# **Reaction of Diphenylcyclopropenethione with Pyridinium Imines**

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Reaction of diphenylcyclopropenethione with a variety of N-substituted pyridinium imines in refluxing benzene gives 2,4,5-trisubstituted-6H-1,3-oxazin-6-thiones in good to excellent yields. The structure of 2,4,5-triphenyl-6H-1,3-oxazin-6-thione prepared in this manner was proven by oxidation and by hydrolysis to the known 2,4,5-triphenyl-6H-1,3-oxazin-6-one. In the preparation of 4,5-diphenyl-2-ethoxy-6H-1,3-oxazin-6-thione changing the heteroaromatic residue in the imine from pyridine to 3-picoline to 3,5-lutidine had little effect on the yield (about 60%).

La réaction de la diphénylcyclopropènethione avec une variété d'imines de pyridinium N-substituées dans le benzène à reflux donne des trisubstituées-2,4,5-6H-1, oxazine-3-thione-6 avec un excellent rendement. La structure de la triphényl-2,4,5-6H-1, oxanine-3-thione-6 préparée de cette manière est prouvée par oxydation et par hydrolyse jusqu'à la triphényl-2,4,5-6H-1, oxazine-3-one-6 qui est connue. Dans la préparation de la diphényl-4,5-éthoxy-2-6H-1, oxanine-3-thione-6, le changement du résidu hétéroatomique dans l'imine de la pyridine à la picoline-3 et à la lutidine-3,5 a un faible effet sur le rendement (autour de 60%).

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Since its initial preparation by Breslow *et al.* (1) and Vol'pin *et al.* (2) diphenylcyclopropenone **1** has proven to be a versatile synthetic intermediate leading to *e.g.* 3,4,6-triaryl-2*H*-pyran-2-ones (3), indolizine derivatives (1,4), cyclic dienones (5,6), a 4-pyridazone (7), aziridinyl enamides (8), methylene cyclopropenes (9), pyrroles (10), pyrrolines (10), furans (11–13), 4-oxazolines (11–13), a 3,4-benzo-tropone (10), and pyrrolo[1,2-*b*]pyridazines (4), 2,3,6-triphenylphenol, and esters of 3,5-hexadienoic acid (14). Its sulfur analog diphenyl-



cyclopropenethione 2 might be expected to

exhibit similar synthetic potential but to date

relatively little success has been obtained with

this compound which is thermally less stable

than its oxygen counterpart. Compound **2** reacts with pyridinium ylides to give 3,4,6-triaryl-2*H*pyran-2-thiones (3), and with 1-(*N*-pyrrolidino)-1-propene to form 2,3-diphenyl-5-methyl-4-(*N*-pyrrolidino)-2-cyclopentenethione(15), while reaction with heteroaromatic nitrogen compounds provides thionpyrazolo[1,2-*a*]pyridazine, 2,3-diphenyl-1-thionpyrazolo[1,2-*a*]benzo-[*c*]cinnoline, di-(7,8-diphenylpyrrolo[1,2-*a*]pyrazinyl)-6-sulfide, and related structures (16).

We report the reaction of diphenylcyclopropenethione with pyridinium imines which yields a variety of 6H-1,3-oxazin-6-thiones in good to excellent yields.

For example treatment of a suspension of pyridinium-N-(benzoyl)-imine (3) with an equimolar quantity of diphenylcyclopropenethione (2) in dry benzene under reflux for 12 h afforded 2,4,5-triphenyl-6H-1,3-oxazin-6thione (4) in 88% yield as a deep orange crystalline solid (Scheme 1). The spectral characteristics of 4 and similar structures are very similar to



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those of the 3,4,6-triaryl-2*H*-pyran-2-thiones formed in the analogous reaction of pyridinium ylides on 2 (3). The structure of 4 was proven conclusively by conversion with *m*-chloroperbenzoic acid (17) to the known 2,4,5-triphenyl-6*H*-1,3-oxazin-6-one (5) which was also prepared independently by the reaction of the pyridinium imine 3 on diphenylcyclopropenone (Scheme 2).

After this paper was submitted for publication, Sasaki *et al.* reported the similar formation of 2,4,5-trisubstituted-6H-1,3-oxazin-6-ones by the reaction of pyridinium imines on diphenylcyclopropenone (18).

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Compound 5 had previously been synthesized by Sprio by the oxidation of 2,4,5-triphenylpyrrole with peracetic acid (19).

Hydrolysis of 4 with sodium methoxide in methanol followed by acidification with hydrochloric acid also gave the 6H-1,3-oxazin-6-one (5) (Scheme 3). Since the intermediate stage after alkaline hydrolysis is soluble in water, from which the orange solid 5 is precipitated upon acidification, it is plausibly represented by the salt 6.

The generality of this preparation of 2,4,5trisubstituted-6H-1,3-oxazin-6-thiones is demonstrated by the variety of substituted pyridinium imines which react with **2**. The analytical

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and spectral data on the new compounds are summarized in Tables 1 and 2.

In the preparation of 4,5-diphenyl-2-ethoxy-6H-1,3-oxazin-6-thiones, changing the heteroaromatic residue in the imine, and therefore the leaving group in the cyclization step from pyridine to 3-picoline to 3,5-lutidine had a minimal effect on the yield. The range of 6H-1,3-oxazin-6-thiones made available by this procedure is evident from the 2-substituents which include aryl, alkoxy, arenoyl, and heterocyclic groups. This preparation of 6H-1,3oxazin-6-thiones represents an extension of the apparently general principal of the ring expansion of triafulvenes (20) with pyridinium betaines, phosphonium ylides, and sulfonium ylides (14).

The mechanism of such processes has been examined by Eicher and his coworkers (14). Three alternative pathways have been considered and recent evidence favors that involving initial attack by the  $\alpha$  carbon of the betaine or ylide on C-1 position of the triafulvene followed by formation of a ketene with cyclization of the latter to the products. The latter intramolecular process is evidently rapid in this case compared with possible intermolecular reaction of the ketene with a protic solvent since reaction of diphenylcyclopropenethione with N-benzoylpyridinium imine in methanol-benzene gave 4 in 80% yield with no trace of an ester byproduct.

## Experimental

Melting points were determined on a Fisher-Johns apparatus and are uncorrected. The i.r. spectra were recorded on a Perkin-Elmer model 421 spectrophotometer, and only the principal sharply defined peaks are reported. The n.m.r. spectra were recorded on Varian A-60 and A-100 analytical spectrometers. The spectra were measured on approximately 10-15% (w/v) solutions in CDCl<sub>3</sub>, with tetramethylsilane as a standard. Line positions are reported in p.p.m. from the reference. Mass spectra were determined on an Associated Electrical Industries MS-9 double focusing high resolution mass spectrometer. The ionization energy, in general, was 70 eV. Peak measurements were made by



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			Found				Calculated				
R*	Yield (%)	point (°C)	С	H N	S	Molecular ion (mass spectrum)	C	н	N	S	Molecular ion (mass spectrum)
	63	135	69.69 5	,10 4.5	10.63	309.0816	69.85	4.89	4.53	10.36	309.0823
p-CH₃OC₅H₄	90	175–177			8.52	371.0980			3.77	8.63	371.0942
p-CH <sub>4</sub> C <sub>6</sub> H <sub>4</sub>	94	180-181	77.88 4	.71 3.98	9.11	355.1030	77.71	4.82	3.94	9.02	355.1031
$m - CH_{4}C_{6}H_{4}$	83	138-140		3.7′	8.62	355.1026			3.94	9.02	355.1031
0-CH <sub>1</sub> C <sub>6</sub> H <sub>4</sub>	50	154-156	77.89 5	.01 4.12	8.99	355.1025	77.71	4.82	3.94	9.02	355.1031
p-CIC,H	74	136-138		3.6	8.20	375.0480			3.73	8.53	375.0485
C <sub>e</sub> H <sub>e</sub>	88	180	77.54 4	.58 4.10	9,19	341.0868	77.40	4,43	4.10	9.39	341.0874
C <sub>6</sub> H <sub>5</sub> CH=CH	61	185	78.13 4	.82 3.98	9.07	367.1030	78.44	4.66	3.81	8.73	367.1031
Сн=сн-	48	170171	70.54 4	.10 3.5	1.75	373.0590	70.75	4.05	3.75	17.17	373.0596
	50	129-133		4.20	9.80	331.0662			4.23	9.68	331.0667
	47	123-125		— 4.3:	5 18.01	347.0435			4.03	18.46	347.0439

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 TABLE 1.
 2,4,5-Trisubstituted-6H-1,3-oxazin-6-thiones

Ç₀H, \_C₀H, <sup>\_</sup>s

## TABLE 2. Spectroscopic data on 2,4,5-trisubstituted-6H-1,3-oxazin-6-thiones

	n.m.r			·			
R*	Vinyl and arom	atic protons	Methyl protons	v (KBr disc)			
C <sub>2</sub> H <sub>5</sub> O	6.9-7.6 (10H)m	4.60 (2H)q (methylene-H)	1.48 (3H)t	950	1052	1300	1483
<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub>	8.31, 6.99 (4H)ABq J = 9 Hz	7.0-7.6 (10H)m	3.87 (3H)s	954	1126	1257	1477
$p-MeC_6H_4$	7.30, 8.24 (4H)ABq J = 8 Hz	7.1–7.55 (10H)m	2.42 (3H)s	953	1115	1278	1477
m-MeC <sub>6</sub> H <sub>4</sub>	8.05-8.3 (2H)m	7.1-7.6 (12H)m	2.43 (3H)s	950	1116	1287	1472
o-MeC <sub>6</sub> H <sub>4</sub>	8.1-8.4 (1H)m	7.0-7.6 (13H)m	2.80 (3H)s		1110	1285	1472
p-ClC <sub>6</sub> H <sub>4</sub>	8.36-7.53 (2H)ABq	7.1-7.5 (12H)m		952	1120	1290	1475
C <sub>6</sub> H₅	8.2-8.6 (2H)m	6.9–7.7 (13H)m		953	1120	1276	1478
C <sub>6</sub> H <sub>5</sub> —CH=CH—	8.04, 6.86 (2H)ABq J = 16.5 Hz	7.05-7.8 (15H)m		950	1120	1278	1475
Сн=сн-	8.10, 6.64 (2H)ABq J = 15.5 Hz	6.9–7.6 (13H)m			1114	1273	1470
		7.0-8.2 (13H)m			1110		1490
$\sqrt{s}$		7.0-8.3 (13H)m		950	1110	1270	1473

\*Refers to formula 7.

comparison with perfluorotributylamine at a resolving power of 15 000. Kieselgel DF-5 (Camag, Switzerland) and Eastman Kodak precoated sheets were used for t.l.c. Microanalyses were carried out by Dr. C. Daesslé, Organic Microanalysis Ltd., Montreal, Quebec and by Mrs. D. Mahlow of this Department.

#### Preparation of Pyridinium Imines

The pyridinium imines required in this study were prepared and purified by the general procedures given by Sasaki *et al.* (21) and Snieckus and coworkers (22). New imines prepared by these procedures are summarized in Tables 3 and 4.

## Diphenylcyclopropenethione

This compound was prepared by the method of Eicher and Frenzel (23), see also (17).

## Reactions of Diphenylcyclopropenethione with

#### Pyridinium Imines

The reaction conditions and purification procedures are illustrated by the following three examples. The analytical and spectral properties of other compounds similarly prepared are summarized in Tables 1 and 2.

(a) Reaction of N-(p-Toluoyl)pyridinium Imine with

Diphenylcyclopropenethione

A suspension of 1.06 g (5 mmol) of N-(p-toluoyl)pyridinium imine and 1.11 g (5 mmol) of diphenylcyclopropenethione in 25 ml of dry benzene was refluxed for 12 h during which time the solution became dark red. Removal of the solvent *in vacuo* and trituration of the residual oil with

cold methanol afforded the 4,5-diphenyl-2-(p-tolyl)-6H-1,3oxazin-6-thione as a bright orange solid m.p. 180-181°, 1.68 g (94% yield).

Anal. Calcd. for  $C_{23}H_{17}NOS$  (mol. wt. 355.1031): C, 77.71; H, 4.82; N, 3.94; S, 9.02. Found (355.1030 (mass spectrum)): C, 77.88; H, 4.71; N, 3.98; S, 9.11.

The n.m.r. spectrum  $\delta_{TMS}(CDCl_3)$ : 2.42 (s, 3H, aromatic CH<sub>3</sub>); 7.1-7.43 (ABq, 4H, tolyl protons); 7.1-7.55 (m, 10H, aromatic protons). The i.r. spectrum  $\nu$  (KBr disc) 953, 1115, 1278, 1477 cm<sup>-1</sup>.

(b) Reaction of N-(Carboethoxy)pyridinium Imine with Diphenylcyclopropenethione

A suspension of 0.84 g (5 mmol) of N-(carboethoxy)pyridinium imine and 1.11 g (5 mmol) of diphenylcyclopropenethione in 25 ml of dry benzene was heated under reflux for 12 h. Removal of the solvent *in vacuo* and trituration of the residual oil with methanol afforded 4,5-diphenyl-2-ethoxy-6H-1,3-oxazin-6-thione as orange crystals, m.p. 135°, 0.95 g (63% yield).

Anal. Calcd. for  $C_{18}H_{15}NO_2S$  (mol. wt. 309.0823): C, 69.85; H, 4.89; N, 4.53; S, 10.36. Found (309.0816 (mass spectrum)): C, 69.69; H, 5.10; N, 4.57; S, 10.63.

The n.m.r. spectrum  $\delta_{TMS}(CDCl_3)$ : 1.48 (t, 3H,  $CH_3CH_2$ ) 4.60 (q, 2H,  $CH_3CH_2$ ); 6.9–7.6 (m, 10H, aromatic protons). The i.r. spectrum (KBr disc), 950, 1052, 1300, 1483 cm<sup>-1</sup>.

The identical product was obtained by the reaction of diphenylcyclopropenethione with (i) N-(carboethoxy)-3-methylpyridinium imine, (ii) N-(carboethoxy)-4-methylpyridinium imine, and (iii) N-(carboethoxy)-3,4-dimethylpyridinium imine in 60, 58, and 54% yields, respectively.

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TABLE 3. N-Substituted pyridinium imines

		Maldara			Found		-		Calculated	1
R*	Yield (%)	Melting point (°C)	С	н	N	Molecular ion (mass spectrum)	с	н	N	Molecular ion (mass spectrum)
p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	86	145	68.47	5.03	11.19	228.0894	68.39	5.30	12.27	228.0899
$p-CH_3 - C_6H_4$	81	164-166	73.36	5.78	13.36	212.0944	73.55	5.70	13.20	212.0949
m-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	88	87-88			13.06	212.0946			13.20	212.0949
o-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	82	104	73.31	5.64	12.85	212.0947	73.55	5.70	13.20	212.0949
$p-Cl-C_6H_4$	80	186-187	61.82	3.90	11.71	232.0400	61.92	3.90	12.05	232.0404
C <sub>6</sub> H <sub>5</sub> —CH—CH	90	149-150	75.14	5.63	12.61	224.0948	74.96	5.46	12.50	224.0950
Сн=сн-	87	125-126	62.07	4.53	12.21 (S:13.72)	230.0516	61.84	4.33	12.03 (S:13.73)	230.0515
	78	223-224	63.56	4.27	14.57	188.0583	63.80	4.29	14.88	188.0586
$\sqrt{s}$	91	208–209	58.83	4.38	13.64 (S:15.99)	204.0354	58.79	3.95	13.72 (S:15.70)	204.0358

\*Refers to formula 8:  $R \rightarrow C - \bar{N} - Py^+$ 

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TABLE 4. Spectroscopic data on N-substituted pyridinium imines

	n.m.r. spectrum $\delta_{TMS}$ (CDCl <sub>3</sub> )								
R*	Vin	nyl and Aromatic Proto	Methyl Protons	v (KBr disc)					
p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	8.75–9.0 (2H)m	6.96, 8.18 (4H)ABq J = 9 Hz	7.2–8.0 (3H)m	3.95 (3H)s	1630 (w)				
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	8.75-9.0 (2H)m	7.26, 8.11 (4H)ABq J = 8 Hz	7.4–7.9 (3H)m	2.38 (3H)s	1610 (w)				
$m-CH_3-C_6H_4$	8.75-9.0 (2H)m	7.15-8.15 (7H)m		2.41 (3H)s	1613 (w)				
o-CH <sub>3</sub> —C <sub>6</sub> H <sub>4</sub>	8.65-8.90(2H)m	7.10-7.9 (7H)m		2.58 (3H)s	1610 (w)				
p-Cl—C <sub>6</sub> H <sub>4</sub>	8.8-9.0 (2H)m	7.2-8.2 (7H)m			1607 (w)				
C <sub>6</sub> H <sub>5</sub> —CH=CH	8.65-8.95(2H)m	6.6-8.0 (10H)m			1634 (s)				
Сн=сн-	8.6–9.0 (2H)m	6.3-8.0 (8H)m			1633 (s)				
	8.7–9.0 (2H)m	6.8-8.2 (6H)m			1619 (w)				

\*Refers to formula 8.

## (c) Reaction of N-(Cinnamoyl)pyridinium Imine with Diphenylcyclopropenethione

A mixture of 1.12 g (5 mmol) of *N*-(cinnamoyl)pyridinium imine and 1.11 g (5 mmol) of diphenylcyclopropenethione in 25 ml of dry benzene was heated at 100° under nitrogen in a sealed tube for 24 h. Evaporation of the solvent gave a dark red oil, trituration of which with cold methanol gave 4,5-diphenyl-2-*trans*-styryl-6H-1,3-oxazin-6-thione 1.08 g, (61% yield), m.p. 185–186° (from benzene-methanol).

Anal. Calcd. for  $C_{24}H_{17}NOS$  (mol. wt. 367.1031): C, 78.44; H, 4.66; N, 3.81; S, 8.73. Found (367.1030 (mass spectrum)): C, 78.97; H, 14.82; N, 3.98; S, 8.82.

The n.m.r. spectrum  $\delta_{TMS}(CDCl_3)$ : 6.86, 8.04 (ABq, J = 16.5 Hz, 2H, *trans*-styryl protons); 7.05–7.8 (m, 15H, aromatic protons). The i.r. spectrum v(KBr disc): 950, 1120, 1278, 1475 cm<sup>-1</sup>.

## Reaction of 2,4,5-Triphenyl-6H-1,3-oxazin-6-thione with m-Chloroperbenzoic Acid

To a stirred solution of 0.68 g (2 mmol) of 2,4,5-triphenyl-1,3-oxazin-6-thione in 20 ml of dichloromethane was added dropwise a solution of 0.43 g (2 mmol) of 80% *m*-chloroperbenzoic acid in 20 ml of dichloromethane over 10 min. A 10% aqueous solution of sodium sulfite was added to decompose the unreacted *m*-chloroperbenzoic acid and the organic layer was washed successively with 5% sodium hydrogen carbonate solution and water and then dried (CaSO<sub>4</sub>). Removal of the solvent *in vacuo* gave 2,4,5-triphenyl-6*H*-1,3-oxazin-6-one 0.52 g (80% yield) which was purified by recrystallization from dichloromethane-methanol, m.p. 205-207° (11: m.p. 207° (19)) as a pale green solid. The i.r. spectrum v(KBr) C=O 1725 cm<sup>-1</sup>. The mass spectrum: 325, C<sub>22</sub>H<sub>15</sub>NO<sub>2</sub> requires M, 325.

#### Reaction of Diphenylcyclopropenone with N-Benzoyl Pyridinium Imine

A suspension of 1.03 g (5 mmol) of diphenylcyclopropenone and 1.0 g (5 mmol) of N-benzoyl pyridinium imine

in 30 ml of dry benzene was heated under reflux for 12 h during which time the solution turned dark green. The excess of solvent was removed *in vacuo* and trituration of the residue with cold methanol afforded 2,4,5-triphenyl-6H-1,3-oxazin-6-one as a light green solid which was purified by recrystallization from benzene-methanol 1.16 g (71% yield) m.p. 205-207°.

The i.r. spectrum of this compound was superimposable with that obtained in the oxidation reaction described above.

#### Reaction of Diphenylcyclopropenethione with N-Benzoyl Pyridinium Imine in Benzene-Methanol

A solution of 1.11 g (5 mmol) of diphenylcyclopropenethione and 1.0 g (5 mmol) of N-benzoyl pyridinium imine in 30 ml of 1:1 benzene-methanol was heated at 90° in a sealed tube for 12 h, during which time the solution became dark red. The solvent was removed in vacuo and trituration of the residual oil with cold methanol afforded 2,4,5-triphenyl-6H-1,3-oxazin-6-thione (4) as a bright orange solid 1.36 g (80% yield), m.p. 178–180°. The product was identical with that obtained in the absence of methanol.

#### Hydrolysis of 2,4,5-Triphenyl-6H-1,3-oxazin-6-thione with Sodium Methoxide in Methanol

A mixture of 0.34 g (1 mmol) of 2,4,5-triphenyl-1,3oxazin-6-thione and 25 ml of a methanol solution of sodium methoxide (prepared from 1.0 g of sodium in 100 ml of methanol) was refluxed for 3 h during which time the orange solution became light green in color. The excess of methanol was removed *in vacuo*, the residue diluted with water and the solution extracted with ether ( $3 \times 20$  ml). The organic layer was dried (CaSO<sub>4</sub>) and the solvent evaporated to give a trace of a green oil. Acidification of the aqueous layer resulted in the precipitation of 2,4,5-triphenyl-6H-1,3oxazin-6-one (5) as a light orange solid, m.p. 207°. The i.r. spectrum of this compound was superimposable with that of the authentic material.

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# An Electron Spin Resonance Study of a Rhodium(I) Molecular Oxygen Complex in Solution

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Electron spin resonance studies on the oxygenation of the rhodium(I) cyclooctene complex  $[RhCl(C_8H_{14})_2]_2$ , in N,N-dimethylacetamide (DMA) solution containing chloride show the presence of a paramagnetic species. This is thought to involve a rhodium(II)-superoxide (O<sub>2</sub><sup>-</sup>) species which is likely responsible for some previously reported autoxidation reactions.

Les études e.s.r. sur l'oxygénation du complexe rhodium(I) cyclooctène [RhCl( $C_8H_{14}$ )<sub>2</sub>]<sub>2</sub>, dans une solution de N,N-diméthylacétamide (DMA) contenant du chlore, indiquent la présence d'espèces paramagnétiques. Il est supposé qu'une espèce rhodium(II)-superoxyde ( $O_2^-$ ) est impliquée et que celle-ci est probablement responsable des réactions d'auto-oxydation précédemment rapportées.

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In recent communications from this laboratory (1, 2), we have reported on the catalytic activity of  $[RhCl(C_8H_{14})_2]_2$  for the oxidation by molecular oxygen of DMA, cyclooctene, and cumene under mild conditions. The complex initially forms a molecular oxygen complex (one  $O_2$  per Rh atom) in benzene, 1,2-dichloroethane, *etc.*, and also in DMA containing lithium chloride; the dimer initially dissociates to an active monomeric species. Gas uptake kinetic