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Furan–Unsaturated 1,4-Diketone Interconversions. Reactions with Phosphorus Chlorides and Halogen. *cis*-Reductive-furanization[1]

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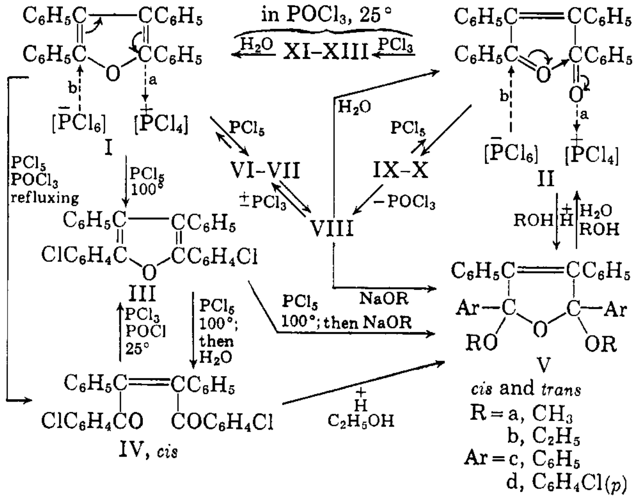
Phosphorus pentachloride oxidizes tetraphenylfuran reversibly, and chlorinatively deoxygenates *cis*- (but not *trans*-) dibenzoylstilbene, to a furan dichloride or a phosphorus pentachloride complex which is converted by water or alkoxide ion into *cis*-dibenzoylstilbene or its stereoisomeric cyclic ketals. Under elevated temperature and conditions maintaining equilibrium amounts of free furan, irreversible *para*-chlorinations of the α-phenyl groups occur. Phosphorus trichloride reductively furanizes *cis*-dibenzoylstilbene but not the *trans* isomer. Chlorine in dry solvent converts tetraphenylfuran without *p*-chlorination into a dichloride which is hydrolyzed to *cis*-dibenzoylstilbene. Chlorine adds to the double bond of *cis*- but not *trans*-dibenzoylstilbene. Bromine in ether containing water or ethanol rapidly oxidizes tetraphenylfuran to *cis*-dibenzoylstilbene or its cyclic ketals. In dry solvents the instability of the bromine–furan complex allows ready α-phenyl *p*-bromination. The scope, steric requirements and mechanism of *cis*-reductive-furanization of unsaturated 1,4-diketones are discussed. Simultaneous reduction and *p*-bromination of 1,2-dimethyldiaroylethylenes by hydrogen bromide in acetic acid has been reinterpreted.

This investigation deals with oxidative and reductive interconversions of *cis* unsaturated 1,4-diketones and furans. Oxidations of substituted furans (*e.g.*, I) to the necessarily *cis* unsaturated 1,4-diketones (*e.g.*, II) have been effected by a wide variety of reagents including nitric and chromic–acetic acid mixtures,[3–8] lead tetraacetate,[9,10] hydrogen peroxide,[11,12] ozone[8,13] photoöxidation,[8,14] halogen,[3,9,15–18] and phosphorus pentahalide.[3,15,19a] The initial step is assumed to be electrophilic α-attack by the reagent (*e.g.*, Ia; *cf.* ref. 12) and formation of a resonance stabilized cation or σ-complex (*e.g.*, VI), with or without reversible formation of unstable polar 2,5 (or 2,3)-adducts (*e.g.*, VII) or bridged counterparts[3,7,17] which, however, may be incidental and unnecessary to progress of the reaction.[5b] Derivatives of 2,5-adducts have been isolated, *e.g.*, 2,5-diacetoxy-, dimethoxy- and dipiperidyldihydrofurans[9,11,18,19]; and the bridged complexes are related to Diels–Alder adducts[20] and to the one known peroxide.[8]

The counterpart of the furan oxidations is the reduction of unsaturated 1,4-diketones with accompanying or subsequent furanization (*cf.* ref. 12). In certain cases furanization seems to be a necessary part of the reduction process and dependent on an initial *cis* configuration of the unsaturated diketone, with *cis*-carbonyl group interaction (*cf.* II) evidently playing an essential role in the mechanism.[21–23] For these cases the specific hyphenated term "*cis*-reductive-furanization" is suggested. In the same vein those specific additions and accompanying furanizations of unsaturated 1,4-diketones which are dependent on initial *cis* configuration and in which an activating *cis* group effect seems to be operating,[26,27] will be designated by the analogous hyphenated term "*cis*-addition-furanization."



Phosphorus Pentachloride Reactions.[3]—Tetraphenylfuran (I) upon treatment with refluxing phosphorus oxychloride–pentachloride mixture, evaporation and quenching with water or ethanolic sodium ethoxide, gave, respectively, *cis*-di-*p*-chlorobenzoylstilbene (IV)[6] or a mixture of its cyclic diethyl ketals Vd.[28,29] The

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[2] Philip Francis du Pont Fellowships, 1959, 1960.

[3] W. J. Welstead, Jr., Ph.D. Dissertation, University of Virginia, June, 1961.

[4] R. E. Lutz and F. N. Wilder, *J. Am. Chem. Soc.*, **56**, 978 (1934).

[5] (a) R. E. Lutz and W. P. Boyer, *ibid.*, **63**, 3189 (1941). (b) The fact that 2-*p*-bromophenyl-5-mesitylfuran but not 2,5-dimesitylfuran undergoes ready nitric acid oxidative cleavage to the *cis* unsaturated 1,4-diketone supports the view that 2,5-adducts are not necessary intermediates in furan oxidations.

[6] N. Zinin, *Ber.*, **4**, 973 (1871).

[7] R. G. Bass, Ph.D. Dissertation, University of Virginia, June, 1961.

[8] R. E. Lutz, W. J. Welstead, Jr., R. G. Bass and J. I. Dale, *J. Org. Chem.*, **27**, 1111 (1962).

[9] N. Elming and N. Clausen-Kaas, *Acta Chem. Scand.*, **6**, 535 (1952).

[10] C.-K. Dien and R. E. Lutz, *J. Org. Chem.*, **22**, 55 (1957).

[11] N. Clausen-Kaas and J. Fakstorp, *Acta Chem. Scand.*, **1**, 216 (1947).

[12] R. E. Lutz and C.-K. Dien, *J. Org. Chem.*, **23**, 1861 (1958).

[13] P. S. Bailey and H. O. Colomb, *J. Am. Chem. Soc.*, **79**, 4238 (1957).

[14] H. H. Wasserman and A. Liberles, *ibid.*, **82**, 2086 (1960).

[15] (a) R. E. Lutz and F. N. Wilder, *ibid.*, **56**, 2145 (1934); (b) R. E. Lutz, W. R. Tyson, A. J. Sanders and C. K. Fink, *ibid.*, **56**, 2679 (1934); (c) R. E. Lutz and W. M. Eisner, *ibid.*, **56**, 2698 (1934); (d) R. E. Lutz, F. N. Wilder and W. C. Conner, *ibid.*, **56**, 2145 (1934) [*cf.* also, (e) R. E. Lutz, A. H. Stuart, F. N. Wilder and W. C. Connor, *ibid.*, **59**, 2314 (1937)].

[16] Z. Zinin, *Ber.*, **5**, 1105 (1872).

[17] R. E. Lutz, R. G. Bass, W. J. Welstead, Jr., and C. L. Dickerson, a paper presented at the Southeast Regional A.C.S. Meeting, Richmond, Va., November, 1959; Abstr.: *The Bulletin*, Va. Section, A.C.S., **36**, 203 (1959).

[18] N. Clausen-Kaas, T. Limbory and J. Fakstorp, *Acta Chem. Scand.*, **2**, 109 (1948).

[19] (a) R. E. Lutz and M. G. Reese, *J. Am. Chem. Soc.*, **81**, 3397 (1959); (b) W. Madelung and M. E. Oberwegner, *Ann.*, **490**, 201 (1931): this reference had been missed in ref. 19a.

[20] A. P. Dunlop and F. N. Peters, "The Furans," A.C.S. Monograph Series, Reinhold Publ. Corp., New York, N. Y., 1953, p. 54.

[21] R. E. Lutz, *J. Am. Chem. Soc.*, **51**, 3008 (1929).

[22] R. E. Lutz, C. R. Bauer, R. G. Lutz and J. S. Gillespie, *J. Org. Chem.*, **20**, 218 (1955).

[23] (a) Phosphorus tribromide reduces *cis*-dibenzoylstilbene types: (b) C. F. Wilcox, Jr., and M. R. Stevens, *J. Am. Chem. Soc.*, **84**, 1258 (1962); (c) Our manuscript, although written subsequently, presents the background, results and ideas essentially as originally conceived[3,17] and modified,[8,24] and without essential change.[25]

[24] R. E. Lutz and W. J. Welstead, Jr., *J. Org. Chem.*, **27**, 2763 (1962).

[25] The few added experiments here referenced, most of which had been previously planned, were carried out since ref. 23 by D. W. Boykin, Jr.

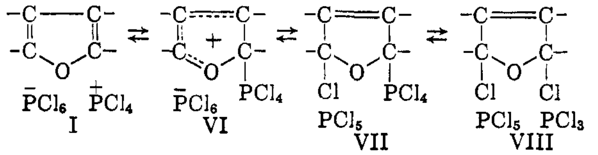
[26] R. E. Lutz and C.-K. Dien, *J. Org. Chem.*, **21**, 1492 (1956), and references cited therein.

[27] R. E. Lutz and M. G. Reese, *J. Am. Chem. Soc.*, **81**, 127 (1959).

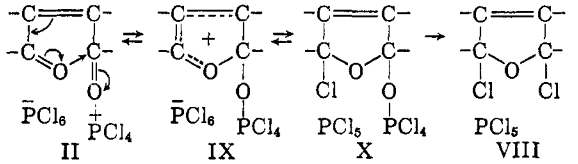
[28] M. G. Reese, Ph.D. Dissertation, University of Virginia, 1957.

[29] Synthesis and proof of structure of this diketone and the location of the 2,5-di-*p*-chlorine atoms are reported in a separate paper; R. E. Lutz, C. L. Dickerson, W. J. Welstead and R. G. Bass, *J. Org. Chem.* **28**, 711 (1963).

function of phosphorus oxychloride simply as a polar solvent was shown by the stability of the furan in refluxing solution, and by the equal effectiveness of benzoyl chloride as the solvent in one typical experiment. When the reaction was run at the lower temperature, 25°, followed by evaporation and then treatment of the products with water or sodium alkoxide, there was produced the chlorine-free *cis*-dibenzoylstilbene (II) or its cyclic ketal stereoisomer mixture Vc, respectively. An independent experiment in which sodium alkoxide, although combining with *cis*-dibenzoylstilbene to give a cyclic anion,[24] does not cause conversion into the cyclic ketals, proves that there must have been formed in the phosphorus pentachloride reactions an intermediate complex or dichloride, *e.g.*, VI–VIII.

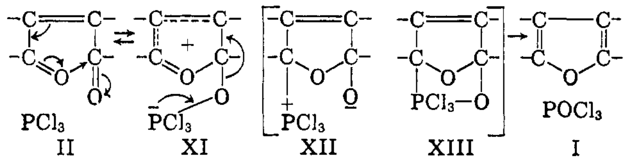


Phosphorus pentachloride in phosphorus oxychloride at 25° converted *cis*- (but not *trans*-) dibenzoylstilbene into a complex which doubtless is the same as the furan–phosphorus pentachloride complex VI–VIII and which reacted with water or alkoxide ion to give *cis*-dibenzoylstilbene or its cyclic ketals V, respectively. Thus chlorinative deoxygenation had occurred, permitted and favored by the *cis* configurational relationship between the two carbonyl groups. This constitutes another case of a reaction which goes with difficulty if at all with the *trans* isomer but which is greatly facilitated by *cis*-carbonyl group interaction and participation. The reaction doubtless proceeds through equilibrations involving IX–X and one irreversible oxygen-abstraction step X → VIII. Only with phosphorus trichloride or some comparable reducing agent can there be reversion from the furan–phosphorus pentachloride complex VI–VIII to the furan I (*cf.* XI–XIII).



trans-Dibenzoylstilbene did not react with phosphorus pentachloride–oxychloride mixture at 25°, but apparently it did so at refluxing; *cis–trans* equilibration did not occur, however, and hydrolysis regenerated *trans*-dibenzoylstilbene.

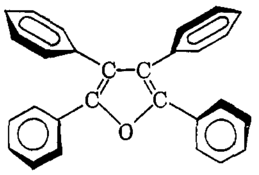
Tetraphenylfuran with phosphorus pentachloride gave quite different results when the solvent phosphorus oxychloride was omitted. At 100–120° it gave chiefly 2,5-di-*p*-chlorotetraphenylfuran (III) and some of the di-*p*-chlorinated unsaturated diketone IV. It would be expected that α-phenyl-*para*-complexes necessary for *p*-chlorinations would not form as easily as furan–α-nuclear complexes such as VI–VIII, and it became obvious that the results were best expressed in terms of reversibility of the furan α-nuclear reactions.



The phosphorus trichloride which is produced in both the furan oxidation step and in the α-phenyl *p*-chlorinations must by its reducing action serve to suppress the unsaturated diketone and thereby maintain large equilibrium quantities of the free furans (I and III). Such a reducing action, illustrated in XI–XIII → I, was demonstrated in independent experiments and is discussed below (*cf.* ref. 23). It may be supposed that in phosphorus oxychloride as solvent, the volatile phosphorus trichloride was lost or was highly diluted so that the equilibrium lay well over on the side of the furan–phosphorus pentachloride complex VI–VIII, thus accounting for the production of the *cis* unsaturated diketone in spite of its known and extraordinarily facile reducibility (*cf.* ref. 22). As a further test of this conclusion the phosphorus pentachloride reaction without solvent at 100° was carried out directly on the di-*p*-chlorotetraphenylfuran (III) and under reduced pressure to minimize the amount of phosphorus trichloride present[25] (the boiling point of phosphorus trichloride is not raised significantly by dissolved phosphorus pentachloride). It gave exclusively the expected oxidation product, *cis*-di-*p*-chlorobenzoylstilbene (IV), which was isolated as the cyclic ketal stereoisomer mixture V.

Wilcox and Stevens came to similar general conclusions in the corresponding phosphorus tri- and pentabromide reactions.[23]

The striking fact that the α-phenyl groups are the unequivocal choice over the β-phenyls for *para* chlorinative substitution is consistent with the generally greater activity of free α-furan positions over β-. Both α- and β-phenyls are in vinyl or dienyl conjugation with the furan oxygen atom which must in some degree affect the phenyl reactivities just as conjugation directly with the ether oxygen atom causes *para*-activation in anisole. The preference for α- over β-phenyl attack must be attributable to more effective resonance stabilization in the intermediate δ-complexes involved. A very important and perhaps overriding factor is the steric suppression of resonance in the conjugated furan–β-phenyl system by the relative noncoplanarity of the sandwiched β-phenyl groups with the furan nucleus as pictured in XIV. The furan–α-phenyl systems should be effectively through-conjugated and normally reactive because of their relatively much closer approach to planarity.



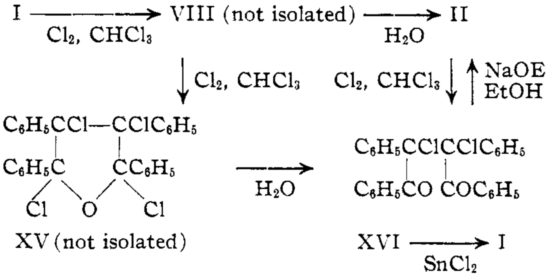
XIV

It is noteworthy that both *p*-chlorination and oxidative ring cleavage of 3,4-dichloro-2,5-diphenylfuran by phosphorus pentachloride, with or without phosphorus oxychloride as solvent, are significantly more difficult than those of tetraphenylfuran as is shown by the considerably higher reaction temperature required and by the failure of the α-phenyl groups to undergo *p*-chlorination.[4] The basis for these effects must be the much stronger electron attraction by 3,4-chlorine atoms than by 3,4-phenyl groups.

In view of the low temperature at which many of the phosphorus pentachloride reactions were carried out and the consequently small extent of dissociation into phosphorus trichloride and chlorine, and because of the evidently significant role of the phosphorus atom as a complexing element, it was deemed important to carry out some experiments on tetraphenylfuran (I) using *free* chlorine.

In chloroform one molecule of chlorine evidently added to the furan nucleus with formation of the 2,5-

dichloride VIII which proved to be very active and eluded isolation; and upon work-up its hydrolysis product *cis*-dibenzoylstilbene (II) was obtained in good yield. When an excess of chlorine was used under otherwise similar conditions the product evidently was the furan tetrachloride XV which, like the dichloride VIII, was very reactive and was not isolated. Upon work-up it underwent partial hydrolysis to a crystalline dichloro compound which was shown by the following facts to be dibenzoylstilbene dichloride (XVI): It had a strong infrared carbonyl band; it could be prepared in another way by direct addition of one molecule of chlorine to *cis*-dibenzoylstilbene; stannous chloride reduced it to tetraphenylfuran, a 4-hydrogen-equivalent process, with elimination of the two chlorine atoms which were thereby shown to be non-aromatic; and refluxing ethanolic sodium ethoxide reductively eliminated the two chlorine atoms but regenerated *cis*-dibenzoylstilbene. The failure of the furan I to undergo *p*-chlorination in the 2,5-phenyl groups is explainable in terms of high speed and essential irreversibility of the formation of the relatively stable furan 2,5-dichloride VIII which lacks the α-phenyl–diene–ether conjugation and has a positive dihydrofuran–nuclear polarity; however, the absence of a complexing agent may be an important factor here.



In contrast to the *cis* isomer, *trans*-dibenzoylstilbene did not react with chlorine in chloroform solution. This constitutes another significant chemical difference between the *cis* and *trans* isomers. It is suggested that the *cis* reaction occurs as a consequence of the quasi-chelation depicted in II which renders one of the ethylenic carbons sterically and electronically more vulnerable than the other toward initiating electrophilic attack by chlorine. This interesting problem is being studied further.

***cis*-Reductive-furanization.**[17]—In accord with the prediction, *cis*-dibenzoylstilbene (II), which is incapable of ordinary addition and furanization, underwent reductive-furanization to the furan I by phosphorus trichloride; this reagent was used as its own solvent at reflux temperature, or it could be used with equal effectiveness in dilute phosphorus oxychloride solution at 25°. The *trans* isomer did not react with phosphorous trichloride under refluxing conditions. A similar relationship held for the 1,2-dichloro-1,2-dibenzoylethylene pair; the *cis* isomer underwent phosphorus trichloride reduction to the furan, but exceedingly slowly, whereas the *trans* isomer was unaffected under the same conditions. Obviously these reductions must involve the same *cis*-carbonyl group proximity effect which operates to facilitate the sodium borohydride, lithium aluminum hydride and aluminum isopropoxide reductions of *cis*- over *trans*-dibenzoylstilbene[22]; but, unlike the hydride reductions, hydride ion transfer cannot be involved here.

The "*cis*-group effect" in this reduction, which is presumed to stem from the quasi-chelation illustrated in II, is potential or real depending on definitions and degrees of bondings involved. It would invite acid or base attack by the reducing agent which may function in the sense of (or with the help of) a Lewis acid or a base. The reduction by phosphorus trichloride may be initiated by one or the other (or both) of the attacks indicated in II $\rightleftarrows$ XI—XIII with formation of a σ-complex such as XI, or XII or a 2,5-bridged adduct XIII; and the reaction may be completed by an essentially irreversible reductive break-up step with abstraction of an oxygen atom by the phosphorus moiety as is suggested in the formulations XI–XIII → I. It will be noted that XI can be regarded as a σ-complex between phosphorus oxychloride and tetraphenylfuran; however, such a complex does not appear to form by direct interaction of the furan with phosphorus oxychloride, and as an intermediate it would presumably be very unstable.[30]

Specific comparative comments on the interesting relationships between the phosphorus trihalide and hydride *cis*-reductive-furanizations is reserved pending reappraisal of the latter type on the basis of further study in progress.

The reduction of a fully substituted unsaturated 1,4-diketone by a thiol[23b] is of interest and doubtless will prove to be a case of true *cis*-reductive-furanization. It can be explained in terms of the above concepts involving cyclic hemithioketal or thioketal complexes related to V (or VI–VIII) which should form under acid catalysis; these should be relatively unstable by virtue of the mild but real reducing effectiveness of the sulfide atom and subject to reductive break-up into the furan with conversion of the sulfide sulfur ultimately into disulfide.

The above preferential and facile reductions of *cis* over *trans* isomers have appeared so far only in the unsaturated 1,4-diketone pairs which carry substituents on both ethylenic carbon atoms, and where both the *cis* and *trans* configurations are stable enough to withstand the experimental conditions. They are brought about by an interesting assortment of reducing agents which are capable in some degree of coördinating in the Lewis acid and base sense; and, in contrast, zinc–acetic acid, sodium hydrosulfite and stannous chloride in acetic acid–hydrochloric acid mixture, under comparable conditions in each case, reduce *both* the *cis* and the *trans* isomers[31] with seemingly comparable though doubtless actually somewhat different ease.

With no ethylenic substituent the *cis* unsaturated diketone configuration is extremely labile, and specific *cis*-group effects such as those described above are not demonstrable; this is the case with stannous chloride reduction of *trans*-dibenzoylethylene (XX) to 2,5-diphenylfuran. A number of mechanisms and step sequences might be written here, including but not requiring the type suggested above for true *cis*-reductive-furanization. Pertinent examples of the related addition-and-furanizations where *cis*-group proximity effects probably are not involved are the phosphorus pentachloride conversion of *trans*-dibenzoylethylene (XX) into the chlorofuran XXIII[15] (discussed below), and the recently reported addition of (rather than reduction by) phosphorus trichloride, with ultimate formation of the 3-furylphosphonic acid.[32]

In the true *cis*-reductive-furanizations several factors of importance evidently stem from the presence of the two necessary ethylenic substituents. By their steric bulk these substituents should (and do) greatly di-

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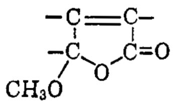
(30) The over-all phosphorus trichloride reaction including the reductive break-up step is in many respects related to the Wittig reaction (*Cf.* S. Trippett, "Advances in Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., Vol. 1, 1960, p. 83). Also it is analogous to the phosphorous trichloride reductive-abstraction of oxygen from pyridine N-oxide.

(31) (a) R. E. Lutz and C. R. Bauer, *J. Am. Chem. Soc.*, **73**, 3456 (1951); (b) J. I. Dale, Ph.D. Dissertation, University of Virginia, 1962.

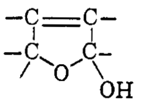
(32) C. E. Griffin and J. T. Brown, *J. Org. Chem.*, **26**, 853 (1961).

minish the competing α,β-unsaturated ketone addition activity which nevertheless does appear under some circumstances (*cf.* ref. 19). These substituents also should seriously disrupt the planarity and effectiveness of the quinone-like conjugated ene–dione system and thereby diminish the readiness of this system to undergo facile conjugate or 1,6-reduction by raising somewhat the energy levels in the acyclic semiquinone-like intermediate stages, an effect which should be much more pronounced in *cis* relative to *trans* isomers. The nevertheless striking *cis*-group facilitation of reductions is explainable in terms of the stabilizing effect of the all-important ethylenic substituents on the various *cyclic* intermediates which would be directly formed *only* from *cis* isomers. This type of steric phenomenon has appeared in a more obvious form and has been extensively studied in other connections. For example, the *cis*-β-aroylacrylic acids and their derivatives carrying two ethylenic substituents, *e.g.*, two methyl groups,[33b] show ring chain tautomerism,[33] and in this series, in contrast to less favorably substituted types, the cyclic forms are strongly favored; and the acid, which is exclusively in the cyclic or γ-hydroxy unsaturated lactone form, is reductively dehydroxylated with very great ease to the unsaturated lactone.[33c]

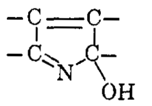
It should be emphasized that the synchronous type mechanism of true *cis*-reductive-furanization at the key reduction step is presumed to involve a resonance and sterically stabilized transition state if there is two-electron transfer, or a semiquinone-like intermediate radical if the reduction is written as two successive one-electron transfers. These reductions are related to the similarly facile reductions of the conjugated systems of oxygenated ring compounds such as XVII[34] and XVIII,[35] and of nitrogen ring analogs such as XIX.[31b,36]



XVII

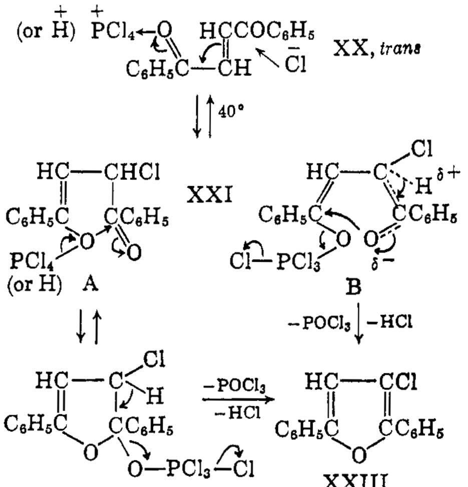


XVIII



XIX

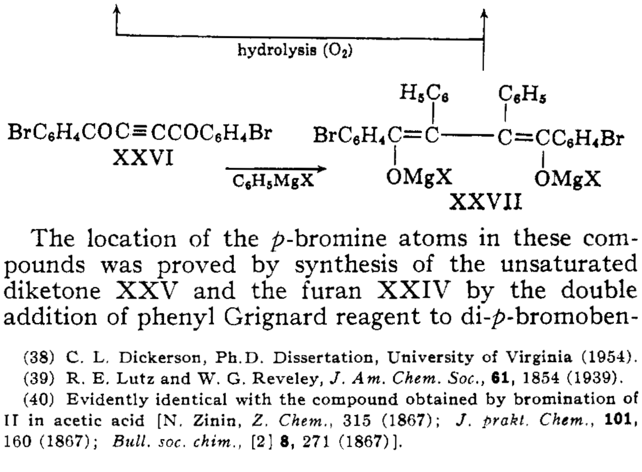
Mechanism of Addition-and-furanization by Phosphorus Pentachloride.—Only unsaturated 1,4-diketones with at least one ethylenic hydrogen can undergo this type of reaction; *e.g.*, phosphorus pentachloride converts *trans*-1,2-dibenzoylethylene (XX) into 3-chloro-2,5-diphenylfuran (XXIII).[15] A true "*cis*-addition-furanization" can hardly be imagined here. Two types of mechanisms might be suggested for the cyclization step following initial 1,4-addition–enolization; (a) ring-chain tautomerism and dehydration *via* XXIA–XXII[27,37a]; and (b), as suggested by Newman and Wood,[37b] attraction of the carbonyl oxygen atom to the α-carbon of the enolate group *via* XXIB.[37c,d] It is hoped that O^{18} tracer studies on suitable examples will show which oxygen atom of unsymmetrically substituted diketones supplies the furan oxygen, and will throw light on mechanistic alternatives.



Action of Bromine on the Furans.—Further study was suggested by the fact that tetraphenylfuran (I), the cyclic ether of a di-enol, is oxidized by bromine with surprising speed to *cis*-dibenzoylstilbene (II).[38] Bromine and iodine have been used to oxidize di-enolates such as XXVII obtained in reductions and phenyl Grignard reactions of unsaturated 1,4-diketones.[39]

Iodine was found to be unreactive toward tetraphenylfuran,[38] even in the presence of water to effect hydrolysis of unstable complexes that might be formed.

An excess of bromine in a mixture of ether and water converted tetraphenylfuran (I) practically quantitatively into *cis*-dibenzoylstilbene (II); and in absolute ether–ethanol mixture it gave *cis*-dibenzoylstilbene diethyl cyclic ketal (Vbc). However, an excess of bromine in *absolute* ether gave a nearly quantitative yield of 2,5-di-*p*-bromotetraphenylfuran (XXIV[40]); and bromine in chloroform gave similar results except that a small yield of the *cis*-unsaturated diketone XXV was obtained also. Bromine in ether–water mixture converted the di-*p*-bromo furan XXIV into the *cis* unsaturated diketone XXV.



The location of the *p*-bromine atoms in these compounds was proved by synthesis of the unsaturated diketone XXV and the furan XXIV by the double addition of phenyl Grignard reagent to di-*p*-bromoben-

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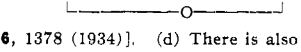
(33) For information and references, see (a) R. E. Lutz and H. Moncure Jr., *J. Org. Chem.*, **26**, 246 (1961); *cf.* also R. E. Lutz and M. Couper, *ibid.*, **6**, (b) 77, (c) 91 (1941).

(34) R. E. Lutz, *J. Am. Chem. Soc.*, **56**, 1378 (1934).

(35) These relationships will be considered in a later paper: R. E. Lutz, C. L. Dickerson and J. I. Dale, manuscript in process.

(36) D. W. Boykin, Jr., M.S. Thesis, University of Virginia, August, 1962; work to be published shortly.

(37) (a) *Cf.* Addition-and-furanization of *cis*- and *trans*-dibenzoylchloroethylenes by hydrogen chloride [R. E. Lutz and F. N. Wilder, *J. Am. Chem. Soc.*, **56**, 1193 (1934)]. (b) M. S. Newman and L. L. Wood, Jr., *ibid.*, **81**, 4300 (1959). (c) XXIB is in some analogy to the facile cyclization in boiling acetic acid of the γ-methoxy-β,γ-unsaturated acid, $CH_3OC(C_6H_4Br)=C(CH_3)CH_2COOH$, to the γ-methoxy-γ-lactone



$$\underbrace{\mathrm{CH_3OC(C_6H_4Br)CH(CH_3)CH_2CO}}_{\mathrm{O}}$$

[R. E. Lutz, *ibid.*, **56**, 1378 (1934)]. (d) There is also the possibility that under these conditions XXI may ketonize to the α-chloro saturated diketone *before* furanization (*cf.* ref. 26).

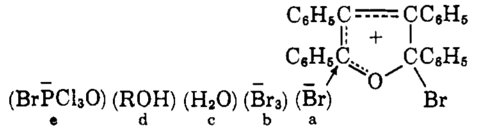
(38) C. L. Dickerson, Ph.D. Dissertation, University of Virginia (1954).

(39) R. E. Lutz and W. G. Reveley, *J. Am. Chem. Soc.*, **61**, 1854 (1939).

(40) Evidently identical with the compound obtained by bromination of II in acetic acid [N. Zinin, *Z. Chem.*, 315 (1867); *J. prakt. Chem.*, **101**, 160 (1867); *Bull. soc. chim.*, [2] **8**, 271 (1867)].

zoylacetylene (XXVI) and hydrolysis of the resulting di-enolate XXVII in the presence of air.[41]

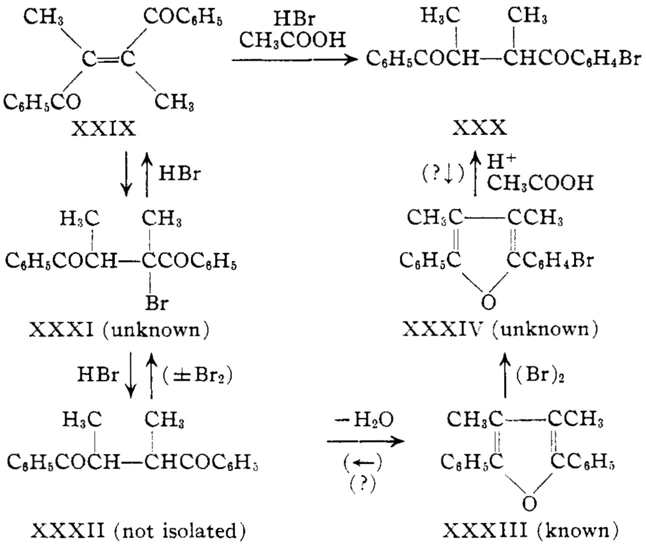
These bromination experiments show that the reaction with tetraphenylfuran (I) in *dry* solvent is primarily one of *para* substitution into the 2,5-phenyl groups, catalyzed perhaps by bromine itself acting as a complexing agent. A reversibly formed and relatively unstable σ-complex XXVIIIa or b or a 2,5-adduct doubtless is formed in small equilibrium amounts much faster than a complex involving an α-phenyl *para* position which would lead irreversibly to substitution, and is solvolyzed rapidly by water or alcohol through XXVIIIc or d to the bromine-free unsaturated diketone II or its cyclic ketals Vc. These results are in contrast to the prompt addition of chlorine in the absence of a complexing agent such as phosphorus pentachloride, without *p*-α-phenyl chlorination, to give a relatively more stable dihalide which, however, in the end is also hydrolyzed to the halogen-free unsaturated diketone II.



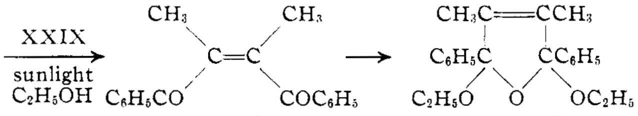
XXVIII

Because phosphorus oxychloride had proved to be an effective solvent for the phosphorus pentachloride reactions, it was employed also in bromination. When 2.3 molecules of bromine were used and the reaction mixture was hydrolyzed, chiefly the 2,5-di-*p*-bromofuran XXIV resulted. However, with 4.6 molecules of bromine the main product was *cis*-di-*p*-bromobenzoylstilbene (XXV) rather than the furan XXIV which had been obtained when dry ether or chloroform had been used as solvent. This suggests that possibly in phosphorus oxychloride a complex does actually build up, one different from and somewhat more stable than XXVIIIa–b and involving phosphorus oxychloride, namely, XXVIIIe, but formed reversibly and thus permitting *para* bromination of free tetraphenylfuran, yet persisting to the point of hydrolysis and accounting for the final over-all oxidative hydrolysis to the unsaturated diketone XXV. However, it is also possible that at the moment of hydrolysis the phosphorus oxychloride, which hydrolyzes slowly in cold water, is serving as a moist solvent like moist ether (above), and that the furan α-complex is formed and hydrolyzed rapidly to the unsaturated diketone.

Reduction and Bromination by Hydrogen Bromide.[42,43]—The foregoing results make possible a reasonable explanation of the partially understood hydrogen bromide–acetic acid reduction-and-bromination of 1,2-dimethyldiaroylethylenes to the *p*-brominated saturated diketones or furans.[43] Of especial interest is the conversion of *trans*-dibenzoyldimethylethylene (XXIX) to its *p*-bromo saturated diketone XXX in poor yield but as the only crystalline product, and the fact that in spite of various attempts to make it, the mono-*p*-bromofuran XXXIV remains unknown whereas the corresponding bromine-free furan XXXIII and its di-*p*-bromo derivative are easily obtainable. These facts suggest that the unsymmetrical substitution has a determinative effect. A reasonable mechanism *via* intermediates XXXI–XXXIV is suggested (although alternatives are possible[44]). The first step is reversible 1,4-addition of hydrogen bromide with formation of the adduct XXXI which in the presence of hydrogen bromide would act reversibly as a brominating agent and go to the saturated diketone XXXII. This diketone would then undergo rapid furanization to XXXIII followed by mono-*p*-bromination giving the mono-*p*-bromofuran XXXIV and thereby utilizing the bromine released in XXXI → XXXII. The suggested alternative mechanism for the *p*-bromination step, namely, 1,6-addition of hydrogen bromide to the benzoyl group itself,[43] (*cf.* also ref. 23b) is rejected because it is unnecessary and because it would involve intermediate disruption of the stable benzoyl group conjugation. The final step is the surprising but quite conceivably prompt hydrolysis of the mono-*p*-bromo furan XXXIV to the actually-isolated *p*-bromo saturated diketone XXX which *in that form* would not be susceptible to the second *para* bromination. This hydrolysis is attributable to β-methyl group activation of the furan nucleus toward proton catalysis and to dissymmetric activation of the furan nucleus by electron attraction of the lone *p*-bromine atom which would particularly affect the corresponding α-furan position; and it supposes hydrolysis in the symmetrical 2,5-diphenyl-3,4-dimethylfuran (XXXIII) and its 2,5-di-*p*-bromo derivative to be suppressed by the balanced opposition of electronic effects at the two α,α'-positions.



Interestingly to this subject, a structure can now be assigned to the unidentified compound of m.p. 103°[42] obtained by the action of sunlight on an absolute ethanol solution of *trans*-dimethyldibenzoylethylene (XXIX). This compound from analysis and analogy[19] obviously must be the cyclic diethyl ketal XXXVI of the as yet unknown *cis*-dimethyldibenzoylethylene (XXXV).



XXXV (not isolated) XXXVI

Elaboration on these questions will await the outcome of an experimental review and extension of the work in this field.

Experimental[45]

Action of Phosphorus Pentachloride on Tetraphenylfuran (I).[6] (**A**).—A mixture of 3.0 g. of the furan I and 6.0 g. of phosphorus pentachloride upon heating for 15 min. at 100°, cooling and hydrolyzing in ice-water, gave 1.4 g. (40%) of 2,5-di-*p*-chloro-

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[41] This subject is treated in detail in a separate paper (see ref. 29).

[42] R. E. Lutz and R. J. Taylor, *J. Am. Chem. Soc.*, **55**, 1599 (1933).

[43] M. Couper and R. E. Lutz, *J. Org. Chem.*, **7**, 79 (1942).

[44] *E.g.*, acid-catalyzed cyclization of XXXI followed by loss of a bromonium moiety, and intermediation of a cyclic bromohemiketal (3,4-dimethyl-2,5-diphenyl-2-hydroxy-4,5-dibromotetrahydrofuran).

[45] All melting points are "corrected"; infrared absorption spectra: Perkin-Elmer Infracord, using KBr pellet; ultraviolet absorption spectra: Perkin-Elmer Spectracord 4000A; 5 × 10^{-5} *M* absolute ethanol solution.

tetraphenylfuran (III); recrystallized from glacial acetic acid, m.p. 168.5–170° (lit.[6] 169°); structure proved by identity with a sample prepared by the action of phenyl Grignard reagent on di-*p*-chlorobenzoylacetylene.[29]

(**B**).—A mixture of 1.0 g. of I, 2.0 g. of phosphorus pentachloride and 30 ml. of phosphorus oxychloride, after 30 min. at room temperature (shaking to dissolve), was evaporated under reduced pressure and hydrolyzed with ice-water. Crystallization of the solid product from glacial acetic acid gave 0.95 g. (91%) of *cis*-dibenzoylstilbene (II); identified by mixture m.p. and infrared spectra.

(**C**).—A similar mixture (using 2.0 g. of I) was treated as in (B). After evaporation of the phosphorus oxychloride the product was extracted with five 30-ml. portions of petroleum hexane. This solution was poured into 75 ml. of absolute methanol containing 5 g. of dissolved sodium. Upon dilution with water, extraction with ether, evaporation, and fractionally crystallizing the residue from a methanol–benzene mixture, the two stereoisomeric cyclic ketals Vac were obtained; the higher-melting (169–171°), 1.4 g. (60%); the lower-melting (137–139°), 0.2 g. (9%).

(**D**).—A mixture of 0.5 g. of I, 1 g. of phosphorus pentachloride and 25 ml. of benzoyl chloride was shaken for 30 min. at room temperature and the resulting solution was poured into aqueous ammonia. The resulting solid upon crystallization from glacial acetic acid was identified as the unsaturated diketone II (0.4 g., 80%).

(**E**).—A mixture of 1.0 g. of I, 2 g. of phosphorus pentachloride and 30 ml. of carbon tetrachloride was shaken for 30 min. at room temperature, evaporated, and hydrolyzed; the furan I was recovered and identified.

(**F**).[28]—A mixture of 1.0 g. of I, 10 g. of phosphorus pentachloride and 20 ml. of phosphorus oxychloride was refluxed for 15 min. and evaporated to dryness under reduced pressure. The residue was extracted with 50 ml. of dry benzene and the extract was treated with 50 ml. of absolute ethanol (refluxing for 30 min.). Evaporation, solution of the residue in ether, drying over sodium sulfate, again evaporating, then crystallization from petroleum hexane, gave a crystalline product which was fractionally recrystallized from absolute ethanol. The two stereoisomeric cyclic diethyl ketals (Vbd) were obtained; the higher-melting (210–213°), 0.18 g. (15%); the lower-melting (176–178.5°), 0.3 g. (26%).[28]

Action of Chlorine on Tetraphenylfuran (I).—A solution of 0.10 g. (0.0014 mole) of chlorine and 0.5 g. (0.0013 mole) of I in 25 ml. of chloroform was allowed to stand for 30 min. (moisture excluded only up to this point), and it was then evaporated under reduced pressure. Treatment of the residue with warm petroleum hexane and cooling gave 0.5 g. (98%) of *cis*-dibenzoylstilbene (II, identified).

Action of Iodine on Tetraphenylfuran (I).—Subjection of I to a large excess of iodine in an ether–water mixture (shaking for 15 min.) was without effect; compound I was recovered quantitatively unchanged.

cis-**Dibenzoylstilbene** (II). (**A**).—After refluxing a solution of 0.5 g. of II in 25 ml. of methanol containing 0.3 g. of dissolved sodium, simulating conditions of formation of Vac from the furan I, II was recovered practically quantitatively.

(**B**).—A mixture of 1.0 g. of II, 2 g. of phosphorus pentachloride and 15 ml. of phosphorus oxychloride was shaken periodically at room temperature for 30 min., and was evaporated under reduced pressure. A petroleum hexane extract of the residue was added to 100 ml. of absolute ethanol containing 2.5 g. of dissolved sodium. After evaporation to small volume and pouring into water the resulting solid was fractionally recrystallized from absolute ethanol. The products were the stereoisomeric cyclic diethyl ketals Vbc; the higher-melting isomer, 0.1 g. (10%) (identified by mixture m.p. with an authentic sample[19]); the lower melting isomer (see below), 0.5 g. (5%).

2,5-Dimethoxy-2,3,4,5-tetraphenyldihydrofuran (the cyclic dimethyl ketals Vac): crystallizations were from methanol–benzene mixture; **higher melting isomer**, m.p. 169–171° (lit.[19b] 164°); absorption maxima: 3.5 μ (OCH_3); none at *ca.* 6.0 μ; 259 mμ, ε 15,600. *Anal.* Calcd. for $C_{30}H_{26}O_3$: C, 82.92; H, 6.03. Found: C, 82.54; H, 6.03.

Lower-melting isomer, m.p. 137–139°; absorption maxima: 3.5 μ (OCH_3); none at *ca.* 6.0 μ; 252 mμ, ε 12,000. *Anal.* Calcd. for $C_{30}H_{26}O_3$: C, 82.92; H, 6.03. Found: C, 82.83; H, 6.11.

2,5-Diethoxy-2,3,4,5-tetraphenyldihydrofuran (the cyclic diethyl ketals): **higher melting isomer**, m.p. 156.5–157.5° (see ref. 19); **lower-melting isomer**, crystallized from absolute ethanol, m.p. 153–155°; absorption maxima: 3.5 μ (CH_3 of OC_2H_5); none at *ca.* 6 μ; 252.5 mμ, ε 13,800. *Anal.* Calcd. for $C_{32}H_{30}O_3$: C, 83.08; H, 6.54. Found: C, 83.17; H, 6.56.

Dibenzoylstilbene Dichloride (**XVI**).—The furan I (0.5 g.) and *cis*-dibenzoylstilbene (II) (1.0 g.) were treated with two and one equivalents, respectively, of chlorine in 20 and 40 ml. of chloroform (24 hr. standing at room temperature). Evaporation under reduced pressure and crystallization from absolute ethanol–benzene mixture gave 0.4 g. (67%) and 0.7 g. (60%), respectively, of the dichloride XVI, m.p. 220–221°. The two samples showed no mixture m.p. depression; absorption maxima: 5.89, 5.96 μ (carbonyl group); 254 mμ, ε 16,840.

Anal. Calcd. for $C_{28}H_{30}Cl_2O_2$: C, 73.21; H, 4.39. Found: C, 73.09; H, 4.34.

Action of sodium ethoxide (0.03 g. of sodium dissolved in 20 ml. of ethanol) on 0.2 g. of XVI (refluxing for 1 hr.), gave 0.07 g. (39%) of *cis*-dibenzoylstilbene (II, identified).

Reductions of *cis*-**Dibenzoylstilbene** (II). (**A**).—A solution of 1.0 g. of II in 20 ml. of phosphorus trichloride was refluxed for 30 min. and evaporated under reduced pressure. The solid residue was washed with water and crystallized from ethanol–benzene mixture and from glacial acetic acid; yield of furan I, 0.8 g. (83%), m.p. 172–174°.

(**B**).—A solution of 1.0 g. of II and 1.35 g. of phosphorus trichloride in 25 ml. of phosphorus oxychloride, after shaking for 30 min. at room temperature, was evaporated under reduced pressure. The residue was hydrolyzed with ice-water and recrystallized from glacial acetic acid; yield of the furan I, 0.79 g. (82%).

(**C**).—A mixture of 0.5 g. of II and 2 g. of stannous chloride in 12 ml. of glacial acetic acid and 4 ml. of concd. hydrochloric acid was refluxed for 25 min. and poured into ice-water. The precipitate was crystallized from glacial acetic acid, 0.45 g. (90%) and identified as the furan I.

trans-**Dibenzoylstilbene** was recovered unchanged after treatment according to the various procedures above with (A) phosphorus trichloride, (B) phosphorus trichloride–oxychloride mixture, (C) phosphorus pentachloride–oxychloride mixture at 25°, (D) stannous chloride and (E) chlorine in chloroform solution (48 hr.). Although *trans*-dibenzoylstilbene is difficultly soluble in ordinary organic solvents at room temperature, it has considerable solubility in phosphorus trichloride, phosphorus oxychloride and mixtures of these; and the differences in solubilities of the stereoisomers appear to be of no consequence to the reactions run in these solvents. On the other hand, in the stannous chloride treatment (D above) failure to undergo reduction seems to be attributable to the extreme insolubility of the *trans* isomer, as shown by the fact that in another experiment reduction actually did occur slowly.[31b]

(**F**) Mixtures, each of 1.0 g. of *trans*-dibenzoylstilbene, 6 g. of phosphorus pentachloride and 60 ml. of phosphorus oxychloride, were refluxed, one for 4 hr. and the others for 0.5 hr., all seemingly with similar results. These were hydrolyzed by ice-water, each over *ca.* 15 min. In one case filtration of the crude product and take-up in *ca.* 30 ml. of benzene at room temperature gave only *ca.* 10–20% of the difficultly-soluble *trans*-diketone. In another case the benzene solution was chromatographed on a column of alumina and gave *ca.* 75% of *trans*-diketone. In two other runs the crude filtered product was treated with ether and with benzene, respectively, and *ca.* 80% of the *trans*-diketone separated immediately. A systematic study of this reaction would seem worthwhile.

Action of Phosphorus Pentachloride on 2,5-Di-*p*-chlorophenyl-3,4-diphenylfuran (III). (**A**).—In a side-arm test-tube fitted with a vacuum-tight rubber-sleeved stirring rod, 0.5 g. of the furan III and 2 g. of phosphorus pentachloride were intimately mixed and heated at 100° for 30 min. under aspirator vacuum. The residue was hydrolyzed with water and the product was crystallized from absolute ethanol; 0.56 g., m.p. 195–205°. It was identified as a mixture of the cyclic ketals Vbd by infrared spectra, and was hydrolyzed by a mixture of 35 ml. of glacial acetic acid and 5 ml. of concd. hydrochloric acid (refluxed for 1 hr.). Precipitation by addition of water and recrystallization from hexane–benzene mixture gave 0.42 g. (82%) of the unsaturated diketone IV, m.p. 196–199° (identified by infrared spectra and mixture m.p.).

(**B**).—A mixture of 0.5 g. of III, 1.2 g. of phosphorus pentachloride and 25 ml. of phosphorus oxychloride was shaken occasionally over 30 min., evaporated under reduced pressure and hydrolyzed with ice-water. The precipitate was crystallized from absolute ethanol; 0.55 g., m.p. 193–200°, identified as a mixture of cyclic ketals Vbd by infrared spectra. Hydrolysis as in (A) gave 0.44 g. (85%) of the unsaturated diketone IV (identified).

cis-**Di-(*p*-chlorobenzoyl)-stilbene** (**1,4-Di-*p*-chlorophenyl-3,4-diphenylbutane-2-dione-1,4**) (**IV**).[28,29] (**A**).—A suspension of 1.0 g. of the 2,5-di-*p*-chlorofuran III in 8 ml. of glacial acetic acid and 1 ml. of concd. nitric acid was warmed at 80–85° for 1 hr. and filtered to remove a small amount of undissolved III. Addition of water gave 0.56 g. (55%) of nearly pure diketone IV.

(**B**).[28]—A mixture of 1.0 g. of tetraphenylfuran (I), 10 g. of phosphorus pentachloride and 20 ml. of phosphorus oxychloride, after refluxing for 15 min., was hydrolyzed in ice-water. The resulting solid was filtered, washed with water and recrystallized from glacial acetic acid; yield of the diketone IV, 0.61 g. (50%). Crystallizations were from absolute ethanol, m.p. 198.5–201°; ultraviolet maximum: 260 mμ, ε 33,090.

Anal. Calcd. for $C_{28}H_{18}Cl_2O_2$: C, 73.53; H, 3.97. Found: C, 73.78; H, 3.96.

2,5-Di-*p*-chlorophenyl-2,5-diethoxydihydrofuran (**Vbd**)[28] was prepared from tetraphenylfuran (I) as described above (F): **higher melting isomer**, crystallized from absolute ethanol, m.p. 210–213°; ultraviolet maximum: 260 mμ, ε 14,160. *Anal.* Calcd. for $C_{32}H_{28}Cl_2O_3$: C, 72.31; H, 5.31. Found: C, 72.44; H, 4.92. **Lower melting isomer,**[28] m.p. 176–178.5°; ultraviolet maximum: 260 mμ, ε 15,570. *Anal.* Calcd. for $C_{32}H_{28}Cl_2O_3$: C, 72.31; H, 5.31. Found: C, 72.58; H, 5.00.

Isomerization of *cis*-di-(*p*-chlorobenzoyl)-stilbene (IV) to the *trans* isomer was effected by refluxing for 24 hr. a mixture of 0.3 g. of IV, 0.2 g. of potassium hydroxide and 6 ml. of ethanol. The insoluble *trans* isomer precipitated during the course of the reaction; 0.1 g. (33%), m.p. 231–233°, identified by mixture m.p. with a sample prepared from di-*p*-chlorobenzoylacetylene.[29]

Phosphorus Trichloride Reduction of *cis*-Di-*p*-chlorobenzoylstilbene (IV).—A solution of 0.5 g. of IV and 0.6 g. of phosphorus trichloride in 20 ml. of phosphorus oxychloride was shaken at room temperature for 30 min. The solvent was evaporated under reduced pressure and the residue was hydrolyzed with water and crystallized from glacial acetic acid; 0.4 g. (83%), identified as the furan III by m.p. 171–173° and mixture m.p.

Action of Bromine on Tetraphenylfuran (I). (A).—In moist ether in an experiment similar to that carried out by Dickerson,[38] a solution of 1.0 g. of I in 100 ml. of ether was shaken with a solution of 1.4 g. (3.2 molecular equivalents) of bromine in 100 ml. of water (20 min). The precipitate which separated together with a second crop obtained upon evaporation of the ether was recrystallized from glacial acetic acid; 0.95 g. (91%, identified as *cis*-dibenzoylstilbene (II)).

(**B**) **In Ether–Ethanol.**—A solution of 1.5 g. of bromine (3.5 molecular equivalents) in 20 ml. of absolute ethanol was added to a solution of 1.0 g. of the furan I in 75 ml. of ether. After periodic shaking over 75 min. at room temperature and evaporation under reduced pressure, fractional crystallization of the residue gave *ca.* 0.4 g. of unchanged furan I, and 0.65 g. of the higher-melting cyclic ketal Vbc (*ca.* 90% calculated from the furan actually used up in the reaction).

(**C**) **In Dry Ether.**—A mixture of 1.0 g. of I, 2 g. (4.6 molecular equivalents) of bromine and 50 ml. of absolute ether was allowed to react for 3 hr. at room temperature. Evaporation under reduced pressure and crystallization of the residue from petroleum hexane and then from glacial acetic acid gave 0.8 g. (56%) of the 2,5-di-*p*-bromo furan XXIV, m.p. 193.5–195° (identified).[40]

(**D**) **In Chloroform.**—A solution of 0.5 g. of I and 1.0 g. (4.6 molecular equivalents) of bromine in 15 ml. of chloroform after 30 min. at room temperature was evaporated under reduced pressure. The residue was treated with aqueous sodium thiosulfate and then crystallized from glacial acetic acid; yield 0.28 g. (40%), identified as the dibromo furan XXIV. The filtrate was evaporated and the residue was crystallized from absolute ethanol; 0.2 g. (27%), identified as *cis*-di-*p*-bromobenzoylstilbene (XXV).

(**E**) **In Phosphorus Oxychloride.**—A solution of 1.0 g. of I and 1.0 g. (2.3 molecular equivalents) of bromine in 20 ml. of phosphorus oxychloride, after standing for 30 min. at room temperature, was hydrolyzed in water. The product was crystallized from glacial acetic acid; yield 1.25 g. (89%), m.p. 195–196°, identified as the di-*p*-bromofuran XIV.

(**F**) **In phosphorus oxychloride,** carried out exactly as above in (E) but using 2 g. of bromine (4.6 molecular equivalents). The yield of *cis*-di-*p*-bromobenzoylstilbene (XXV) was 1.3 g. (89%), m.p. 223–224° (identified).

Action of Phenyl Grignard Reagent on Di-*p*-bromobenzoylacetylene (XXVI).—To a stirred solution of phenyl Grignard reagent made in the usual way from 10 g. of magnesium and 7 g. of bromobenzene in 50 ml. of absolute ether and cooled in an ice–salt-bath was added portionwise 5 g. of di-*p*-bromobenzoylacetylene[46] (*cf.* ref. 29) with further stirring for 20 min. Hydrolysis and fractional crystallizations of the mixture of products first from glacial acetic acid, and then the alcohol–benzene mixture and from petroleum hexane, gave two pure compounds: 0.50 g. (20%) of the unsaturated 1,4-diketone XXV (from air oxidation of the di-enolate of reaction) and 0.15 g. (3%) of the furan XXIV.

cis-**Di-(*p*-bromobenzoyl)-stilbene** (1,4-di-*p*-bromophenyl-2,3-diphenyl-2-butene-1,4-dione) (XXV), m.p. 223.5–225°; absorption maxima: 6.01, 6.07 μ (carbonyl groups); 268 mμ, ε 23,100.

Anal. Calcd. for $C_{28}H_{16}Br_2O_2$: C, 61.56; H, 3.32. Found: C, 61.85; H, 3.33.

2,5-Di-*p*-bromophenyl-3,4-diphenylfuran (XXIV), m.p. 194–196°; ultraviolet maxima: 236.5, 265, 335 mμ, ε 20,200, 16,000, 24,300.

Anal. Calcd. for $C_{28}H_{18}Br_2O_2$: C, 63.42; H, 3.40: Found: C, 63.26; H, 3.54.

Action of Bromine Water on the Furan XXIV.—A mixture of 0.20 g. of XXIV, 3 g. of bromine, 20 ml. of ether and 10 ml. of water was shaken for 15 min. The excess bromine was reduced by sodium thiosulfate and the ether solution was evaporated. Crystallization of the residue from glacial acetic acid gave 0.15 g. (75%) of the unsaturated diketone XXV, m.p. 224–226° (identified).

Acknowledgment.—We are indebted to Millard G. Reese[28] and David W. Boykin, Jr.,[25,36] for carrying out certain of the experiments included or referred to above.

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[46] R. E. Lutz and W. R. Smithey, Jr., *J. Org. Chem.*, **16**, 51 (1951).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA 4, PENNA.]

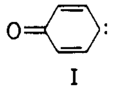
Reactions of 3,5-Dimethylbenzene-1,4-diazoöxide

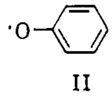
BY TOYOKI KUNITAKE[1] AND CHARLES C. PRICE

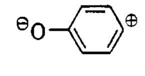
RECEIVED NOVEMBER 1, 1962

When 3,5-dimethylbenzene-1,4-diazoöxide was heated or irradiated with ultraviolet light in chlorinated hydrocarbons, the corresponding diazonium salt was obtained. When heated in chlorobenzene, the diazoöxide formed a mixture of hydroxybiphenyls and the diazonium salt. These results suggest the formation of an intermediate with free radical character. With boron trifluoride, a hydrated complex was obtained. The decomposition of the diazoöxide in tetrahydrofuran, thermally or photochemically, gave a one-to-one copolymer with the solvent. The product was crystalline under certain conditions. A cationic mechanism for this copolymerization is suggested.

The photochemical decomposition of benzene-*p*-diazoöxide has been studied in various solvents. Süs and co-workers[2] irradiated a methanolic solution of the diazoöxide with ultraviolet light and obtained *p*-methoxyphenol. In aromatic solvents, *p*-arylphenols were obtained. However, Wang[3] obtained a solid (m.p. 300°) having characteristics of a phenol along with a trace amount of *p*-phenylphenol, when a benzene solution was irradiated at room temperature. Irradiation of a toluene solution gave a mixture including *p*-benzylphenol, and in boiling ethanol, quantitative conversion to 4,4′-dihydroxyazobenzene occurred. A carbene (I) or its electromers (II or III) were assumed to be the intermediate.


I


II


III

Stille[4] observed the quantitative conversion of the simple *p*-diazoöxide into a polymeric material ([η] 0.12) by irradiation in tetrahydrofuran. However, the rather low melting point reported for the polymer (120–130°) indicated it was not the expected poly-1,4-phenylene oxide.

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[1] Taken in part from the doctoral dissertation of T. Kunitake, Univ. of Pennsylvania, 1962.

[2] O. Süs, K. Möller and H. Heiss, *Ann.*, **598**, 123 (1956).

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