Heating with the iodine–phosphorus–acetic acid reagent, with sodium methylate, or with 85% phosphoric acid, was without effect on the compound. A **2,4-dinitrophenylhydrazone** was obtained in the usual way and crystallized from ethyl acetate–ethanol mixtures and from acetone; m. p. 187.5–188° (corr.) (yellow).

Anal. Calcd. for $C_{28}H_{32}O_4N_4$: N, 11.5. Found: N, 11.4.

The **semicarbazone** was obtained as colorless crystals by refluxing for twenty-four hours a methanol solution of XV with semicarbazide hydrochloride and sodium acetate; m. p. 177.5–178° (corr.).

Anal. Calcd. for $C_{23}H_{33}ON_3$: N, 11.5. Found: N, 11.6.

The **oxime** was prepared by heating an ethanol solution of XV, hydroxylamine hydrochloride, and sodium acetate for two hours. It crystallized from methanol; m. p. 154.5–155.5° (corr.).

Anal. Calcd. for $C_{22}H_{29}ON$: N, 4.3. Found: N, 4.6.

1,4-Dimesitylbutanol-2, XVI.—Four-tenths gram of dimesitylbutanone-2 was reduced with 2 g. of sodium and 25 cc. of absolute ethanol under nitrogen. On diluting with water and distilling under diminished pressure, 0.46 g. of colorless crystals was separated and recrystallized from methanol; m. p. 125.5–126° (corr.).

Anal. Calcd. for $C_{22}H_{30}O$: C, 85.0; H, 9.7. Found: C, 84.7, 84.3; H, 9.8, 9.6.

The **urethan** was prepared by refluxing for eight hours a petroleum ether solution of 0.1 g. of XVI and 0.5 cc. of phenyl isocyanate. On cooling 0.13 g. of product was obtained and crystallized several times from ligroin and from methanol; m. p. 122–122.5° (corr.).

Anal. Calcd. for $C_{29}H_{35}O_2N$: N, 3.3. Found: N, 3.3, 2.9.

1,4-Dimesityl-2-iodobutane, XVII.—A mixture of 0.2 g. of dimesitylbutanol-2, XVI, 0.05 g. each of iodine and red phosphorus, 8 cc. of concd. acetic acid, 3 drops of water, and 7 drops of hydriodic acid (sp. gr. 1.7) was boiled for two and one-half hours and filtered into a sodium bisulfite solution. The organic material was extracted into ether, freed from acetic acid by washing with sodium hydroxide, and isolated as an oil on evaporation of the solvent. On digestion with ethanol 0.13 g. of crystals was obtained which was recrystallized from absolute ethanol and melted at 105.5–106° (corr.).

Anal. Calcd. for $C_{22}H_{29}I$: C, 62.9; H, 7.0. Found: C, 62.8; H, 7.1.

Summary

The preparations and proof of structures of dimesitylbutanones-1 and -2 and the corresponding monohydric alcohols are described.

In the preparation of dimesitylbutanone-1 the two possible unsaturated ketones were obtained and their structures demonstrated.

CHARLOTTESVILLE, VA. RECEIVED JANUARY 18, 1938

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

2,5-Dimesityl- and 2,5-Di-(bromomesityl)-furans

BY ROBERT E. LUTZ, ELIZABETH C. JOHNSON AND JOHN L. WOOD

2,5-Diarylfurans generally can be made by dehydration of the 1,4-diaroyl-1,4-diketones with acetic anhydride and sulfuric acid, although occasionally substituents on the chain hinder the reaction.[1] Few dimesityl compounds have been considered in this connection, however. Acetoxydimesitylfuran is obtainable by the action of acetic anhydride and sulfuric acid on di-(trimethylbenzoyl)-hydroxyethane,[2] and 2,5-dimesityl-3,4-dimethylfuran is formed with exceptional ease from the corresponding saturated 1,4-diketone by this method.[3] Furan ring closure is the chief result in zinc–acetic acid reduction of both *cis* and *trans* di-(trimethylbenzoyl)-dimethylethylenes,[3] a type of reaction which has been observed in relatively few cases[4] and which does not occur in the reduction of di-(trimethylbenzoyl)-ethylene itself.

The dimesityl- and di-(bromomesityl)-1,4-diketones, I and VII, which are unsubstituted on the chain, do not undergo furan ring closure under the usual conditions with acetic anhydride or acetyl chloride and sulfuric acid. Di-(trimethylbenzoyl)-ethane, I, undergoes slow dehydration when subjected to the prolonged action of boiling hydrochloric acid and acetic acid mixtures, to give dimesitylfuran, IV, but the reaction is difficult to bring to completion and is therefore unsatisfactory as a method of preparation. Heating directly with 85% phosphoric acid gives only traces of the furan but brings about chiefly fission of the molecule to mesitylene and succinic acid, a type of reaction which is characteristic of mesitylenic ketones.[5] Both

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[1] *Cf.* the dibenzoyldibromoethanes, Lutz, THIS JOURNAL, **48**, 2916 (1926).

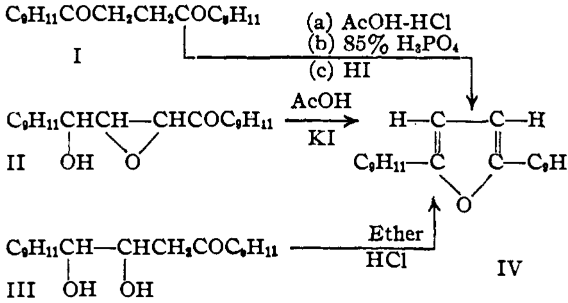
[2] Lutz and Wood, *ibid.*, **60**, 229, 705 (1938).

[3] Lutz and Taylor, *ibid.*, **55**, 1593 (1933).

[4] Lutz, *ibid.*, **51**, 3008 (1929).

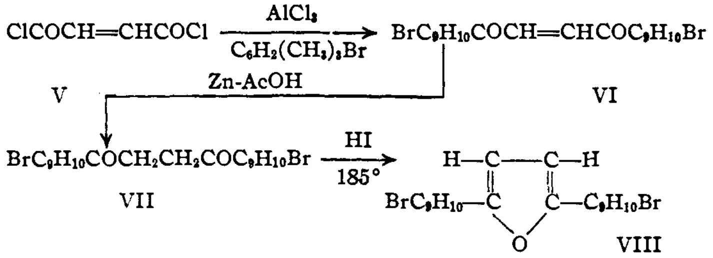
[5] *Cf.* Klages and Lickroth, *Ber.*, **32**, 1549 (1899); Klages, *ibid.*, **37**, 924, 1715 (1904).

saturated diketones I and VII are dehydrated in good yield, however, by heating with concd. hydriodic acid, the reactions being suitable for use on a preparative scale.



In this connection it should be noted that dimesitylfuran is produced[2] also by the action of potassium iodide in concd. acetic acid on dimesityl-4-hydroxy-2,3-epoxybutanone-1, II, and by the action of ethereal hydrogen chloride on dimesityl-3,4-dihydroxybutanone-1, III, as is illustrated in the above diagram.

The synthesis of the di-(bromomesityl)-furan, VIII, was carried out according to the following scheme



It is clear from these facts that 1,4-dimesityl-1,4-diketones can in general be converted into furans without particular difficulty although in some instances the reactions proceed less easily than with the diphenyl analogs and a certain amount of steric hindrance appears to be involved.

The dimesityl- and di-(bromomesityl)-furans are being studied further with a view toward obtaining compounds such as 2,5-di-(bromomesityl)-3,4-dibromofuran which should show diastereoisomerism due to restricted rotation of the planes of the three rings involved.

Experimental

1,2-Di-(trimethylbenzoyl)-ethane, I.—A convenient preparation of the saturated 1,4-diketones is illustrated as follows: 35 g. of di-(trimethylbenzoyl)-ethylene was dissolved in 100 cc. of boiling concd. acetic acid, and the solution poured into a mixture of 250 cc. of concd. acetic acid, 200 cc. of concd. hydrochloric acid and 125 g. of stannous chloride. The mixture was boiled and stirred for five minutes and cooled, the saturated 1,4-diketone crystallizing in a yield of 32 g. of nearly pure material.

Reduction of a sample of di-(trimethylbenzoyl)-ethylene in alcohol with palladium on calcium carbonate and hydrogen gave a quantitative yield of I (nearly pure), the reaction coming to a definite stop. Attempts to carry the reduction further with palladium and platinum catalyst, even after several days of shaking, failed.

Refluxing concd. hydrochloric acid for twenty-four hours was without effect on the saturated diketone I.

Treatment under a variety of conditions with acetyl chloride or acetic anhydride and sulfuric acid gave only unchanged material or intractable products. In the case of acetic anhydride and sulfuric acid, at 80°, sulfonation occurred slowly, giving a difficultly water soluble sulfonate which could be isolated as fine needles melting with decomposition at about 230°.

2,5-Dimesitylfuran, IV.—Of the following methods of preparation, (d) proved to be the best.

(a) Samples of di-(trimethylbenzoyl)-ethylene were treated with mixtures of 3 parts concd. acetic acid, 2 parts concd. hydrochloric acid, and an excess of tin, refluxing for thirteen hours. The yellow color was quickly bleached, and (as was shown in independent experiment) the unsaturated diketone was completely reduced to the saturated diketone within five minutes. The product, at the end of the long heating, was fractionally crystallized from ethanol and separated into the components, namely, the saturated diketone, I, and dimesitylfuran.

(b) In another experiment dry hydrogen chloride was passed into a refluxing solution of I in 97% acetic acid for five hours, with similar results.

(c) When 3.2 g. of the saturated diketone, I, was heated with 30 cc. of 85% phosphoric acid at 120–130° an oil was obtained which was extracted into ether, washed with sodium hydroxide to remove acids and then distilled, giving 1.1 g. (47% of theoretical) of mesitylene (b. p. 158–165°) which was identified by conversion into the trinitro derivative and comparison with an authentic sample. From the sodium hydroxide solution on acidification a small amount of succinic acid was isolated. In one (of several) experiments 0.05 g. of dimesitylfuran was isolated from the residue after distillation of the mesitylene, and was identified.

(d) A 5-g. sample of I was suspended in 15 cc. of hydriodic acid (sp. gr. 1.7) and the mixture refluxed for five hours with mechanical stirring (using ground glass joints and mercury seal). On cooling the product usually solidified (seeded) and was filtered immediately on a hardened filter paper and recrystallized. The yield of nearly pure material melting at 79–81° was 4.4 g.

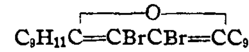
The furan was purified by repeated crystallization from ethanol and melted at 82–83 (corr.).

Anal. Calcd. for $C_{22}H_{24}O$: C, 86.9; H, 8.0. Found: C, 86.5, 86.9; H, 7.9, 8.0.

Attempted reduction with sodium and alcohol under drastic conditions was without effect on the furan.

A nitro derivative was obtained by treating the above furan in 5 cc. of concd. acetic acid at 22° with 1 cc. of concd. nitric acid. It crystallized from ethanol and melted at 107.5–108° (corr.).

Anal. Calcd. for $C_{22}H_{23}O_3N$: C, 74.7; H, 6.5; N, 4.0. Found: C, 75.3; H, 6.5; N, 4.1.



$C_9H_{11}C{=}CBrCBr{=}CC_9H_{11}$, **2,5-Dimesityl-3,4-dibromofuran.**—Attempts at direct bromination of the dimethylfuran gave oils. Only when the amount of bromine added was limited to two molecules was a crystalline product obtained. This proved to be the dibromo compound. It was best obtained by stepwise addition of bromine to a carbon tetrachloride solution of the furan. It was crystallized from ethyl acetate, acetone, and ether–butanone mixtures, and melted at 146.5–147°.

Anal. Calcd. for $C_{22}H_{22}OBr_2$: C, 57.14; H, 4.8. Found: C, 57.45; H, 4.9.

When bromination of IV or VIII was carried out in carbon disulfide with ferric bromide as catalyst, a product was obtained which appeared to be a pentabromo compound. This is being investigated further.

The reaction between phosphorus pentabromide and di-(trimethylbenzoyl)-ethylene gave di-(trimethylbenzoyl)-dibromoethane. From I only intractable products were obtained.

1,2-Di-(3-bromo-2,4,6-trimethylbenzoyl)-ethylene, VI.—Ten grams of fumaryl chloride, V, was added slowly to a well-stirred mixture of 150 cc. of carbon disulfide, 30 cc. of bromomesitylene, and 60 g. of aluminum chloride, the mixture being allowed to stand with stirring for forty-five minutes and decomposed in ice in the usual way. The product was obtained in a yield of 50%; it was crystallized from chloroform and ethyl acetate; m. p. 228–230° (pale yellow).

Anal. Calcd. for $C_{22}H_{22}O_2Br_2$: C, 55.2; H, 4.6; Br, 33.4. Found: C, 55.0; H, 4.9; Br, 33.8.

1,2-Di-(3-bromo-2,4,6-trimethylbenzoyl)-ethane, VII, was prepared by adding an excess of zinc dust to a boiling solution of 3 g. of VI in 150 cc. of glacial acetic acid, allowing the mixture to boil gently for one minute and filtering and washing the zinc residue with more hot acetic acid. On diluting with a little water and cooling, 3 g. of nearly pure VII separated and was recrystallized from ethyl acetate; m. p. 183–184°.

Anal. Calcd. for $C_{22}H_{24}O_2Br_2$: C, 55.0; H, 4.5. Found: C, 55.0; H, 5.3.

2,5-Di-(3-bromo-2,4,6-trimethylphenyl)-furan, VIII.—Attempts to dehydrate VII with acetic anhydride and sulfuric acid failed, also heating with mixtures of concd. hydriodic acid and concd. acetic acid.

Half a gram of VII with 1.5 cc. of hydriodic acid (sp. gr. 1.7) was sealed in a tube and heated at 182–185° for one hour. The tube was cooled in ice, opened, and the hydriodic acid decanted from the resinous product which was washed with cold water and digested with methanol, the furan crystallizing. It was recrystallized from ethanol–ethyl acetate mixtures and melted at 92–94°.

Anal. Calcd. for $C_{22}H_{22}OBr_2$: C, 57.1; H, 4.8. Found: C, 57.3; H, 4.9.

Summary

The preparations of 2,5-dimesityl- and 2,5-di-(bromomesityl)-furans are described and the effect of the mesityl groups on the ease of furan ring closure is discussed.

CHARLOTTESVILLE, VA. RECEIVED JANUARY 18, 1938

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

Catalytic Hydration of Alkylacetylenes[1]

BY ROBERT J. THOMAS, KENNETH N. CAMPBELL AND G. F. HENNION

Introduction

Surprisingly little work has been reported in the literature concerning the hydration of alkylacetylenes to ketones.

$$R{-}C{\equiv}CH + HOH \longrightarrow R{-}CO{-}CH_3$$

Propyne,[2] 1-pentyne,[3] 2-hexyne,[4,5] 1-heptyne,[6] 3-heptyne,[7] 1-octyne[6,8] and 2-octyne[7] have been converted to their corresponding ketones by the action of strong sulfuric acid. The yields obtained by this method are low because of polymerization and charring. Desgrez[9] was able to obtain ketones from several alkylacetylenes by heating them with water in sealed tubes at high temperatures. In this case also the yields were low.

Kutscheroff[10] succeeded in hydrating propyne to acetone under mild conditions by the use of dilute sulfuric acid and mercuric salts as catalysts. As is well known this method finds commercial application in the production of acetaldehyde from acetylene. Carter[11] and Conaway[12]

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[1] Paper XXIV on the chemistry of the alkylacetylenes and their addition compounds; previous paper, THIS JOURNAL, **60**, 568 (1938).

[2] Schrohe, *Ber.*, **8**, 367 (1875).

[3] Faworski, *J. prakt. Chem.*, [2] **37**, 388 (1888).

[4] Faworski, *ibid.*, [2] **37**, 428 (1888).

[5] Michael, *Ber.*, **39**, 2147 (1906).

[6] Béhal, *Ann. chim.*, [6] **15**, 267 (1888).

[7] Béhal, *ibid.*, [6] **15**, 408 (1888).

[8] Béhal, *Bull. soc. chim.*, [2] **47**, 33 (1887).

[9] Desgrez, *Ann. chim.*, [7] **3**, 209 (1894).

[10] Kutscheroff, *Ber.*, **17**, 13 (1884).

[11] Carter, U. S. Patent 1,896,161 (1933); *C. A.*, **27**, 2458 (1933).

[12] Conaway, U. S. Patent 1,967,225 (1934); *C. A.*, **28**, 5834 (1934).