the extract with water, evaporation and crystallization of the residue gave 3 g. of colorless prisms which after repeated crystallizations from ethanol melted at 120–120.5°.

Anal. Calcd. for $C_{17}H_{14}Br_2O_2$: Br, 39.0. Found: Br, 38.93.

Summary

Bromination of 3-methyl-2,5-diphenylfuran involves successive substitutions in the furan β-position, the phenyl para positions and in the methyl group.

The various brominated furans of this series have been oxidized to *cis* unsaturated diketones and these in turn have been reduced. The diketones of the di-*p*-bromophenyl series have become available through these reactions.

CHARLOTTESVILLE, VA. RECEIVED JULY 16, 1942

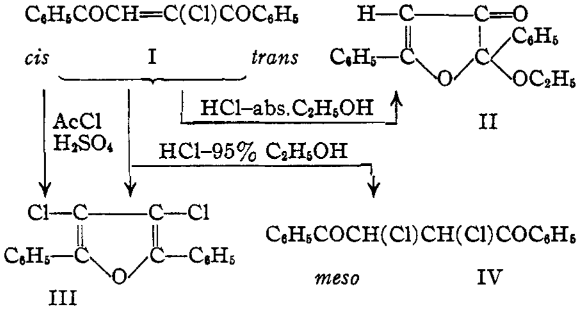
[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY OF THE UNIVERSITY OF VIRGINIA]

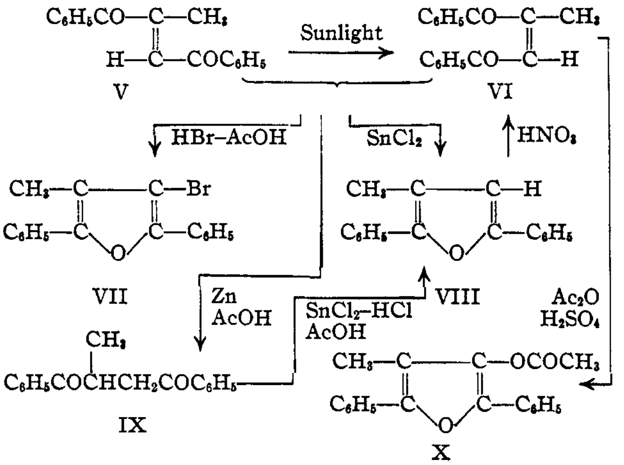
The Conversion of Unsaturated 1,4-Diketones into Furans and Hydroxyfuranones

BY ROBERT E. LUTZ AND C. EDWARD MCGINN[1]

It would be expected that *cis* unsaturated 1,4-diketones would be somewhat more reactive than *trans*. This is the case with the stereoisomeric dibenzoylchloroethylenes (I) where only the *cis*-isomer reacts under the usual conditions with acetic anhydride and with acetyl chloride (with sulfuric acid as catalyst) to give, respectively, the acetoxychlorodiphenylfuran and dichlorodiphenylfuran (III).[2] However, both the *cis*- and *trans*-dibenzoylchloroethylenes react easily with hydrogen chloride in 95% ethanol to give the same mixture of dichlorodiketone (IV) and furan (III)[3], and in absolute ethanol to give the ethoxyfuranone (II).[4] This report deals with more reactions of these types.

Certain of the *cis* unsaturated diketones which have been difficult if not impossible to make from the *trans*-isomers by the sunlight inversion can now be made in good yield through the corresponding furan by oxidation by means of nitric acid. This method has been applied successfully in the preparation in quantity of *cis*-dibenzoylmethylethylene (VI) as is outlined in the diagram.





The *cis*- and *trans*-dibenzoylmethylethylenes (VI and V) are converted readily into the bromofuran (VII) by hydrogen bromide in acetic acid, but it has not been possible under the experimental conditions to determine the relative ease of reaction in the two cases. In the reaction with acetic anhydride and sulfuric acid at room temperature, on the other hand, the *trans*-compound did not react whereas the *cis*-isomer was converted in good yield into the acetoxyfuran (X). Similarly the *trans*-compound did not react with benzoic anhydride and sulfuric acid whereas the *cis*-isomer did (although, unfortunately, not to give a crystalline product). Incidentally, it has since been found that in the medium acetic anhydride, acetic acid and zinc chloride, *trans*-dimesitoylethylene is reduced catalytically to the saturated diketone in the normal fashion whereas the *cis*-isomer in-

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[1] Present location, National Aniline Division, Allied Chemical and Dye Corp., Buffalo.

[2] Lutz, Stuart, Wilder and Connor, THIS JOURNAL, **59**, 2314 (1937).

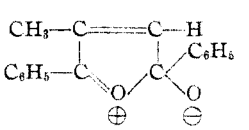
[3] Lutz and Wilder, *ibid.*, **56**, 1193 (1934).

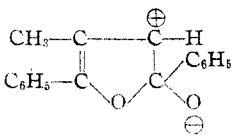
[4] Lutz, Wilder and Parrish, *ibid.*, **56**, 1980 (1934).

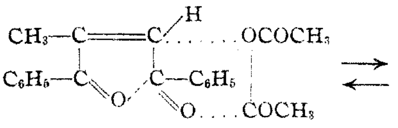
stead is converted into the acetoxyfuran by addition and dehydration.[5]

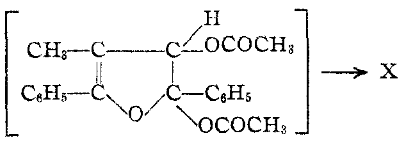
There probably is some special reason, other than the slightly higher energy content, for the greater reactivity of the *cis* as compared with the *trans* unsaturated 1,4-diketone. Possibly actual interaction of the two spatially proximate carbonyl groups is involved to give resonance hybrids such as XI and XII, which might facilitate the reaction with acetic anhydride or combination with the catalyst (*cf.* XIII, XIV).[6]

Each of the compounds discussed above carries in the chain position a hydrogen atom which makes possible elimination of an acid molecule or its equivalent to form the double bond needed to complete the conjugated system of the furan nucleus (*cf.* XIV). If this chain hydrogen were not available, as is the case with completely substituted unsaturated diketones such as XV, the


XI

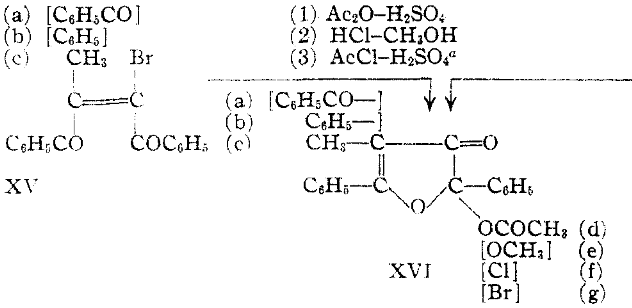

XII


XIII


XIV

formation of a furan would be impossible. However, with an oxygen or halogen atom at one of these chain positions, a reaction still could proceed by a mechanism similar to that suggested above but with the formation in the end of a 2,3-hydroxyfuranone derivative of the type XVI or XVII. This latter type of reaction has in fact been observed even when a chain hydrogen is available and where both the furan and the hydroxyfuranone theoretically might result [*cf.* the conversion of the *cis*- and *trans*-dibenzoylchloroethylenes (I) into the ethoxyfuranone (II[3,4])].

The formation of hydroxyfuranone types from suitably substituted unsaturated 1,4-diketones has already been utilized in a method of synthesis of 4-benzoyl-2-hydroxy-2,5-diphenylfuranone-3.[7] Other examples of this type of reaction have been sought and found; these reactions, including both old and new ones, are illustrated in the following diagram.



[a] Not carried out on tribenzoylbromethylene.

The *trans* unsaturated diketones corresponding to XV-b and c are not known and work is being undertaken to complete some suitably substituted *cis–trans* pairs for comparison with respect to relative facility of this type of reaction.

Experimental

***trans*-2-Methyl-1,4-diphenyl-2-butenedione-1,4 (V).**—Earlier preparations[8] were not satisfactory. From a long series of experiments carried out under varied conditions, it was found that temperature control and rapid working-up of the product were very important factors. The directions finally evolved were practically identical with those which have since been published.[9]

***cis*-2-Methyl-1,4-diphenyl-2-butenedione-1,4 (VI).**—A mixture of 10 ml. of concd. nitric and 30 ml. of concd. acetic acids at 10° was added to a solution of 10 g. of the furan (VIII) in 50 ml. of concd. acetic acid (also at 10°). Immediate reaction occurred with evolution of oxides of nitrogen, and after standing for five minutes 200 ml. of water was added. The viscous resinous precipitate was isolated by extraction with ether and evaporating. The product crystallized from ethanol; 8.7 g. (81%). It was identified by mixture melting point with a sample made by the sunlight inversion method.[10] The yields were lowered when the reactions were carried out at higher temperatures or over longer periods of time.

Reduction with zinc dust and concd. acetic acid at 100° gave the saturated diketone (IX) in excellent yields.

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(5) Lutz, Reveley and Mattox, THIS JOURNAL, **63**, 3171 (1941).

(6) The idea of interaction of the two carbonyls to give a ring form in an equilibrium or oscillating system is not new [*cf.* the peroxide formula for *cis*-dibenzoylethylene suggested by Smedley [*J. Chem. Soc.*, **75**, 219 (1909)].

(7) Lutz and Smith, THIS JOURNAL, **63**, 1148 (1941).

(8) Lutz and Taylor, *ibid.*, **55**, 1177 (1933); Stuart, Dissertation, University of Virginia, 1936, p. 100.

(9) Fuson, Fleming and Johnson, *ibid.*, **60**, 1994 (1938).

(10) Lutz and Taylor, *ibid.*, **55**, 1168 (1933).

Attempts to obtain a crystalline ethylene oxide from the *cis*-compound (VI) by the action of hydrogen peroxide were unsuccessful and only non-crystalline products were obtained.

3-Methyl-2,5-diphenylfuran (VIII).—A mixture of 250 ml. of concd. acetic acid and 200 ml. of concd. hydrochloric acid was heated to boiling, and 128 g. of stannous chloride was added, followed by 35 g. of *trans*-dibenzoylmethylethylene (V) in 100 ml. of concd. acetic acid. Heating was continued for five minutes during which time an oil separated. Upon cooling and diluting with 700 ml. of water and crystallizing the product once from ethanol, 31.3 g. (96%) of nearly pure furan was obtained (m. p. 58–59°). This melting point corresponds with that given in the literature.[11]

Equally good results were obtained using the *cis* unsaturated diketone (VI).

3-Bromo-2,5-diphenyl-4-methylfuran (VII).[12]—A solution of 1 g. of the furan (VIII) in 20 ml. of chloroform was treated with 0.8 ml. of bromine. The bromine color was discharged and hydrogen bromide was evolved. Evaporation and crystallization of the residue from ethanol gave 1.1 g. of the bromofuran (VII).

In another experiment, 5 g. of the *cis* unsaturated diketone (VI) was suspended in 50 ml. of acetic anhydride and treated with 10 ml. of 30% hydrogen bromide in concd. acetic acid at 0°. Three drops of concd. sulfuric acid were added and after fifteen minutes the mixture was hydrolyzed with water. The product was crystallized from ethanol and identified as the bromofuran (VII) (yield 5.1 g.).

3-Acetoxy-4-methyl-2,5-diphenylfuran (X).—A solution of 5 g. of the *cis* unsaturated diketone (VI) in 20 ml. of acetic anhydride was cooled to $-5°$ and three drops of concd. sulfuric acid were added. The temperature was not allowed to rise above $-1°$. After standing for five minutes the solution was poured into 200 ml. of water. When crystallization was complete the product was recrystallized from isopropanol (yield 3.7 g. or 68%).

In a similar experiment on a larger scale in which the temperature was allowed to rise to 25° the yield was lower (about 50%).

The compound crystallizes as yellowish needles but undergoes vacuum evaporation onto a cold-finger condenser as colorless needles of m. p. 94–95°.

Anal. Calcd. for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52. Found: C, 78.18; H, 5.58.

Attempts to obtain a chlorofuranone from this compound by means of phosphorus pentachloride, thionyl chloride and phenyliodochloride produced only non-crystalline materials. In the case of thionyl chloride a small yield (5%) of the dimolecular oxidation product, 2-bis-(4-methyl-2,5-diphenylfuranone-3), was obtained and identified by mixture m. p.[12]

2-Bromo-4-methyl-2,5-diphenylfuranone-3 (*cf.* XVI-c,g).—A solution of 0.8 g. of bromine in 8 ml. of carbon tetrachloride was added to a solution of 1.0 g. of the acetoxyfuran (X) in 15 ml. of the same solvent. The color was discharged by refluxing for a short time. Evaporation and crystallization of the residue from ligroin gave 1 g. of colorless prisms which after repeated crystallizations from ligroin melted at 88–89°.

Anal. Calcd. for $C_{17}H_{13}BrO_2$: C, 62.02; H, 3.98. Found: C, 62.98, 62.67; H, 4.22, 4.33. (The high values for carbon and hydrogen are accounted for by the instability of the compound and evident loss of some of the bromine through hydrolysis.)

When treated immediately with ethanol under refluxing for five minutes, the ethoxyfuranone was obtained in good yield and identified by mixture melting point.

***cis*-2-Bromo-3-methyl-1,4-diphenyl-2-butenedione-1,4**[12] **(XV-c).**—A mixture of 5 ml. of concd. nitric and 15 ml. of concd. acetic acid was added to a solution of 5.1 g. of the bromofuran (VII) in 25 ml. of concd. acetic acid with heating at 80° for one hour. Dilution with water gave 4.2 g. of nearly pure *cis* unsaturated diketone (XV-c).

A suspension of 1 g. of (XV-c) in 10 ml. of acetic anhydride at 0° was treated with two drops of concd. sulfuric acid. After fifteen minutes at this temperature, the solution was hydrolyzed with a large volume of water. The resulting oil was crystallized from ethanol (0.5 g.) and identified as the acetoxyfuranone (XVI-c,d).

A drop of concd. sulfuric acid was added to a suspension of 1 g. of (XV-c) in 10 ml. of acetyl chloride at 0° and the mixture was allowed to stand at this temperature for fifteen minutes and hydrolyzed in an excess of water. The resulting yellow solid was crystallized from ligroin (0.2 g.) and identified as the chlorofuranone (XVI-c,f).

A solution of 1 g. of the bromo unsaturated diketone (XV-c) in 20 ml. of 99% of methanol saturated with dry hydrogen chloride was allowed to stand at room temperature for twenty hours in a glass-stoppered flask. Upon cooling 0.6 g. of the methoxyfuranone (XVI-c,e) crystallized and was identified.

3-Bromo-2,4,5-triphenylfuran[13] was prepared in excellent yield by the action of 30% hydrogen bromide in concd. acetic acid on dibenzoylphenylethylene. The reaction was complete within two to three minutes at room temperature and the product crystallized on cooling.

***cis*-2-Bromo-1,2,4-triphenyl-2-butenedione-1,4**[14] **(XV-b)** was prepared by adding a mixture of 50 ml. of concd. nitric and 30 ml. of concd. acetic acids to a solution of 10 g. of 3-bromotriphenylfuran in 50 ml. of concd. acetic acid. The mixture was heated for fifteen minutes at 100° and poured into cold water. The product was crystallized from ethanol (7.2 g.).

Two drops of concd. sulfuric acid were added to a solution of 1 g. of (XV-b) in 10 cc. of acetic anhydride. The mixture was allowed to stand for fifteen minutes at room temperature and was hydrolyzed in an excess of water. Crystallization of the product from isopropanol gave 0.73 g. of the acetoxyfuranone (XVI-b,d).

In a similar experiment, using acetyl chloride instead of acetic anhydride, the chlorofuranone (XVI-b,f) was obtained in 85% yield.

A solution of 0.5 g. of (XV-b) in 10 ml. of methanol saturated with hydrogen chloride was allowed to stand for eighteen hours in a glass-stoppered flask; 0.3 g. of methoxyfuranone (XVI-b,e) was obtained.

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(11) Lauer and Spielman, THIS JOURNAL, **55**, 4924 (1933).

(12) Lutz and Stuart, *ibid.*, **59**, 2316 (1937).

(13) Japp and Klingemann, *J. Chem. Soc.*, **57**, 674 (1890); Allen, THIS JOURNAL, **49**, 2110 (1927).

(14) Lutz, Tyson, Sanders and Fink, THIS JOURNAL, **56**, 2679 (1934).

Summary

Several *cis* unsaturated 1,4-diketones are shown to be much more susceptible than the *trans* isomers toward furanization through addition and dehydration. A mechanism is suggested to account for this.

The analogy between these furanizations and the formation of 2,3-hydroxyfuranones is considered and new examples of the latter reaction are described.

CHARLOTTESVILLE, VA. RECEIVED JULY 16, 1942

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

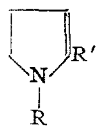
Basicity Studies of Tertiary Vinyl Amines

BY ROGER ADAMS AND J. E. MAHAN

The introduction of a double bond into a primary or secondary amine lowers the basic strength constant, that is, decreases the degree of ionization.[1] Hixon and co-workers[2] measured the ionization constants of several 2-alkyl substituted 4,5-dihydropyrroles (2-ethyl, 2-benzyl, 2-phenyl, and 2-cyclohexyl-Δ^2-pyrrolines) and of the corresponding saturated compounds (pyrrolidines). The saturated molecules were, in all cases, stronger bases than the unsaturated by 2.4 to 3.3 pK_H units.[2a] In the case of tertiary amines the same general effect as for primary and secondary amines might be expected but no examples were found in the literature. Vinyl tertiary amines, excluding the pseudo bases or anhydro bases formed from pyridinium type salts which are not entirely comparable have also, with one exception, not been studied. The normal assumption would be that they are weaker bases than the corresponding saturated amines.

An attempt to locate the relative position of a double bond to the nitrogen atom in retronecine, a base from the plants of the genera *Crotalaria*, *Senecio* and *Trichodesma*, was initiated by comparative basicity studies[3] of retronecine, desoxyretronecine and their reduction products. These substances were all tertiary amines containing pyrrolizidine rings. For purposes of comparison, a variety of tertiary vinyl amines and the corresponding reduced compounds have been synthesized and their relative basicity measurements made.

A series of 1,2-dialkyl-Δ^2-pyrrolines (I–IV) was first investigated, since such molecules are very closely related in structure to the products under study. The basic strengths of these pyrrolines and the analogous pyrrolidines are shown in Table I. It is to be noticed that in every case the unsaturated compound is more basic than the saturated. This interesting observation stimulated us to study analogous 6-membered ring compounds, namely, 1,2-dialkyl-Δ^2-tetrahydropyridines and the corresponding piperidines.



I. $R = CH_3$; $R' = CH_3$
II. $R = CH_3$; $R' = C_4H_9$
III. $R = C_2H_5$; $R' = CH_3$
IV. $R = C_4H_9$; $R' = CH_3$

TABLE I

Name	Obs. pK_H	T, °C.	pK_H (25°)[4]	Diff.	Lit.
1,2-Dimethyl-Δ^2-pyrroline	11.94	25	11.94		
1,2-Dimethylpyrrolidine	10.24	26	10.26	1.68	9.8[5]
1-Methyl-2-*n*-butyl-Δ^2-pyrroline	11.88	26	11.90		
1-Methyl-2-*n*-butylpyrrolidine	10.24	25	10.24	1.66	9.8[5]
1-Ethyl-2-methyl-Δ^2-pyrroline	11.88	27	11.92		
1-Ethyl-2-methylpyrrolidine	10.60	27	10.64	1.28	
1-*n*-Butyl-2-methyl-Δ^2-pyrroline	11.90[a]	26			
1-*n*-Butyl-2-methylpyrrolidine	10.43[a]	28		1.47	

[a] Taken in 25% aqueous methanol.

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(1) Hixon and Johns, THIS JOURNAL, **49**, 1786 (1927).

(2) Craig and Hixon, *ibid.*, **53**, 4367 (1931); Starr, Bulbrook and Hixon, *ibid.*, **54**, 3971 (1932).

(2a) The constant pK_H will be used in this paper to indicate the basic strengths. It is related to the more usual constant K_{ion}, by the expression $pK_H = pK_w - pK_{ion}$, where K_w is the ion product for water.

(3) Adams, Carmack, and Mahan, *ibid.*, **64**, 2593 (1942).

(4) Corrected to 25° employing the negative temperature coefficient of the constant as given by Hall and Sprinkle, *ibid.*, **54**, 3469 (1932), for amines of various basicity. Since these data are valid only for aqueous solutions the pK_H constants measured in aqueous methanol were not corrected to 25°.

(5) Craig, *ibid.*, **55**, 2543 (1933).