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Reaction of 3-aroylaziridines with diphenylcyclopropenone. Synthesis and properties of novel 4-aroyl-4-oxazolines

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3-Aroylaziridines and 3-acylaziridines react with diphenylcyclopropenone with the formation of novel 4-aroyl-4-oxazolines and 4-acyl-4-oxazolines respectively. The unusual physical and chemical properties of these reactive heterocycles are discussed.

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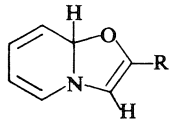
4-Oxazolines represent an almost completely unexamined heterocyclic system, although they have been postulated as intermediates in several reactions, e.g. in the Lewis acid catalyzed rearrangement of 3-aroylaziridines leading to the formation of oxazoles (1) and in the synthesis of oxazoles by the addition of iminoethers to α-aminocarbonyl compounds (2). A 4-oxazoline structure **1** was suggested many years ago for a pyridinium ylid (3) but has since been rejected in favor of the enol betaine structure **2** (4).



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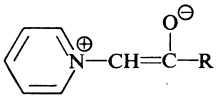
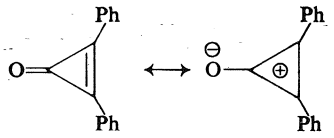


2 R = $C_6H_3(SC_2H_5)_2CH_3$

We recently described the preparation of 4-aroyl-4-oxazolines by the addition of azomethine ylids to diphenylcyclopropenone (5, 6). Very recently Baldwin *et al.* reported the preparation of 4-oxazolines of a different type by the valence rearrangement of isoxazolines via an acylaziridine intermediate (7), eq. [1]. The aziridine probably opens to an azomethine ylid which subsequently ring closes on the adjacent carbonyl group to give the 4-oxazoline. The 4-aroyl-4-oxazolines described in the present work show unusual physical and chemical properties and undergo a variety of [2 + 3] cycloadditions with activated multiple bonds.

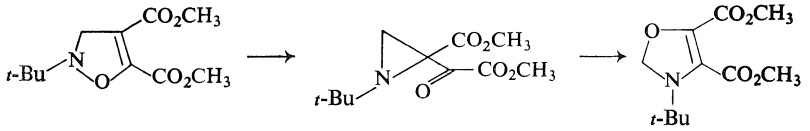
Azomethine ylids may be conveniently prepared *in situ* by heating solutions of 3-aroylaziridines in inert solvents, eq. [2], and 1,3-dipolar addition products have been reported with dipolarophiles such as acetylenic esters, olefins, and aryl isothiocyanates (8–22). Their addition to carbonyl bonds has been reported only once (23). The carbonyl bond in diphenylcyclopropenone (DPP) (24) is highly polarizable owing to resonance of the type shown:



Consequently, DPP reacts readily with azomethine ylids derived from 3-aroylaziridines; however, the reaction takes a different course after the initial 1,3 dipolar addition.

Treatment of either *cis*- or *trans*-3-benzoyl-1-cyclohexyl-2-phenylaziridine (25) with one molar

[1]



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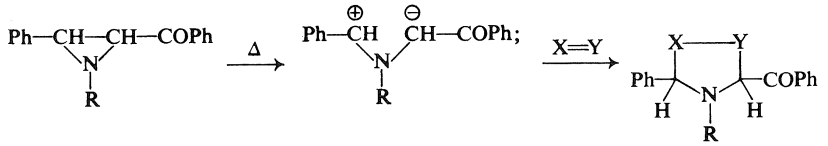
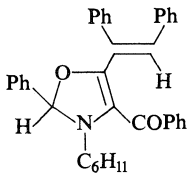


[1]N.R.C.C. Postdoctoral fellow 1967–1968.
[2]N.R.C.C. Studentship holder 1967–1969.



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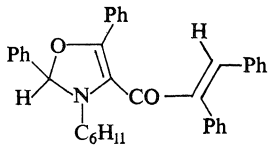

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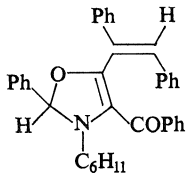

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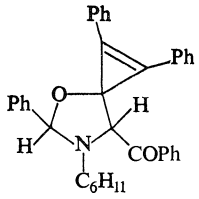

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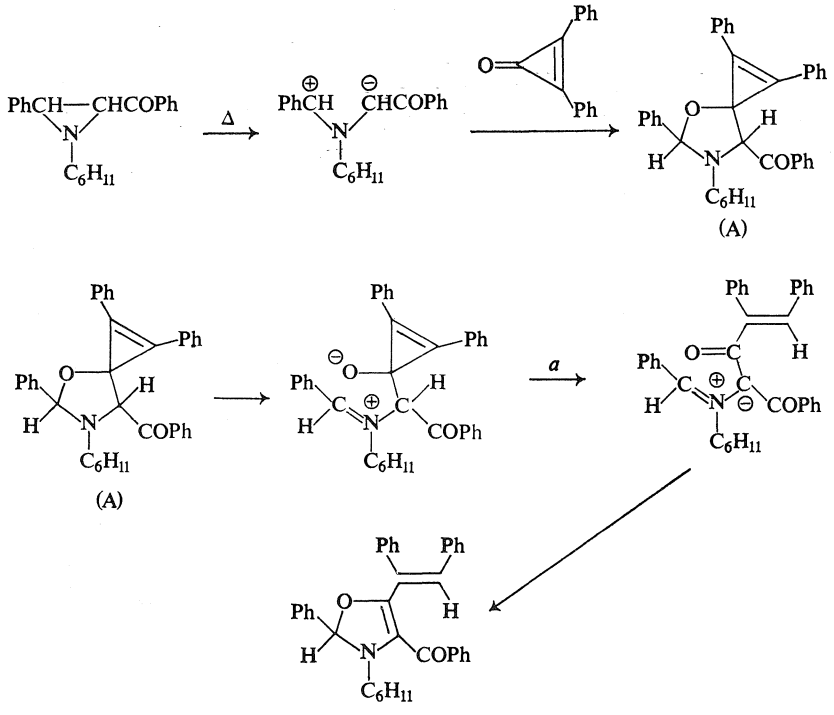
equivalent of DPP in refluxing benzene gives a deep-red solution and followed by chromatographic separation, affords a photochromic crystalline product m.p. 163° in 46.5% yield, which is assigned the 4-oxazoline structure **3**. The structural assignment rests on spectral evidence and the unusual chemical properties described below. The product exhibits an infrared (i.r.) band at 1695 cm^{-1} characteristic of an aromatic ketone (26*a*), consistent with **3** since space filling models indicate steric hindrance will prevent conjugation with the ring double bond.

The carbonyl frequency of **4** would represent an α,β unsaturated ketone and would absorb at 1665–1685 cm^{-1} (26*b*). In addition, in unsaturated ketones of this type the C=C stretch absorption at 1650–1600 (27) is of comparable intensity and no such band is visible in the spectrum of the product. Mass spectral evidence also supports **3** (see the following paper). For these reasons we reject **4**. Structure **5** is rejected on the basis of the known chemistry of DPP since nucleophile catalyzed ring opening proceeds in a *cis* fashion (24). Similarly **6** is rejected since there is no proton in the nuclear magnetic resonance (n.m.r.) spectrum corresponding to the 4 proton of the oxazolidine structure. Also, heating the product with deuterium oxide under base catalyzed conditions did not result in any deuterium incorporation. These facts together with the observed lack of dependence on the stereochemistry of the 3-aroylaziridine lend support to the rationalization shown in Scheme 1.



SCHEME 1

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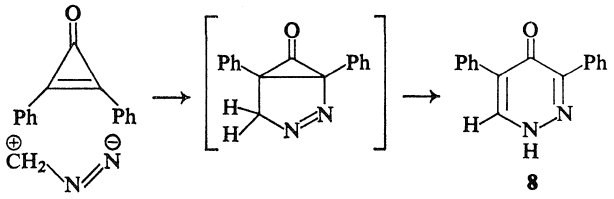
[3] 

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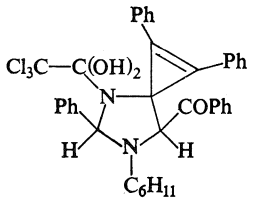
Experiments are currently underway with specifically 3-deuterated aziridines to examine the possibility of a concerted step for the ring opening *a*. The isolation of **7** in the analogous additions of iminocyclopropenes to azomethine ylids supports the intermediacy of the spiro-oxazolidine (A). This work will be reported in a subsequent publication.



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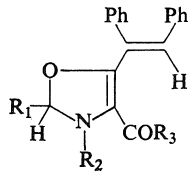
The observed reaction of DPP with azomethine ylids to produce 4-oxazolines is in marked contrast to that with other 1,3 dipoles e.g. diazomethane where primary addition occurs at the carbon–carbon double bond with the formation of a pyridazone **8** (28), eq. [3]. In view of the successful [2 + 3] cycloaddition of azomethine ylids to the carbonyl group in DPP described above, and to *p*-nitrobenzaldehyde (23), the obvious approach was made to confirm structure **3** i.e. via the reaction shown in eq. [4], so that the tetrahydro reduction product of **3** could be compared with the expected product **9**. There was no addition since the aliphatic aldehyde is not sufficiently reactive for 1,3 dipolar addition to the azomethine ylid.

A series of substituted 4-oxazolines was synthesized from DPP by this procedure. Best results were obtained by using highly purified aziridines in a molar ratio of 4:3, aziridine:DPP, at a temperature of about 80°. Contamination of the aziridine with a trace of amine hydrobromide and/or the presence of a greater proportion of DPP results in another reaction in which a furan predominates (see below). The choice of solvent is critical and we have examined (*a*) benzene, (*b*) acetonitrile, (*c*) methylene chloride, and (*d*) toluene. Solvents (*a*) and (*b*) give 4-oxazolines in good yield, (*d*) gives only furan, whilst (*c*) at the boiling point yields unreacted starting material in reduced yield. Having demonstrated that both *cis* and *trans* 3-aroylaziridines upon reaction with DPP give rise to 4-oxazolines, *cis–trans* mixtures of the aziridines were used for the general procedure. The analytical and spectral data on the 4-oxazolines are summarized in Tables 1 and 2. The scope of the synthesis is seen to extend to aroyl or acyl groups at position 4; biphenylyl or aryl (with either electron withdrawing or electron donating groups) at position 2, and with *N*-substituent of cyclohexyl, isopropyl, or methyl.

The numbering of substituents in Tables 1 and 2 refer to structure **10**.



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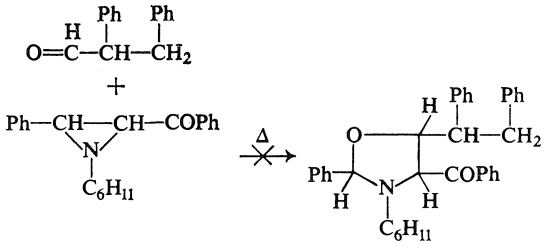
[4] 

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TABLE 1

4-Oxazolines

						Calculated				Found			
						%				%			
10	R_1	R_2	R_3	Melting point	Yield %	C	H	N	Molecular ion	C	H	N	Molecular ion
	C_6H_5	CH_3	C_6H_5	145°	20*	83.92	5.69	3.16	443.1885	83.80	5.60	3.25	443.1879
a	C_6H_5	$(CH_3)_2CH$	C_6H_5	175°	23.5*	84.05	6.20	2.97	471.2198	84.15	6.35	3.45	471.2192
b	C_6H_5	$(CH_3)_2CH$	$pCH_3C_6H_4$	165–166°	31*	84.10	6.44	2.89	485.2355	84.00	6.85	3.10	485.2358
c	C_6H_5	C_6H_{11}	C_6H_5	163°	65	84.50	6.51	2.74	511.2511	84.20	6.40	2.65	511.2510
d	$pCH_3OC_6H_4$	C_6H_{11}	C_6H_5	158–160°	23*	82.07	6.47	2.59	No molecular ion	82.02	6.45	2.62	—
e	$mNO_2C_6H_4$	C_6H_{11}	C_6H_5	165–166°	27*	77.70	5.76	5.04	556.2368	77.65	6.03	4.97	556.2362
f	$pNO_2C_6H_4$	C_6H_{11}	C_6H_5	180–182°	64	77.70	5.76	5.04	No molecular ion	77.46	5.75	5.19	—
g	$pC_6H_5C_6H_4$	C_6H_{11}	C_6H_5	122–123°	100	85.82	6.35	2.38	No molecular ion	85.64	6.28	2.32	—
h	C_6H_5	C_6H_{11}	$pCH_3OC_6H_4$	175.5–176.5°	79	82.07	6.47	2.59	541.2616	82.27	6.49	2.50	541.2614
i	C_6H_5	C_6H_{11}	$pCH_3C_6H_4$	176–176°	20*	84.53	6.72	2.67	525.2668	84.50	6.60	2.40	525.2665
j	C_6H_5	C_6H_{11}	$pNO_2C_6H_4$	191–192.5°	23	77.70	5.76	5.04	556.2362	77.56	6.03	4.76	556.2373
k	C_6H_5	C_6H_{11}	CH_3	80–82°	84	82.85	6.90	3.12	499.2355	82.65	7.04	3.03	449.2353
l	$pC_6H_5C_6H_4$	C_6H_{11}	CH_3	144–142°	59	84.53	6.72	2.67	525.2668	84.32	6.68	2.58	525.2675

*Indicates made by 1:1 aziridine: DPP; otherwise by 4:3 aziridine: DPP.

TABLE 2

Spectroscopic data of 4-oxazolines

					Nuclear magnetic resonance* (δ) ($CDCl_3$)				
10	R_1	R_2	R_3	Infrared cm^{-1} ($CHCl_3$)	2 Proton	Cyclohexyl CH_2 or $(CH_3)_2CH$— or CH_3	Cyclohexyl CH or $(CH_3)_2CH$—	Aryl + vinyl protons	Aryl substituent and acetyl protons
	C_6H_5	CH_3	C_6H_5	1700	4.3 (1) s	2.15 (3) s		6.75–8.0 (21) m	
a	C_6H_5	$(CH_3)_2CH$	C_6H_5	1700	4.95 (1) s	0.73 (3) d J = 6.5 Hz 0.81 (3) d J = 6.5 Hz	3.43 (1) m	6.75–8.15 (21) m	
b	C_6H_5	$(CH_3)_2CH$	$pCH_3C_6H_4$	1695	4.91 (1) s	0.72 (3) d J = 6.5 Hz 0.8 (3) d J = 6.5 Hz	3.39 (1) m	6.80–8.10 (20) m	2.42 (3) s CH_3
c	C_6H_5	C_6H_{11}	C_6H_5	1698	4.95 (1) s	0.35–1.75 (10) m	2.72–3.05 (1) m	6.8 –8.0 (21) m	
d	$pCH_3OC_6H_4$	C_6H_{11}	C_6H_5	1695	4.90 (1) s	0.50–1.66 (10) m	2.70–3.17 (1) m	6.75–8.08 (20) m	3.78 (3) s OCH_3
e	$mNO_2C_6H_4$	C_6H_{11}	C_6H_5	1696	4.96 (1) s	0.50–1.78 (10) m	2.67–3.24 (1) m	6.82–8.12 (20) m	
f	$pNO_2C_6H_4$	C_6H_{11}	C_6H_5	1696	5.03 (1) s	0.42–1.73 (10) m	2.70–3.15 (1) m	6.84–8.25 (20) m	
g	$pC_6H_5C_6H_4$	C_6H_{11}	C_6H_5	1700	5.10 (1) s	0.40–2.0 (10) m	2.30–3.30 (1) m	6.70–8.30 (25) m	
h	C_6H_5	C_6H_{11}	$pCH_3OC_6H_4$	1700	4.95 (1) s	0.38–1.95 (10) m	2.55–3.15 (1) m	6.78–8.10 (20) m	3.85 (3) s OCH_3
i	C_6H_5	C_6H_{11}	$pCH_3C_6H_4$	1695	4.96 (1) s	0.50–1.75 (10) m	2.65–3.0 (1) m	6.70–8.05 (20) m	2.42 (3) s CH_3
j	C_6H_5	C_6H_{11}	$pNO_2C_6H_4$	1699	5.05 (1) s	0.65–1.80 (10) m	2.54–2.94 (1) m	6.75–8.06 (19) m 8.16 (1) s	
k	C_6H_5	C_6H_{11}	CH_3	1703	5.14 (1) s	0.66–2.15 (10) m	3.10–3.56 (1) m	7.32–8.50 (16) m	2.02 (3) s CH_3
l	$pC_6H_5C_6H_4$	C_6H_{11}	CH_3	1700	4.86 (1) s	0.55–2.10 (10) m	2.80–3.55 (1) m	6.65–8.10 (20) m	1.90 (3) s CH_3

*s = singlet; m = multiplet; d = doublet.

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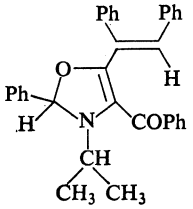
Properties of 4-Aroyl-4-oxazolines

In view of their novelty and their marked reactivity in [2 + 3] cycloadditions (in this respect they resemble sydnones) the properties of these heterocycles have been examined in some detail.

The n.m.r. spectra summarized in Table 2 are consistent with the proposed structures. Those with an isopropyl group bonded to the nitrogen show non-equivalent methyl groups, indicating proximity to an asymmetric center in accordance with structure **10***a* for example.



10*a*

The ultraviolet (u.v.) spectra are dominated by two intense absorption bands in the region (227.5–232) and (265–275.5) mμ (Table 3). The i.r. spectra show the characteristic aryl ketone absorption at 1695–1700 cm^{-1}. In the high resolution mass spectrum a common major mode of scission involves cleavage to the anil, a direct counterpart of the thermal cleavage involved in the [2 + 3] cycloaddition described below (see Table 4).

TABLE 3

Ultraviolet absorption spectra of 4-aroyl-4-oxazolines and their visible absorption on addition of *p*-toluene sulfonic acid

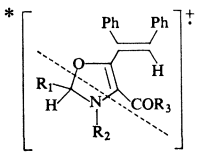
	Absorption spectrum		Acid added*	
Structure **10**	λ_{max} (CH_3CN) (mμ)	log ε	λ_{max}	λ_{max} (visible)
b	232 265	4.16 3.80	228 275 317	528
c	227 267	4.19 3.82	232 277 311	527
d	230 275	4.29 3.76	229 266 316	525
e	231 268	4.29 4.14	229 268	524
f	229 276	4.21 4.09	229 282	530
h	233 274	4.16 3.87	229 275 326	534
j	228 273	4.24 4.19	228 276 350	532
l	225 260	4.26 4.31	—	—
m	227 260	4.35 4.38	—	—

*Trace quantity of *p*-toluenesulfonic acid added, log ε was not determined since concentration of colored species is unknown.

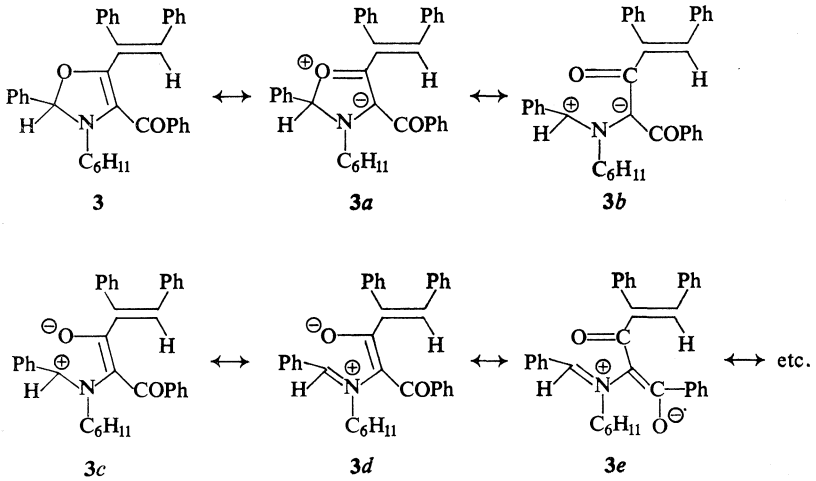
TABLE 4

Principal fragmentations in the high resolution mass spectra of 4-aroyl-4-oxazolines*

Structure **10**	Molecular ion *m/e*	Relative abundance %	Anil *m/e*	Relative abundance %	M^+-Anil *m/e*	Relative abundance %
c	511	5	187	100	324	75
d	541	—	217	100	324	16
e	556	1	232	19	324	100
f	556	—	232	91	324	20
g	587	—	263	5	324	100
h	541	1	187	100	354	19
j	556	6	187	85	369	39
k	449	19	187	12	262	100
l	525	5	263	100	262	100



The dotted line shows the principal fragmentation mode.

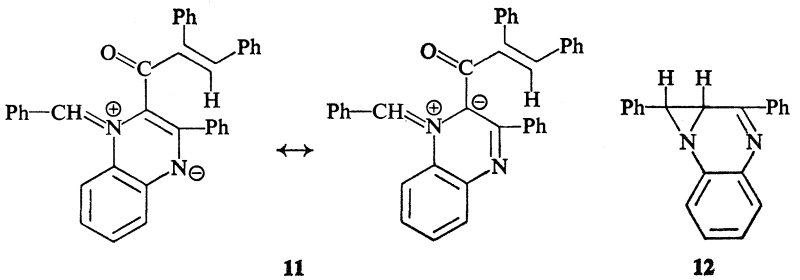


Another characteristic property of the 4-aroyl-4-oxazolines is their marked photochromism in the solid state where the white crystalline solids turn pinkish-red on exposure to light and revert to white in the dark. The phenomenon is reversible and no detectable decomposition occurs. In addition, all the oxazolines give bright red melts, and solutions in hot benzene, toluene, or xylene adopt a wine-red coloration. These phenomena may plausibly be associated with contributions from dipolar species. In the limit, substantial contributions from the canonical forms **3***b*, **3***c*, **3***d*, and **3***e* are equivalent to photochemical or thermal ring-chain valence isomerism to a new azomethine ylid. This situation exists in the case of **11** synthesized from the corresponding tricyclic aziridine **12** (21) and DPP. Compound **11** gives blood red crystals and behaves like a typically highly polar substance and has accordingly been assigned the zwitter ionic ylid structure.

Supporting evidence for these proposals is provided by the observed facile ring opening and [2 + 3] cycloaddition reactions described in this and in the accompanying paper.

The photochromism and thermochromism displayed by 4-aroyl-4-oxazolines is reminiscent of that shown by some 1,3 dipolar addition products of azomethine imines (29) and of the ring–chain isomerism exhibited by 2(biphenylyl)-3-acyl-(or 3-carbalkoxy)2,3-dihydro-1,3,4-oxadiazoles (30) e.g. eq. [5].

The appearance of the vivid red color of solutions of 4-oxazolines is enhanced by the addition of acids. Treatment with *p*-toluenesulfonic acid under mild conditions produces a strong visible absorption band at 530 mμ (see Table 3) and proved useful in substantially reducing the reaction time for various [2 + 3] cycloadditions of 4-oxazolines and evidently assists in the separation of the anil moiety (see accompanying paper). At room temperature the 4-oxazoline can be recovered in excellent yield from this acid treatment. The position of protonation on the 4-oxazolines (C, O, or N) unfortunately cannot be assigned with confidence



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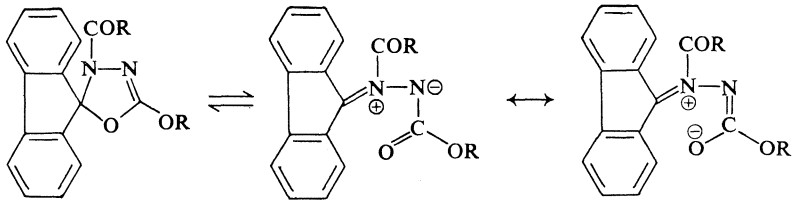
[5] 

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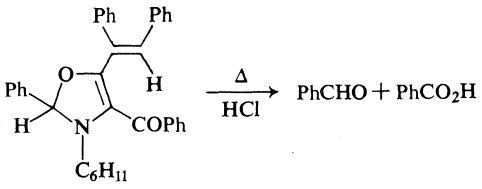
since addition of sufficient acid to affect the n.m.r. spectrum results in decomposition.

Benzaldehyde and benzoic acid were isolated from the controlled hydrolysis of **3** with hydrochloric acid, eq. [6]. A similar hydrolysis of **14**

[6] 

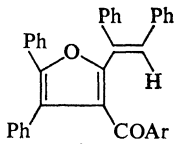
3

afforded *p*-nitrobenzaldehyde and benzoic acid, eq. [7].

The 4-aroyl-4-oxazolines are stable to alkali and to nucleophiles e.g. **3** was recovered unchanged after refluxing with (*a*) potassium carbonate in aqueous tetrahydrofuran, (*b*) potassium thiocyanate in acetone, and (*c*) sodium iodide in acetone. The solution turns red in the case of (*b*) and (*c*). A systematic study of the necessary structural features in the 4-oxazolines required for the photochromism and facile ring cleavage has been undertaken but is not yet complete. However a 2-aryl group and a 4-aroyl or acyl group seem to be essential. Baldwin *et al.* described the preparation of a 4-oxazoline via the valence rearrangement of an isoxazoline. The product lacked a 2-aryl group and has carbomethoxy groups at the 4 and 5 positions. No mention was made of any photochromism or tendency for [2 + 3] cycloadditions although it was remarked that the compound was unstable (7).

Chemical Reactions of 4-Aroyl-4-oxazolines

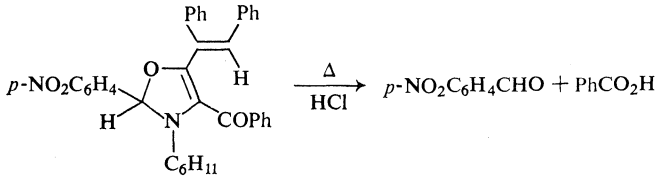
It was noted earlier that under certain conditions of the preparation of 4-aroyl-4-oxazolines that a common side reaction was formation of yellow crystalline furans of structure **15**. If the



15

3-aroylaziridine is contaminated with some cyclohexylamine hydrobromide, or in the presence of excess DPP, furans like **15** are the only product of the reaction. While this type of reaction was found to have wider implications and its mechanism will be discussed more fully in the accompanying paper, we may represent the formation of furans under these conditions as shown schematically in Scheme 2.

Scheme 2 is supported by the following experiments. Treatment of **3** with one equivalent of DPP in refluxing toluene for 18 h, then chromatography on alumina gave furan **15** (Ar = Ph). The anil moiety is normally hydrolyzed to benzaldehyde in the work-up procedure and in this instance was characterized as the 2,4-dinitrophenylhydrazone. Occasionally however the anil is isolated intact. In a separate experiment **3** was allowed to react with diphenylacetylene (eq. [8]) and gave the same furan **15** in good yield, although the reaction was slower. However the possibility of thermal decarbonylation of DPP to diphenylacetylene under the

[7] 

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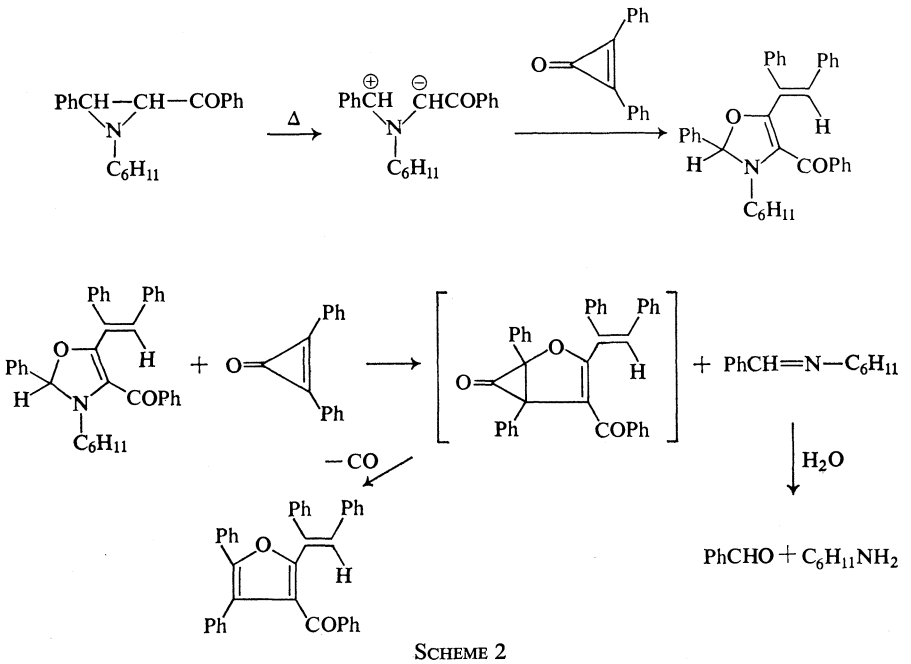


SCHEME 2

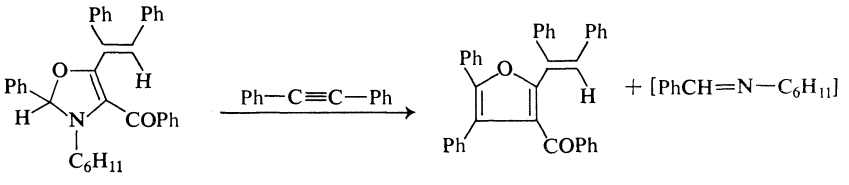
reaction conditions obtaining in the preparation of the 4-aroyl-4-oxazolines was discounted by a separate control reaction.

Another example in support of the reaction path in Scheme 2 is provided by the reaction of **3** with cycloheptenocyclopropenone (24) which gives the bicyclic furan **16**, eq. [9]. In this case, prior decarbonylation is even less likely.

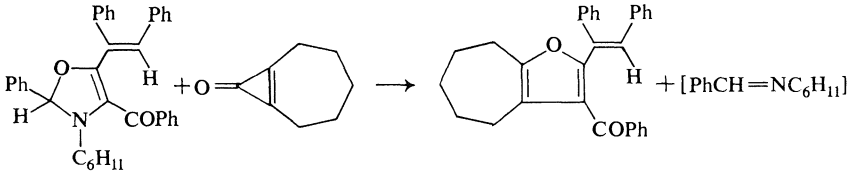
Addition of DPP to 3-aroylaziridines via the azomethine ylid therefore involves competing 1:1 and 2:1 reactions to form **3** and **15** respectively. Other things being equal, higher reaction temperatures (e.g. refluxing toluene rather than benzene) and the presence of the amine hydrobromide favor the formation of the furans **15**. The amine hydrobromide is a by-product of the Gabriel synthesis of aziridines.

Experimental

Melting points were determined on a Fisher–Johns apparatus and are uncorrected. Infrared spectra were recorded on a Perkin–Elmer model 421 spectrophotometer, and only the principal, sharply defined peaks are reported. Nuclear magnetic resonance spectra were

[8] 

3

[9] 

3 **16**

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recorded on Varian A-60 and A-100 analytical spectrometers. The spectra were measured on approximately 10–15% (w/v) solutions in $CDCl_3$, with tetramethylsilane as a standard. Line positions are reported in parts per million (p.p.m.) from the reference. Absorption spectra were recorded in 'spectro'-grade solvents on a Beckman DB recording spectrophotometer. 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 comparison with perfluorotributylamine at a resolving power of 15 000. Kieselgel DF-5 (Camag, Switzerland) and Eastman Kodak precoated sheets were used for thin-layer chromatography (t.l.c.). Microanalyses were carried out by Dr. C. Daesslé, Organic Microanalysis Ltd., Montreal, Quebec and by Mrs. D. Mahlow of this department.

General Preparation of 3-Aroylaziridines

The compounds required in this study were prepared by established methods involving Claisen–Schmidt condensations to form chalcones, then addition of bromine to form the dibromochalcones, and treatment of the latter with primary amines to provide 3-aroylaziridines (22 and references therein). The analytical and spectroscopic data on new aziridines prepared by this procedure are summarized in Tables 5 and 6.

Preparation of 4-Aroyl-4-oxazolines

General

The control experiments between diphenylcyclopropenone and isomerically pure samples of *cis* and *trans*-3-aroylaziridines employing a molar ratio of 1:1 are described in detail.

Thereafter 4-oxazolines and substituted furans were prepared using *cis–trans* mixtures of various aroylaziridines and in the case of the former, the improved technique using a 4:3 molar ratio of aziridine:DPP was used. Representative preparations are described in full and the analytical and spectroscopic data on the other 4-oxazolines prepared by similar procedures are summarized in Tables 1 and 2.

Control Experiments between Stereoisomerically Pure 3-Aroylaziridines and Diphenylcyclopropenone (1:1 Molar)

4-Benzoyl-3-cyclohexyl-5-(cis-1,2-diphenylvinyl)-2-phenyl-4-oxazoline

(*a*) A solution of 3.05 (0.01 mole) of *cis*-3-benzoyl-1-cyclohexyl-2-phenylaziridine (25) and 2.06 g (0.01 mole) of diphenylcyclopropenone (24) in 60 ml of dry benzene was heated under reflux for 24 h. Removal of the solvent *in vacuo* from the resulting deep red solution yielded an oily residue which was chromatographed on 200 g of alumina (B.D.H.). Elution with benzene caused the rapid separation of a pale orange band which was collected in 3 × 50 ml fractions. Removal of the solvent yielded an orange syrup which crystallized on trituration with heptane to give 4-benzoyl-3-cyclohexyl-5-(*cis*-1,2-diphenylvinyl)-2-phenyl-4-oxazoline as a pale pink solid 2.4 g, (46.5% yield); m.p. 162–163° (EtOH). The solid is strongly photochromic and the initially pink crystals become colorless when set aside in the dark.

Anal. Calcd. for $C_{36}H_{33}NO_2$: C, 84.50; H, 6.51; N, 2.74. Found: C, 84.2; H, 6.4; N, 2.65.

Mol. Wt. Calcd.: 511.2511. Found (mass spectrum): 511.2510.

The i.r. spectrum showed ν_{max} ($CHCl_3$), 1695 cm^{-1} (C=O); n.m.r., δ_{TMS} ($CDCl_3$), 2.7–3.05 (multiplet, 1H, cyclohexyl C*H*), 0.35–1.75 (multiplet 10H, cyclohexyl CH_2), 4.95 (singlet 1H, oxazoline 2 proton), 6.8–8.0 (multiplet, 21H, aromatic protons and vinyl proton).

Further elution of the column with benzene (200 ml) gave 0.25 g of unreacted 3-aroylaziridine, then elution with chloroform gave 0.6 g of a yellow oil consisting largely of benzaldehyde (identified as the 2,4-dinitrophenylhydrazone m.p. 238°; mixed m.p. undepressed on admixture with an authentic sample, and by the characteristic aldehyde absorption at 9.78 in the n.m.r. spectrum). Finally elution with ethanol yielded 0.5 g of unreacted diphenylcyclopropenone; m.p. 119°.

(*b*) A similar reaction was carried out between 2.44 g (0.008 mole) of *trans*-3-benzoyl-1-cyclohexyl-2-phenylaziridine (25) and 1.65 g (0.008 mole) of diphenylcyclopropenone in benzene and worked up as described above to yield 4-benzoyl-3-cyclohexyl-5-(*cis*-1,2-diphenylvinyl)-2-phenyl-4-oxazoline, 1.5 g (37% yield); m.p. 162–163° (EtOH) identical in all respects to that obtained with the *cis* stereomer of the 3-aroylaziridine described in (*a*) above.

Addition Reactions Employing Other Solvents with 1:1 Molar Ratio of 3-Aroylaziridine to Diphenylcyclopropenone

(*c*) A similar reaction between 1.5 g (0.005 mole) of *cis*-3-benzoyl-1-cyclohexyl-2-phenylaziridine and 1.03 g (0.005 mole) of diphenylcyclopropenone was carried out in refluxing acetonitrile. The reaction was worked up by a similar procedure to give 4-benzoyl-3-cyclohexyl-5-(*cis*-1,2-diphenylvinyl)-2-phenyl-4-oxazoline, 1.2 g (46.5% yield); m.p. 162–163° (EtOH).

(*d*) A similar reaction between 1.96 g (0.06 mole) of 1-benzyl-2-phenyl-3-toluoylaziridine and 1.24 g (0.06 mole) of diphenylcyclopropenone was performed in 60 ml of refluxing methylene chloride for 5 days followed by chromatography afforded unreacted starting materials in reduced yields.

(*e*) A solution of 3.05 (0.01 mole) of a mixture of *cis* and *trans*-3-benzoyl-1-cyclohexyl-2-phenylaziridine (25) and 2.06 g (0.01 mole) of diphenylcyclopropenone in 60 ml dry toluene was heated under reflux for 24 h. Removal of the solvent and chromatographic separation of the resulting oil on 300 g of alumina (B.D.H.) using benzene as eluent caused the rapid separation of a yellow band which was collected as 3 × 50 ml fractions. Removal of the solvent yielded a yellow oil which on trituration with heptane gave 3-benzoyl-4,5-diphenyl-2-(*cis*-1,2-diphenylvinyl)-furan as a pale yellow solid 1.45 g (28.9% yield). The product crystallized from ethanol as yellow crystals; m.p. 195–196°.

Anal. Calcd. for $C_{37}H_{26}O_2$: C, 88.41; H, 5.21; Found: C, 88.31; H, 5.18.

Mol. Wt. Calcd.: 502.1933. Found (mass spectrum): 502.1935.

The i.r. spectrum showed ν_{max} ($CHCl_3$), 1695 cm^{-1} (aryl C=O); n.m.r., δ_{TMS} ($CDCl_3$), 8.0–6.7 (multiplet, 25H, aromatic protons); 7.99 (singlet, 1H, vinyl proton).

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TABLE 5

3-Acyl and 3-aroyl aziridines

R_1	R_2	R_3	Melting point	Yield %	Calculated % C	Calculated % H	Calculated % N	Calculated Molecular ion	Found % C	Found % H	Found % N	Found Molecular ion
$pC_6H_5C_6H_4$	C_6H_{11}	C_6H_5	127°	100	85.00	7.14	3.67	381.2093	84.90	7.23	3.64	381.1974
$mNO_2C_6H_4$	C_6H_{11}	C_6H_5	95°	88	72.00	6.29	8.00	350.1630	71.70	6.17	8.02	350.1634
C_6H_5	C_6H_{11}	$pCH_3OC_6H_4$	126–127°	75	78.81	7.46	4.18	335.1885	78.76	7.36	4.10	335.1888
C_6H_5	C_6H_{11}	CH_3	oil	85*	79.01	8.71	5.72	243.1623	78.90	8.83	5.75	243.1623

*For dibromochalcone see reference 33.

TABLE 6

Spectroscopic data on aziridines

R_1	R_2	R_3	Infrared cm^{-1} (O ‖ C ⟨ $CHCl_3$)	Nuclear magnetic resonance (δ) ($CDCl_3$)* Ring protons	Cyclohexyl CH_2 or $(CH_3)_2CH$	Cyclohexyl CH or $(CH_3)_2CH$	Aryl protons	Aryl substituent + acetyl protons
$pC_6H_5C_6H_4$	C_6H_{11}	C_6H_5	1680 (*cis*) 1665 (*trans*)	3.23 (2) s 3.53 (2) s	1.0–2.1 (10) m	2.2–3.0 (1) m	7.2–8.3 (14) m	
$mNO_2C_6H_4$	C_6H_{11}	C_6H_5	1681 (*cis*) 1667 (*trans*)	3.24 (1) $J = 7$ Hz 3.44 (1) 3.22 (2) s	0.83–2.06 (10) m	2.35–2.85 (1) m	7.30–8.30 (9) m	
C_6H_5	C_6H_{11}	$pCH_3OC_6H_4$	1658 (*trans*)	3.53 (2) s	0.85–2.00 (10) m	2.36–2.77 (1) m	6.83–8.14 (9) m	2.83 (3) s OCH_3
C_6H_5	C_6H_{11}	CH_3	1699	2.83 (1) s 2.88 (1) s 3.24–3.36 (2) d	1.00–2.00 (10) m	2.15–2.75 (1) m	7.26–7.46 (5) d	2.27 (3) s CH_3

*s = singlet; d = doublet; m = multiplet.

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Further elution with benzene yielded an oil containing benzaldehyde and unreacted 3-aroylaziridine. Continued elution with chloroform and then ethanol gave unreacted diphenylcyclopropenone.

Control Attempted Deuterium Exchange of the 2-Proton of 4-Benzoyl-3-cyclohexyl-5-(cis-1,2-diphenylvinyl)-2-phenyl-4-oxazoline

A solution of 0.10 g of 4-benzoyl-3-cyclohexyl-5-(*cis*-1,2-diphenylvinyl)-2-phenyl-4-oxazoline in 25 ml of dry tetrahydrofuran was heated under reflux for 4 h with 2 ml of deuterium oxide and 0.05 g of anhydrous potassium carbonate. The solution was evaporated to dryness, and the process repeated with 25 ml of dry tetrahydrofuran, 0.05 g of potassium carbonate, and 1 ml of deuterium oxide. Examination of the n.m.r. spectrum of the product indicated that no exchange of the 2-proton had occurred. Accurate mass measurement (mass spectrum) also indicated no incorporation of deuterium had taken place.

Attempted Addition of 2,3-Diphenylpropanal to 3-Benzoyl-1-cyclohexyl-2-phenylaziridine

A solution of 0.05 g (0.005 mole) of 2,3-diphenylpropanal (31) and 1.05 g (0.005 mole) of 3-benzoyl-1-cyclohexyl-2-phenylaziridine in 60 ml of benzene was heated under reflux for 25 h, allowed to cool, and the solvent removed *in vacuo*. Chromatographic separation of the residual oil (2.05 g) afforded only unreacted starting materials and uncharacterized decomposition products.

Representative Improved Procedure for the Synthesis of 4-Aroyl-4-oxazolines Employing 4:3 Molar Ratio of 3-Aroylaziridine to Diphenylcyclopropenone

4-Anisoyl-3-cyclohexyl-5-(cis-1,2-diphenylvinyl)-2-phenyl-4-oxazoline

A solution of 0.62 g (0.00185 mole) of isomeric 3-anisoyl-1-cyclohexyl-2-phenylaziridine and 0.29 g (0.0014 mole) of diphenylcyclopropenone in 30 ml of benzene was heated under reflux for 24 h. The deep red solution was then cooled and the solvent removed *in vacuo*, yielding a red oil which was chromatographed on 40 g of alumina (B.D.H.). Elution with a 4:1 benzene:hexane mixture afforded a red oil which crystallized on trituration with ethanol to give 4-anisoyl-3-cyclohexyl-5-(*cis*-1,2-diphenylvinyl)-2-phenyl-4-oxazoline, 0.60 g (79% yield); m.p. 175–176.5° (from absolute ethanol).

Anal. Calcd. for $C_{37}H_{35}NO_3$: C, 82.07; H, 6.47; N, 2.59. Found: C, 82.27; H, 6.49; N, 2.50.

Mol. Wt. (mass spectrum) Calcd.: 541.2616. Found: 541.2614.

The i.r. spectrum showed ν_{max} ($CHCl_3$), 2850 (OCH_3), 1700 (C=O), 832 (1,4 disubst. ring) cm^{-1}; u.v., λ_{max} (CH_3CN), 233.5 mμ log ε 4.16, 274 mμ log ε 3.87; n.m.r. ($CDCl_3$), 0.38–1.95 (10H, multiplet cyclohexyl CH_2), 2.55–3.15 (multiplet, 1H, cyclohexyl CH), 3.85 (3H, singlet, methoxy protons), 4.95 (1H, singlet, 2 proton), 6.78–8.10 (multiplet, 20H, aryl protons plus vinyl proton).

Acid Hydrolysis of 4-Benzoyl-3-cyclohexyl-5-(cis-1,2-diphenylvinyl)-2-(p-nitrophenyl)-4-oxazoline

4-Benzoyl-3-cyclohexyl-5-(*cis*-1,2-diphenylvinyl)-2-(*p*-nitrophenyl)-4-oxazoline (0.30 g, 0.00054 mole) was heated under reflux in 25 ml of 2 *N* hydrochloric acid for a period of 3½ h. On cooling the orange mixture, a yellow residue appeared in the flask while a white sublimate was observed in the condenser and was isolated. The mixture was then extracted with ether (3 × 20 ml) to give an organic layer, an aqueous layer, and an insoluble yellow residue. (*i*) White sublimate: this was found to be benzoic acid 0.007 g, m.p. 116–118°, and was identified by spectral comparison with authentic material. (*ii*) Ether extract: this was dried ($MgSO_4$) and the ether removed *in vacuo* to yield a yellow oil 0.035 g which partly crystallized on standing. It was found to be *p*-nitrobenzaldehyde on the basis of its compatibility in i.r. and n.m.r. spectra with authentic material, and by its 2,4-dinitrophenylhydrazone derivative m.p. 317–318° (lit. 320° (32)) having an identical i.r. spectrum and undepressed mixed melting point with the same derivative of authentic *p*-nitrobenzaldehyde. (*iii*) Yellow residue: no structure could be assigned to this semi solid (0.02 g) which possessed a carbonyl stretching frequency in the i.r. spectrum (Nujol) of 1754 cm^{-1} and from the mass spectrum was seen to correspond to *m/e* 324 (i.e. parent oxazoline–anil moiety). (*iv*) Aqueous solution: this contained only cyclohexylamine hydrochloride.

Acid Hydrolysis of 3-Cyclohexyl-5-(cis-1,2-diphenylvinyl)-4-(p-nitrophenyl)-2-phenyl-4-oxazoline

0.40 g (0.00072 mole) of 3-cyclohexyl-5-(*cis*-1,2-diphenylvinyl)-4-(*p*-nitrophenyl)-2-phenyl-4-oxazoline was heated under reflux in 25 ml of 2 *N* hydrochloric acid for a period of 3½ h. From this reaction 4 products were isolated in the manner described above. The white sublimate (0.008 g) and the ether extract (0.050 g) were found to consist of benzoic acid (m.p. 119–120.5°), while the aqueous layer contained cyclohexylamine hydrochloride. As before, no structural assignment could be given to the brown residue (0.12 g, m.p. 85°) whose physical data was as follows. Mol. Wt. (mass spectrum): 369 (which corresponds to oxazoline–anil); the i.r. spectrum showed $\nu_{CHCl_3}^{max}$ 1766 (C=O) 1695 cm^{-1} (C=O); n.m.r. ($CDCl_3$), 6.7–8.5 (multiplet, aryl protons).

Acid Hydrolysis of 4-Benzoyl-3-cyclohexyl-5-(cis-1,2-diphenylvinyl)-2-phenyl-4-oxazoline

0.20 g (0.00039 mole) of 4-benzoyl-3-cyclohexyl-5-(*cis*-1,2-diphenylvinyl)-2-phenyl-4-oxazoline was heated under reflux in 25 ml of 50% (w/w) sulfuric acid for a period of 3 h. As in the procedure described above, benzoic acid was sublimed out in the condenser and benzaldehyde was obtained from the ether extract.

Reaction of 4-Benzoyl-3-cyclohexyl-5-(cis-1,2-diphenylvinyl)-2-phenyl-4-oxazoline with Nucleophiles and Bases.

(a) Potassium Thiocyanate

A solution of 0.064 g (0.125 mmole) of the title 4-oxazoline and 0.0032 g (0.025 mmole) of potassium thiocyanate in 10 ml of acetone was heated under reflux for 26 h; during which time it adopted a pink color. The solution was cooled, the solvent removed *in vacuo*, and the residue extracted with benzene affording 0.056 g (87.5% recovery) of unchanged 4-oxazoline; m.p. 158° (heptane), mixed m.p. 158° with authentic material.

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(b) Sodium Iodide

Similarly, a solution of 0.064 g (0.125 mmoles) of the title 4-oxazoline and 0.005 g (0.025 mmoles) of sodium iodide in 10 ml of acetone was heated under reflux for 3 h, during which time it adopted a deep red color. The solution was allowed to cool when it reverted to the original straw color, the solvent removed *in vacuo*, and the organic material recovered by extraction with benzene affording 0.054 g (84.1% recovery) of unchanged 4-oxazoline; m.p. 156° (heptane) identical with authentic material.

(c) Dimethyl Sulfoxide

A solution of 0.511 g (0.001 mole) of the 4-oxazoline and 0.234 g (0.003 mole) of dimethyl sulfoxide in 30 ml of benzene was heated under reflux for 24 h. The solvent was removed *in vacuo* and the resulting red oil chromatographed on 30 g of Fisher alumina with a 1:1 mixture of heptane and benzene as eluant. The main fraction was a pink solid of the unchanged 4-oxazoline 0.408 g (80% recovery) m.p. 160°.

(d) Potassium Carbonate in Aqueous Tetrahydrofuran

As described above in the attempted deuterium exchange, the 4-oxazoline was completely inert to prolonged refluxing with potassium carbonate in tetrahydrofuran–deuterium oxide mixtures.

(e) Sodium Hydroxide

A suspension of 0.51 g of the 4-oxazoline in 25 ml of 10% aqueous sodium hydroxide was heated under reflux for 3 h. The mixture was then cooled and the solid material collected, washed with water, and dried, affording 0.47 g of the unchanged 4-oxazoline m.p. 161°, undepressed by admixture with the starting material.

3-Cyclohexyl-5-(cis-1,2-diphenylvinyl)-3-phenyl-4-(p-toluoyl)-4-oxazoline and 4,5-Diphenyl-2-(cis-1,2-diphenylvinyl)-3-(p-toluoyl) furan

A solution of 1.6 g (0.005 mole) 1-cyclohexyl-2-phenyl-3-(*p*-toluoyl)aziridine (25) and 1.03 g (0.005 mole) of diphenylcyclopropenone in 60 ml of dry benzene, was heated under reflux for 12 h. The residual oil obtained after removal of the solvent was chromatographed on 120 g alumina as in the previous experiments. The benzene eluants gave on evaporation, an orange oil which when dissolved in 20 ml heptane and cooled yielded, 4,5-diphenyl-2-(*cis*-1,2-diphenylvinyl)-3-(*p*-toluoyl) furan, m.p. 180 °C (0.3 g) which recrystallized from ethanol as pale yellow crystals, m.p. 186–187 °C, and which was identical (mixed m.p. undepressed, superimposable i.r. spectrum) with the product obtained from the reaction of 3-cyclohexyl-5-(*cis*-1,2-diphenyl)-3-phenyl-4-(*p*-toluoyl)-4-oxazoline with diphenylacetylene described below.

Anal. Calcd. for $C_{38}H_{28}O_2$: C, 88.34; H, 5.46. Found: C, 88.5; H, 5.4.

Mol. Wt. Calcd.: 516.2089. Found (mass spectrum): 516.2089.

The i.r. spectrum showed ν_{max} ($CHCl_3$), 1693 cm^{-1} (aryl C=O); n.m.r. spectrum δ_{TMS} ($CDCl_3$), 7.8–6.7 (multiplet, 24H, aromatic protons) 8.05 (singlet, 1H, vinyl proton) 2.35 (singlet, 3H, methyl protons).

Concentration and further cooling of the heptane solution yielded 3-cyclohexyl-4-(*cis*-1,2-diphenylvinyl)-2-phenyl-4-(*p*-toluoyl)-4-oxazoline, m.p. 168–170 °C, 0.65 g, (20% yield) pink crystals, m.p. 175–176 °C (EtOH) which slowly became colorless on standing in the dark.

Anal. Calcd. for $C_{37}H_{35}NO_2$; C, 84.53; H, 6.72; N, 2.67. Found: C, 84.5; H, 6.7; N, 2.6.

Mol. Wt. Calcd.: 525.2668. Found (mass spectrum): 525.2665.

The i.r. spectrum showed ν_{max} ($CHCl_3$), 1695 cm^{-1} (aryl C=O); δ_{TMS} ($CDCl_3$), 8.0–6.7 (multiplet, 20H, aromatic protons and vinyl proton); 4.96 (singlet, 1H, '2' proton); 2.42 (singlet, 3H, CH_3 protons); 2.65–3.0 (multiplet, 1H) and 1.8–0.4 (multiplet 10H, cyclohexyl protons).

4,5-Diphenyl-2-(cis-1,2-diphenylvinyl)-3-(p-toluoyl)-furan from Reaction of 4-Aroyl-4-oxazoline and Diphenylacetylene

A solution of 0.1 g (0.0002 mole) of 5-(*cis*-1,2-diphenylvinyl-3-isopropyl-2-phenyl-4-(*p*-toluoyl)-4-oxazoline and 0.05 g (0.00028 mole) of diphenylacetylene in 20 ml dry toluene was heated under reflux for 48 h. Treatment of the reaction mixture as in the previous experiments gave 4,5-diphenyl-2-(*cis*-1,2-diphenylvinyl)-3-(*p*-toluoyl)furan 0.075 g (70.5% yield) which crystallized from ethanol, m.p. 185–186 °C. The product was identical in all respects with the sample obtained from the reaction of 1-cyclohexyl-2-phenyl-3-(*p*-toluoyl)aziridine with diphenylcyclopropenone.

3-Benzoyl-4,5-diphenyl-2-(cis-1,2-diphenylvinyl)-furan from Reaction of 4-Aroyl-4-oxazoline with (a) Diphenylcyclopropenone and with (b) Diphenylacetylene

(*a*) A solution of 0.2 g (0.00039 mole) of 4-benzoyl-3-cyclohexyl-5-(*cis*-1,2-diphenylvinyl)-2-phenyl-4-oxazoline and 0.08 g (0.00039 mole) of diphenylcyclopropenone in 25 ml dry toluene was heated under reflux for 18 h. The resulting pale yellow solution was evaporated to a small volume and the residual oil chromatographed on 30 g alumina using benzene as eluent. A yellow band which rapidly separated, was evaporated to dryness and the residual semi-solid on trituration with cold heptane gave 3-benzoyl-4,5-diphenyl-2-(*cis*-1,2-diphenylvinyl)-furan as a yellow solid, which crystallized from ethanol m.p. 196 °C (0.04 g (20.5% yield)). The product obtained was identical in all respects to the furan previously isolated from the reaction of 3-benzoyl-1-cyclohexyl-2-phenyl-aziridine with diphenylcyclopropenone in toluene described above.

(*b*) A solution of 0.2 g (0.00039 mole) of 4-benzoyl-3-cyclohexyl-5-(*cis*-1,2-diphenylvinyl)-2-phenyl-4-oxazoline and 0.1 g (0.0056 mole) of diphenylacetylene in 25 ml dry toluene was heated under reflux for 18 h. Treatment of the reaction mixture as in the previous experiment gave 3-benzoyl-4,5-diphenyl-2-(*cis*-1,2-diphenylvinyl)-furan, 0.145 g (75.5% yield) m.p. 196 °C.

Control Attempted Thermal Decarbonylation of Diphenylcyclopropenone under the Reaction Conditions of Formation of 4-Aroyl-4-oxazolines and 3-Aroylfurans

A solution of 1 g of diphenylcyclopropenone and 50 mg of isopropylamine in 20 ml of dry benzene was heated under reflux for 24 h. Evaporation of the solvent gave unreacted diphenylcyclopropenone 0.95 g m.p. 118° (24).

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A similar control experiment using toluene as solvent containing a trace of cyclohexylamine resulted in recovery of unchanged diphenylcyclopropenone.

Reaction of Cycloheptenocyclopropenone with 4-Benzoyl-3-cyclohexyl-5-(cis-1,2-diphenylvinyl)-2-phenyl-4-oxazoline

A solution of 0.061 g (0.005 mole) of cycloheptenocyclopropenone (24) and 0.25 g (0.005 mole) of 4-benzoyl-3-cyclohexyl-5-(*cis*-1,2-diphenylvinyl)-2-phenyl-4-oxazoline in 10 ml of toluene was heated under reflux for 27 h, allowed to cool, and solvent removed *in vacuo* leaving a yellow oil. Chromatography of the product on alumina (B.D.H.) with hexane/benzene (60:40) as eluant afforded 3-benzoyl-4,5-cycloheptено-2-(*cis*-1,2-diphenylvinyl)furan 0.067 g (32% yield) m.p. 160 °C (benzene/heptane).

Anal. Calcd. for $C_{30}H_{26}O_2$; C, 86.08; H, 6.27. Found: C, 84.83; H, 6.32.

Mol. Wt. Calcd.: 418.1933. Found (mass spectrum): 418.1935

The i.r. spectrum showed ν_{max} ($CHCl_3$), 1690 cm^{-1} (broad, arylketone); n.m.r. ($CDCl_3$), 1.8–2.3 (multiplet, 4H, 1,1′,5,5′-cycloheptenyl protons), 1.2–1.8 (multiplet, 6H, 2,2′,3,3′,4,4′-cycloheptenyl protons), 6.9–8.1 (multiplet, 10H, aryl protons and vinyl proton).

Reaction of 1,1a-Dihydro-1,2-diphenylazirino[1,2-a]-quinoxaline with Diphenylcyclopropenone

A solution of 2.08 g (0.007 mole) of 1,1*a*-dihydro-1,2-diphenylazirino[1,2-*a*]quinoxaline (21) and 1.45 g (0.007 mole) of diphenylcyclopropenone in 50 ml of dry benzene was heated under reflux for 24 h, during which time the solution adopted a blood red color. Evaporation of the solvent *in vacuo* left a red semi-solid which was subjected to chromatography on basic alumina in benzene. The main fraction appeared on the column as a deep red band and elution and evaporation of the solvent gave a red oil ca. 2.0 g. Trituration with hexane and chilling resulted in the deposition of small dark red crystals 0.43 g (12.7% yield) of 3-(*cis*-1,2-diphenylvinyl)-1-phenyl-4-phenyl-1H-oxazolo-[3,4-*a*]-quinoxaline, m.p. 101° (soften).

Anal. Calcd. for $C_{36}H_{26}N_2O$: C, 86.02; H, 5.22; N, 5.58. Found: C, 85.60; H, 5.65; N, 5.56.

Mol. Wt. Calcd.: 502.2045. Found (mass spectrum): 502.2040.

The i.r. spectrum showed ν_{max} ($CHCl_3$) 1625 cm^{-1}; n.m.r. spectrum, δ_{TMS} ($CDCl_3$), 6.05 (singlet, 1H, vinyl proton); 6.68–7.72 (multiplet, 24H, aromatic protons).

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