

## The Reaction between 2,4,6-Triarylpyrylium Salts and Sodium Nitrite\*

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The reaction between a series of 2,4,6-triarylpyrylium salts and sodium nitrite in various solvents has been examined. When the reaction was carried out in acetonitrile the main reaction led to 3,5-diaroyl-4-arylisoxazoles. If the reaction was carried out in alcoholic solvents, complex mixtures were formed. The main product in most of these cases consisted of 2,4,6-triaryl-2,6-dialkoxy-5-nitro-5,6-dihydro-2*H*-pyrans. Besides this, various by-products were isolated and characterized. The mechanism and scope of the reactions are discussed.

In continuation of our previous studies of the reactions of pyrylium salts,<sup>2</sup> this examination of the reaction between 2,4,6-triarylpyrylium salts and sodium nitrite (nitrite-nitrous acid) was instigated.

Rather complex reaction mixtures resulted in most cases; a variety of products could be isolated, and the product distribution was found

to be highly dependent on solvent as well as other variables, *e.g.*, the pyrylium counter ion and the oxygen concentration.

A number of the types of product isolated would be very hard to synthesize by known methods. Thus we directed our studies towards making the reactions potentially useful for synthetic purposes, as well as towards understanding the mechanisms involved. Our study was met with a certain degree of success, since we were able to find conditions where one or the other of the main products dominated. Furthermore a mechanistic scheme that explains the main reactions was derived.

Most of the detailed studies employed 2,4,6-triphenylpyrylium tetrachloroferrate as substrate. The product distribution from this substrate in a typical experiment is illustrated by Chart 1.

\* For a preliminary account of part of this work, see Ref. 1.

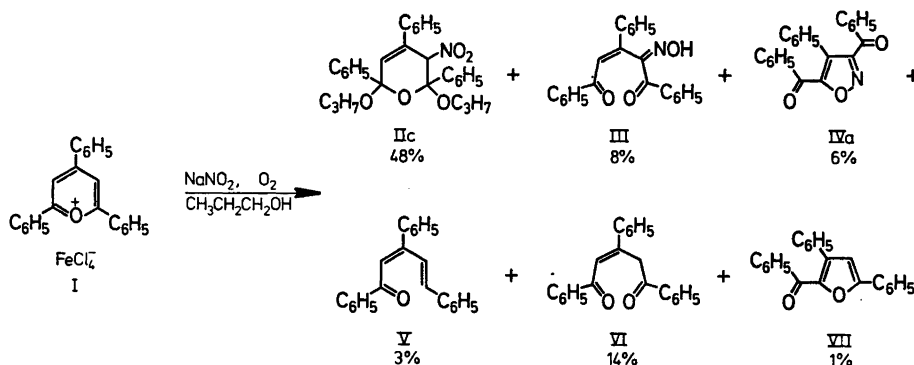


Chart 1.

## RESULTS

In this section the synthetically useful results are discussed, whereas some results which are especially useful in our attempt to unravel the mechanistic picture will be presented in the discussion section.

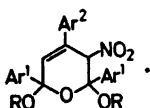
a. *The formation of dihydropyrans (II) using monovalent alcohols as the solvent.* A series of experiments were performed with 2,4,6-triphenylpyrylium tetrachloroferrate (I) as substrate and a monoalcohol both as solvent and one of the reagents. The reaction vessels were open, and thus oxygen from the air was present. The results are summarized in Table 1.

b. *The reaction between glycols and 2,4,6-triphenylpyrylium tetrachloroferrate.* In this series of experiments it was found that ethylene glycol

and 1,3-propanediol gave the bicyclic dihydropyrans VIII and IX, respectively (Chart 2), whereas 1,4-butanediol did not lead to a dihydropyran in observable amounts. In this case the only isolated product consisted of IVa (Table 2). It should be noted that the reactions with monoalcohols and glycols as a rule were discontinued before all pyrylium ion was consumed, since the dihydropyrans were slowly decomposed under the reaction conditions.

From the results it appears that the formation of dihydropyrans is a very general reaction. However, steric crowding was observed to be a limiting factor. By using secondary or tertiary butyl alcohol as solvents and reagents, we were not able to isolate any dihydropyran, but only compound IVa (Table 2). Furthermore, it should be noted that the so-called pseudobase VI was

Table 1. Dihydropyrans IIa - r,



	Ar <sup>1</sup>	Ar <sup>2</sup>	R	Yield (%)
a	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	27
b	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	CH <sub>2</sub> CH <sub>3</sub>	46
c	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	48
d	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	71
e	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	48
f	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	(CH <sub>3</sub> ) <sub>2</sub> CH	43
g	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	(CH <sub>3</sub> ) <sub>2</sub> CCH <sub>3</sub>	21
h	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	(-)-CH <sub>3</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )CH <sub>3</sub>	66
i	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub>	24
j	C <sub>6</sub> H <sub>5</sub>	<i>p</i> -CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	80
k	C <sub>6</sub> H <sub>5</sub>	<i>m</i> -NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>	CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	19
l	C <sub>6</sub> H <sub>5</sub>	<i>p</i> -Pr <sup>i</sup> -C <sub>6</sub> H <sub>4</sub>	CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	91
m	<i>p</i> -Br-C <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	40
n	<i>p</i> -CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	89
o	<i>p</i> -Cl-C <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	60
p	<i>p</i> -CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	<i>p</i> -CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	50
q	<i>p</i> -Cl-C <sub>6</sub> H <sub>4</sub>	<i>p</i> -Cl-C <sub>6</sub> H <sub>4</sub>	CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	47
r	C <sub>6</sub> H <sub>5</sub>	<i>p</i> -Br-C <sub>6</sub> H <sub>4</sub>	CH <sub>2</sub> CH <sub>3</sub>	57

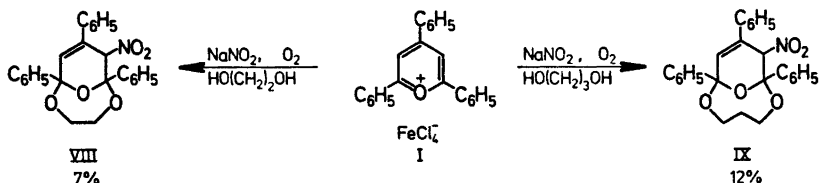


Chart 2.

formed in all experiments using alcohols as solvents.

c. *The influence of oxygen, and the pyrylium counter ion, on the dihydropyran formation.* The 2,4,6-triphenylpyrylium salts were also in this study chosen as model substrates, and as the alcohol was used 1-propanol. In an experiment with 2,4,6-triphenylpyrylium tetrachloroferrate, where oxygen was carefully excluded, we observed a decrease in the yield of dihydropyran IIc (from  $\approx 48\%$  to  $< 7\%$ ). Concurrently the yield of oxime (III) increased (from  $8\%$  to  $20\%$ ) as did that of pseudobase VI (from  $14\%$  to  $60\%$ ). The influence of the counter ion was adequately demonstrated by a comparison with 2,4,6-triphenylpyrylium tetrafluoroborate, which only gave  $11\%$  of dihydropyran IIc, while the yield of oxime (III) increased to  $61\%$ .

d. *Dihydropyrans from other 2,4,6-triarylpyrylium derivatives.* The reaction in which the dihydropyrans were generated was found to be rather independent of substituents in the aryl groups (Table 1), although there is undoubtedly a limit to this.

In all of the above experiments, some minor products were formed, but as a rule it was not tried to isolate them quantitatively. However, in Chart 1 such a quantitative experiment is depicted.

e. *Formation of isoxazoles (IV), and the oxime (III).* The isoxazoles (IV) were formed to some extent in all our experiments, and it was attempted to find conditions, whereby the yield of this product could be increased to the point where it became of synthetic usefulness. The reaction between 2,4,6-triphenylpyrylium ion and nitrite ion was therefore examined in a series of solvents (Table 2). From the table it emerges that the best yield of isoxazoles is obtained with acetonitrile as solvent under refluxing conditions. Furthermore, as can be seen in Table 2, this reaction is also general for 2,4,6-triarylpyrylium salts. It was found that a tetrafluoroborate counter ion gave better yields than when the tetrachloroferrate was employed. In the former case, it was furthermore observed, that the benzoate of the oxime, X, was formed (Chart 3). If oxygen was excluded, an almost quantitative yield of the oxime III was ob-

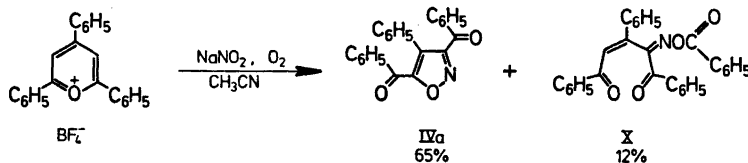
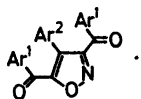


Chart 3.

Table 2. Isoxazoles IVa - d,



	Solvent	Ar <sup>1</sup>	Ar <sup>2</sup>	Counter ion	Yield (%)
a	H <sub>2</sub> O/CH <sub>3</sub> COCH <sub>3</sub> (5/95)	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	FeCl <sub>4</sub> <sup>-</sup>	44
a	CH <sub>3</sub> CH <sub>2</sub> CHOHCH <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	FeCl <sub>4</sub> <sup>-</sup>	29
a	(CH <sub>3</sub> ) <sub>3</sub> COH	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	FeCl <sub>4</sub> <sup>-</sup>	25
a	CH <sub>3</sub> CH <sub>2</sub> COH(CH <sub>3</sub> ) <sub>2</sub>	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	FeCl <sub>4</sub> <sup>-</sup>	15
a	HO(CH <sub>2</sub> ) <sub>4</sub> OH	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	FeCl <sub>4</sub> <sup>-</sup>	23
a	CH <sub>3</sub> CN	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	BF <sub>4</sub> <sup>-</sup>	65
b	CH <sub>3</sub> CN	C <sub>6</sub> H <sub>5</sub>	<i>m</i> -Cl-C <sub>6</sub> H <sub>4</sub>	BF <sub>4</sub> <sup>-</sup>	33
c	CH <sub>3</sub> CN	C <sub>6</sub> H <sub>5</sub>	<i>p</i> -NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>	BF <sub>4</sub> <sup>-</sup>	26
d	CH <sub>3</sub> CN	<i>p</i> -CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	BF <sub>4</sub> <sup>-</sup>	39

Table 3. Nuclear magnetic resonance spectra of compounds IIa-r, VIII and IX.<sup>a</sup>

Com- pound	Aromatic	H <sup>b</sup>	H <sup>b</sup>	Alkoxy
IIa	2.12-2.88 (15 H)	3.35	4.20	6.76, 6.84 (-CH <sub>3</sub> , 6 H)
IIb	2.03-2.71 (15 H)	3.25	4.14	6.05-6.92 (-OCH <sub>3</sub> , 4 H) 8.85, 8.87 (-CH <sub>3</sub> , 6 H)
IIc	2.02-2.70 (15 H)	3.25	4.12	6.16-7.10 (-OCH <sub>3</sub> , 4 H) 8.08-8.87 (-CH <sub>3</sub> CH <sub>3</sub> , 4 H) 8.93-9.37 (-CH <sub>3</sub> , 6 H)
IIId	2.04-2.69 (15 H)	3.25	4.11	6.12-6.93 (-OCH <sub>3</sub> , 4 H) 8.28-8.85 (-OCH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> , 8 H) 8.93-9.37 (-CH <sub>3</sub> , 6 H)
IIe	2.07-2.74 (15 H)	3.28	4.15	6.16-7.15 (-OCH <sub>3</sub> , 4 H) 8.17-9.00 (-OCH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> , 12 H) 9.00-9.33 (-CH <sub>3</sub> , 6 H)
IIIf	1.97-2.71 (15 H)	3.15	4.04	5.45-6.35 (-OCH <sub>3</sub> , 2 H) 8.71, 8.80, 8.89, 9.38 (-CH <sub>3</sub> , 12 H)
IIg	2.05-2.69 (15 H)	3.19	4.15	6.47-7.30 (-OCH <sub>3</sub> , 4 H) 9.12, 9.14 (-CH <sub>3</sub> , 18 H)
IIh	2.00-2.94 (15 H)	3.23	4.08	6.22-7.18 (-OCH <sub>3</sub> , 4 H) 8.83-9.50 (-CH(CH <sub>3</sub> )CH <sub>2</sub> CH <sub>3</sub> , 18 H)
IIi	1.81-2.81 (25 H)	3.00	3.92	5.10-5.83 (-OCH <sub>3</sub> , 4 H)
IIj	2.03-2.90 (14 H)	3.30	4.13	6.15-7.08 (-OCH <sub>3</sub> , 4 H) 8.18-8.78 (-CH <sub>3</sub> CH <sub>3</sub> , 4 H) 8.93-9.35 (-CH <sub>3</sub> , 6 H)
IIk	1.45-2.54 (14 H)	3.00	4.03	6.22-7.02 (-OCH <sub>3</sub> , 4 H) 8.15-8.72 (-CH <sub>2</sub> CH <sub>3</sub> , 4 H) 8.93-9.33 (-CH <sub>3</sub> , 6 H)
III <sup>d</sup>	2.05-2.95 (14 H)	3.28	4.14	6.23-7.44 (-OCH <sub>3</sub> , (CH <sub>3</sub> ) <sub>3</sub> CH-C <sub>6</sub> H <sub>4</sub> , 5 H) 8.10-8.82 (-CH <sub>2</sub> CH <sub>3</sub> , 4 H) 8.95-9.37 (-CH <sub>3</sub> , 6 H)
IIIm	2.14-2.55 (13 H)	3.21	4.05	6.15-7.07 (-OCH <sub>3</sub> , 4 H) 8.17-8.62 (-CH <sub>2</sub> CH <sub>3</sub> , 4 H) 8.93-9.33 (-CH <sub>3</sub> , 6 H)
IIIn	2.20-2.87 (13 H)	3.28	4.15	6.28-7.08 (-OCH <sub>3</sub> , 4 H) 8.20-8.77 (-CH <sub>2</sub> CH <sub>3</sub> , 4 H) 8.95-9.37 (-CH <sub>3</sub> , 6 H)
IIo	2.17-2.80 (13 H)	3.36	4.18	6.23-7.20 (-OCH <sub>3</sub> , 4 H) 8.08-8.83 (-CH <sub>2</sub> CH <sub>3</sub> , 4 H) 8.93-9.37 (-CH <sub>3</sub> , 6 H)
IIp	2.20-3.03 (12 H)	3.35	4.18	6.31-7.16 (-OCH <sub>3</sub> , 4 H) 8.10-8.82 (-CH <sub>2</sub> CH <sub>3</sub> , 4 H) 8.95-9.38 (-CH <sub>3</sub> , 6 H)
IIq	2.17-2.73 (12 H)	3.38	4.25	6.18-7.06 (-OCH <sub>3</sub> , 4 H) 8.12-8.78 (-CH <sub>2</sub> CH <sub>3</sub> , 4 H) 8.92-9.38 (-CH <sub>3</sub> , 6 H)
IIr	2.12-2.93 (14 H)	3.35	4.25	6.15-6.96 (-OCH <sub>3</sub> , 4 H) 8.86, 8.88 (CH <sub>3</sub> , 6 H)
VIII	1.75-2.55 (15 H)	3.36	4.15	5.67-6.47 (-OCH <sub>2</sub> CH <sub>3</sub> O-, 4 H)
IX	1.69-2.69 (15 H)	3.43	4.02	5.82-6.42 (-OCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> O-, 4 H) 7.57-9.22 (-CH <sub>3</sub> -, 2 H)

<sup>a</sup> The spectra were recorded at 60 MHz in CDCl<sub>3</sub> with TMS as internal reference. Chemical shifts are in  $\tau$ -values. Relative intensities are given in parenthesis. <sup>b</sup> Singlets. The integrals of all signals correspond to one proton. <sup>c</sup>  $J(\text{CH}-\text{CH}_3) = 6$  Hz for all four methyl groups. <sup>d</sup>  $J(\text{CH}-\text{CH}_3) = 7$  Hz.

tained. No attempts to maximize the other by-products (Chart 1) were undertaken.

## STRUCTURE ELUCIDATION

*a. The dihydropyrans (II).* The structure of the product, IIr, from 2,6-diphenyl-4-(4-bromophenyl)pyrylium tetrachloroferrate, sodium nitrite and ethanol was unambiguously determined by X-ray crystallography.<sup>1</sup> The molecule has the following geometrical features: 1, Five of the atoms of the dihydropyran ring are coplanar, whereas the carbon atom in the 6-position is 0.59 Å out of this plane. 2, The phenyl groups in the 2- and 6-positions, and the nitro group are on the same side of the dihydropyran ring, and thus the ethoxy groups are *cis* to each other. The structures of the analogues of IIr were determined on the basis of their elemental analysis (Table 7), and by comparison of their NMR spectra (Table 3) and their IR and UV spectra (Table 4) with those of compound IIr.

*b. The isoxazoles (IV).* The elemental analysis (Table 7) and the mass spectrum of compound IVa, *i.e.*, the product from 2,4,6-triphenyl-

pyrylium tetrafluoroborate and sodium nitrite in acetonitrile, established its formula as C<sub>23</sub>H<sub>15</sub>NO<sub>3</sub>. However, although its spectra (NMR, only aromatic protons; IR, strong absorption at 1670 cm<sup>-1</sup>) (Tables 5 and 6) agree with our structural assignment, they do not permit its identification. We thus particularly base the assigned structure on its formation from the oxime (III), which by oxidation with air yielded compound IVa (Chart 4).

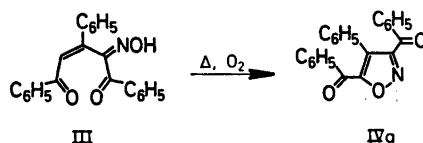


Chart 4.

*c. The oxime (III).* This compound was identified as 4-oximino-1,3,5-triphenyl-2-pentene-1,5-dione on the basis of its elemental analysis (Table 7) and its spectra. In the NMR spectrum (Table 5) were found signals due to the aromatic protons and at very low field a singlet (-2.20 τ), which disappeared upon

Table 4. Characteristic infrared and ultraviolet absorptions of compounds IIa-r, VIII and IX.

Compound	IR <sup>a</sup> cm <sup>-1</sup>	UV (96 % ethanol)					
		$\lambda_{\max}$ nm	log $\epsilon$	$\lambda_{\max}$ nm	log $\epsilon$	$\lambda_{\max}$ nm	log $\epsilon$
IIa	1555	209	4.47	251	4.16		
IIb	1555	210	4.29	249	4.10		
IIc	1555	212	4.27	248	4.10		
IId	1555	211	4.23	248	4.05		
IIe	1560	214	4.25	248	4.14		
IIf	1555	209	4.30	247	4.06		
IIg	1560	210	4.34	246	4.11		
IIh	1560						
IIi	1560						
IIj	1555	210	4.42	254	4.23		
IIk	1560	211	4.32	248	4.29		
III	1560	211	4.31	254	4.16		
IIIm	1555	210	4.31	228	4.31	242 <sup>sh</sup>	4.15
IIIn	1555	216	4.33	248	4.20		
IIo	1560	212 <sup>sh</sup>	4.33	223	4.36	248	4.20
IIp	1555	220	4.34	256	4.25		
IIq	1555	226	4.36	258	4.28		
IIr	1550	211	4.11	259	3.98	298 <sup>sh</sup>	3.21
VIII	1560	212	4.22	249	4.10		
IX	1555	210	4.27	244	4.09		

<sup>a</sup> The spectra of compounds IIh, i were recorded in CHCl<sub>3</sub>, all other compounds in KBr.

Table 5. Nuclear magnetic resonance spectra of compounds III, IVa-d, X and XI<sup>a</sup>.

Compound	Aromatic	Other
III	1.78–2.75 (15 H)	2.17 (alkene, 1 H), –2.20 (OH, 1 H) <sup>b</sup>
IVa	1.61–2.64	
IVb	1.80–2.87	
IVc	1.68–2.72	
IVd	1.97–2.93 (13 H)	7.60 (methyl, 6 H)
X	1.38–2.75	
XI	1.93–2.98 (16 H)	1.82 (methine, 1 H) <sup>b</sup>

<sup>a</sup> The spectra were recorded at 60 MHz with TMS as internal reference. Chemical shifts are in  $\tau$ -values. Relative intensities are given in parenthesis. The spectrum of compound III was recorded in DMSO-*d*<sub>6</sub>, those of the other compounds in CDCl<sub>3</sub>.

<sup>b</sup> These singlets disappeared after shaking with D<sub>2</sub>O.

Table 6. Characteristic infrared and ultraviolet absorptions of compounds III, IVa-d, X and XI.

Compound	IR in KBr, cm <sup>-1</sup>	UV (96 % ethanol)							
		$\lambda_{\max}$ nm	log $\epsilon$	$\lambda_{\max}$ nm	log $\epsilon$	$\lambda_{\max}$ nm	log $\epsilon$	$\lambda_{\max}$ nm	log $\epsilon$
III	3290(OH), 1680, 1660(C=O)	209	4.43	264	4.46	310	4.32		
IVa	1670(C=O)	208	4.44	263	4.41	287 <sup>sh</sup>	4.10		
IVb	1680(C=O)	208	4.43	264	4.30	289 <sup>sh</sup>	4.04		
IVc	1670(C=O), 1515(–NO <sub>2</sub> )	207	4.38	270	4.41				
IVd	1670(C=O)	208	4.37	274	4.11				
X	1760, 1660, 1650(C=O)	206	4.34	237	4.28	264	4.28	311 <sup>sh</sup>	4.16
XI	1705, 1645(C=O), 1570(–NO <sub>2</sub> )	206	4.40	256	4.24	284 <sup>sh</sup>	4.11	343 <sup>sh</sup>	3.72

shaking with D<sub>2</sub>O. This singlet is believed to be due to the oxime proton; the signal due to the vinyl proton is found at 2.17  $\tau$ , and is unchanged upon shaking with D<sub>2</sub>O. Its IR spectrum (Table 6) showed two carbonyl absorptions, and a broad band at 3300 cm<sup>-1</sup> from the oxime function.

*d. Compound XI (4-nitro-1,3,5-triphenyl-2-pentene-1,5-dione).* The assignments of structure to this compound is based on its generation from the corresponding dihydropyran, IIc, by mild acid hydrolysis (Chart 5).

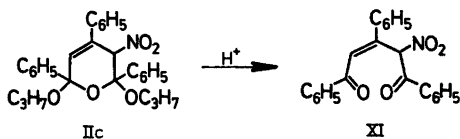


Chart 5.

Furthermore, its spectroscopic features support the proposed structure (Tables 5 and 6).

*e. 4-O-Benzoyloximino-1,3,5-triphenyl-2-pentene-1,5-dione (X).* This compound is assigned its structure on the basis of its IR and NMR spectra (Tables 5 and 6). Furthermore, its molecular weight was confirmed by mass spectrometry. 1,3,5-Triphenyl-2-pentene-1,5-dione (VI),<sup>3</sup> 1,3,5-triphenyl-2,4-pentadiene-1-one (V)<sup>4</sup> and 2-benzoyl-3,5-diphenylfuran (VII)<sup>5</sup> were identical (m.p.'s and IR spectra) to the respective authentic samples.

## DISCUSSION

The reactions between 2,4,6-triarylpopyrium salts and nitrite ion represent a complicated sequence of reactions, and consequently no complete understanding of the reaction pathways leading to each individual product could

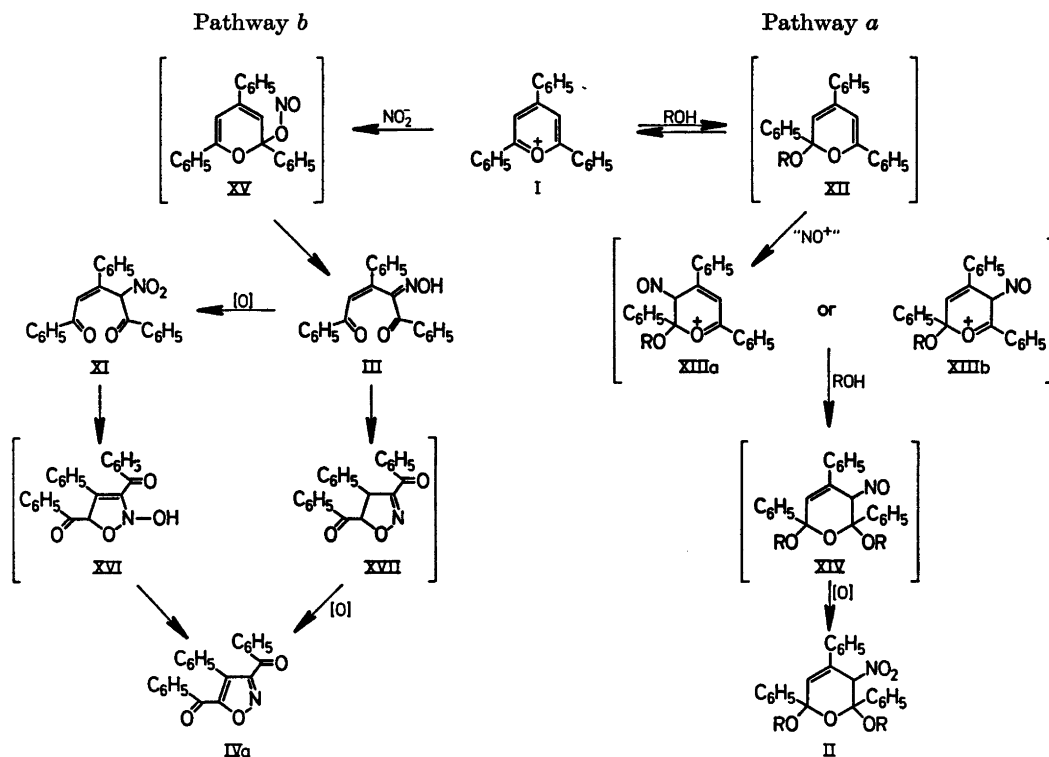


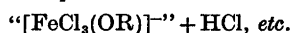
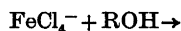
Chart 6.

be obtained. However, in order to obtain some understanding of the reaction mechanisms some further experiments have been performed, again using the 2,4,6-triphenylpyrylium ion as substrate.

We believe that the following represents the main pattern of events.

There are two mutually independent types of nucleophilic attack on the pyrylium ion (Chart 6), namely by alcohol (Pathway *a*) and by nitrite (Pathway *b*). After the initial steps, the reactions presumably proceed like shown in the scheme. This assumption is based on: (1) the pH-dependency of the dihydropyran formation, (2) the isolation of intermediates.

(1) The formation of IIc from I and 1-propanol was investigated with either tetrachloroferrate or tetrafluoroborate as counterions. It turns out that tetrachloroferrates solvolyze slowly in protic solvents as seen from pH measurements (eqn. 1), whereas tetrafluoroborates do not under the experimental condi-



(1)

tions employed.

By using the tetrachloroferrate salt of I, a yield of 48 % of IIc was obtained, whereas with the tetrafluoroborate only 11 % of IIc could be obtained; concurrently, the yield of the oxime III increased from 8 % to 61 %. In each experiment the reaction vessels were open to the air.

The influence of pH was corroborated by doing an experiment with the tetrafluoroborate salt with added phosphoric acid, whereby the yield of dihydropyran (IIc) could be increased to 37 %, and the yield of oxime (III) was 34 %. This clearly illustrates the influence of pH, but it is not disproved that the tetrachloroferrate does not have some specific effect, like *e.g.*, increasing the oxidation potential.

(2) That two independent pathways to the main products (II and IV) exist was further

consolidated by isolating and examining possible intermediates. Thus the oxime (III) could be generated almost quantitatively when  $I, BF_4^-$  and sodium nitrite was allowed to react in boiling acetonitrile with exclusion of air. If boiling of the reaction mixture was continued in the presence of air the oxime III was converted to isoxazole IVa in the same yield as could be obtained from  $I, BF_4^-$  and nitrite if air was present from the beginning. This clearly demonstrates that III is the precursor for IVa in acetonitrile, and probably also in other solvents (note that III could also be isolated from reaction mixtures with propanol as solvent as shown in Chart 1). Furthermore, by following the reaction in acetonitrile with air present, by thin layer chromatography, it was observed that the oxime concentration increased in the beginning of the reaction whereafter it slowly disappeared in favor of isoxazole (IVa). Furthermore, a number of attempts were undertaken to convert the oxime III to dihydropyran (IIc), but in all cases the only product observed was IVa.

The nitro compound XI could also have been a possible intermediate for both isoxazole and dihydropyran formation. It was only detected in the reaction between  $I, FeCl_4^-$  and sodium nitrite in 2-propanol and could be isolated in 38 % yield, but its formation is probably due to partial degradation of the dihydropyran, IIc. Compound XI was most conveniently prepared from the dihydropyran, IIc, by acid hydrolysis. All attempts to convert it back to dihydropyran, IIc, failed; instead the isoxazole, IVa, was formed.

*In conclusion* we postulate that the dihydropyran is formed from XII by attack of nitrous acid or maybe  $NO^+$  to give XIII, which reacts with the alcohol to give intermediate XIV which in turn is oxidized to the dihydropyran (II). The isoxazole is assumed to be formed *via* initial attack of nitrite on I to give intermediate XV which in turn rearranges to III. The reaction of III to give the product IV may go *via* either of the two pathways shown.

Most probably the main reaction goes *via* intermediate XVII, since refluxing of the nitro compound, XI, gave IVa and a 20 % yield of the furan (VII) (Chart 1). This contrasted with results from reacting  $I, BF_4^-$  and sodium nitrite

in acetonitrile, which only gave compounds IVa and X.

The furan (VII) could be isolated in very low yield from  $I, FeCl_4^-$  and sodium nitrite in propanol, but since it can also be generated from the pseudo base (VI) (Chart 1) by mild oxidations,<sup>5</sup> VI may be the progenitor.

The pentadienone (V) (Chart 1) is most likely formed directly from I. It was shown to be the main product upon reduction of 2,4,6-triphenylpyrylium tetrafluoroborate with sodium borohydride, or phenylsilane.<sup>6</sup>

## EXPERIMENTAL

Microanalysis was carried out in the microanalysis department of this laboratory. Melting points (uncorrected) were determined on a Reichert melting point microscope or a Büchi melting point apparatus. Infrared spectra were recorded on a Perkin Elmer model 337 grating infrared spectrophotometer. Ultraviolet spectra were recorded on a Perkin Elmer model 137 UV spectrophotometer. Nuclear magnetic resonance spectra were recorded on a Varian A60A spectrometer. Mass spectra were obtained with an A.E.I. MS-902 instrument, using direct sample insertion into the ion source. The electron energy was maintained at 70 eV. Preparative layer chromatography (PLC) was performed on 20 × 100 cm plates with a 2.5 mm thick layer of silica gel (Merck PF<sub>254+366</sub>). The plates were developed 2–3 times with benzene or benzene-petroleum ether (1:1). The fractions were isolated by continuous extraction with chloroform in a Soxhlet apparatus.

*Pyrylium salts.* The tetrachloroferrates were prepared according to Ref. 6 and the tetrafluoroborates according to Ref. 7.

*Reaction of pyrylium salts with sodium nitrite in different alcohols.* In all preparations except with the very involatile glycols the following procedure was used: e.g. 2,4,6-triphenylpyrylium tetrachloroferrate (5.00 g, 9.9 mmol) and sodium nitrite (1.37 g, 19.8 mmol) were suspended in propanol (100 ml) and the mixture was stirred at room temperature for 64 h. After this, 2.26 g of unreacted pyrylium salt was removed by filtration and the reaction mixture was evaporated to dryness and extracted with benzene. After evaporation of the benzene, the resulting oil was separated by PLC (eluent: benzene/petroleum ether 1:1) into: (1) 2,4,6-triphenyl-2,6-dipropoxy-5-nitro-5,6-dihydro-2H-pyran (IIc) (1.27 g, ~48 %),\* (2) 3,5-dibenzoyl-4-

\* This compound was contaminated with about 3 % of 1,3,5-triphenyl-2,4-pentadiene-1-one (V) as measured by NMR-spectroscopy. Direct isolation of compound V was only possible when the reaction was run in methanol. In that case compound V was obtained in 4 % yield.



Table 7. Melting points and elemental analyses of compounds IIa-r, III, IVa-d and VIII-XI.

Com- pound <sup>a</sup>	M.p. °C	Formula	Analyses		% H		% N		% halogen	
			% C calc.	found	calc.	found	calc.	found	calc.	found
IIa <sup>c</sup>	164-165	C <sub>25</sub> H <sub>23</sub> NO <sub>5</sub>	71.93	71.85	5.55	5.60	3.36	3.29		
IIb <sup>d</sup>	158-159	C <sub>27</sub> H <sub>27</sub> NO <sub>5</sub>	72.79	72.70	6.11	6.33	3.14	3.20		
IIc <sup>e</sup>	142-143	C <sub>28</sub> H <sub>31</sub> NO <sub>5</sub>	73.55	73.44	6.60	6.78	2.96	3.00		
II d <sup>e</sup>	114-115	C <sub>31</sub> H <sub>35</sub> NO <sub>5</sub>	74.23	74.10	7.03	7.05	2.79	2.76		
IIe <sup>e</sup>	71-73	C <sub>33</sub> H <sub>39</sub> NO <sub>5</sub>	74.83	74.60	7.42	7.44	2.64	2.61		
II f <sup>e</sup>	163-164	C <sub>28</sub> H <sub>31</sub> NO <sub>5</sub>	73.55	73.80	6.60	6.73	2.96	2.90		
II g <sup>e</sup>	152-155	C <sub>33</sub> H <sub>39</sub> NO <sub>5</sub>	74.83	74.70	7.42	7.45	2.64	2.46		
II h <sup>e</sup>	<sup>b</sup>	C <sub>33</sub> H <sub>39</sub> NO <sub>5</sub>								
II i <sup>e</sup>	124-125	C <sub>37</sub> H <sub>39</sub> NO <sub>5</sub>	73.90	73.70	6.82	6.84	2.87	2.70		
II k <sup>e</sup>	162-164	C <sub>30</sub> H <sub>33</sub> NO <sub>5</sub>	67.17	67.12	5.83	5.97	5.40	5.52		
III <sup>f</sup>	117-119	C <sub>38</sub> H <sub>39</sub> O <sub>7</sub>	74.54	74.43	7.23	7.30	2.72	2.66		
II m <sup>f</sup>	167-168	C <sub>33</sub> H <sub>37</sub> Br <sub>2</sub> NO <sub>5</sub>	55.17	55.18	4.63	4.73	2.22	2.15	25.31	25.58
II n <sup>f</sup>	149-151	C <sub>31</sub> H <sub>35</sub> NO <sub>5</sub>	74.23	74.32	7.03	7.10	2.79	2.76		
II o <sup>d</sup>	146-148	C <sub>30</sub> H <sub>29</sub> Cl <sub>2</sub> NO <sub>5</sub>	64.21	64.29	5.39	5.42	2.72	2.58		
II p <sup>d</sup>	143-145	C <sub>32</sub> H <sub>33</sub> NO <sub>5</sub>	74.54	74.56	7.23	7.34	2.72	2.73		
II q <sup>f</sup>	159-160	C <sub>28</sub> H <sub>29</sub> Cl <sub>2</sub> NO <sub>5</sub>	60.38	60.26	4.89	4.91	2.43	2.39	18.44	18.43
II r <sup>e</sup>	125-127	C <sub>27</sub> H <sub>29</sub> Br <sub>2</sub> NO <sub>5</sub>	61.83	61.75	5.00	5.11	2.67	2.58	16.24	16.39
III <sup>e</sup>	156-168	C <sub>23</sub> H <sub>17</sub> NO <sub>3</sub>	77.73	78.00	4.82	5.00	3.94	3.93		
IV a <sup>e</sup>	122-123	C <sub>25</sub> H <sub>15</sub> NO <sub>3</sub>	78.17	78.02	4.28	4.29	3.96	3.97		
IV b <sup>c</sup>	126-127	C <sub>23</sub> H <sub>14</sub> ClNO <sub>3</sub>	71.22	71.45	3.64	3.87	3.61	3.34	9.14	9.25
IV c <sup>e</sup>	113-114	C <sub>23</sub> H <sub>19</sub> NO <sub>5</sub>	69.34	69.20	3.54	3.73	7.03	6.98		
IV d <sup>e</sup>	118-119	C <sub>25</sub> H <sub>19</sub> NO <sub>3</sub>	78.72	78.90	5.02	5.18	3.67	3.68		
VIII <sup>e</sup>	158-159	C <sub>25</sub> H <sub>21</sub> NO <sub>5</sub>	72.28	72.82	5.10	5.20	3.37	3.37		
IX <sup>e</sup>	-	C <sub>26</sub> H <sub>23</sub> NO <sub>5</sub>	72.71	74.20	5.40	5.86	3.26	2.97		
X <sup>c</sup>	153-154	C <sub>30</sub> H <sub>21</sub> NO <sub>4</sub>	78.41	78.12	4.61	4.77	3.05	2.96		
IX <sup>e</sup>	126 <sup>d</sup>	C <sub>23</sub> H <sub>17</sub> NO <sub>4</sub>	74.38	74.50	4.61	4.73	3.77	3.75		

<sup>a</sup> Recrystallization solvents; <sup>c</sup> Methanol, <sup>d</sup> Ethanol, <sup>e</sup> Benzene/petroleum ether and <sup>f</sup> ethanol/benzene. <sup>b</sup> Compounds IIh,i were isolated as oils.

phenylisoxazole (IVa) (0.12 g ~ 6%), (3) 2-benzoyl-3,5-diphenylfuran (VII) (0.017 g ~ 1%), (4) 1,3,5-triphenyl-1,5-pentenedione (VI) (0.25 g ~ 14%), and (5) 4-oximino-1,3,5-triphenyl-2-pentene-1,5-dione (III) (0.16 g ~ 8%).

The experiment with 2,4,6-triphenylpyrylium tetrafluoroborate and phosphoric acid was carried out as described above; pyrylium salt (1.00 g ~ 2.52 mmol), 90% phosphoric acid (0.14 g ~ 1.26 mmol) and sodium nitrite (0.35 g ~ 5.04 mmol) were suspended in propanol (20 ml). PLC gave the dihydropyran IIc (0.44 g ~ 37%) and the oxime III (0.30 g ~ 34%).

In those preparations where glycols were used, a slightly different procedure was employed: After stirring for five days at room temperature, 200 ml of water was added, and the mixture was extracted three times with chloroform. After evaporation, the residue was extracted with benzene. The resulting oil was separated as above.

*Reaction of pyrylium salts with sodium nitrite in acetonitrile.* Compounds IVa-d were all prepared according to the following procedure: e.g. 2,4,6-triphenylpyrylium tetrafluoroborate (1.50 g, 3.8 mmol) was dissolved in acetonitrile (30 ml) and sodium nitrite (0.79 g, 11.4 mmol) was added. The mixture was refluxed for 20 h\* and evaporated to dryness. The resulting oil was extracted with chloroform and the crude material from evaporation of the chloroform was recrystallized from methanol to give 0.79 g ~ 59% of 3,5-dibenzoyl-4-phenylisoxazole (IVa). By the method of PLC (eluent: benzene) a further product was found. Separation of the residue from the chloroform extraction (the same amount of starting materials were used) gave (1) 3,5-dibenzoyl-4-phenylisoxazole (0.87 g ~ 65%) and (2) a compound believed to be the benzoate of 4-oximino-1,3,5-triphenyl-2-pentene-1,5-dione (X) (0.22 g ~ 12%).

*Preparation of 4-oximino-1,3,5-triphenyl-2-pentene-1,5-dione (III).* This compound was prepared in the same way as compounds IVa-d except that the reaction mixture was very carefully protected against air. The crude product from the chloroform extraction was recrystallized from benzene/petroleum ether to give an almost quantitative yield of III. Protection against air was not found necessary during the work up.

*Preparation of 4-nitro-1,3,5-triphenyl-2-pentene-1,5-dione (XI).* Compound IIc (0.50 g) was dissolved in chloroform (5 ml). To this solution was added concentrated hydrochloric acid (1 ml) and the resulting two phase system was stirred vigorously for 10 min. Water and additional chloroform was added and the organic phase was separated and dried over anhydrous sodium sulfate. After evaporation of the chloroform, the residue was recrystallized from ben-

zene/petroleum ether to give an almost quantitative yield of compound XI.

*Thermolysis of compound XI.* Compound XI (0.40 g) was dissolved in acetonitrile (20 ml) and the solution was refluxed for 2 h. After evaporation of the solvent the residue was separated by PLC (eluent: benzene) into (1) 3,5-dibenzoyl-4-phenylisoxazole (IVa) (0.20 g ~ 52%) and (2) 2-benzoyl-3,5-diphenylfuran (VII) (0.07 g ~ 20%).

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\* However, in the preparation of IVd it was necessary to reflux for 7 days.