Summary

The pronounced effectiveness of benzylalkali compounds in some interconversion reactions of organometallic compounds made desirable improved and convenient directions for the preparation of benzyl types. Benzylpotassium, now available for the first time in workable quantities, is readily prepared in 82% yield from toluene, chlorobenzene and potassium. Benzylsodium can be obtained in 80% yield by heating p-tolylsodium (from p-chlorotoluene and sodium in 80% yield) in petroleum ether; and in 80% yield by heating phenylsodium (from chlorobenzene and sodium in 87% yield) with toluene.

There is a lateral migration of sodium to give benzylsodium when o-, m-, or p-tolylsodium is heated. p-Tolyllithium is stable under these conditions. However, n-butyllithium metalates toluene laterally to give benzyllithium (0.2% yield).

In addition to other lateral metalations, an account is given of rates of carbonation, thermal stabilities, reaction mechanisms and some hazards in manipulating organopotassium compounds and potassium.

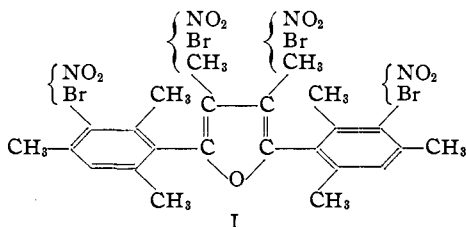## Some Substituted 2,5-Dimesitylfurans

BY ROBERT E. LUTZ AND CHARLES J. KIBLER

This investigation has been made in order to study the effect of substitution of mesityl groups on the reactions of the furan nucleus, and also to test the possibility of stereoisomerism involving restricted rotation on the inter-nuclear bonds.


I

Five 2,5-dimesitylfurans of the type I have been prepared by methods in which the final step has completed the introduction of groups requisite for diastereoisomerism due to restricted rotation. In no case was there found any evidence of the existence of isomers. It would appear, therefore, that under the somewhat drastic preparative conditions involved in all but one case, stereoisomers are not stable enough for independent existence, as would be expected since interference effects in this type of compound should be small. It is, of course, possible that labile isomers, once formed, might be stable enough to exist under ordinary conditions; and further investigation should be made, including an attempt to resolve a suitable derivative which presumably would have the more stable trans-dl configuration.

In the preparation and study of the compounds mentioned above, it was found that the mesityl groups offer very little hindrance to nitration and bromination at the furan β-positions and that these β-positions are generally more reactive than the unsubstituted positions in the mesityl nuclei. The results parallel those obtained in the halogenation of 2,5-diphenylfuran.[1]

The most striking generalization arising from this investigation concerns oxidative ring fission, which is a reaction characteristic of 2,5-diarylfurans with no ortho substituents in the aryl nuclei. The cis unsaturated 1,4-diketone is produced whenever this stereoisomer is stable under the reaction conditions,[2] as is illustrated in the case of the oxidation of diphenyldimethylfuran (II) to the new cis unsaturated diketone, III. There are
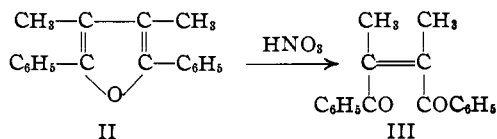
over 25 examples of this reaction among the 2,5-diaryl types alone, and there is now no authentic failure of the reaction when tried. Substituents in these compounds in the para position of the phenyls include chlorine and bromine, and in the furan β-positions, chlorine,[1,2] methyl,[3] chloromethyl,[3] phenyl,[1,2] and mesityl.[4] On the other

(1) Lutz and Wilder, THIS JOURNAL, **56**, 2145 (1934); Lutz, Tyson, Sanders and Fink, ibid., **56**, 2679 (1934).

(2) Lutz and Wilder, ibid., **56**, 978 (1934), and references cited; cf. also examples cited by Gilman and Wright, Chem. Rev., **11**, 523 (1932).

(3) Lutz and McGinn, results to be published shortly.

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

hand, 2,5-dimesitylfuran and a large number of derivatives are now known, including a number described in the experimental part of this paper. Among the substituents are bromine and nitro in the mesityl nuclei, and bromine, nitro, methyl, phenyl[5] and mesityl[6] in the furan β-positions. These compounds consistently have resisted oxidative ring fission under the usual conditions effective for the 2,5-diphenyl types. If they have reacted at all, they have undergone only nitration or decomposition; in no case was there any evidence of simple ring fission to the unsaturated 1,4-diketone.

These results are significant in connection with the mechanism of the oxidative ring fission. It has been suggested[2,7] that the reaction involves addition of nitric acid or its equivalent (an anhydride or a mixed anhydride) to the diene system of the furan, followed by break-up and loss of the equivalent of nitrous acid, the ethylene linkage being formed before the break in the oxygen bridge of the ring with the consequent production of a *cis* product whenever this isomer is stable under the conditions of the experiment. The failure consistently of 2,5-dimesitylfurans to undergo the oxidative ring fission is readily understandable if one assumes that the α-mesityl groups offer hindrance to addition at the ends of the diene system involved, and supports the hypothesis that α-substitution in general, including displacement of one group by another, involves 1,4-addition and elimination at the α-carbons. Since substitution in the β-positions is not hindered to any significant extent by α-mesityl groups, it might be supposed also that β-substitution proceeds either direct or by addition and elimination at the vinyl ether system, —$\overset{|}{C}$=$\overset{|}{C}$—O—, but without involving addition at the α-carbon.

Experimental Part

2,5 - Di - (bromomesityl) - 3,4 - dimethylfuran (VI).—The preparation of this furan, VI, was accomplished in two ways. One synthesis began with the Friedel–Crafts reaction between dimethylfumaryl chloride (IV) and bromomesitylene. The desired unsaturated diketone, di-(bromotrimethylbenzoyl)-ethylene (V), was ob-

tained but in extremely poor yield. Zinc and acetic acid reduction of this and dehydration of the product with acetic anhydride and sulfuric acid gave di-(bromomesityl)-dimethylfuran (VI) in good yield.

The first step in the above synthesis was entirely impractical because under the necessary conditions of the Friedel–Crafts reaction bromomesitylene undergoes dismutation to mesitylene and di- and tribromomesitylene, a reaction for which there are many analogies[8] and one which proceeds more rapidly than the desired Friedel–Crafts reaction. Under the most favorable conditions a very difficultly separable mixture was obtained which contained large amounts of di-(trimethylbenzoyl)-ethylene and only a small amount of the desired di-(bromomesityl) derivative, V; laborious fractional crystallization was necessary for separation. This synthesis, however, in conjunction with the second preparation to be described below, shows the structure of the final product and the location of the bromine atoms in the mesityl nuclei. The two halogens of the furan, VI, are not removable by means of zinc dust and acetic acid but are eliminated by catalytic hydrogen.
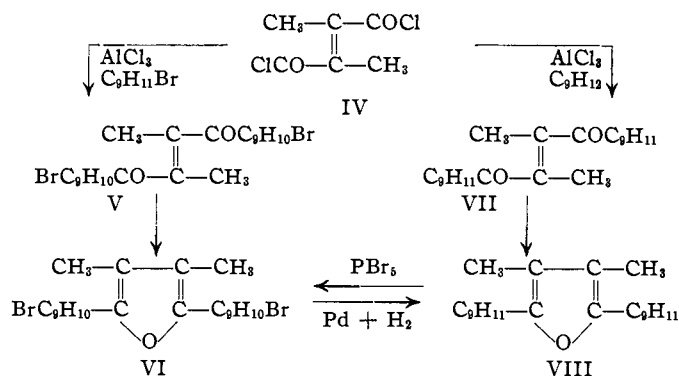
The best preparation of di-(bromomesityl)-dimethylfuran (VI) was through direct bromination of dimesityldimethylfuran (VIII) with phosphorus pentabromide.

The Friedel–Crafts Reaction between Dimethylfumaryl Chloride and Bromomesitylene.—A series of reactions was run using aluminum chloride as catalyst and carbon

(5) Lutz and Kibler, THIS JOURNAL, **61**, 3010 (1939).

(6) Lutz and Kibler, *ibid.*, **62**, 360 (1940).

(7) Freure and Johnson, *ibid.*, **53**, 1142 (1931).

(8) α- and β-bromonaphthalenes with aluminum chloride and toluene at 100° give a mixture of bromotoluenes and naphthalene, and in carbon disulfide (refluxing) α-bromonaphthalene gives β-bromonaphthalene and 1,2-dibromonaphthalene [Roux, *Ann. chim. phys.*, [6] **12**, 345 (1887)]; bromobenzene and aluminum chloride at high temperature give benzene and dibromobenzene [Dumreicher, *Ber.*, **15**, 1867 (1882)]; and *o*-dichlorobenzene, methyl chloride, and aluminum chloride at 100° give trichloromesitylene [Friedel and Crafts, *Ann. chim. phys.*, [6] **10**, 418 (1887)].

disulfide as solvent, with variation in temperature, proportion of materials and time of reaction. The following compounds were isolated: dibromomesitylene, tribromomesitylene, di - (trimethylbenzoyl) - dimethylethylene (VII), the desired di - (bromotrimethylbenzoyl) - dimethylethylene (V), and 1 - bromomesityl - 2,3 - dimethyl - 4-mesityl-2-butenedione-1,4. The bromomesitylene used was carefully purified and had the b. p. 117° at 25 mm. and m. p. −0.1°. Three typical experiments were as follows:

(a) Bromomesitylene (69 g.) was added to 300 cc. of carbon disulfide and 136 g. of anhydrous aluminum chloride, followed quickly by 31 g. of dimethylfumaryl chloride, added dropwise with stirring, allowing the mixture to reflux gently for one hour. This gave 81 g. of a mixture of diketones. Tribromomesitylene (2.3 g.) was obtained from the residues (identified by m. p. 227–228° and analysis). The diketone mixture was fractionally crystallized from acetone, butanone, ethyl acetate, and other solvents until 10 mg. of nearly pure monobromo derivative remained, the melting point becoming constant.

(b) In another run, the temperature was held to 22°. From this all three diketones were isolated. At 0° to −5° no reaction occurred.

(c) With a large excess of bromomesitylene, the product was nearly pure di-(trimethylbenzoyl)-ethylene (yield, 78%). Steam distillation of the residues gave unchanged bromomesitylene, and then dibromomesitylene which solidified in the condenser; the yield was 68% based on disproportionation to mesitylene and dibromomesitylene. The dibromomesitylene was identified by m. p. 64° and b. p. 278–279°.

trans - 4 - **Bromomesityl - 2,3 - dimethyl - 1 - mesityl-2-butenedione-1,4**, $BrC_9H_{10}COC(CH_3){=}C(CH_3)COC_9H_{11}$.—This compound was obtained in only very small amounts by fractional crystallization of the mixtures of diketones, the best sample melting from 124–127° (rosets of blade-shaped plates).

Anal. Calcd. for $C_{24}H_{27}O_2Br$: C, 67.6; H, 6.4. Found: C, 65.3; H, 6.0.

trans - 1,4 - **Di - (bromomesityl) - 2,3 - dimethyl - 2 - butenedione-1,4, V.**—The best sample obtained melted at 140–143°.

Anal. Calcd. for $C_{24}H_{26}O_2Br_2$: C, 56.9; H, 5.2. Found: C, 56.9; H, 5.0.

A mixture of 0.07 g. of V with 0.5 cc. of concd. acetic acid, 1 cc. of acetic anhydride and 0.5 g. of zinc dust was boiled for one minute and filtered. One drop of concd. sulfuric acid was added to the filtrate; then, when worked up in the usual way, the furan, VI, was obtained in good yield.

2,5-Dimesityl-3,4-dimethylfuran, VIII.—Attempts to oxidize the furan with concd. nitric acid in acetic or propionic acid gave only resinous products even at −10°.

2,5-Di-(bromomesityl)-3,4-dimethylfuran, VI.—A mixture of 0.2 g. of dimesityldimethylfuran, VIII, and 0.8 g. of phosphorus pentabromide (50% excess) was heated at 100° for three minutes and allowed to cool slowly (ten minutes). Decomposition in water gave an oil which solidified. Crystallization from isopropanol gave 0.28 g. of nearly pure product (rhomboids); m. p. 111.5–113°.

Anal. Calcd. for $C_{24}H_{26}OBr_2$: C, 58.8; H, 5.3. Found: C, 58.4, 58.9; H, 5.2, 5.5.

Runs on a large scale gave poorer yields ranging from 65–75%.

The furan was not appreciably affected by zinc dust and concd. acetic acid. Hydrogenation with palladium on barium sulfate catalyst proceeded with absorption of approximately two molecules of hydrogen, and 2,5-dimesityl-3,4-dimethylfuran, VIII, was isolated and identified.

3,4 - Dibromo - 2,5 - di - (bromomesityl)-furan (XVII).—This furan (XVII) was prepared in three ways. The best synthesis started with dimesitylfuran, XIV. Bromination directly[9] gives mixtures which are not easily handled, but the 3,4-dibromo derivative, XV, has actually been made in this way and isolated.[9] Using phosphorus pentabromide at 90°, the desired tetrabromo derivative, XVII, is produced in excellent yield; when an insufficient quantity of this reagent is used, a difficultly separable mixture of the tri- and tetrabromo compounds, XVIII and XVII, is obtained; but at a higher temperature with an excess of the reagent there is produced the pentabromo derivative, XVI.
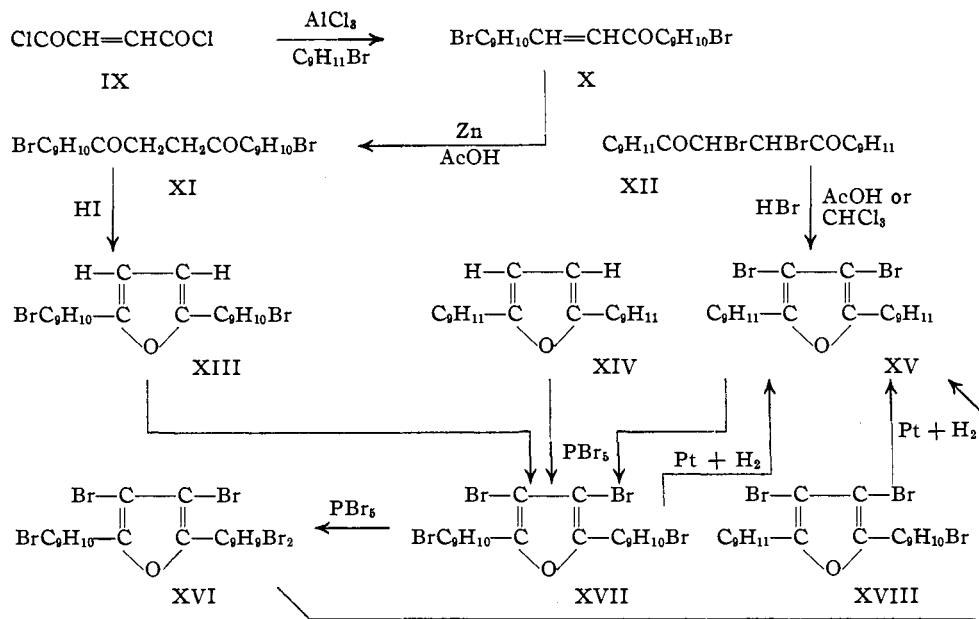
A second synthesis started with the Friedel–Crafts reaction between fumaryl chloride and bromomesitylene.[9] Here dismutation of bromomesitylene does not interfere seriously although it occurs to some extent. Reduction of the resulting unsaturated diketone to the saturated diketone, XI, was followed by dehydration to the furan, XIII, with hydriodic acid; and finally bromination with phosphorus pentabromide gave the tetrabromo derivative, XVII, in good yield.

The third synthesis utilized 3,4-dibromodimesitylfuran, XV, which was prepared by an improved method through the action of hydrogen bromide in acetic acid or chloroform on di-(trimethylbenzoyl)-dibromoethane, XII. The furan, XV, reacted with phosphorus pentabromide to give the tetrabromo derivative, XVII, in excellent yield.

Attempts to make the tetrabromo furan, XVII, by dehydration of the dibromide of di-(bromotrimethylbenzoyl)-ethylene (X) were unsuccessful.
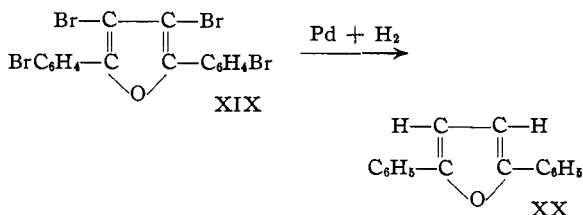
The positions of the halogens in the tetrabromo furan, XVII, are established by two of the syntheses described above involving different orders of introduction of halogens and starting from the dibromo derivatives, XI and XII, in which the location of the halogens is known, and by the reductions described below.

(9) Lutz, Johnson, and Wood, THIS JOURNAL, **60**, 716 (1938).

ClCOCH=CHCOCl $\xrightarrow[\text{C}_9\text{H}_{11}\text{Br}]{\text{AlCl}_3}$ BrC$_9$H$_{10}$CH=CHCOC$_9$H$_{10}$Br

IX   X

BrC$_9$H$_{10}$COCH$_2$CH$_2$COC$_9$H$_{10}$Br $\xleftarrow[\text{AcOH}]{\text{Zn}}$ C$_9$H$_{11}$COCHBrCHBrCOC$_9$H$_{11}$

XI   XII

HI   HBr | AcOH or CHCl$_3$

H—C——C—H   H—C——C—H   Br—C——C—Br
BrC$_9$H$_{10}$—C   C—C$_9$H$_{10}$Br   C$_9$H$_{11}$—C   C—C$_9$H$_{11}$ C$_9$H$_{11}$—C   C—C$_9$H$_{11}$
      \O/   \O/   \O/
      XIII   XIV   XV

PBr$_5$ Pt + H$_2$ Pt + H$_2$

Br—C——C—Br   Br—C——C—Br   Br—C——C—Br
BrC$_9$H$_{10}$—C   C—C$_9$H$_9$Br$_2$ $\xleftarrow{\text{PBr}_5}$ BrC$_9$H$_{10}$—C   C—C$_9$H$_{10}$Br   C$_9$H$_{11}$—C   C—C$_9$H$_{10}$Br
      \O/   \O/   \O/
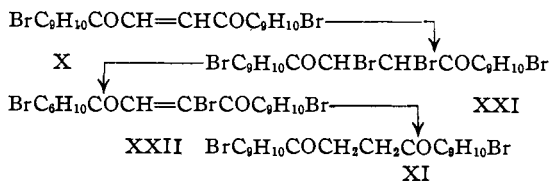   XVI   XVII   XVIII

Reductive elimination of the halogens could not be brought about by means of zinc and acetic acid since no aliphatic halide groupings were involved. Hydrogenation with a palladium catalyst removed halogens from the mesityl nuclei in four compounds which were tested, namely, di-(bromomesityl)-dimethylfuran (VI), and the tri-, tetra- and pentabromo furans, XVIII, XVII and XVI. In the latter three cases the bromines in the β-positions of the furan nucleus resisted the catalytic reduction and remained untouched. Reduction, then, distinguishes between the two types of halogens, those in the mesityl nuclei being the more active and reducible.

The resistance of the halogens in the furan β-positions toward reduction was observed only in the 2,5-dimesitylfuran series, however; 3,4-dibromo-2,5-di-(bromophenyl)-furan, XIX, under comparable conditions is readily reduced by palladium and hydrogen to diphenylfuran, XX, with elimination of all four halogens including those in the furan β-positions. Probably the resistance to reduction of the β-halogens in the dimesitylfuran series is to be attributed to steric hindrance by the adjacent mesityl groups.

Br—C——C—Br
BrC$_6$H$_4$—C   C—C$_6$H$_4$Br $\xrightarrow{\text{Pd + H}_2}$
      \O/
   XIX

H—C——C—H
C$_6$H$_5$—C   C—C$_6$H$_5$
      \O/
      XX

The various reactions described above show clearly that both in dimesityl- and diphenylfuran the β-positions in the furan nucleus are consistently more reactive toward bromination than the free positions in the aryl nuclei. Each mesityl or phenyl nucleus can subsequently be brominated once in each ring. The introduction finally of a second bromine into either mesityl nucleus meets with resistance, and disubstitution could be brought about in only one of the two rings under the most drastic conditions which were employed, the pentabromo derivative, XVI, being the result.

Some Halogen Derivatives of the Dimesityl 1,4-Diketones.—Incidental to this research, the following reactions were carried out. The dibromide of di-(bromotrimethylbenzoyl)-ethylene was made by direct addition of bromine to the unsaturated diketone, X. When a solution of the dibromide (XXI) in concd. acetic acid was refluxed, hydrogen bromide was quickly eliminated with formation of the bromo unsaturated diketone, XXII. The structure of this compound was proved by analysis and reduction to the saturated diketone, XI.

BrC$_9$H$_{10}$COCH=CHCOC$_9$H$_{10}$Br

X → BrC$_9$H$_{10}$COCHBrCHBrCOC$_9$H$_{10}$Br

BrC$_6$H$_{10}$COCH=CBrCOC$_9$H$_{10}$Br XXI

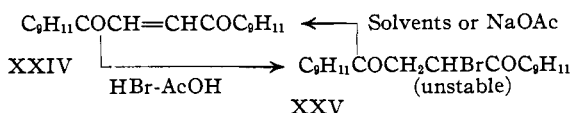XXII   BrC$_9$H$_{10}$COCH$_2$CH$_2$COC$_9$H$_{10}$Br
XI

In the dimesityl series the dibromo diketone,

XII, was made by the action of 8% hydrogen bromide in concd. acetic acid on di-(trimethylbenzoyl)-bromoethylene, XXIII, the reaction proceeding quickly at room temperature. The conversion of the product by dehydration into the dibromo furan, XV, required longer standing under similar conditions with 30% hydrogen bromide in concd. acetic acid; while the yield was poor, no unchanged material was left to complicate the separation of the product.

$$C_9H_{11}COCH=CBrCOC_9H_{11} \xrightarrow{\text{HBr-AcOH (8\%)}}$$

XXIII $\qquad$ $C_9H_{11}COCHBrCHBrCOC_9H_{11}$
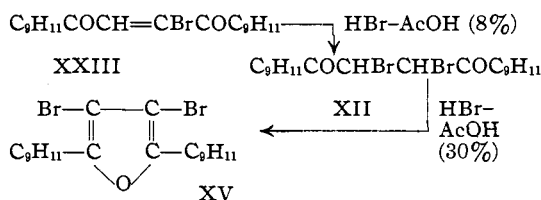
Di-(trimethylbenzoyl)-ethylene, XXIV, itself reacts with hydrogen bromide in concd. acetic acid at 10° to give the addition compound, XXV, which was isolated and was moderately stable in the solid state. This product lost hydrogen bromide when treated with sodium acetate or upon standing in contact with solvents, particularly during crystallization, the unsaturated diketone, XXIV, being regenerated.

$$C_9H_{11}COCH=CHCOC_9H_{11} \xleftarrow{\text{Solvents or NaOAc}}$$

XXIV $\qquad$ $\xrightarrow{\text{HBr-AcOH}}$ $C_9H_{11}COCH_2CHBrCOC_9H_{11}$ (unstable)

XXV

In connection with the relative stabilities of halides in the various saturated 1,4-diketones of the type under discussion, it is worthy of note that the chloro analog of XXV, namely, di-(trimethylbenzoyl)-chloroethane, also is unstable.[10] The dibenzoylchloro and bromoethanes require higher temperatures for decomposition, usually fusion temperature. The dihalides, both in the dimesityl and in the dibenzoyl series, decompose on melting or in boiling solvents with loss of halogen acid to give the halogeno unsaturated diketones. The dimesityl mono- and dihalogeno compounds in general, however, lose halogen acid with definitely greater ease than do the diphenyl analogs, perhaps due to the greater negativity of the mesityl groups as compared with phenyls.

Little is known about the corresponding halogeno compounds with an aryl group substituted on the ethylene linkage, but it should be pointed out that the two pairs of stereoisomers of the

(10) Lutz and Wood, THIS JOURNAL, **60**, 229 (1938).

1,2,4-trimesityl halogeno 1,4-diketones, C_9H_{11}-$COCH(C_9H_{11})CH(X)COC_9H_{11}$, are known and are remarkably stable, resistant even to the action of sodium acetate in boiling ethanol.[6]

Meso - 1,4 - dimesityl - 2,3 - dibromobutanedione - 1,4, XII, was obtained when the unsaturated bromo diketone, XXIII, was dissolved at room temperature in 8% hydrobromic–concd. acetic acid, the dibromo diketone separating within two minutes.

1,4 - Dimesityl - 2 - bromobutanedione - 1,4 (Di-(trimethylbenzoyl)-bromoethane), XXV.—One gram of XXIV was added to 18 cc. of 13% hydrobromic acid in concd. acetic acid at 10°, the solid dissolving quickly. After standing for fifteen minutes and diluting with water, a gum was obtained which solidified. Crystallization from methanol gave a small amount of the dibromide, XII, formed by the brominating action of the bromo diketone, XXV, under these conditions.[11] The filtrate deposited 0.83 g. of the addition compound, XXV. It was difficult to purify any lost hydrogen bromide during crystallization. By careful manipulation and crystallization at moderate temperatures a sample of m. p. 81.5–82° was obtained. The analysis for bromine was low, indicating some loss of hydrogen bromide on standing, but it showed beyond question that one and only one bromine was present.

Anal. Calcd. for $C_{22}H_{25}O_2Br$: Br, 19.9. Found: Br, 18.9.

A small sample, when refluxed in ethanol for ten minutes with sodium acetate, gave di-(trimethylbenzoyl)-ethylene, XXIV, in quantitative yield.

trans - 1,4 - Di - (bromomesityl) - 2 - butenedione - 1,4, X, was prepared by the Friedel–Crafts reaction[9] between fumaryl chloride and bromomesitylene. From the residues of the run, by steam distillation, dibromomesitylene of m. p. 63–64° was obtained and identified.

2,3 - Dibromo - 1,4 - di - (bromomesityl) - butanedione-1,4, XXI.—To a stirred suspension of 8 g. of X in 400 cc. of concd. acetic acid, heated to 60–65°, was added 2.68 g. of bromine in concd. acetic acid, the stirring being continued with heating for a short time after addition. The suspended solid went into solution as the bromine was added, and the difficultly soluble dibromide separated. On cooling and filtering 10 g. was obtained (82%). It crystallized from acetic acid or benzene as long flat rectangular prisms which melted with decomposition at about 250°.

Anal. Calcd. for $C_{22}H_{22}O_2Br_4$: C, 41.4; H, 3.5. Found: C, 41.2; H, 3.3.

Attempts to furanize this compound with 30% hydrobromic acid in concd. acetic acid failed, and only unchanged material was obtained after standing for five months in contact with the reagent. When refluxed with this reagent the hydrogen bromide was expelled and the bromo unsaturated diketone, XXII, was isolated. Reduction of the dibromide with zinc dust and concd. acetic acid in the usual way gave the saturated diketone, XI.

trans - 2 - Bromo - 1,4 - di - (bromomesityl) - 2 - butenedione-1,4, XXII.—A suspension of the dibromide, XXI, in

(11) *Cf.* Lutz and Stuart, *ibid.*, **59**, 2324 (1937).

concd. acetic acid was refluxed for one hour and diluted with water. A good yield of the bromo unsaturated diketone, XXII, was obtained and crystallized from isopropanol; light yellow needles of m. p. 154–155°.

Anal. Calcd. for $C_{22}H_{21}O_2Br_3$: C, 47.4; H, 3.8. Found· C, 47.1; H, 3.8.

Reduction with zinc dust and concd. acetic acid in the usual way gave the saturated diketone, XI.

2,5-Dimesitylfuran, XIV.—Attempts to dehydrate the saturated diketone with dry hydrogen chloride in boiling concd. acetic acid (twenty-seven hours) or chloroform at room temperature (standing for six months), were not successful as preparative methods for the furan because the reactions were not complete. The hydriodic acid method was used.[9]

Oxidation with potassium permanganate in acetone, water or concd. acetic acid gave only small amounts of mesityl carboxylic acid.

2,5-Di-(bromomesityl)-furan, XIII, was made by hydroiodic acid dehydration of XI.

3,4-Dibromo-2,5-dimesitylfuran, XV, was prepared[9] by stepwise bromination of dimesitylfuran, XIV, but the yields were poor and uncertain. The dehydration of the dibromo diketone, XII, was studied in order to find effective conditions. Acetic anhydride and 30% hydrobromic acid in concd. acetic acid had no effect. With chloroform or concd. acetic acid, saturated with dry hydrogen chloride and allowed to stand, respectively, for one and six months, there were obtained impure mixtures that were difficult to purify. The following two experiments were highly successful, the latter being of advantage only when the material was needed quickly.

(a) A solution of 5 g. of the dibromo diketone, XII, in 50 cc. of dry chloroform, saturated with dry hydrogen bromide, was allowed to stand at room temperature for six months. The progress of the reaction was followed by withdrawing samples at intervals, evaporating the solvent under an air blast, and determining the melting point. The entire product was worked up in this way, 3.6 g. being obtained (m. p. 130–137°). Crystallization from ethanol gave 3.1 g. melting at 139–142°. The yield of dibromofuran (60%) does not take into account the material withdrawn for tests.

(b) A suspension of 10 g. of XII in 80 cc. of 30% hydrogen bromide–concd. acetic acid was allowed to stand at room temperature, the reaction being complete in two weeks. The resinous product obtained by diluting the mixture with water was crystallized three times from ethanol giving a 37% yield of nearly pure furan. A large amount of resinous material was formed in this reaction.

Attempts to hydrogenate the furan with platinum oxide or palladium on barium sulfate as catalysts were without result, the bulk of the furan being recovered unchanged.

3,4 - Dibromo - 2,5 - di - (bromomesityl) - furan, XVII.—This furan was prepared by the bromination of the furans, XIV, XV, XIII and XVIII, by the same procedure described below, using phosphorus pentabromide. A large excess of reagent was necessary due to loss of bromine. With an insufficient amount a difficultly separable mixture of tri- and tetrabromo furans was obtained. The temperature was not allowed to go above 90° in order to avoid formation of the pentabromo derivative. 2,5-Dimesityl-

furan was used in large scale preparations because it was the most easily obtained of the starting materials.

A mixture of 0.2 g. of dimesitylfuran and 1.5 g. of phosphorus pentabromide was ground together thoroughly and heated at 88–90° for forty-five minutes. The red melt was then hydrolyzed in water, the oily product coagulating on standing. The yield of crude but nearly pure material was 0.41 g. (m. p. 170–172.5°). It crystallized from ethanol, isopropanol, and ethyl acetate; long rectangular plates; m. p. 177°.

Anal. Calcd. for $C_{22}H_{20}OBr_4$: C, 42.6; H, 3.25; Br, 51.55. Found: C, 42.34; H, 3.6; Br, 51.2.

The furan occurs in two distinct modifications. As usually obtained it was in the form of long rectangular plates melting at 175–177°, but these were usually contaminated by traces of the second form (rhombic). The presence of the rhombic form, visible under the microscope, probably accounted for the unsharp melting point. The rhombic form was obtained free from the other modification only once, after filtration of a hot solution of the compound in isopropanol. It melted sharply at 166° and, after solidifying in the capillary tube, remelted sharply at 177°.

Reduction of 0.4 g. of XVII with hydrogen and palladium on barium sulfate as catalyst (0.5 g.) in 25 cc. of ethanol involved absorption of two molecules in nine hours and 0.29 g. of 3,4-dibromo-2,5-dimesitylfuran, XV, was isolated and identified.

2 - Bromomesityl - 3,4 - dibromo - 5 - mesitylfuran, XVIII.—In the first brominations carried out under somewhat milder conditions than those described above, a mixture of this furan, XVIII, and the tetrabromo derivative, XVII, was obtained and separated by laborious fractional crystallization and by sublimation under reduced pressure.

A mixture of 4 g. of XIV and 25 g. of phosphorus pentabromide was heated for thirty minutes at 70°, giving 8 g. of product. It was repeatedly crystallized from ethyl acetate and isopropanol, giving the tetrabromo compound pure. The residues were subjected to fractional sublimation in the vacuum oven at 150°. The tribromo compound distilled first and was finally purified by crystallization from isopropanol, the sample obtained melting at 125.5–126.5° (blade-shaped scales).

*Anal.* Calcd. for $C_{22}H_{21}OBr_3$: Br, 44.4. Found: Br, 41.3.

From analyses it was evident that the sample still contained some impurity, probably the dibromo derivative, but not enough material was left for further purification.

2 - Bromomesityl - 3,4 - dibromo - 5 - dibromomesityl-furan,[9] XVI.—Nine grams of bromine (7 moles) in 10 cc. of carbon disulfide was added slowly to a mixture of 2 g. of dimesitylfuran, 5 cc. of carbon disulfide, and 0.5 g. of iron filings; the mixture was then refluxed gently for four hours. A quantitative yield of the pentabromo derivative was obtained; m. p. 280–282.5°.

Zinc dust and concd. acetic acid had no effect on this compound. Hydrogenation using palladium on barium sulfate gave 3,4-dibromo-2,5-dimesitylfuran (XV).

The pentabromide was prepared also by the action of phosphorus pentabromide at 100° on the tetrabromo compound, XVII.

3,4 - Dibromo - 2,5 - di - (nitromesityl) - furan (XXVII).—This furan was prepared by the action of a 1–3 mixture of concd. nitric and acetic acids at refluxing temperature on 3,4-dibromodimesitylfuran (XV). The mononitro derivative, XXVI, was obtained under similar conditions when a lower concentration of nitric acid was used.
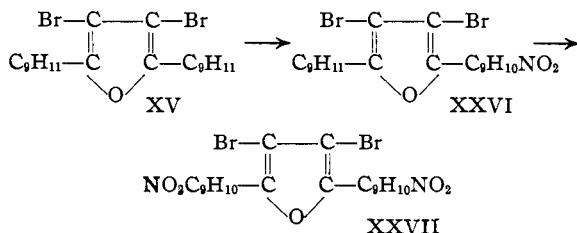
3,4 - Dibromo - 2 - mesityl - 5 - nitromesitylfuran, XXVI.—Dimesityldibromofuran, XV, did not react with 1–10 mixture (by vol.) of concd. nitric and acetic acids at 100°. Nitration was brought about as follows: a solution of 0.38 g. of XV in 20 cc. of concd. acetic acid and 3.8 cc. of concd. nitric acid was refluxed for thirty minutes and diluted with water. Crystallization of the product from ethanol gave 0.28 g. of nearly pure mononitro derivative; needles of m. p. 121.5–122.5°.

Anal. Calcd. for $C_{22}H_{24}O_3NBr_2$: C, 52.1; H, 4.2; N, 2.75. Found: C, 52.5; H, 4.0; N, 2.3.

Nitration further with 1–4 (by vol.) concd. nitric-acetic acid mixture (refluxed) gave the dinitro derivative, XXVII.

Zinc dust and concd. acetic acid (refluxed) gave a solid of m. p. 150–153° which has not been investigated further.

3,4 - Dibromo - 2,5 - di - (nitromesityl) - furan, XXVII.—A mixture of 0.8 g. of dibromodimesitylfuran (XV), 5 cc. of concd. nitric acid and 15 cc. of concd. acetic acid was refluxed for five minutes and diluted with water. The product was crystallized from ethanol; yield 0.57 g. It crystallized from ethanol and isopropanol as tapered needles melting at 204–205°.

Anal. Calcd. for $C_{22}H_{20}O_5N_2Br_2$: C, 47.85; H, 3.65; N, 5.1. Found: C, 47.5; H, 3.8; N, 5.2.

A thorough examination of the residues from this preparation failed to reveal any trace of another compound.

2,5 - Di - (bromomesityl) - 3,4 - dinitrofuran (XXX).—The logical synthesis of this furan by nitration of di-(bromomesityl)-furan (XIII) was unsuccessful because of the surprising resistance to the substitution of the second nitro group. The desired furan was prepared from dimesitylfuran (XIV) by successive substitutions of two nitro groups in the β-positions in the furan nucleus, followed by bromination with phosphorus pentabromide.
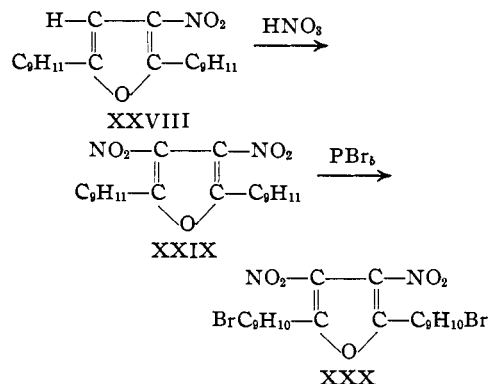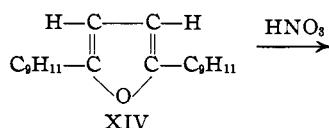
The first step in the above synthesis involved introduction of one nitro group into a β-position in the furan nucleus to give XXVIII; this is evident from the following facts. Bromination of the mononitro product, XXVIII, gave di-(bromomesityl)-nitrofuran (XXXI) which was made in a second way by nitration of di-(bromomesityl)-furan (XIII). The positions of the bromine atoms in XXXI are demonstrated conclusively by this second synthesis. The position of the nitro group of both XXVIII and XXXI in the furan β-position is evident from the following considerations: it has been shown that the nitro groups in dinitrodi-(nitromesityl)-furan (XXXII) effectively block bromination in the remaining vacant positions in the mesityl nuclei; therefore, bromination of XXVIII could not have involved both mesityl groups if one of them already carried the nitro group as a substituent; instead, bromination in only one (the unsubstituted) mesityl nucleus or/and the two β-positions in the furan ring would have occurred, whereas actually the bromines are known to have gone one to each mesityl group.
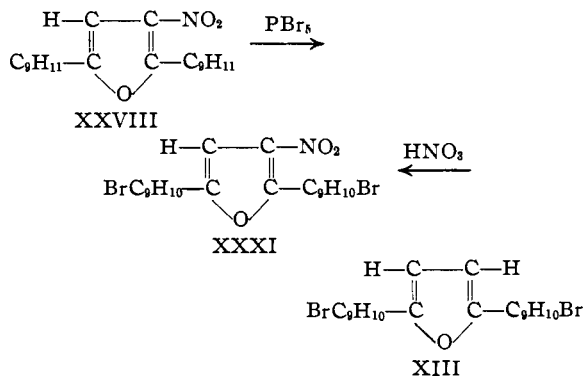
From these facts, then, it is evident that the first nitro group enters a furan β-position. The presence of this nitro group blocks substitution of

bromine in the remaining furan β-position and halogens then enter the two mesityl nuclei.

Unfortunately, further nitration of the 2,5-di-(bromomesityl)-3-nitrofuran (XXXI) could not be controlled successfully to give the desired dinitro derivative, XXX; when the reaction was forced it went too far and there was produced a compound which apparently contained five nitro groups. Thus, a simple proof of structure for XXX could not be obtained and it was necessary to be content with indirect evidence.

In nitration of dimesitylnitrofuran (XXVIII) it might be supposed that the second nitro group would not be able to enter the remaining furan β-position, but would, like bromine, enter a mesityl nucleus. However, from the fact that only one more nitro group (the second) entered, it is to be presumed that it went to the second furan β-position since, otherwise, substitution in both and not just one mesityl group would be expected. Furthermore, the formula XXIX for the dimesityldinitrofuran best explains the introduction subsequently of two bromines by the action of phosphorus pentabromide; if the alternative structure with the second nitro group in a mesityl nucleus were assumed, then bromination of the dinitro compound could have introduced only one bromine atom and this in the unsubstituted mesityl nucleus, because, as has just been shown, a nitro group in one furan β-position blocks bromination at the other β-position, and because, as will be shown below, a nitro group in a mesityl group hinders further substitution in this nucleus. Since this reasoning is involved, the evidence is not as conclusive as could be desired.

2,5-Dimesityl-3-nitrofuran, XXVIII,[9] reacts with 1–4 (by vol.) concd. nitric–acetic acid mixture (boiling for two minutes) to give the dinitro derivative, XXIX.

2,5-Dimesityl-3,4-dinitrofuran, XXIX.—A solution of 1 g. of dimesitylfuran, XIV, in 15 cc. of concd. acetic acid and 5 cc. of concd. nitric acid was refluxed for five minutes and cooled, the dinitro derivative, XXIX, crystallizing; yield 0.5 g. A crystalline impurity, visible under the microscope, was removed by repeated crystallization from isopropanol and from concd. acetic acid. The dinitrofuran crystallized as hexagonal plates of m. p. 213°. It is difficultly soluble in the alcohols.

Anal. Calcd. for $C_{22}H_{24}O_5N_2$: C, 67.0; H, 5.6; N, 7.1. Found: C, 66.7, 67.1; H, 5.4, 5.6; N, 7.0.

From the mother liquors 0.2 g. of mesityl carboxylic acid was isolated.

2,5-Di-(bromomesityl)-3,4-dinitrofuran, XXX.—A mixture of 0.28 g. of dimesityldinitrofuran, XXIX, and 0.7 g. of phosphorus pentabromide was heated at 90° for thirty minutes, then 0.3 g. more of the reagent was added and

heating continued for fifteen minutes at the same temperature. Hydrolysis gave an oil which solidified. Washing with methanol several times on the filter left 0.36 g. (92%) of nearly pure dibromo compound, XXX. It crystallized from isopropanol or concd. acetic acid as colorless rhombic plates melting at 200.5–201.5°.

Anal. Calcd. for $C_{22}H_{20}O_5N_2Br_2$: C, 47.8; H, 3.65. Found: C, 47.7; H, 3.8.

2,5-Di-(bromomesityl)-3-nitrofuran, XXXI.—A solution of 0.1 g. of di-(bromomesityl)-furan (XIII) in a 1–3 mixture (by vol.) of concd. nitric and acetic acids was refluxed for five minutes. On cooling 0.06 g. of the nitro derivative, XXXI, separated and was purified from isopropanol; m. p. 130–130.5°.

Anal. Calcd. for $C_{22}H_{21}O_3NBr_2$: C, 52.1; H, 4.2. Found: C, 51.7, 51.6; H, 4.0, 4.2. (Carbon analyses on known compounds were running consistently 0.3% low when these were made.)

This furan, XXXI, was obtained in a second way as follows: a mixture of 0.1 g. of 2,5-dimesityl-3-nitrofuran, XXVIII, and 0.3 g. of phosphorus pentabromide was heated at 90–93° for fifteen minutes and hydrolyzed. The product was crystallized from isopropanol giving 0.05 g. of pure XXXI.

NO₂—C————C—NO₂
NO₂C₉H₁₀—C   C—C₉H₁₀NO₂   **3,4 - Dinitro - 2,5-**
            \O/
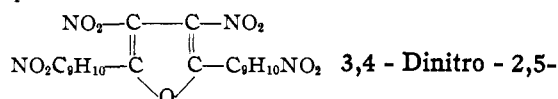
di - (nitromesityl) - furan, XXXII.—This tetranitro derivative was made by nitration of dimesityldinitrofuran, XXIX, using a stronger nitric–acetic acid mixture. The symmetrical structure, XXXII, has been assigned because the only alternative would be one in which at least one of the mesityl nuclei carried two nitro groups, an unlikely possibility. Further substitution of nitro groups was not accomplished, and phosphorus pentabromide at 100° was without action on the compound.
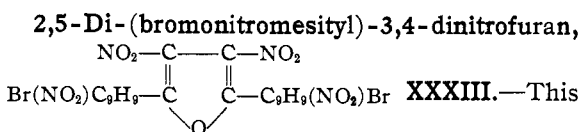
A suspension of 0.15 g. of dimesityldinitrofuran, XXIX, in 4 cc. of a 1–1 (by vol.) mixture of concd. nitric and acetic acids, was refluxed for five minutes and diluted with water, the product crystallizing. Recrystallizing from ethyl acetate gave 0.1 g. of nearly pure product; m. p. 266–267°.

Anal. Calcd. for $C_{22}H_{20}O_9N_4$: N, 11.56. Found: N, 11.8.

Nitration of 2,5-Di-(bromomesityl)-furan and the 3-Nitro Derivative.—When the furans, XIII and XXXI, were treated with a 1–1 mixture (by vol.) of fuming nitric and concd. acetic acids at 90–94° for five minutes, a product was obtained which crystallized from isopropanol or concd. acetic acid as long rectangular plates of m. p. 287–288°. It gave no mixture melting point depression with XXXIII of m. p. 251–252°. But in view of the analysis and this difference in melting point, there is little doubt of non-identity with XXXIII.

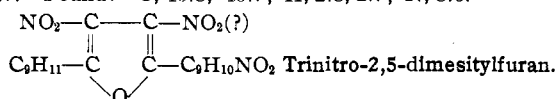*Anal.* Calcd. for $C_{22}H_{17}O_{11}N_5Br_2$: C, 38.45; H, 2.5. Found: C, 38.7, 38.14; H, 3.1, 3.14.

2,5-Di-(bromonitromesityl)-3,4-dinitrofuran,

$$\underset{\underset{\text{Br}(NO_2)C_9H_9-C}{\big\|}}{\overset{\overset{\text{NO}_2-C}{\big\|}}{}}\underset{\underset{C-C_9H_9(NO_2)Br}{}}{\overset{C-NO_2}{}}$$

XXXIII.—This furan could not be made by bromination of the tetranitro compound, XXXII; but it was obtained through a different order of introducing the groups, namely, by nitration of dinitro-di-(bromomesityl)-furan (XXX) with a 1–1 fuming nitric-concd. acetic acid mixture, as follows:

A solution of 0.3 g. of di-(bromomesityl)-dinitrofuran, XXX, in 6 cc. of a 1–1 (by vol.) mixture of fuming nitric and concd. acetic acids was allowed to stand for thirty minutes at 90°. On cooling 0.18 g. of nearly pure material separated. From the filtrate 0.23 g. of partly reacted material was obtained, which was nitrated again by the same procedure, giving 0.17 g. of product. It crystallized from concd. acetic acid as colorless rhombic plates which melted with decomposition at 245° (at 251–252° in an evacuated tube).

Anal. Calcd. for $C_{22}H_{18}O_9N_4Br_2$: C, 41.1; H, 2.8; N, 8.7. Found: C, 40.8, 40.7; H, 2.8, 2.7; N, 8.6.

$$\underset{\underset{C_9H_{11}-C}{\big\|}}{\overset{\overset{\text{NO}_2-C}{\big\|}}{}}\underset{\underset{C-C_9H_{10}NO_2}{}}{\overset{C-NO_2(?)}{}}$$
Trinitro-2,5-dimesitylfuran.

—A suspension of 0.3 g. of dimesitylfuran (XIV) was allowed to stand in 8 cc. of a 1–1 (by vol.) mixture of concd. nitric and acetic acids at room temperature until a thick paste formed. The mixture was then refluxed for three minutes and diluted with water. The amorphous product on standing overnight in ethanol became crystalline and was recrystallized from ethanol; tapered needles of m. p. 158–160°.

Anal. Calcd. for $C_{22}H_{21}O_7N_3$: C, 60.1; H, 4.8. Found: C, 60.3; H, 4.95.

After standing for several days the first filtrate deposited 0.03 g. of nitromesityl carboxylic acid which was identified by mixture melting point with a sample prepared by nitration of mesityl carboxylic acid.

cis - 2,3 - Dimethyl - 1,4 - diphenyl - 2 - butenedione - 1,4 (*cis*-Dibenzoyldimethylethylene), III.—A suspension of dimethyldiphenylfuran (II) in 4 cc. of propionic acid was made by dissolving the furan in the hot solvent and chilling to obtain fine crystals free from lumps; this mixture was maintained at −10° and treated with 0.2 cc. of concd. nitric acid in 0.6 cc. of propionic acid, also at −10°. The crystals dissolved quickly. On standing for fifteen minutes at −10° and diluting with water, the diketone, III, separated crystalline in practically quantitative yield. It crystallized from isopropanol or acetic acid–water mixtures as slender needles melting at 86.5–87°.

Anal. Calcd. for $C_{18}H_{16}O_2$: C, 81.8; H, 6.1. Found: C, 81.4; H, 5.8.

The structure of this compound was demonstrated by reduction with zinc dust and concd. acetic acid (boiling one minute) followed by treatment of the filtrate directly with acetic anhydride and a trace of concd. sulfuric acid to give the furan, II, in 90% yield.

3,4 - Dibromo - 2,5 - di - (4 - bromophenyl) - furan, XIX.—Catalytic reduction of 0.4 g. with 0.5 g. of palladium on barium sulfate in ethanol was complete in three hours. 4 molecules of hydrogen being absorbed; 0.16 g. of diphenylfuran, XX, was isolated, purified and identified.

Summary

1. In a study of five suitably substituted compounds, no evidence of diastereoisomerism due to restricted rotation on the internuclear 2,5-dimesitylfuran bonds has been found.

2. 2,5-Dimesityl groups prevent the oxidative fission of the furan nucleus by nitric and acetic acids, a reaction which is shown to be general for furans with 2,5-diaryl groups carrying no ortho substituents. The bearing of these results on the mechanism of furan reactions is considered.

3. The reactions involved in the synthesis and proof of structure of the various substituted 2,5-dimesitylfurans are described and discussed.

4. Catalytic hydrogen eliminates the bromines from the mesityl nuclei of four substituted 2,5-dimesitylfurans, but is without effect on bromines substituted in the β-positions. In the case of 2,5-di-(p-bromophenyl)-3,4-dibromofuran all four bromines are eliminated by catalytic reduction.

5. Some new halogeno saturated 1,4-diketones of the dimesityl series are described, and the relative ease of elimination of halogen acid is considered.

6. 3,4-Dibromo-2,5-dimesitylfuran is nitrated stepwise in the mesityl nuclei.

7. 2,5-Di-(bromomesityl)-3-nitro- and -3,4-dinitrofurans have been prepared by stepwise nitration and bromination of dimesitylfuran. Evidence for the structures is discussed.

8. Disubstitution in the 2,5-dimesityl groups was accomplished only in the nitration of 2,5-di-(bromomesityl)-3,4-dinitrofuran to the di-(bromonitromesityl) derivative.