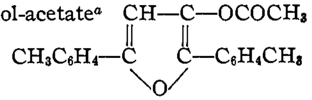
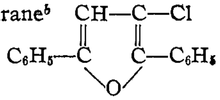
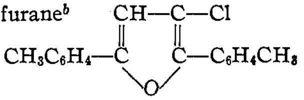
1,4-Diphenyl-furanol-acetate.  .—To 4 g. of *trans*-dibenzoylethylene, suspended in acetic anhydride, a few drops of concd. sulfuric acid were added. A rapid exothermic reaction took place with the formation of a dark-colored solution. On decomposing the product with water and recrystallizing several times from alcohol, 3 g. of colorless crystals was obtained; m. p., 95°.[12]

Anal. Calcd. for $C_{18}H_{14}O_3$: C, 77.0; H, 5.1. Found: C, 76.8; H, 5.4.

Other Derivatives of 1,4-Diphenylfurane.—The substances described in Table I were synthesized by the same procedure as used in the preparation of 1,4-diphenyl-2-furanol-acetate. All were purified by repeated recrystallization from alcohol, and were colorless.

Table I

Other Derivatives of 1,4-Diphenylfurane

		M. p., °C.	Analysis	
			Calcd., %	Found., %
1,4-Ditolyl-2-furanol-acetate[a]		100.5	C, 78.4 H, 5.9	78.6 6.3
1,4-Diphenyl-2-chlorofurane[b]		76	Cl, 13.9	14.0
1,4-Ditolyl-2-chlorofurane[b]		85	Cl, 12.0	12.5

[a] The ditolylfurane derivatives were prepared and analyzed in the Chemical Laboratory of Harvard University with Professor J. B. Conant.

[b] Acetyl chloride was used in place of acetic anhydride.

1,4-Ditolyl-2-chlorofurane was prepared also in nearly quantitative yield from the colorless addition product of hydrogen chloride and ditoluylethylene by dehydration in the usual manner.

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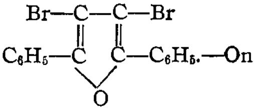
[10] (a) Zinin, *Z. Chem.*, 3, 313 (1867); (b) *Jahresber. Fort. Thier-Chem.*, 409 (1875). (c) Dorn, *Ann.*, 153, 358 (1870). (d) Magnanini and Angeli, *Ber.*, 22, 853 (1889).

[11] Dibenzoyl-styrene is readily reduced to triphenylfurane (see Ref. 6) and dibenzoylmethoxy-ethylene to diphenylmethoxyfurane (see Ref. 5).

[12] Melting points of compounds prepared in this research are corrected for exposed mercury column.

Action of Acetyl Chloride and Acetic Anhydride on Dibenzoyl-chloroethylene (Beta) and Dibenzoyl-acetylene.—In no case did appreciable reaction take place when 0.2 g. of the substance was heated and allowed to stand for 15–30 minutes with 10 cc. of solvent (acetyl chloride or acetic anhydride) and 8–10 drops of concd. sulfuric acid.

1,4-Diphenyl-2,3dibromofurane.



—One g. of dibenzoyl-dibromo-ethane (alpha) was treated with 5 cc. of acetic anhydride, 3 cc. of acetyl chloride and 8 drops of concd. sulfuric acid, the mixture being warmed to 50°. After standing for 15 minutes, the mixture was poured into water and the solid product was separated and extracted with petroleum ether; a residue of 0.75 g. of unchanged dibromide was recovered. The filtrate yielded 0.175 g. of colorless crystals which were recrystallized from alcohol and melted at 88.5–89°.

Anal. Calcd. for $C_{16}H_{10}OBr_2$: Br, 42.2. Found: 42.6.

In an identical experiment a sample of the high-melting (beta) dibenzoyl-dibromoethane was used and brought completely into solution by heating to boiling. A quantitative recovery of unchanged material was effected.

Summary

1. Acetic anhydride and traces of sulfuric acid react with dibenzoyl- and ditoluyl-ethylene to give 1,4-diphenyl- and 1,4-ditolyl-furanol-acetate.

2. In a similar manner acetyl chloride reacts to give 1,4-diphenyl- and 1,4-ditolyl-2-chlorofurane. Under the same conditions the hydrogen chloride addition compound of ditoluyl-ethylene is dehydrated to the furane.

3. Under certain definite conditions the alpha (low-melting) stereoisomer of dibenzoyl-dibromo-ethane can be dehydrated to give 1,4-diphenyl-2,3-dibromofurane, while the beta isomer fails to react.

4. The mechanism of the reactions of unsaturated 1,4-diketones with acetic anhydride and acetyl chloride is discussed.

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