tion of phenyllithium was prepared under nitrogen from 0.9 g. of lithium in 25 ml. of dry ether by dropwise addition of 5.3 ml. (0.05 mole) of distilled, dried bromobenzene in 25 ml. of dry ether over a period of 20 min. with stirring and slight warming to initiate the reaction. After stirring for an additional 1.5 hr. a solution of 5 g. (0.02 mole) of 1,2-dibenzoylcyclopropane (II) in 250 ml. of ether was added under gentle refluxing over a period of 30 min. Hydrolysis, washing with water, drying the ether solution over sodium sulfate, and evaporating under reduced pressure, gave a colorless solid which was recrystallized from benzene-ligroin mixture, m.p. 169.5–171.5°, yield 6.26 g. (77%).

Anal. Calcd for $C_{29}H_{26}O_2$: C, 85.68; H, 6.45. Found: C, 85.37; H, 6.19. Infrared absorption: 2.8, 9.93 μ.

In a similar experiment using phenylmagnesium bromide, except that hydrolysis was with 10% sulfuric acid, the yield of the glycol (I) was 33%.

One gram of the glycol after heating at 200–210° for 5 min. was recovered almost quantitatively.

1,2,5,5-Tetraphenyl-4-pentene-1-one (VI). A suspension of 0.5 g. (0.00123 mole) of the glycol (I) in 10 ml. of acetic acid was brought rapidly to boiling and refluxed for one min. Upon cooling a white precipitate of VI formed and was recrystallized from absolute ethanol, m.p. 130.5–132.5°; yield 0.36 g. (75%).

Anal. Calcd. for $C_{29}H_{24}O$: C, 89.65; H, 6.22; mol. wt. 388.5. Found: C, 89.43; H, 5.91; mol. wt. (Rast), 408. Ultraviolet absorption in absolute ethanol (2.02×10^{-5} *M*): λ_{max}, 248.5; ϵ, 16,530. Infrared absorption: 5.94, 6.23, 6.67, 6.9, very slight peak at 9.95 μ.

In another experiment, 5 g. (0.0123 mole) of the glycol (I) dissolved rapidly in 40 ml. of thionyl chloride with the evolution of gas. The red solution was warmed on a steam bath for 20 min., and the excess thionyl chloride was evaporated under reduced pressure. Ligroin was added and evaporated. The residue was recrystallized from benzene-ligroin mixture or from absolute ethanol; m.p. 131.5–132.5°; yield 3.0 g. (61%).

Numerous *ozonolysis* attempts were unsuccessful.

Potassium permanganate oxidation (cf. Ref. 10). A solution of 4 g. of VI (0.0103 mole) in 100 ml. of pyridine and 30 ml. of water on a steam bath was treated with six 2.1-g. portions of potassium permanganate (a total of 0.08 mole) at 1-hr. intervals. Upon steam distillation 0.69 g. (32%) of benzophenone, m.p. 44–46.5°, was obtained and identified by a mixture melting point determination. Work-up of the residue from steam distillation produced 1.6 g. (64%) of the calculated two equivalents of benzoic acid, m.p. 119–120° (identified by a mixture melting point determination).

Chromic acid oxidation.[11] A solution of 5 g. (0.0128 mole) of VI in 30 ml. of chloroform and 39 ml. of acetic acid at 45–50° was treated dropwise over 10 min. under stirring with a solution of 4.8 g. (0.048 mole) of chromic acid in 4 ml. of water and 26 ml. of acetic acid. After stirring for an additional 20 min. at this temperature and treatment dropwise with methanol to destroy excess reagent, the reaction mixture was concentrated on a steam bath under reduced pressure and evaporated to near dryness at room temperature under reduced pressure. The residue was triturated with ether, filtered, and placed in 150 ml. of water. Extraction of ether, washing with 10% hydrochloric acid, drying over sodium sulfate, evaporation under reduced pressure, and trituration of the viscous residue with ether, gave 0.9 g. of a white crystalline solid, m.p. 153–160°; recrystallized from dilute ethanol, m.p. 163–165°. It was identified as VI by a correct analysis, and by mixture m.p. with, and identity of the infrared absorption spectrum with that of an authentic sample prepared as described below.

β-Benzoyl-β-phenylpropionic acid. This synthesis is based on a procedure outlined briefly by Ali, *et al.*[12] To a solution of 0.5 g. of sodium in 15 ml. of absolute ethanol was added portion-wise 5 g. (0.0254 mole) of desoxybenzoin (m.p. 52–5°). After all of the ketone had been added, the mixture was treated with 2.8 ml. (4.2 g., 0.0252 mole) of distilled ethyl bromoacetate and was refluxed for 5 hr.; the alcohol was then evaporated. A solution of the residue and 1.5 g. of sodium hydroxide in 25 ml. of ethanol was refluxed for 30 min., cooled, diluted with water, and neutralized with concentrated hydrochloric acid. The resulting white precipitate was recrystallized from dilute ethanol; m.p. 163–165°; (A[12], m.p. 168°); yield 3.6 g. (55%).

CHARLOTTESVILLE, VA.

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

Lead Tetraacetate Oxidations of 2,5-Diarylfurans*,[1a]

CHI-KANG DIEN[1b] AND ROBERT E. LUTZ

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Lead tetraacetate in chloroform solution oxidized five 2,5-diarylfurans to the *cis* unsaturated 1,4-diketones and converted three β-acetoxy-2,5-diarylfurans into the corresponding 2-acetoxy-3-furanones. 2,5-Dimesitylfuran and 3,4-dichloro-2,5-diphenylfuran did not react under these conditions.

In refluxing concentrated acetic acid lead tetraacetate, behaving differently, brought about two-stage oxidations of three 2,5-diarylfurans to the 2-acetoxy-3-furanones. In one of these cases the reaction could be stopped at the first stage of oxidation with production of the 3-acetoxyfuran. Four 3-acetoxy-2,5-diarylfurans were oxidized to 2-acetoxy-3-furanones.

These reactions are consistent with expectations based on known behaviors of the reagent, effects of different types of substituents, and present views of mechanism.

Numerous 2,5-diarylfurans (I), including one carrying a sterically hindering mesityl group at one of the two α-positions, undergo oxidative-cleavage by nitric-acetic acids to *cis* unsaturated 1,4-diketones (II),[2] but 2,5-dimesitylfurans (Ij)[3] resist this

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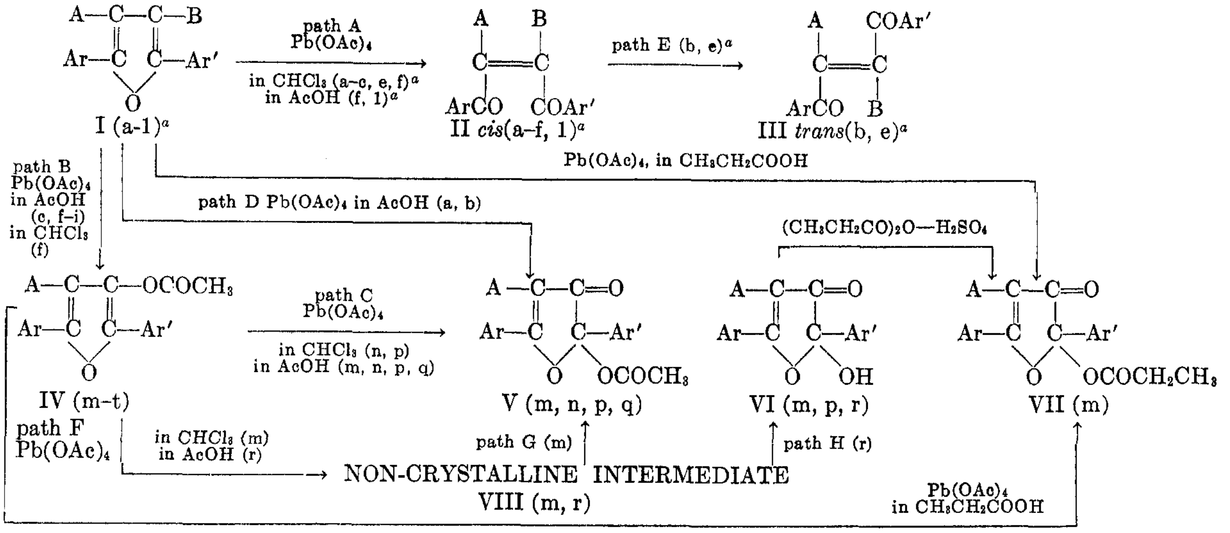
[*] This paper is a contribution in honor of Lyndon F. Small, former Editor of the Journal.

(1) (a) This investigation was supported in part by a contract with the Office of Ordnance Research, U. S. Army, and in part by a grant-in-aid from the National Science Foundation. (b) Present location, National Aniline Div. Allied Chemical & Dye Corp., Buffalo, N. Y.

(2) (a) A. P. Dunlap and F. N. Peters, *The Furans*, Reinhold Publishing Corp., N. Y., 1953, and references cited therein; see especially p. 50. (b) R. E. Lutz and F. N. Wilder, *J. Am. Chem. Soc.*, 56, 978 (1934); (c) R. E. Lutz and W. P. Boyer, *J. Am. Chem. Soc.*, 63, 3189 (1941).

CHART I



I^a–VIII	Substituents^b			Reaction path:	
	Ar, Ar'	A	B	CHCl$_3$^{c}	AcOH^{a,c}
a	C_6H_5	H	H	A^d	D^e
b	BrC_6H_4^{b}	H	H	A^d, E	D
c	C_6H_5	Cl	H	A	B
d	C_6H_5	Cl	Cl	N^b	E
e	C_6H_5	CH_3	CH_3	A, E^d	E^f
f	C_6H_5	C_6H_5	H	A, B	A, B
g	C_6H_5	C_6H_5CO	H	N^b	B
h	C_6H_5	BrC_6H_4CO	H	—	B
i	C_6H_5	$C_9H_{11}CO$	H	—	B
j	C_9H_{11}	H	H	N^b	R^b
k	C_9H_{11}, BrC_6H_4	H	H	R^{b,e}	R^b
l	C_6H_5	H	OCH_3	R^b	A
m	C_6H_5	H	—	F, G	C
n	BrC_6H_4	H	—	C	C
o	C_9H_{11}	H	—	N^{b,e}	—
p	C_6H_5	Cl	—	C	C
q	C_6H_5	C_6H_5	—	—	C
r	C_6H_5	C_6H_5CO	—	—	F, H
s	C_6H_5	BrC_6H_4CO	—	—	—
t	C_6H_5	$C_9H_{11}CO$	—	—	—

[a] The first column designates by letters a–t the formulas I–VIII. The letters under the formulas and above the arrows specify those compounds of the list which reacted according to the several paths A–H. [b] Abbreviations: AcOH = CH_3COOH; BrC_6H_4 = *p*-bromophenyl; C_9H_{11} = mesityl; N = no reaction occurred; R = reaction occurred but product did not crystallize. [c] Reaction temperature was refluxing unless otherwise specified: [d] at 30°; [e] at 50°; [f] the reaction undoubtedly proceeded through IIe but IIe was not isolated or detected.

reaction. A mechanism involving attack at one unhindered α-position without completion of a 1,4-addition was suggested to account for the results.[2c] Clausen-Kaas[4] in recent studies on the action of other oxidizing agents such as lead tetraacetate, hydrogen peroxide, and the halogens, on simpler furans, has isolated completed-addition compounds or derivatives of them (*e.g.* 2,5-diacetoxy and 2,5-dimethoxy compounds analogous to XI). The present paper deals with some results of a further examination of the 2,5-diarylfurans in respect to the action of oxidizing agents, specifically lead tetraacetate,[5,6] and the marked effects of the solvents chloroform and acetic acid on the mode of reaction. The results are outlined in formulas I–VIII which show the several oxidation paths involved (A–H).

Lead tetraacetate reactions in chloroform solution at 30° with 2,5-diphenyl- and 2,5-di-(*p*-bromophenyl)-furans (Ia, b), gave chiefly the *cis* unsaturated diketones (IIa, b). In the latter case, IIb, where the *cis* compound is relatively very labile, a small amount of the stable *trans* isomer IIIb was obtained also. 3-Chloro-2,5-diphenylfuran (Ic) reacted but only at refluxing temperature and also gave the *cis* unsaturated diketone IIc. 3,4-Dichloro- and 3-benzoyl-2,5-diphenylfurans (Id and g) failed to react at refluxing temperature. 3,4-Di-

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(3) R. E. Lutz and C. J. Kibler, *J. Am. Chem. Soc.*, **62,** 1520 (1940).

(4) (a) N. Clauson-Kass, *Kgl. Danske Videnskab. Selskab, Mat-fys. Medd.*, 24, 6 (1947). (b) N. Elming and N. Clauson-Kass, *Acta Chem. Scand.*, 6, 535 (1952). (c) N. Clauson-Kaas, *Acta Chem. Scand.*, 6, 569 (1952). (d) N. Elming, *Acta Chem. Scand.*, **6,** 578 (1952). See also references cited in reference 2(a).

(5) Empirically the reagent lead tetraacetate is said to react in three ways, by addition of two acetoxyls to a double bond, by substitution of an acetoxyl for an "active" hydrogen, and by abstraction of two suitably located hydrogens of systems such as that in a 1,2-glycol (*cf.* W. A. Waters, *Organic Chemistry,* H. Gilman, 1953, Vol. IV, p. 1185). The 2,5-diarylfurans are capable of only the first two.

(6) For recent studies see: (a) W. A. Mosher and C. L. Kehr, *J. Am. Chem. Soc.*, **75,** 3172 (1953); (b) H. E. Barron, G. W. K. Cavill, E. R. Cole, P. T. Gilham, and D. H. Solomon, *Chemistry & Industry,* 76 (1954); (c) G. W. K. Cavill, E. R. Cole, P. T. Gilham and D. J. McHugh, *J. Chem. Soc.*, 2785 (1954); (d) G. W. K. Cavill and D. H. Solomon, *J. Chem. Soc.*, 1404, 3943 (1954); (e) R. Criegee, *Ann.*, **481,** 263 (1930); (f) R. Criegee and H. Beuker, *Ann.*, **541,** 218 (1939); (g) F. V. Brutcher and F. J. Vara, *J. Am. Chem. Soc.*, **78,** 5695 (1956).

methyl-2,5-diphenylfuran (Ie) reacted smoothly at 30° to give largely the *cis* unsaturated diketone IIe together with a small yield of the stable *trans* isomer IIIe which was doubtless formed by stereoisomerization. It is noteworthy that as would be expected the electron-attracting groups chlorine and benzoyl in the β-position of the furan ring retard the reaction while the electron-repelling methyl group facilitates it.

The reaction with 2,3,5-triphenylfuran (If) deviated from the above pattern; in addition to a sizable yield of *cis* unsaturated diketone IIf there was produced some of the β-acetoxy furan IVq.

2,5-Dimesitylfuran (Ij) was largely recovered after reaction at refluxing temperature but an unidentified product of high oxygen content was produced in small yields. 2-Mesityl-5-*p*-bromophenylfuran (Ik) resisted reaction at room temperature but gave a non-crystalline product at refluxing temperature. Evidently two α-mesityl groups by steric interference with addition at the α-carbons slow down the oxidation reaction in chloroform solution as they do the nitric-acetic acid oxidation.[3]

3-Methoxy-2,5-diphenylfuran (Il) reacted readily, as expected because of the activating β-methoxyl group, but gave an intractable resin.

The reaction between the lead tetraacetate-chloroform reagent and 2,5-diarylfurans carrying the activating β-acetoxyl group, in the main followed a course different from the above, one which was followed also in acetic acid as solvent. Attack was at the adjacent α-position. 3-Acetoxy-2,5-diphenylfuran (IVm), 3-acetoxy-4-chloro-2,5-diphenylfuran (IVp), and 3-acetoxy-2,5-di-(*p*-bromophenyl)furan (IVn) reacted somewhat more slowly than those unsubstituted in the 3,4-positions. In the case of the latter two (IVn and p) the products were the corresponding acetoxyfuranones (Vn,p). In the case of 3-acetoxy-2,5-diphenylfuran (IVm) the product was an oil (VIII) which was believed to contain the completed addition product, the triacetoxydihydrofuran XIV or XV, which under the action of refluxing acetic acid then produced the acetoxyfuranone Vm in significant amounts. 3-Acetoxy-2,5-dimesitylfuran (IVo) constituted an exception to the above generalization; it failed to react with the reagent in chloroform, presumably because of steric hindrance at the α-carbons.[7]

It should be emphasized that in chloroform solution β-acetoxylation did not take place in any of the compounds studied except in the triphenyl series (If → IVq).

The lead tetraacetate reactions in acetic acid in many cases exhibited striking differences from those in chloroform. The 2,5-diarylfurans Ia and b, instead of undergoing the one-step oxidation-cleavage to the *cis* unsaturated diketone II, underwent a two-fold rise in oxidation level and gave the corresponding 2-acetoxy-2,5-diaryl-3-furanones (Vm,n). The best yields (*ca.* 70%) were obtained at refluxing temperature using two molar equivalents of reagent. The possibility that the different course of the reaction in the two solvents was due to a temperature rather than a solvent effect was eliminated by experiments on 2,5-diphenylfuran (Ia) in acetic acid at refluxing temperature and at 40–50°; from these reactions only the 2-acetoxy-3-furanone, Vm could be obtained.

The 3-chloro-, 3-benzoyl-, 3-(*p*-bromobenzoyl)-, and 3-mesitoyl-2,5-diphenylfurans (Ic,g-i) reacted under similar conditions but underwent a rise in oxidation level of only one stage by substitution of acetoxyl for the β-hydrogen to give the corresponding β-acetoxy furans (IVp,r-t).

3-Acetoxy-2,5-diphenyl- and 3-acetoxy-2,5-di-(*p*-bromophenyl)furans (IVm,n), which might be presumed to be the intermediates in the two-stage reactions with the parent 2,5-diarylfurans (Ia,b), actually did react readily in separate experiments to give the corresponding 2-acetoxy-3-furanones (Vm,n). 3-Acetoxy-4-chloro-2,5-diphenylfuran (IVp) reacted similarly but required prolonged heating and an excess of reagent. 3-Acetoxy-4-benzoyl-2,5-diphenylfuran (IVr) reacted still more slowly and gave an oil which presumably consisted largely of a triacetoxyl addition compound of the type XIV or XV because it was converted into the 2-hydroxy-3-furanone VI upon treatment with alcoholic potassium hydroxide.

In these reactions it is seen, again, that an electron-attracting substituent in the β-position retards reaction. On the other hand, a β-acetoxyl group specifically directs attack at the adjacent α-carbon.

The possibility in the above formation of the 3-acetoxyfurans and 2-acetoxy-3-furanones of a reaction path involving initially the oxidative cleavage of the parent diarylfurans to *cis*-diaroylethylenes (II) followed by *cis*-addition-cyclization, was tested and shown to be unlikely by a series of experiments in which both *cis* and *trans*-dibenzoylethylenes (IIa and IIIa) and *cis*-1-chloro-1,2-dibenzoylethylene (IIc) were subjected to the above reaction conditions. In each case unreacted materials were recovered, and it is certain in these cases at least that neither the 3-acetoxyfuran nor the 2-acetoxy-3-furanone, which could easily have been detected, was produced in any significant amount.

In contrast to the above results 3-methoxy-2,5-diphenylfuran (Il) upon treatment with the lead tetraacetate–acetic acid reagent at refluxing temperature gave as the only tractable product *cis*-1-methoxy-1,2-dibenzoylethylene (IIl) although in only 24% yield. 3,4-Dichloro- and 3,4-dimethyl-2,5-diphenylfurans (Id,e) both of which are incapable of simple β-substitution, reacted with lead

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(7) *cf.* Similar resistance to nitric acid oxidative cleavage (ref. 3).

tetraacetate in boiling acetic acid, with some difficulty in the former case and more readily in the latter. In the case of the 3,4-dichlorofuran (Id) the noncrystalline product evidently contained the low-melting *cis*- unsaturated diketone (IId) (or possibly the intermediate diacetoxy compound XII because it gave a sizable yield of the easily crystallizable *trans* unsaturated diketone (IIId) when placed in chloroform solution containing iodine and subjected to the action of sunlight. In the case of the 3,4-dimethylfuran (Ie) the reaction produced the unsaturated diketone in its stable *trans* form (IIIe) in 20% yield.

2,3,5-Triphenylfuran (If) reacted with lead tetraacetate in acetic acid as it did in chloroform to give a mixture of both the *cis* unsaturated triketone (IIf) and the 3-acetoxyfuran (IVq), but in this case the acetoxyfuran was produced in a relatively much greater yield. Thus the solvent effect in this borderline case is operative although it does not dominate as in the other cases studied.

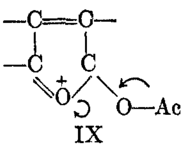
Reactions by lead tetraacetate in acetic acid with 2,5-dimesitylfuran and 2-mesityl-5-(*p*-bromophenyl)furan (Ij and k) took place rapidly but unfortunately gave non-crystalline materials (in the former case a small amount of unidentified high-melting product was obtained).

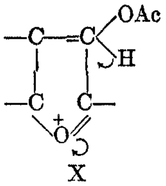
It should be noted that in the oxidation of a 3-acetoxyfuran to a 2-acetoxy-3-furanone, the 3-acetoxy group has been eliminated and a 2-acetoxy group gained. When propionic acid was used as solvent rather than acetic acid in typical oxidations of either 2,5-diphenylfuran (Ia) or 3-acetoxy-2,5-diphenylfuran (IVm), as was to be expected, the product was the 2-propionoxyfuranone-3[8] (VIIm). This product was subsequently synthesized in another way by the action of propionic anhydride and sulfuric acid on the 2-hydroxy-3-furanone (VI). It was shown in an independent experiment that the exchange of propionoxyl for or by acetoxyl does not occur in the furanone (Vm,VIIm) under the reaction conditions. The formation of the propionoxy compound in the above oxidation therefore must have involved either a group exchange in the lead tetraacetate before reaction or pick-up of a solvent molecule at the 2-position during but not after completion of the formation of the furanone system.

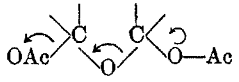
Discussion of results. In spite of frequently poor yields and formation of sizable amounts of resinous products, it is possible to draw some limited and tentative conclusions. The reactions of the 2,5-diarylfurans with lead tetraacetate, summarized in formulations I–VIII, involve three one-stage processes, paths A, B, and C. One of these (A) is the oxidative cleavage of the ring to give the *cis*-unsaturated 1,4-diketone (II). This is the favored reaction in chloroform solution, but it has been observed in a few instances in acetic acid as solvent, notably where both β-positions were occupied by substituents other than acetoxyl; and significantly it occurred in the case of the β-phenyl and β-methoxy compounds (If and l).

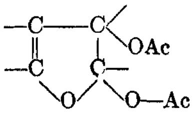
The second mode of attack (B) is substitution of acetoxyl for a β-hydrogen to give 3-actoxyfurans (IV), and is favored in acetic acid. The third process (C) which applies only to the 3-acetoxyfurans (IV), leads to 2-acetoxy-3-furanones (V) and takes place both in chloroform and in acetic acid solution. The two processes B and C often occur as successive steps in one-operation oxidations (D) to 2-acetoxy-3-furanones (V) of furans which have an open β-position. However, it is to be noted that when there is present one β-acetoxyl which would direct the primary attack alpha to that group, a second (β′) acetoxylation has not been observed.

In all of these reactions there is a fundamental similarity expressible in terms of "oxidation" or electrophilic attack at "active" or nucleophilic points on an enol or diene-ol ether system, —C=C—O— or —C=C—C=C—O—, whatever form or direction the completion of the reactions may take.[9] Thus the furan system may be pictured as responsive toward both α- and β-attack by $\overset{+}{O}COCH_3$ or its equivalent, possibly through prior complexing with $Pb(OCOCH_3)_4$.[9] This attack would be followed by break-up of the resulting cation IX[10] or X, or of a completed 1,4- or 1,2-diacetoxyl-addition product XI or XII, and would lead to unsaturated 1,4-diketones of necessarily *cis* configuration, or to 3-acetoxyfurans.

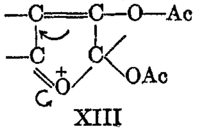

IX

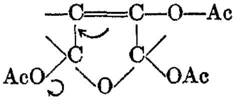

X


XI


XII

The β-acetoxyl group specifically directs reaction to the adjacent α-position to give the 2-acetoxy-3-furanones (V) and these reactions also can be rationalized, *cf. e.g.*, XIII, XIV, XV.


XIII


XIV

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[8] *cf.* The analogous oxidation of mesitol with lead tetraacetate in propionic acid to 2,4,6-trimesityl-2-propionoxycyclohexadienone (Cavill and co-workers, ref. 6).

[9] For comprehensive review and analysis of organic oxidation reactions see L. S. Levitt, *J. Org. Chem.*, 20, 1257 (1955).

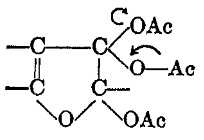
[10] *cf.* Suggested mechanism of nitric acid oxidation of 2-(*p*-bromophenyl)-5-mesitylfuran (2c).

TABLE I

LEAD TETRAACETATE OXIDATIONS

					Reaction			
Compound	G.	$Pb(OAc)_4$, G.	Solvent	Ml.	Temp., C.	Time, min.	Recovered, %	Product, %
Ia	1	2.2	$CHCl_3$	30	20–30°	300	—	IIa, 59
Ia	1	2.2	$CHCl_3$	20	Reflux	15	35	IIa, 12
Ia	2	4.5	AcOH	40	40–50°	120	61	Vm, 14^{a}
Ia	1	4	AcOH	20	Reflux	5	—	Vm, 69
Ia	1	6	AcOH	20	Reflux	5	—	Vm, 21^{b}
Ia	2	4.5	C_2H_5COOH	40	Reflux	5	52	VIIm,^{c} 25
IIa	0.85	1.5	AcOH	20	Reflux	5	—	IIIa, 16.5^{b}
IIIa	2	4	AcOH	40	Reflux	5	10.5	^{b}
VIIm	0.5	1	AcOH	10	Reflux	5	91	—
Vm	0.5	1	C_2H_5COOH	10	Reflux	5	82	—
Ib	1	1.5	$CHCl_3$	20	20–30°	180	—	IIb, 43
					50–60°	20	—	IIIb, 9
Ib	5	7.5	AcOH	80	Reflux	15	28	Vn,^{c} 42
Ic	2	5	$CHCl_3$	40	Reflux	40	—	IIc, 60^{a}
Ic	2	5	AcOH	30	Reflux	5	—	IVp, 51
IIc	1	2.5	AcOH	20	Reflux	5	48	—
Id	0.8	1.6	$CHCl_3$	25	Reflux	25	94	—
Id	0.8	1.6	AcOH	20	Reflux	15	60	^{b,d}
Ie	1	2	$CHCl_3$	30	20–30°	240	—	IIe, 35; IIIe, 14
Ie	1	2	AcOH	20	Reflux	15	—	IIIe, 20^{b}
If	1	2	$CHCl_3$	25	Reflux	20	—	IVq, 26; IIf, 53
If	1	2	AcOH	25	Reflux	10	—	IVq, 49: IIf, 36
Ig	1	2	$CHCl_3$	30	Reflux	20	91	—
Ig	1	2	AcOH	20	Reflux	15	—	IVr, 35
Ih	1	1.5	AcOH	20	Reflux	10	—	IVs, 31^{e}
Ii	1	2	AcOH	20	Reflux	10	—	IVt, 12^{b,e}
Ij	2	4	$CHCl_3$	50	50–60°	60	60	^{f}
Ij	2	4	AcOH	40	Reflux	15	—	^{b,g}
Ik	2	4	$CHCl_3$	50	20–30°	600	—	^{b,h}
Ik	2	5	AcOH	40	Reflux	5	—	^{b,i}
Il	0.5	1	$CHCl_3$	15	40–50°	20	—	^{b}
Il	1	1	AcOH	20	Reflux	5	—	IIl, 24^{b}
IVm	1	2	$CHCl_3$	25	Reflux	10	25	^{b,j}
IVm	1	2	AcOH	20	Reflux	5	—	Vm, 65
IVm	1	2	C_2H_5COOH	25	Reflux	5	—	VIIm, 41
IVn	2	2.6	$CHCl_3$	40	Reflux	15	56	Vn, 27
IVn^{c}	1	1.3	AcOH	30	Reflux	10	—	Vn, 70
IVo	0.6	1.5	$CHCl_3$	20	Reflux	15	83	—
IVo	0.8	2	AcOH	20	Reflux	5	65	^{k}
IVp	0.8	1.6	$CHCl_3$	20	Reflux	20	—	Vp,^{c} 65
IVp	0.7	1.5	AcOH	30	Reflux	30	—	Vp,^{c} 75
IVq	1	2	AcOH	25	Reflux	30	—	Vq, 77
IVr	1	2	AcOH	30	Reflux	60	18	^{b,l}

[a] At room temperature. No reaction occurred. [b] The product or major product was noncrystalline. [c] New compound; see Experimental for details. [d] The oil was converted to IIId in 30% yield from Id by exposing a chloroform solution of it containing a trace of iodine to sunlight for 2 hr. [e] C-K. Dien and R. E. Lutz, *J. Org. Chem.*, 21, 1492 (1956). [f] Colorless unknown product (0.12 g.) was isolated; m.p. 180–181°. *Anal.:* C, 54.87; H, 4.61. [g] A small amount (0.04 g.) of yellow unknown product was isolated; m.p. 172–174°. *Anal.:* C, 54.69; H, 4.53. [h] At lower temperatures (0–25°, 2 hr.) starting material was recovered. [i] At lower temperature (40–50°, 30 min.) the product also was an oil; a trace of *p*-bromobenzoic acid was isolated. [j] The oil was converted to Vm in 26% yield after refluxing 10 min. in acetic acid solution. [k] Prolonged heating (30 min.) gave only an oil. [l] The oil was converted to VIr in 28% yield by treatment with alcoholic potassium hydroxide.



XV

In two cases (IVm,r) evidence for the completed additions (XIV or XV) was obtained but unfortunately in neither case was the addition compound actually isolated in pure condition and characterized. Evidently in the series under investigation the 2,5-diaryl groups militate against the stability and isolability of such intermediates.

The above results seem generally consistent with the effect of substituents on diacetoxyl additions to olefins.[11] They are to be compared with lead tetraacetate oxidations in general,[5] and specifically with the oxidations of simple furans[4] where occasionally 1,4-diacetoxy addition compounds have

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(11) R. Criegee, *Newer Methods of Preparative Organic Chemistry* (Bergmann), Interscience Publishers, Inc., N. Y., 1949, p. 1.

been isolated, and with the oxidation of anthracene through or accompanied by 1,4-diacetoxyl additions to produce acetoxyanthracene and acetoxyanthrone.[12]

EXPERIMENTAL[13]

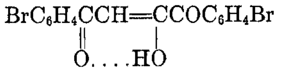
Materials. Lead tetraacetate[14] was recrystallized from acetic acid and dried *in vacuo.* Dry acetic acid was prepared by mixing 100 ml. of concd. acetic acid with 3 ml. of acetic anhydride. Reagent grade chloroform was dried by washing with concd. sulfuric acid.

General oxidation procedure. The furan was treated with lead tetraacetate in dry acetic acid or chloroform solution under the different conditions specified in Table I. The acetic acid solutions were diluted with water and extracted with ether, and the extract was washed, dried, and evaporated. The chloroform solutions were washed with water, dried, and evaporated. The products were crystallized from benzene-ligroin or ethyl acetate-ligroin mixtures. The known compounds were identified by mixture melting point.

3-Acetoxy-2,5-di-(p-bromophenyl)furan (IVn). A mixture of 6 g. of *trans*-di-(*p*-bromobenzoyl)ethylene (IIIb), 40 ml. of acetic anhydride, 20 ml. of acetyl chloride, and 5 drops of concd. sulfuric acid, was allowed to stand at 40–60° for 18 hr. and then on the steam bath for 1 hr. The dark red solution was hydrolyzed with ice water and the resulting product was extracted with ether. Evaporation and crystallization of the residue from ethyl acetate gave 5.6 g. (85%) of nearly colorless product; melting point after repeated recrystallizations from ethyl acetate-methanol mixture, 122–123°.

Anal. Calcd. from $C_{18}H_{12}Br_2O_3$: C, 49.57; H, 2.77. Found: C, 49.54; H, 2.58. λ_{max} 232.5, 332 mμ, ϵ 17,000, 36,500; shoulders at 250, 349 mμ, ϵ 12,000, 26,500; λ_{min} 264 mμ, ϵ 4,400.

2-Acetoxy-2,5-di(p-bromophenyl)furanone-3 (Vn) [prepared from Ib or IVn as described above (see Table I)] was also obtained by treatment of di(*p*-bromobenzoyl)ethanol (XVI)[15] with acetic anhydride and concd. sulfuric acid in the usual way (room temperature, 20 min.); crystallized from benzene-ligroin mixture, m.p. 173–174°.



$$\begin{array}{l}BrC_6H_4\underset{\underset{\textstyle O}{\|}}{C}CH{=}\underset{\underset{\textstyle HO}{|}}{C}COC_6H_4Br\end{array}$$

XVI

Anal. Calcd. for $C_{18}H_{12}Br_2O_4$: C, 47.82; H, 2.68. Found: C, 47.51; H, 2.45. λ_{max} 226, 257, 312 mμ, ϵ 18,500, 9,200, 24,200. λ_{min} 243, 270 mμ, ϵ 7,200, 7,400.

Hydrolysis of 1 g. of Vn by refluxing methanolic sodium hydroxide (15 min.) gave 0.42 g. of XVI, m.p. 168–170°.[15]

2-Acetoxy-2,5-diphenylfuranone-3 (Vm). The ultraviolet absorption spectrum of this compound was determined for reference because it is the parent compound of this type. λ_{max} 245, 309 mμ, ϵ 6,500, 17,600; slight shoulder at 300 mμ, ϵ 16,500; λ_{min} 235, 260 mμ, ϵ 6,100, 4,400. This is not far different from the absorption of the corresponding 2-methoxy analog (λ_{max} 247, 314 mμ, ϵ 8,540, 17,400[16]). Substitution of bromines in the two phenyl *para*-positions has caused a negligible bathochromic shift in the long wave length band and a sizable increase in the absorptivity.

2-Acetoxy-4-chloro-2,5-diphenylfuranone-3 (Vp) was prepared by oxidation of 3-acetoxy-4-chloro-2,5-diphenylfuran (IVp)[17] as described above. It was also obtained by the action of acetic anhydride and concd. sulfuric acid on VIp[18] (which exists chiefly in this cyclic form) at 40–50° for 40 min. It was isolated by crystallizing from ethyl acetate–ligroin mixture; recrystallized from ethyl acetate; m.p. 173–174°.

Anal. Calcd. for $C_{18}H_{13}ClO_4$: C, 65.78: H, 3.99. Found: C, 65.62; H, 3.95. λ_{max} 250, 321 mμ, ϵ 7,800, 15,400; λ_{min} 240, 274 mμ, ϵ 6,500, 3,800.

Hydrolysis with refluxing alcoholic sodium hydroxide (5 min.) regenerated VIp in 65% yield.

2-Propionoxy-2,5-diphenylfuranone-3 (VIIm) was prepared: (*a*) by oxidation of either 2,5-diphenylfuran (Ia) or 3-acetoxy-2,5-diphenylfuran (IVm) in propionic acid as described above; crystallized from ethyl acetate-methanol mixture; m.p. 157–158°.

Anal. Calcd. for $C_{19}H_{16}O_4$: C, 74.01; H, 5.23. Found: C, 73.77; H, 4.84. λ_{max} 245, 309 mμ, ϵ 7,400, 18,500; λ_{min} 235, 261 mμ, ϵ 6,000, 4,600.

(*b*) By treatment of dibenzoylethenol (VIm) with propionic anhydride and concd. sulfuric acid (room temperature, 10 min.) yield 80%; m.p. and mixture m.p. with (a), 155–158°.

When VIIm was refluxed with lead tetraacetate-acetic acid for 5 min. only unchanged material was recovered in 91% yield. Treatment of Vm with lead tetraacetate–propionic acid (refluxing 5 min.) gave also unchanged material in 82% yield.

Hydrolysis of VIIm (0.3 g.) with methanolic potassium hydroxide (room temperature, 15 min.) gave 0.18 g. (73%) of VIm; identified by mixture melting point.

Dibenzoylacetylene was recovered largely unchanged after treatment for 1 hr. with acetic anhydride and sulfuric acid (2 drops in 20 ml.) at 50–60°. This experiment was carried out in the ill-founded hope that addition and cyclization to the acetoxyfuranone (VIm) would occur.

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[12] L. F. Fieser and S. T. Putnam, *J. Am. Chem. Soc.,* **69,** 1038 (1947).

[13] (a) Melting points are "corrected"; (b) microanalyses were by Miss Yuen-May Lai.

[14] L. F. Fieser, *Experiments in Organic Chemistry,* 2nd ed., D. C. Heath and Co., N. Y., 1941, p. 436.

[15] R. E. Lutz, F. N. Wilder, and C. I. Parrish, *J. Am. Chem. Soc.,* **56,** 1980 (1934).

[16] R. E. Lutz, T. Amacker, S. M. King, and N. H. Shearer, *J. Org. Chem.,* **15,** 181 (1950).

[17] R. E. Lutz, A. H. Stuart, F. N. Wilder, and W. C. Connor, *J. Am. Chem. Soc.,* **59,** 2314 (1937).

[18] R. E. Lutz and A. H. Stuart, *J. Am. Chem. Soc.,* **59,** 2322 (1937).