In the series of compounds $RCOCH_2COCH_3$ (R equals *n*-butyl, *i*-butyl, *s*-butyl or *t*-butyl) the effect of branching was to lower greatly the cleavage at the branched end of the molecule, but also to affect the cleavage at the acetyl bond slightly. Thus is demonstrated the weak retarding effect of groups exhibiting +I effects on carbon 3 (Table I of earlier paper).

The dibenzylacetyltrimethylacetylmethane was only very slightly cleaved in glass apparatus. This is in accord with the lack of appreciable cleavage of the unenolized form in the high temperature cleavage without addition of the catalyst. However, the diketone was readily cleaved in the presence of traces of catalyst.

Summary

The relation of the structure of a number of unsymmetrical 1,3-diketones to the proportion of cleavage products under a variety of conditions has been studied. The results have been tabulated and summarized above. A number of these experimental observations have been correlated with the I and T effects of the substituent groups and the mechanism outlined in an earlier paper.

MADISON, WISCONSIN RECEIVED AUGUST 11, 1934

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA, NO. 143]

The 2,3,5-Triphenylfurans and the Related Saturated and Unsaturated 1,4-Diketones

BY ROBERT E. LUTZ, W. R. TYSON,[1] AGNES G. SANDERS AND C. K. FINK

This paper deals with some further studies on the reactions between phosphorus pentahalides and saturated and unsaturated 1,4-diketones and related furans, and on the nitric–acetic acid oxidation of the furans to unsaturated 1,4-diketones.[2]

Dibenzoylphenylethylene (I), dibenzoylphenylethane V, 2,3,5-triphenylfuran III, and 2,3,5-triphenyl-4-acetoxyfuran II, react readily with phosphorus pentachloride to give in each case the known 2,3,5-triphenyl-4-chlorofuran IV[3] which is prepared also by the action of alcoholic hydrogen chloride[3] or acetyl chloride and sulfuric acid on dibenzoylphenylethylene. Phosphorus pentabromide reacts similarly with all of these compounds (excepting dibenzoylphenylethane) yielding however 2,5-di-(*p*-bromophenyl)-3-phenyl-4-bromofuran VI, a substance which is identical with that prepared by Japp and Klingemann by the direct bromination of dibenzoylphenylethylene.[3] In these reactions both of the α- (but not the β-) phenyl groups are brominated in the para positions. The greater reactivity of the α-phenyl groups as compared with the β-phenyls is doubtless due to the influence of the adjacent furan oxygen.

Phosphorus pentabromide reacts with 2,3,5-triphenylfuran III, when the temperature is controlled, brominating only the unoccupied β-position of the furan nucleus to give 2,3,5-triphenyl-4-bromofuran VII (known);[3,4] the latter compound (VII) is brominated further in a second stage under more drastic conditions, giving the 2,5-di-(*p*-bromophenyl) derivative VI. These facts show that the furan nucleus in triphenylfuran III is considerably more reactive than any of the phenyl groups; this is consistent with the so-called superaromatic character of the furan nucleus.[5] These relationships are outlined in diagram 1.

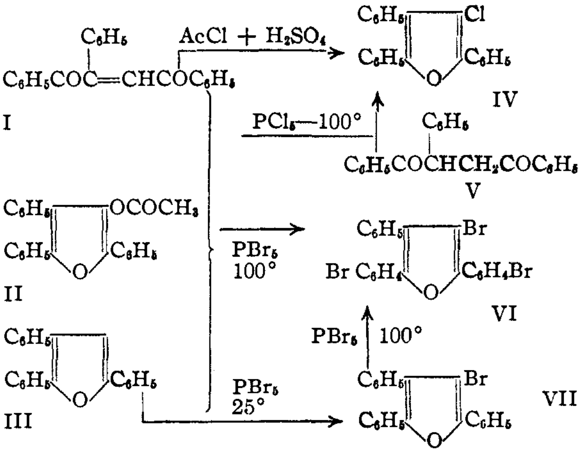

DIAGRAM 1.

The oxidation of triphenylfuran III by the nitric–acetic acid method is described by Japp

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[1] The larger part of this work was presented by Mr. W. R. Tyson in a thesis for a Master's Degree, University of Virginia, 1933.

[2] *Cf.* Lutz and Wilder, THIS JOURNAL, **56**, (a) 2145, (b) 978 (1934).

[3] Japp and Klingemann, *J. Chem. Soc.*, **57**, 674 (1890).

[4] Allen, THIS JOURNAL, **49**, 2110 (1927); **51**, 3591 (1929).

[5] Gilman and Calloway, *ibid.*, **55**, 4197 (1933).

and Klingemann as giving a mononitro derivative of dibenzoylphenylethylene.[3] We have found that under controlled conditions *cis* dibenzoylphenylethylene (I) may be obtained exclusively and that this undergoes nitration to the mononitro derivative in a second stage under more drastic conditions (diagram 2). In view of these circumstances it is very unlikely that the nitration has taken place in one of the phenyl groups. The nitro group is eliminated during reduction with zinc and glacial acetic acid with the formation of dibenzoylphenylethane V; this result would be expected if the nitro group were on the ethylene linkage.[6] The nitro derivative has therefore been assigned the structure VIII (the configuration is uncertain).

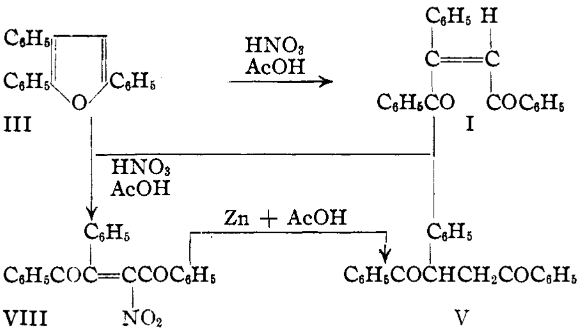
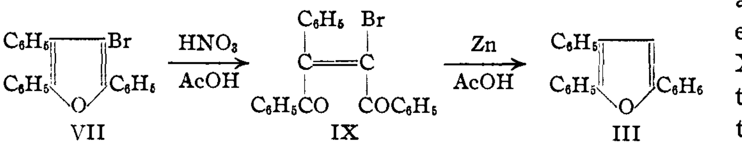


DIAGRAM 2.

Dibenzoylphenylethane V when treated with the nitric–acetic acid reagent is oxidized to dibenzoylphenylnitroethylene VIII, a reaction which very probably proceeds through a primary dehydration to the furan III with subsequent oxidation and nitration.



The oxidation of triphenylbromofuran VII by the nitric–acetic acid method gives dibenzoylphenylbromoethylene IX to which is assigned the *cis* configuration on the basis of the method of synthesis (*cf.* Ref. 2b); the reduction of this with zinc and acetic acid gives largely triphenylfuran. In this reduction, the bromine must be eliminated before the closure of the furan ring because otherwise the bromofuran VII would have been obtained since it is stable under the conditions involved.

Analogous results were obtained in the di-(*p*-bromophenyl) series as is indicated in diagram 3. Di-(*p*-bromobenzoyl)-phenylethane XI (prepared from di-(bromobenzoyl)-ethylene X by the Grignard reaction)[7] gives the corresponding furan XIII upon dehydration with acetic anhydride and sulfuric acid, and reacts with phosphorus pentabromide to give the bromofuran VI. The latter is obtained also by the action of phosphorus pentabromide on dibenzoylphenylethylene and -ethane (I and V). Both furans XIII and VI are oxidized by the nitric–acetic acid method to the corresponding unsaturated 1,4-diketones XII and XIV. The latter are assigned *cis* configurations on the basis of the mode of formation (*cf.* Ref. 2b).

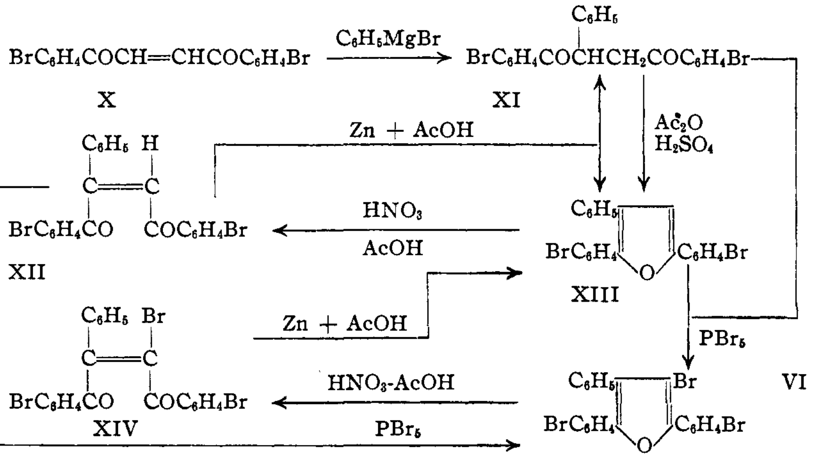


DIAGRAM 3.

Di-(bromobenzoyl)-phenylethylene XII is easily reduced with zinc and glacial acetic acid to a mixture of di-(bromobenzoyl)-phenylethane XI and the furan XIII; since XI is stable under the reducing conditions this is a typical case of 1,6 addition.[8] The di-(bromobenzoyl)-phenylbromoethylene XIV, however, under these conditions gives exclusively the furan XIII. According to the recently postulated mechanism of reduction of α-halogeno ketones of the latter type[6b] involving 1,4-reduction of the system

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(6) *Cf.* the reductive elimination of halogen, hydroxyl, alkoxyl and amino groups during reduction of substituted unsaturated 1,4-diketones (a) Conant and Lutz, THIS JOURNAL, **47**, 881 (1925); (b) Lutz and Wilder, *ibid.*, **56**, 2065 (1934).

(7) Lutz and Tyson, *ibid.*, **56**, 1341 (1934).

(8) Lutz, *ibid.*, **51**, 3008 (1929).

Br—C—C=O, di-(bromobenzoyl)-phenylethylene should be an intermediate product, and both of these reductions should therefore have led to the same result. The discrepancy has been accounted for in the catalytic effect of the zinc bromide produced during the reduction of the bromo compound XIV[9] which favors the formation of the furan during reduction; this result therefore does not invalidate the type of mechanism proposed.

The structure of the 2,5-di-(bromophenyl)-3-phenyl-4-bromofuran VI follows from the transformations outlined in diagram 3. The α-(*p*-bromophenyl) groups are shown by permanganate oxidation which gives two equivalents of *p*-bromobenzoic acid, and by the synthesis of the furan from di-(bromobenzoyl)-ethylene X. The position of the third bromine in the β-position of the furan nucleus is certain from the analogy between the various modes of introduction of halogen in this and in the diphenyl- and di-(bromophenyl)-furans,[2a] and from the ease of reductive elimination of this halogen from the corresponding unsaturated 1,4-diketone XIV obtained from it by oxidation (*cf.* Ref. 6b).

Experimental Part

The action of phosphorus pentahalides on various of the saturated and unsaturated 1,4-diketones and furans as described in the introduction were carried out according to the following standard procedure: a mixture of 1 part of substance to 3 parts of phosphorus pentachloride (or 5 parts of phosphorus pentabromide) was heated on a water-bath for a short time until the reaction subsided. The mixture was then hydrolyzed with water and the organic residue recrystallized from ethanol and identified by mixed melting points. The phosphorus pentachloride reactions (diagram 1) gave 2,3,5-triphenyl-4-chlorofuran in yields of 60–75%. Phosphorus pentabromide in these reactions gave very low yields of 2,5-di-(*p*-bromophenyl)-3-phenyl-4-bromofuran. Triphenylfuran reacted at 25° with phosphorus pentabromide giving triphenylbromofuran, and di-(*p*-bromobenzoyl)-phenylethylene and 2,5-di-(*p*-bromophenyl)-3-phenyl-4-bromofuran at 60° giving 2,5-di-(*p*-bromophenyl)-3-phenyl-4-bromofuran (diagram 3) in yields of 85 and 92%, respectively.

2,5-Di-(*p*-bromophenyl)-3-phenylfuran, XIII.—To a suspension of 4 g. of 1,2-di-(*p*-bromobenzoyl)-phenylethane in 40 cc. of acetic anhydride was added 12 drops of concd. sulfuric acid (heated for ten minutes at 60°). The product was isolated by hydrolysis with water and crystallization from mixtures of ethanol and butanone; yield 69%; thin hexagonal plates of m. p. 114° (corr.).

Anal. Calcd. for $C_{22}H_{14}OBr_2$: Br, 35.28. Found: 35.05.

2,5-Di-(*p*-bromophenyl)-3-phenyl-4-bromofuran, VI.—Prepared according to Japp and Klingemann;[3] crystallized from benzene as thin hexagonal scales of m. p. 202.5–203.5° (corr.).

Anal. Calcd. for $C_{22}H_{13}OBr_3 + H_2O$: H_2O, 3.21; Br, 43.54. Found: H_2O, 3.31; Br, 43.40, 43.11. Calcd. for $C_{22}H_{13}OBr_3$ (dried in vac. at 120°); Br, 45.02; Found: Br, 45.02.

Oxidation of 5 g. with 10 g. of nitric acid (sp. gr. 1.42), with heating for two hours on a steam-bath, gave 3.26 g. of *p*-bromobenzoic acid; the rest of the material was accounted for as an oil (on subsequent oxidation with permanganate this gave 0.2 g. more of bromobenzoic acid), total yield of bromobenzoic acid 1.89 equivalents.

A New Preparation of *Cis*-1,2-dibenzoylphenylethylene, I.—To a solution of 1 g. of triphenylfuran in 10 cc. of glacial acetic acid (at 50°) was added 1 cc. of a 3–1 mixture of nitric acid (sp. gr. 1.42) and glacial acetic acid. The product was isolated by diluting the solution with water and crystallizing from ethanol; yield 80%.

1,2-Dibenzoyl-1-phenyl-2-nitroethylene, VIII, was prepared by the above nitric–acetic acid reaction from dibenzoylphenyl-ethane or -ethylene using a higher temperature (100°) and a somewhat larger amount of nitric acid (*cf.* Ref. 3). Reduction with zinc dust and glacial acetic acid (boiling for two minutes) gave dibenzoylphenylethane.

***Cis*-1,2-di-(*p*-bromobenzoyl)-phenylethylene, XII,** was prepared from 2,5-di-(*p*-bromophenyl)-3-phenylfuran by the nitric–acetic acid oxidation at 50° (see above); yield 67%; crystallized as tufts of needles from ethanol; m. p. 155° (corr.).

Anal. Calcd. for $C_{22}H_{14}O_2Br_2$; Br, 34.00. Found: Br, 34.21.

Reduction of 0.2 g. in 3 cc. of glacial acetic acid with 1 g. of zinc dust (refluxing for two minutes) and subsequent removal of the zinc by filtration, and dilution with water, gave 0.2 g. of crude product. On dissolving this in acetone 0.02 g. of crystalline deposit was obtained and identified by mixed melting point as di-(bromobenzoyl)-phenylethane. From the filtrate 0.9 g. of pure di-(bromophenyl)-phenylfuran was isolated and identified.

***Cis*-1,2-dibenzoyl-1-phenyl-2-bromoethylene, IX,** was prepared by adding a mixture of 1 part of glacial acetic acid and 3 parts of nitric acid (sp. gr. 1.42) cautiously to a hot solution (90–100°) of 1 part of triphenylbromofuran in 10 parts of glacial acetic acid. The mixture was shaken during the addition (ten minutes) and copious evolution of oxides of nitrogen occurred. The product was then precipitated with water and crystallized from ethanol; yield 60–75%; m. p. 63°.

Anal. Calcd. for $C_{22}H_{15}OBr$: Br, 20.44; C, 67.50; H, 3.84. Found: Br, 20.67; C, 67.44; H, 4.14.

Reduction with zinc and glacial acetic acid at refluxing temperature gave mainly triphenylfuran (the bromofuran in a similar reduction experiment is unchanged under these conditions) and a small amount of dibenzoylphenylethane. The yield of the latter was markedly less than in the case of a parallel reduction of dibenzoylphenylethylene, due apparently to the catalytic effect of the zinc bromide produced during the reduction (*cf.* Ref. 9).

***Cis*-1,2-di-(*p*-bromobenzoyl)-1-phenyl-2-bromoethylene, XIV,** was prepared by the nitric–acetic acid oxidation

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(9) *Cf.* Lutz and Palmer, unpublished results.

method (as above) at 95°; yield 87%; crystallized from acetone as truncated rhombohedra; m. p. 142° (corr.).

Anal. Calcd. for $C_{22}H_{13}O_2Br$: Br, 43.59. Found: Br, 43.55.

Reduction of 1 g. with zinc dust in 15 cc. of glacial acetic acid (refluxed for two minutes) gave 0.7 g. (84%) of di-(bromophenyl)-phenylfuran. Both di-(bromobenzoyl)-phenylethane and di-(bromophenyl)-phenylbromofuran are stable under these conditions in the presence of added zinc bromide in the amount that is formed during a reduction. The residues from this reduction were examined carefully and none of the difficultly soluble and easily crystallized di-(bromobenzoyl)-phenylethane was isolated.

Summary

The triphenyl saturated and unsaturated 1,4-diketones and furans react with phosphorus pentahalides giving halogenated furans; phosphorus pentabromide also brominates the α- (but not the β-) phenyl groups of the furans.

The nitric-acetic acid oxidation of triarylfurans leads to the formation of some new *cis* unsaturated 1,4-diketones which have been studied. Some reductions are described.

UNIVERSITY, VIRGINIA RECEIVED AUGUST 11, 1934

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Vapor Pressure of Certain Ketones

BY M. GLENN MAYBERRY[1] AND JOHN G. ASTON

Several ketones of the methyl, isopropyl and the first two members of the cyclohexyl series have been prepared in rather large quantities for other work. Since it was thus possible to obtain pure samples, it was decided to determine the vapor pressures of these ketones, acetone being the only ketone whose vapor pressure curve has been studied.

Experimental

Preparation and Purification of the Ketones.—Methyl ethyl ketone was purified by drying over sodium sulfate and fractionating through an insulated column 46 × 1.5 cm. packed with glass rings.[2] The fraction boiling 78–78.2° was again dried over sodium sulfate and redistilled. For the vapor pressure determination, a 15-cc. portion was collected from the middle of a 100-cc. fraction boiling 78.1° at 728 mm.

Methyl isopropyl ketone was prepared from tertiary amyl alcohol and bromine.[3] The other ketones of the methyl series were prepared through the acetoacetic ester synthesis.[4] These ketones were distilled through a column 25 × 0.8 cm. packed with glass helices.[5]

The ketones of the isopropyl and cyclohexyl series were prepared from the corresponding alcohols by the oxidation method of Faworsky.[6] These ketones were distilled through a column 76 × 1.5 cm.[2]. The diisopropyl ketone was furnished by T. S. Oakwood of this Laboratory.

The boiling point ranges of the ketones used were as follows: methyl ethyl ketone, 78.1° (728 mm.); methyl isopropyl ketone, 92.5–92.8° (727 mm.); methyl propyl ketone, 100.8–101° (726 mm.); methyl isobutyl ketone, 113.4–114° (727 mm.); methyl butyl ketone, 124.5–124.8° (727 mm.); ethyl isopropyl ketone, 112.5–113.2° (734.4 mm.); diisopropyl ketone, 123–124.5° (740 mm.); propyl isopropyl ketone, 132–132.6° (725 mm.); isobutyl isopropyl ketone, 142.5–143.2° (728 mm.); butyl isopropyl ketone, 154.2–154.4° (736 mm.); methyl cyclohexyl ketone, 61.2–61.5° (11 mm.); ethyl cyclohexyl ketone, 75.2–75.7 (11 mm.).

Vapor Pressure Measurements.—The vapor pressures of the ketones of the isopropyl and cyclohexyl series were determined by comparing their boiling points with those of water at the same pressure, using two Cottrell boiling point units in the way described by Woodburn and Whitmore of this Laboratory.[7] The corresponding pressures were then obtained from a table of vapor pressures for water.[8]

The vapor pressures of diisopropyl ketone and the ketones of the methyl series were determined directly by the method of Ramsay and Young.[9] The liquid whose vapor pressure was to be measured was placed in a Cottrell boiling point apparatus which was connected directly to a U-type manometer, the inside diameter of which was 1 cm. The pressure at which the liquid boiled was determined by comparison of the mercury levels with a meter stick, using a cathetometer accurate to 0.05 mm. The cathetometer was placed in such a position that both arms of the manometer and the meter stick were in focus at the same setting of the cathetometer telescope. The meter stick was calibrated to 0.05 mm. by comparison with a standard meter (Bureau of Standards). The system was usually evacuated by means of a water pump (in some cases an oil pump was used) and a capillary air leak used to adjust the pressure. A 5-liter flask was also placed in the system to maintain constant pressure, as the system was entirely closed off from the pump and air leak, before a reading was taken. It was thus possible to get readings with the pressure varying less than 0.1 mm.

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(1) Submitted in partial fulfilment of the requirements for the Ph.D. degree.

(2) Whitmore and Lux, THIS JOURNAL, **54**, 3448 (1932).

(3) "Organic Syntheses," 1933, Vol. XIII, p. 68.

(4) "Organic Syntheses," 1927, Vol. VII, p. 36.

(5) Wilson, Parker and Laughlin, THIS JOURNAL, **55**, 2795 (1933).

(6) Faworsky, *J. prakt. Chem.*, **88**, 641 (1913).

(7) Woodburn and Whitmore, not yet published.

(8) Landolt-Börnstein-Roth-Scheel, "Physikalisch-chemische Tabellen," 1923, Julius Springer, Berlin, p. 1317.

(9) Ramsay and Young, *J. Chem. Soc.*, **47**, 42 (1885).