di-enolates. The unsaturated diketone was obtained by oxidation of the di-enolates.

A crystalline 4-monoenol of the saturated diketone was isolated and evidence given for its structure and configuration. The structural proof included relation to the bromo saturated diketone and bromo-*t*-butyldimesitylfuran.

Evidence for the existence and configuration of the stereoisomeric 4-monoenolate is described.

Evidence for the existence and configurations of three di-enolates is given. The configuration of the di-enolate obtained from mesitoylmesitylmethylfuran is based partly on the probable mechanism of 1,4-addition of Grignard reagent to the α,β-unsaturated ketone system.

A rigorous proof is outlined for 1,4-reduction and 1,4-reductive enolization of a typical α-bromoketone.

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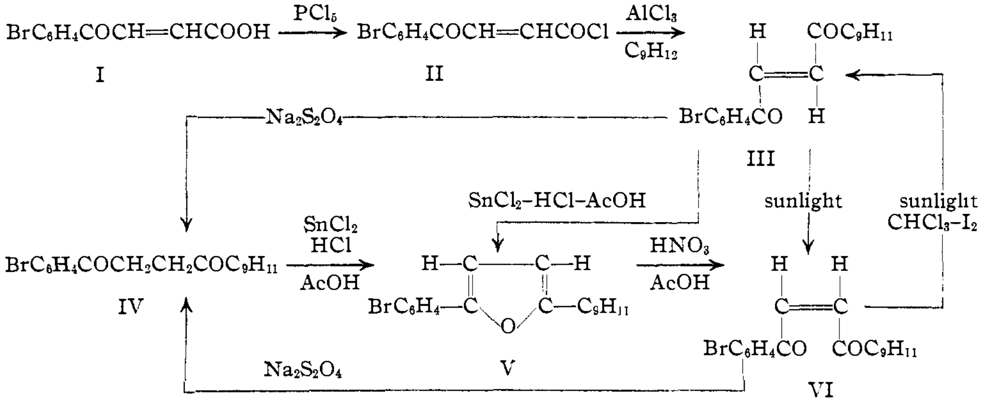
[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

The Mechanism of Oxidative Fission of the Furan Nucleus. Furans with Steric Hindrance by One α-Aryl Group

BY ROBERT E. LUTZ AND WILLIAM P. BOYER

It has been suggested that the characteristic oxidative ring fission of 2,5-diarylfurans to *cis*-unsaturated diketones involves 1,4-addition of the reagent to the diene system followed by break-up, generating necessarily the unsaturated diketone of *cis* configuration.[1] The failure generally of 2,5-dimesitylfurans to undergo this reaction was regarded as consistent with the hypothesis.[1c] The purpose of this investigation was to prepare and test some typical unsymmetrical 2,5-disubstituted furans carrying one and only one sterically hindering α-aryl group. Two compounds of this type have now been studied successfully and are the subject of this report.

2-Bromophenyl-5-mesitylfuran.—In connection with the synthesis of this and related compounds, the following reactions were carried out.



The unsaturated diketone (III) was prepared from *p*-bromobenzoylacrylic acid (I) by the Friedel–Crafts reaction on the acid chloride (II).[2] It was converted into the *cis*-isomer (VI) by the action of sunlight; and the *cis*-compound was converted back into the *trans* by the action of iodine on a chloroform solution with iodine as a catalyst. Reduction of both stereoisomeric unsaturated diketones by means of sodium hydrosulfite gave the saturated diketone (IV). Reduction of the *trans*-isomer by stannous chloride in an acetic–hydrochloric acid mixture gave the furan (V), a reaction which evidently involved first reduction to the saturated diketone. The latter compound in a separate experiment was shown to be convertible readily into the furan under these conditions.

The oxidation of the furan with the nitric–acetic

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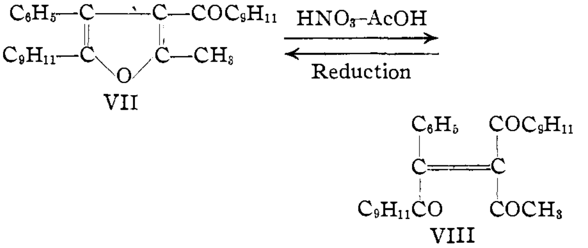
[1] (a) Freure and Johnson, THIS JOURNAL, **53**, 1142 (1931); (b) Lutz and Wilder, *ibid.*, **56**, 978 (1934); (c) Lutz and Kibler, *ibid.*, **62**, 1520 (1940).

[2] Kohler and Woodward, *ibid.*, **58**, 1933 (1936).

acid reagent proceeded with great facility and gave the *cis*-unsaturated diketone which, surprisingly, proved to be sufficiently stable to persist under the conditions of the experiment.

A similar series of experiments in the phenyl-mesityl series was blocked by failure to obtain a crystalline *cis*-unsaturated diketone either from the *trans*-compound or from the furan. These experiments as far as they were carried are described in the experimental section.

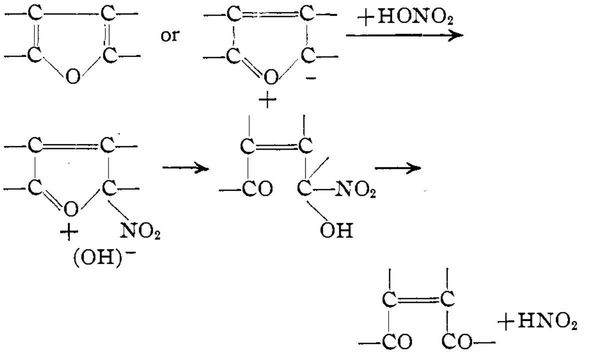
3-Mesitoyl-5-mesityl-2-methyl-4-phenylfuran.—A second example of the oxidative ring fission of an unsymmetrical furan with one and only one sterically hindering α-group was sought and found in the case of 3-mesitoyl-5-mesityl-2-methyl-4-phenylfuran (VII) which had already been prepared in another connection.[3] When treated with the nitric–acetic acid reagent at 40° this furan was converted in 60% yield into the corresponding unsaturated 1,4-diketone (VIII). In view of the degree and kind of substitution involved here the configuration indicated in formula VIII was assigned on the basis of the synthesis.



Independent evidence for the structure of the unsaturated diketone (VIII) is the analysis and the facile reduction to the furan (VII) by means of sodium hydrosulfite, catalytic hydrogen, or stannous chloride. It is noteworthy that furanization dominated and that the saturated diketone was not obtainable by the usual methods. These results are analogous to those observed in the reduction of 1,4-diphenyl-2-mesitylbutenedione[4] and tribenzoylbromoethylene.[5]

Mechanism of Oxidation

It was previously shown that mesityl groups at both α-positions hinder or block the oxidative ring fission of the furan nucleus, and it has now been demonstrated that this reaction can and does occur without noticeable difficulty when one α-position is free from excessive steric hindrance. Obviously, these results are not consistent with a theory of reaction mechanism expressed in the simple classical terms of 1,4-addition of the reagent to the diene system since on that basis steric hindrance at one α-position should be practically as effective as hindrance at both. However, the reaction may satisfactorily be expressed in electronic or ionic terms, and in terms of the conjugated diene-oxy system, C=C—C=C—O, which is analogous to the reactive systems in phenols, phenol ethers, and aromatic amines. A typical and convenient picture is reaction between this system and nitric acid or its equivalent (an anhydride or mixed anhydride), somewhat as follows



This would involve the positive addend going to the unhindered α-carbon, followed by break-up with loss of nitrous acid or its equivalent and formation necessarily of the unsaturated diketone of *cis*-configuration with respect to the newly formed carbonyl groups.

Experimental Part

The Mesityl-phenyl Series

trans-β-**Mesitoylacrylic** acid was prepared as follows: 178 g. of finely ground aluminum chloride was added portionwise with thorough mechanical stirring over a period of eight minutes to a solution of 80 g. of mesitylene and 65 g. of maleic anhydride in 630 cc. of tech. tetrachloroethane. The mixture was then heated to 80° on a water-bath for 10 minutes and decomposed in ice and hydrochloric acid. The tetrachloroethane layer was washed with water and the solvent steam distilled. The residual oil was extracted into ether and this solution shaken successively with four portions of 10% sodium carbonate solution. The sodium salt formed was filtered off after each treatment. The combined crops of sodium salt were suspended in water and treated with an excess of hydrochloric acid to liberate the organic acid; 90.9 g. of β-mesitoylacrylic acid was thus obtained; melting point 134–137° (yield 62.5%).

trans-**1-Mesityl-4-phenyl-2-butenedione-1,4,** C_9H_{11}-$COCH{=}CHCOC_6H_5$.—A modification of a previous procedure[6] is as follows. A mixture of 47 g. of β-mesitoyl-

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

(4) Lutz and Kibler, *ibid.*, **61**, 3007 (1939).

(5) Lutz and Smith, *ibid.*, **63**, 1148 (1941).

(6) Lutz, *ibid.*, **52**, 3423 (1930).

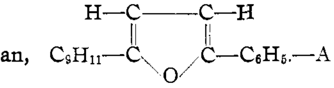
acrylic acid and 400 cc. of pure benzene was cooled in an ice-bath and treated portionwise with 45 g. of phosphorus pentachloride, added with stirring over a period of ten minutes. After another five minutes of stirring 80 g. of powdered anhydrous aluminum chloride was added quickly and the mixture stirred for five minutes. The mixture was then hydrolyzed in ice and hydrochloric acid and stirred mechanically for forty-five minutes to complete the hydrolysis of the phosphorus oxychloride present. The benzene layer was washed with warm water and 10% sodium carbonate to remove any regenerated mesitoylacrylic acid. The solvent was removed by distillation under reduced pressure and the residual oil crystallized from methanol; yield, 21.6 g. (38%); melting point 60–61°. Yields as high as 48% were obtained when the reaction was run on a small scale. Attempts to convert this compound into a *cis* isomer by the action of sunlight failed.

Catalytic reduction with Raney nickel and hydrogen at atmospheric pressure showed continuous absorption of hydrogen beyond one molecule. When the reaction was interrupted at that point a mixture was obtained from which was isolated a compound melting at 202.5–203.5° and another melting at 86–87°. The latter was oxidized by potassium dichromate to mesitylphenylbutanedione and gave the analyses: calcd. for $C_{19}H_{22}O_2$: C, 80.8; H, 7.9; found: C, 81.0, 80.8; H, 7.86, 7.85. This may have been mesitylphenylbutanone-ol, $C_9H_{11}COCH_2CH_2CH(OH)C_6H_5$ or $C_9H_{11}CH(OH)CH_2CH_2COC_6H_5$. These two compounds were not investigated further.

1-Mesityl-4-phenylbutanedione-1,4, $C_9H_{11}COCH_2CH_2COC_6H_5$.—A mixture of 2.5 g. of mesitylphenylbutenedione and an excess of sodium hydrosulfite in 70% ethanol was refluxed for twenty-five minutes, then diluted with water and extracted by means of ether. Upon evaporation of the solvent an oil was obtained which crystallized from ethanol. On repeated recrystallization it melted at 52–53°.

Anal. Calcd. for $C_{19}H_{20}O_2$: C, 81.4; H, 7.2. Found: C, 81.6; H, 7.5.

2-Mesityl-5-phenylfuran,



.—A solution of 8 g. of mesitylphenylbutenedione in 25 cc. of concd. acetic acid was poured into a warm mixture of 60 cc. of concd. acetic acid, 55 cc. of concd. hydrochloric acid, and 32 g. of stannous chloride. After heating to boiling and immediately cooling crystals separated which melted at room temperature. This material was distilled at 5 mm. pressure and the distillate which came over at 175–190° crystallized as cubic prisms of melting point 30.5–31°.

Anal. Calcd. for $C_{19}H_{18}O$: C, 87.0; H, 6.9. Found: C, 86.9; H, 7.1.

Attempts to oxidize this product with acetic and nitric acids at 28° and at −15° gave only intractable oils. Attempts to convert these oils into the *trans*-mesitylphenylbutenedione failed.

The Bromophenyl-mesityl Series

trans-**1-(*p*-Bromophenyl)-4-mesityl-2-butenedione-1,4** (III).—A sample of β-bromobenzoylacrylyl chloride (II) was prepared (*cf.* ref. 2) by treating 20 g. of the acid (I) with 17.2 g. of phosphorus pentachloride at 40–45° in 125 cc. of carbon disulfide (twenty minutes), stirring with ice water for ten minutes, separating and evaporating the carbon disulfide; yield, 17.4 g.; melting point, 100–102°.

A sample of the acid chloride (43.5 g.) was added portionwise with stirring over a period of twelve minutes to a mixture of 57.5 g. of powdered anhydrous aluminum chloride in 400 cc. of technical tetrachloroethane and 39 g. of mesitylene. The temperature rose to 35° and the mixture was stirred for twenty-five minutes and hydrolyzed in ice and hydrochloric acid. The organic layer was washed with hot water and steam distilled. The resulting light yellow oil crystallized from methanol; yield, 45 g. (79%); melting point, 95–95.5°. Repeated crystallization from methanol and from ethyl acetate gave yellow hexagonal prisms melting at 96–97°.

Anal. Calcd. for $C_{19}H_{17}BrO_2$: C, 63.9; H, 4.8. Found: C, 63.9; H, 5.05.

cis-**1-(*p*-Bromophenyl)-4-mesityl-2-butenedione-1,4** (VI).—A solution of 0.5 g. of the *trans*-compound in benzene was exposed to sunlight for ten days. Upon evaporation of the solvent slowly, yellow crystals formed and were collected on a filter and washed with ligroin; yield, 0.45 g. It was recrystallized repeatedly from ethanol and obtained as hexagonal prisms of pale yellowish tint; melting point, 77.5–78° (a mixture melting point with the *trans*-isomer showed a depression of 10°).

Anal. Calcd. for $C_{19}H_{17}BrO_2$: C, 63.9; H, 4.8. Found: C, 63.9; H, 4.95.

Reduction by sodium hydrosulfite as with the *trans*-isomer gave the saturated diketone (IV). The action of sunlight on a chloroform solution of the *cis* compound with a trace of iodine present as catalyst gave the *trans* isomer.

1-(*p*-Bromophenyl)-4-mesitylbutanedione-1,4 (IV).—A mechanically stirred mixture of 1 g. of the *trans* unsaturated diketone (III), 2 g. of sodium hydrosulfite and 50 cc. of 70% ethanol was refluxed for twenty minutes and diluted with water. Ether extraction and evaporation gave 0.9 g. of nearly pure diketone which upon repeated crystallization from ethanol was obtained as flat colorless plates of melting point 99.5–100°.

Anal. Calcd. for $C_{19}H_{17}BrO_2$: C, 63.5; H, 5.33. Found: C, 63.25; H, 5.69.

A sample of the saturated diketone was treated with stannous chloride, hydrochloric acid and acetic acid under the conditions of preparation of the furan from the unsaturated diketone, and the furan was obtained in 76% yield and identified by mixture melting point.

2-(*p*-Bromophenyl)-5-mesitylfuran (V).—A solution of 5 g. of the unsaturated diketone (III) in 15 cc. of warm concd. acetic acid was poured into a boiling mixture of 40 cc. of concd. hydrochloric acid, 30 cc. of concd. acetic acid, and 20 g. of stannous chloride. After refluxing for five minutes and cooling a nearly pure crystalline product separated and was collected on a filter and recrystallized from an ethanol–ethyl acetate mixture; yield, 4.3 g.; melting point, 74–76°. Repeated crystallization from this solvent mixture gave colorless needles of melting point 84°. When the melting point was taken rapidly by immersing the sample in the bath at a temperature just below the melting point, it melted at 78°, solidified and melted again at 84°.

Anal. Calcd. for $C_{19}H_{17}BrO$: C, 66.86; H, 5.0. Found: C, 66.9; H, 5.3.

Oxidative Fission of the Furan.—In order to work at lowered temperature propionic acid was used as the medium instead of the usual acetic acid. One gram of the furan was suspended in 12.5 cc. of propionic acid and 1.5 cc. of concd. nitric acid at −12°. The temperature rose to −3°. Upon chilling again and allowing to stand for a total of fifteen minutes, the mixture was poured into ice water. The resulting yellow oil was extracted into ether and on evaporation of the solvent the compound was obtained in crystalline form; yield, 0.5 g. of melting point 74–75°. Upon repeated crystallization the melting point was 77–78° and the product was identified by mixture melting point with a sample of the *cis*-unsaturated diketone. It gave a 10° mixture melting point depression with the starting material.

Nitric Acid Oxidation of 3-Mesitoyl-5-mesityl-2-methyl-4-phenyl-furan (VII)

2-Acetyl-1,4-dimesityl-3-phenyl-2-butenedione-1,4 (VIII).—It had been found previously[3] that the nitric acid oxidation of the furan (VII) did not go at room temperature and that at the boiling point of the medium only intractable products were obtained. The following procedure was developed to produce the unsaturated triketone (VIII).

To a suspension of 4.5 g. of the furan in 45 cc. of concd. acetic acid was added dropwise 4.5 cc. of concd. nitric acid. The temperature was maintained at 40–45° for twenty-five minutes. On cooling 2.75 g. of crystals separated; melting point, 132–133°. Upon diluting the filtrate with water and crystallizing the resulting amorphous precipitate from ethanol the yield was brought to 3.2 g. After repeated crystallization from ethanol it was obtained as fine colorless needles of melting point 133.5–134.5°.

Anal. Calcd. for $C_{30}H_{30}O_3$: C, 82.16; H, 6.9. Found: C, 82.1; H, 7.3.

Acid hydrolysis (refluxing concd. acetic acid containing 10% by volume of concd. hydrochloric acid) gave intractable products. Alkali hydrolysis (short refluxing in 5% ethanolic sodium hydroxide) gave a new substance which has not yet been investigated.

Reduction.—Attempts to obtain the saturated triketone by reduction failed; in every attempt only the furan (VII) was produced.

(a) A suspension of 0.3 g. of VIII and 0.6 g. of sodium hydrosulfite in 20 cc. of 70% ethanol was refluxed for one and one-half hours, partially evaporated and diluted with water; 0.27 g. of crystals separated and on recrystallization from ethanol was identified as the furan by mixture melting point.

(b) Hydrogenation at atmospheric pressure in ethanol with Raney nickel showed absorption of one molecule of hydrogen and gave the furan in 75% yield.

Summary

The synthesis of two series of unsymmetrical unsaturated 1,4-diketones with one terminal mesityl group is outlined. The nitric acid oxidation of two typical furans with one α-mesityl group proceeded without difficulty and gave the corresponding unsaturated 1,4-diketones. The bearing of this on the mechanism is discussed.

Charlottesville, Virginia
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[Joint Contribution from the Kodak Research Laboratories and the Frick Chemical Laboratory, Princeton University]

Color and Constitution. II.[1] Absorptions of Some Related Vinylene-Homologous Series*

By L. G. S. Brooker, F. L. White, G. H. Keyes, C. P. Smyth and P. F. Oesper

The absorptions of many vinylene homologous series have been examined in the past, and these may be divided into two main categories, those series the members of which have an ionic charge available for resonance, and those in which this is not the case.

Among the latter series may be listed those studied by König and more recently by Hausser and Kuhn of which the first members are furfurol,[2] *p*-dimethylaminobenzaldehyde,[3] acetaldehyde (or crotonaldehyde),[4] crotonic acid,[4] stilbene[5] and furoic acid.[6] These are characterized by showing differences in $\lambda_{max.}$ between successive vinylene homologs which are relatively small, usually less than 500 Å., and these differences diminish as the vinylene series is ascended. Thus in the series $CH_3(CH{=}CH)_nCOOH$, the difference between the values of $\lambda_{max.}$ (in EtOH), where $n = 1$ and $n = 2$, is 500 Å., that between $n = 2$ and $n = 3$ is 400 Å., and the next shift is 330 Å. For the series furyl-$(CH{=}CH)_nCHO$,

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* Communication No. 816 of the Kodak Research Laboratories.

[1] Part I, Brooker, Sprague, Smyth and Lewis, This Journal, **62**, 1116 (1940).

[2] König, *Ber.*, **58**, 2559 (1925).

[3] König, Schramek and Rösch, *ibid.*, **61**, 2074 (1928).

[4] Hausser, Kuhn, Smakula and Hoffer, *Z. physik. Chem.*, **B29**, 371 (1935).

[5] Hausser, Kuhn and Smakula, *ibid.*, **B29**, 384 (1935).

[6] Hausser, Kuhn, Smakula and Deutsch, *ibid.*, **B29**, 378 (1935).