Reaction of 3-aroylaziridines with aryl isothiocyanates

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3-Aroylaziridines react with a variety of aryl isothiocyanates in refluxing benzene to give either (*a*) 4-aroyl-5-arylamino-4-thiazolines by a [2 + 3] cycloaddition and/or (*b*) 2-arylamino-4-aroyl-4-thiazolines. When the *N*-substituent of the aziridine is cyclohexyl or isopropyl the product type (*a*) is isolated in greater quantity, but when the *N*-substituent is methyl, product type (*b*) is isolated in greater quantity. The reactions provide convenient one-step syntheses of new 4-aroyl-4-thiazolines.

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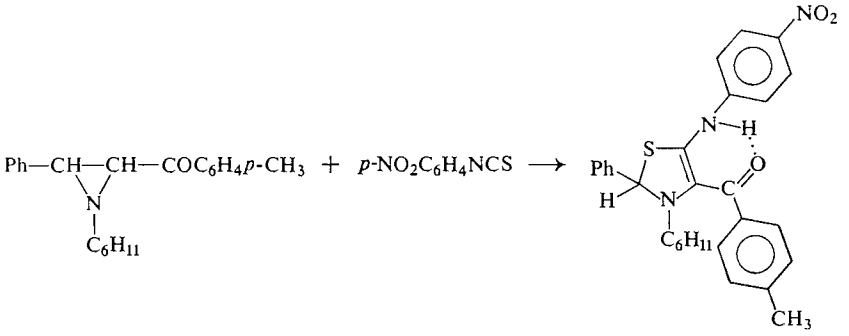
Recently, interest has been shown in the addition reactions of substituted aziridines involving cleavage of the 2–3 bond to an azomethine ylid and subsequent [2 + 3] cycloaddition to the acetylenic bond and to activated alkenes (1–14). We have reported the analogous addition of 3-aroylaziridines to the polarized carbonyl bond of diphenylcyclopropenone with the formation of novel 4-oxazolines (15, 16). In a continuing study of these addition reactions of 3-aroylaziridines to heteromultiple bonds we now report their addition to aryl isothiocyanates.

Treatment of 1-cyclohexyl-2-phenyl-3-*p*-toluoylaziridine with an equimolar quantity of *p*-nitrophenyl isothiocyanate in refluxing benzene, followed by chromatographic separation on alumina, afforded 3-cyclohexyl-5-*p*-nitrophenylamino-2-phenyl-4-*p*-toluoyl-4-thiazoline **3** (Table I) in 54% yield as orange-red crystals, m.p. 206–207°. The analytical and spectral data on this and similar 4-thiazolines is summarized in Tables I and II and are clearly consistent with structure **3**. In particular the strong hydrogen bonding in a favorable six-membered ring is confirmed by the infrared (i.r.) data, 3050 (broad, bonded NH), 1605(s) (aryl ketone strongly shifted hydrogen bonding), 1589(s) (C=N stretch), and the observation of the low field exchangeable hydrogen bonded NH proton at 13.4 δ in the nuclear magnetic resonance (n.m.r.), spectrum.

This reaction is mechanistically rationalized as involving thermal cleavage of the aroylaziridine to an azomethine ylid and concerted [2 + 3] cycloaddition of this species to the C=S bond of the aryl isothiocyanate and tautomerisation of the product to **3**. It has been observed that the C=S bond of an isothiocyanate will undergo [2 + 3] cycloaddition with diazocompounds, ketocarbenes, alkylene oxides and thioketocarbenes to form five-membered ring heterocycles (17), and that the C=S bond in general displays unusually great activity as a dipolarophile (18).

Huisgen has pointed out that the orientation of 1,3 dipolar additions may not be safely predicted on pragmatic grounds of the assignment of nucleophilic and electrophilic centers in



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[1]NRCC Studentship holder 1967–1969.

TABLE I

4-Aroyl-5-arylamino-4-thiazolines*

No.	R_3	R_4	R_5	Melting point	Yield (%)	Observed C	H	N	S	Mol. ion (Mass spec.)	Calculated C	H	N	S	Mol. ion
1.	C_6H_{11}	$pCH_3C_6H_4$	C_6H_5	170–171°	59	76.35	6.90	5.93	6.74	454.2081	76.61	6.65	6.16	7.05	454.2079
2.	$(CH_3)_2CH$	C_6H_5	C_6H_5	158°	31	75.10	5.98	6.92	8.15	400.1608	74.96	6.04	7.00	8.00	400.1610
3.	C_6H_{11}	$pCH_3C_6H_4$	$pNO_2C_6H_4$	206–207°	54	69.44	5.80	8.38	6.48	499.1931	69.71	5.85	8.41	6.42	499.1930
4.	C_6H_{11}	$pCH_3C_6H_4$	$mNO_2C_6H_4$	122°	48	69.84	6.31	—	6.37	499.1931	69.71	5.85	—	6.42	499.1930
5.	$(CH_3)_2CH$	C_6H_5	$mNO_2C_6H_4$	97°	20.5	67.35	5.06	9.45	7.36	445.1458	67.39	5.20	9.43	7.20	445.1460
6.	C_6H_{11}	$pCH_3C_6H_4$	1-naphthyl $C_{10}H_8$	204°	32	78.65	6.32	5.53	6.36	504.2235	78.53	6.39	5.55	6.35	504.2236
7.	C_6H_{11}	$pNO_2C_6H_4$	$pNO_2C_6H_4$	160°	49	63.22	5.11	10.51	6.16	530.1628	63.38	4.94	10.56	6.04	530.1624
8.	C_6H_{11}	$pNO_2C_6H_4$	$mNO_2C_6H_4$	167°	20	63.29	4.69	10.38	6.07	530.1620	63.38	4.94	10.56	6.04	530.1624
9.	C_6H_{11}	$pNO_2C_6H_4$	1-naphthyl $C_{10}H_8$	204°	5	71.94	5.41	7.95	6.00	535.1927	71.75	5.45	7.85	5.99	535.1930
10.	C_6H_{11}	$pNO_2C_6H_4$	$pC_6H_5—C_6H_4$	200°	49	72.86	5.40	7.56	5.87	561.2084	72.70	5.56	7.48	5.71	561.2086
11.	C_6H_5	C_6H_{11}	C_6H_5	156°	20	75.99	6.42	6.38	7.47	440.1927	76.33	6.40	6.36	7.28	440.1923

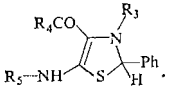
*Compounds of structure 

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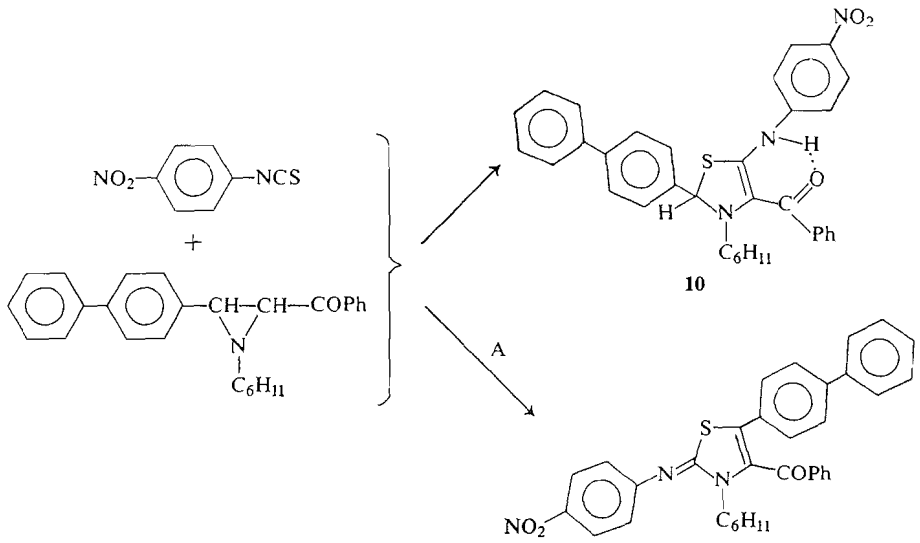
TABLE II

Spectroscopic properties of 4-aroyl-5-arylamino-4-thiazolines

	Infrared spectrum ($CHCl_3$)			Nuclear magnetic resonance ($CDCl_3$)δ						Absorption spectrum (CH_3CN)	
No.	N—H bonded	C=O	C=N	Aryl protons	2-proton	$(CH_3)_2CH$	*N*-Alkyl groups	Aryl methyl	Chelated N—H	λ_{max}	Log ε
1.	3050 br	1610(s)	1595(s)	8.16–6.92 (14H)m	5.90 (1H)s	—	1.96–0.75 (11H)m C_6H_{11}	2.33 (3H)s	13.14 (1H)s	260 350 420	4.16 3.97 4.09
2.	3050 br	1610(s)	1592(s)	8.25–7.0 (14H)m	5.87 (1H)s	3.17(1H) m $J = 7$Hz	1.05–1.09 (3H)d (3H) $J = 7$Hz	—	13.20 (1H)s	250 350 415	4.22 3.10 4.09
3.	3050(m) br	1605(s)	1589(s)	8.4–7.1 (13H)m	6.02 (1H)s	—	2.15–0.75 (11H)m C_6H_{11}	2.32 (3H)s	13.23 (1H)s	255 280 365 440	4.16 4.16 4.09 4.11
4.	3050(m) br	1602(s)	1590(s)	8.31–7.12 (13H)m	6.09 (1H)s	—	2.17–0.77 (11H)m C_6H_{11}	2.36 (3H)s	13.26 (1H)s	233 350 430	3.93 4.05 4.15
5.	3050(m) br	1610(s)	1600(s)	8.36–7.24 (14H)m	6.00 (1H)s	3.18(1H) m $J = 6.5$Hz	1.12 d (6H) $J = 6.5$Hz	—	13.19 (1H)s	252 355 424	4.36 3.98 4.10
6.	2990 br	1600(s)	1592(s)	8.56–6.82 (16H)m	5.97 (1H)s	—	3.31–0.82 (11H)m C_6H_{11}	2.37 (3H)s	13.02 (1H)s	260 350 420	4.31 3.94 4.17
7.	3100 br	1600(s)	1588	8.52–7.10 (13H)m	6.08 (1H)s	—	3.0–0.77 (11H)m C_6H_{11}	—	13.16 (1H)s	250 290 375 460	4.32 4.26 4.09 4.17
8.	3090 br	1590(s)	1580(s)	8.58–7.20 (13H)m	6.10 (1H)s	—	3.10–0.83 (11H)m C_6H_{11}	—	13.07 (1H)s	265 455	4.40 4.14
9.	3050 br	1590(s)	1585(sh)	8.60–6.80 (16H)s	6.01 (1H)s	—	3.25–0.26 (11H)m C_6H_{11}	—	12.96 (1H)s	272 457	4.36 4.16
10.	3050 br	1610(s)	1595(s)	8.54–7.16 (18H)m	6.08 (1H)s	—	3.0–0.68 (11H)m C_6H_{11}	—	13.30 (1H)s	260 340 420	4.71 3.74 3.82
11.	3080 br	1610(s)	1590(s)	8.30–6.90 (15H)m	5.95 (1H)s	—	3.0–0.6 (11H)m C_6H_{11}	—	13.20 (1H)s	250 320 416	4.20 3.98 4.03

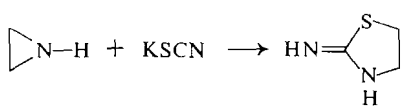


the 1,3 dipole (18). However, in the present reaction, hydrogen bonding of the N—H bond to the carbonyl group uniquely confirms the mode of addition. This reaction therefore provides a useful and facile route to 4-aroylthiazolines and its scope was now explored by examining the reactions of a series of aroylaziridines with a variety of aryl isothiocyanate.

It was anticipated that the above [2 + 3] cycloaddition would in many cases have to compete with nucleophilic attack by the isothiocyanate grouping at the 2-position of the aziridine ring, which Cromwell has pointed out is electrophilic (19).

In the reaction of 3-benzoyl-1-cyclohexyl-2-*p*-biphenylylaziridine with *p*-nitrophenyl isothiocyanate for example products **10** (Tables I and II) and **15** (Tables III and IV) were isolated corresponding respectively to [2 + 3] cycloaddition via the azomethine ylid and to aziridine ring opening at the 2 position and subsequent cyclisation to a 2-arylimino-4-aroyl-4-thiazoline. One of the referees has suggested that compound **15** could also be formed by a [2 + 3] polar cycloaddition.

Gabriel has reported that reaction of aziridine with potassium thiocyanate gives 2-iminothiazolidine (20, 21).



Therefore the initial product of reaction (A) might be expected to be the thiazolidine, and in fact in one example such a thiazolidine was isolated, but in general, the initially formed thiazolidine is dehydrogenated, either during the reaction or in the work-up to the iminothiazoline such as **15**. The iminothiazoline **15** and similar compounds are readily characterized by the observation in the i.r. spectrum of strong C=N stretch and strongly conjugated aryl ketone absorption and the absence of a hydrogen bonded proton characteristic of **10** and similar compounds. In contrast alkyl and aryl isothiocyanates react with aziridines having a free N—H, and gives thioureas (22, 23).

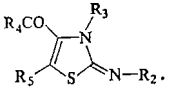
The course of the present reaction of aroylaziridines with aryl isothiocyanates often leads to complex mixtures of oils from which major solid products can be isolated by column chromatography. The data summarized in Table V is given as a preparative guide only, of the dependence of the course of the reaction principally on the nature of the *N*-substituent of the aziridine. While no quantitative conclusions may be drawn from the above observations it is evident in a qualitative sense that when the *N*-substituent of the aziridine is cyclohexyl or isopropyl the [2 + 3] cycloaddition mode is favored in reaction with phenyl isothiocyanate, *p*-nitrophenyl isothiocyanate, *m*-nitrophenyl isothiocyanate, and 1-naphthyl isothiocyanate.

However when the *N*-substituent of the

TABLE III

2-Arylimino-4-aroyl-4-thiazolines*

No.	$\frac{R_2}{R_3}$	$\frac{R_4}{R_5}$	Melting point	Yield (%)	Observed C	H	N	S	Mol. ion (Mass spec.)	Calculated C	H	N	S	Mol. ion
12	$\frac{C_6H_5}{CH_3}$	$\frac{C_6H_5}{C_6H_5}$	219–221°	31	74.40	4.69	7.44	8.31	370.1140	74.57	4.90	7.56	8.65	370.1140
13	$\frac{\text{1-naphthyl } C_{10}H_8}{CH_3}$	$\frac{C_6H_5}{C_6H_5}$	275°	20	76.85	4.97	6.37	7.83	420.1301	76.75	5.25	6.63	7.59	420.1297
14	$\frac{C_6H_5}{CH_3}$	$\frac{pCH_3C_6H_4}{C_6H_5}$	248°	20	74.64	5.40	7.25	8.40	(M^+-1)† 383.1220	74.97	5.24	7.29	8.34	(M^+-1) 383.1219
15	$\frac{pNO_2C_6H_4}{C_6H_{11}}$	$\frac{C_6H_5}{pC_6H_5C_6H_4}$	183°	25	72.68	5.38	7.43	5.74	559.1935	72.96	5.22	7.51	7.53	559.1930

*Compounds of structure 

†Parent peak too small to measure.

TABLE IV

Spectroscopic properties of 2-arylimino-4-aroyl-4-thiazolines*

No.	$\frac{R_2}{R_3}$	$\frac{R_4}{R_5}$	Infrared spectrum ($CHCl_3$) C=O	Infrared spectrum ($CHCl_3$) C=N	Nuclear magnetic resonance $\delta(CDCl_3)$ Aryl protons	Nuclear magnetic resonance $\delta(CDCl_3)$ Alkyl Protons	Absorption spectrum (CH_3CN) λ_{max}	Log ε	λ_{max}	Log ε	λ_{max}	Log ε
12	$\frac{C_6H_5}{CH_3}$	$\frac{C_6H_5}{C_6H_5}$	1615(s)	1597(s)	8.40–7.13 (15H)m	3.78 (3H)s *N*–CH_3	418	3.85	336	3.76	250	4.54
13	$\frac{\text{1-naphthyl } C_{10}H_9}{CH_3}$	$\frac{C_6H_5}{C_6H_5}$	1605(s)	1595(s)	8.35–6.90 (17H)m	3.97 (3H)s *N*–CH_3	420	4.86	320	3.81	250	4.47
14	$\frac{C_6H_5}{CH_3}$	$\frac{pCH_3C_6H_4}{C_6H_5}$	1615(s)	1600(s)	8.30–7.0 (14H)m	2.39(3H)s aryl Me 3.81 (3H)s *N*–Me	420	3.82	340	3.75	255	4.45
15	$\frac{pNO_2C_6H_4}{C_6H_{11}}$	$\frac{C_6H_5}{pC_6H_5C_6H_4}$	1605(s)	1586(s)	8.30–7.15 (18H)m	2.3–0.8 (11H)m C_6H_{11}	420	3.82	340	3.74	260	4.71

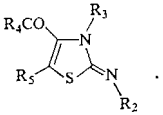
*Compounds of structure 

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TABLE V

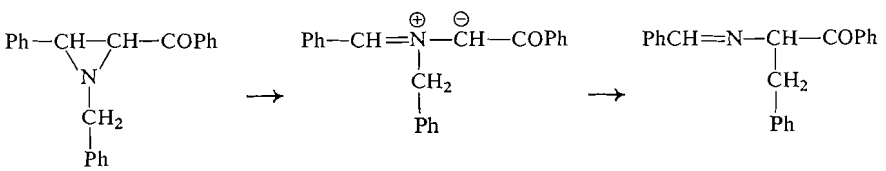
Substituent dependence of the reaction course in the reaction of 3-aroylaziridines with arylisothiocyanates

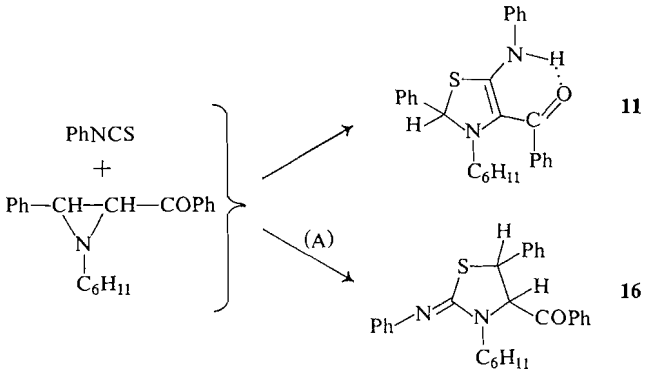
3-Aroylaziridine and number of examples	Product type and % yield range	
	5-Arylamino-4-thiazoline	2-Arylimino-4-thiazoline
Ph-CH—CH-COAr (8) N C_6H_{11}	(59–21)	—
Ph-CH—CH-COAr (2) N $CH(CH_3)_2$	(31–21)	—
Ph-CH—CH-COAr (3) N CH_3	—	(43–20)
pC_6H_5-C_6H_4-CH—CH-COPh (1) N C_6H_{11}	49	25

aziridine is methyl, nucleophilic attack at the 2-position of the aziridine is favored leading to the 2-arylimino-4-thiazoline. The yields in Table V represent isolated and purified products after chromatography and no attempt has been made to optimize the yields. *N*-Benzyl substituted 3-aroylaziridines are found to be unsatisfactory in attempted [2 + 3] cycloadditions in this and in other studies (1, 24) where the superior migratory aptitude of the benzyl group favors a Stevens rearrangement of the intermediate azomethine ylid. The thermolysis of 2,3-diphenylaziridine results in a similar rearrangement (5). 3-Benzoyl-1-cyclohexyl-2-phenylaziridine is exceptional in that upon reaction with phenyl isothiocyanate [2 + 3] cycloaddition affords **11** (Table I) and nucleophilic ring opening and subsequent ring closure given the iminothiazolidine **16** (see Experimental) and not the dehydrogenation product.

Compound **16** isomeric with **11** shows an AB quartet due to the 4,5 protons of the thiazolidine ring, the coupling constant of which, 3Hz, corresponds to a *trans* arrangement (8) of these protons in a five-membered ring and confirms, as predicted, that the original 2–3 bond of the aroylaziridine is still intact. Normally dehydrogenation of the initially formed 2-iminothiazolidine to the 2-iminothiazoline occurs during the reaction but **16** proved to be unusually resistant to dehydrogenation, presumably accounting for its isolation in this reaction.

The dehydrogenation of structurally related thiazolines by quinones has been investigated by Kenner and co-workers (25) who found that 9,10-phenanthrenequinone was often satisfactory whereas higher potential quinones such as 2,3-dichloro-5,6-dicyano-1,4-benzoquinone led to more extensive decomposition. Reaction of **16** with 9,10-phenanthrenequinone in acetic acid





resulted in dehydrogenative elimination of benzaldehyde to form **17.**

Compound **17** gives correct analytical figures, mass spectral parent peak, the i.r. confirms the absence of an aryl ketone band and the 4-vinyl proton is prominent in the n.m.r. spectrum. The above reaction is analogous to decarboxylative dehydrogenation (26). The abnormal resistance to dehydrogenations of this type has been noted in certain other five-membered ring heterocycles (6).

Treatment of **16** with the higher potential quinone tetrachloro-1,2-benzoquinone in benzene afforded the 2-arylaminothiazole **18.** The [2 + 3] cycloaddition of other reactive hetero-multiple bonds to aroylaziridines is currently under investigation.

Experimental

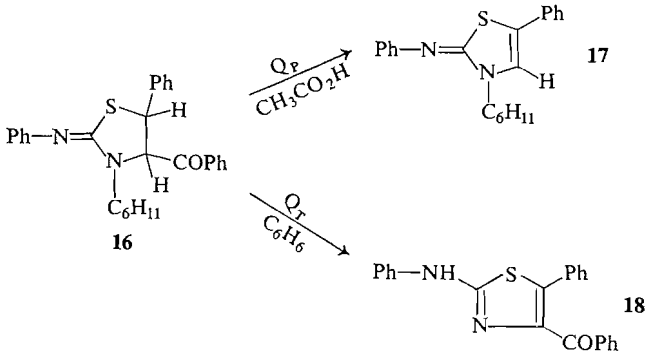
Melting points were determined on a Fisher–Johns apparatus and are uncorrected. Infrared spectra were recorded on a Perkin–Elmer model 421 spectrophotometer, and only the principal, sharply defined peaks are reported. Nuclear magnetic resonance spectra were recorded on Varian A-60 and A-100 analytical 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 'spectrograde' 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 ionisation 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. 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

These compounds were prepared by established methods involving aldol type condensations to form the chalcones, then addition of bromine to form the dibromochalcone and treatment of the latter with primary amines to provide the aroylaziridines. Several new aroylaziridines have been prepared by this method exemplified as follows.

Preparation of 3-Benzoyl-1-isopropyl-2-phenylaziridine

Isopropylamine 24 g, (0.407 mole) was added dropwise to a stirred solution of 50 g (0.136 mole) of 2,3-



Q_P = 9,10-phenanthrenequinone
Q_T = tetrachloro-1,2-benzoquinone

dibromo-3-phenylpropiophenone (Eastman Kodak Co.) in 700 ml of dry benzene at 0°, then the solution was stirred for 1 h at 0° and set aside for 24 h at room temperature. The precipitated isopropylamine hydrobromide was collected (34 g; theoretical yield 34 g) and the yellow filtrate washed with water to remove excess amine, dried ($MgSO_4$), and the solvent removed *in vacuo*. The residual oil consisted of an approximately 1:1 mixture of *cis* and *trans* 3-benzoyl-1-isopropyl-2-phenylaziridines (36 g) 100% yield which crystallized partly on chilling. For reaction with the arylisothiocyanates the mixture of isomeric aroylaziridines was used as in previous work (13) but a small quantity was separated into isomers for analytical purposes by preparative thin-layer chromatography on silica with (3:1) benzene:heptane which afforded the pure *cis* isomer and slightly impure *trans*. The latter could be obtained isomerically pure by further chromatography on Fisher alumina in heptane. The stereochemistry was readily assigned by reference to the n.m.r. spectrum (27).

cis-Isomer, pale-yellow crystals m.p. 90–91° (heptane).

Anal. Calcd. for $C_{18}H_{19}NO$ (mol. wt., 265.1467): C, 81.51; H, 7.17; N, 5.28. Found (mol. wt. (mass spectrum) 265.1468): C, 81.32; H, 7.20; N, 5.34.

Infrared spectrum: ν_{max} ($CHCl_3$); 1683 cm^{-1} (aryl C=O). Nuclear magnetic resonance spectrum ($CDCl_3$): 1.22 (doublet, 6H; J = 5.7Hz; $(CH_3)_2CH$—); 1.86 (septet, 1H, $(CH_3)_2$ C*H*), 3.18 (singlet 2H, aziridine ring protons), 7.00–7.50 and 7.80–8.01 (multiplet 10H, aryl protons).

trans-Isomer, low-melting yellow solid, m.p. <25°.

Anal. Calcd. for $C_{18}H_{19}NO$ (mol. wt., 265): C, 81.51; H, 7.17; N, 5.28. Found (mol. wt. (mass spectrum) 265): C, 81.50; H, 7.39; N, 5.05.

Infrared spectrum: ν_{max} ($CHCl_3$) 1662 cm^{-1} (aryl C=O). Nuclear magnetic resonance spectrum ($CDCl_3$): 0.91 (doublet, 3H; J = 6Hz; 1.18, doublet 3H, J = 6Hz; $(CH_3)_2CH$—), 2.19 (multiplet, 1H, $(CH_3)_2CH$—), 3.46–3.66 (AB quartet, 2H, aziridine ring protons); 7.16–7.58 and 7.96–8.16 (multiplets, 10H, aryl protons).

2,3-Dibromo-3-phenyl-p-nitropropiophenone

Styryl-*p*-nitrophenylketone was prepared in 74% yield m.p. 145–147° (lit. m.p. 149–150°) (28) then brominated to give 2,3-dibromo-3-phenyl-*p*-nitropropiophenone in 85% yield, m.p. 210° by the method of Weygand (29).

1-Cyclohexyl-3-p-nitrobenzoyl-2-phenylaziridine

This aziridine was prepared from 2,3-dibromo-3-phenyl-*p*-nitropropiophenone and cyclohexylamine by the standard procedure in 76% yield as an orange solid m.p. 112–113° (hexane).

Anal. Calcd. for $C_{21}H_{22}N_2O_3$ (mol. wt., 350.1630): C, 72.00; H, 6.29; N, 8.00. Found (mol. wt. (mass spectrum) 350.1634): C, 72.10; H, 6.32; N, 7.94.

Infrared spectrum ($CHCl_3$): ν_{max}: 1681, (C=O *cis* aziridine) 1656 cm^{-1} (C=O *trans* aziridine). Nuclear magnetic resonance spectrum ($CDCl_3$): 0.83–2.00 (multiplet, 10H, cyclohexyl CH_2), 2.33–2.76 (multiplet, 1H, cyclohexyl C*H*), 3.22 (singlet, 2H, *cis* aziridine ring protons) (25), 3.57 (singlet, 2H, *trans* aziridine ring protons), 7.18–8.35 (multiplet, 9H, aryl protons).

3-(p-Biphenylyl)-2,3-dibromo-1-phenyl-1-propanone

A solution of 12.6 g (0.0775 mole) of bromine in 50 ml of chloroform was added dropwise to a stirred solution of 22 g (0.0775 mole) of 4-(*p*-phenyl)-styrylphenyl ketone (32) in 100 ml of chloroform during 30 min. The solution was stirred for 15 min, then the solvent removed *in vacuo* to give the dibromo compound as a yellow solid m.p. 180–181°, 34.4 g, (quantitative yield). The product was purified by recrystallization from benzene: hexane as a white solid m.p. 185.5–186°.

Anal. Calcd. for $C_{21}H_{16}Br_2O$: C, 56.75; H, 3.63; Br, 35.99. Found: C, 56.66; H, 3.56; Br, 36.22.

Infrared spectrum ν_{max} ($CHCl_3$): 1690 cm^{-1} (aryl C=O). Nuclear magnetic resonance spectrum ($CDCl_3$): AB quartet centered at 5.76 and 5.92 (2H, J = 11Hz, 2,3 protons); 7.25–8.3 (multiplet, aryl protons).

3-Benzoyl-2-(p-biphenylyl)-1-cyclohexylaziridine

This aziridine was prepared as a *cis–trans* mixture from 22.2 g (0.05 mole) of 2-(*p*-biphenylyl)-2,3-dibromo-1-phenyl-1-propanone and 54.5 g (0.55 mole) of cyclohexylamine by the standard procedure in approximately quantitative yield as a white solid m.p. 127° (MeOH).

Anal. Calcd. for $C_{27}H_{27}NO$: C, 85.00; H, 7.14; N, 3.67. Found: C, 84.90; H, 7.23; N, 3.64.

Infrared spectrum ($CHCl_3$) ν_{max}: 1680 cm^{-1} (C=O). Nuclear magnetic resonance spectrum ($CDCl_3$): 1.0–3.0 (multiplet, 11H, cyclohexyl protons), 3.23 (singlet, 2H, *cis* aziridine ring protons) (27), 3.53 (singlet, 2H, *trans* aziridine ring protons), 7.2–8.3 (multiplet, 14H, aryl protons).

3-Benzoyl-1-methyl-2-phenylaziridine

This aziridine was prepared as a *cis–trans* mixture m.p. 88–89° by the method of Cromwell and co-workers (30).

3-Benzoyl-1-cyclohexyl-2-phenylaziridine

This aziridine was prepared by the method of Cromwell (31) *cis* isomer m.p. 107–109°; *trans* isomer m.p. 99–101°.

1-Methyl-2-phenyl-3-p-toluoylaziridine

This aziridine was also prepared by the above procedure (31) as a *cis–trans* mixture m.p. 76–78°.

1-Cyclohexyl-2-phenyl-3-p-toluoylaziridine

This aziridine was also prepared by the method of Cromwell (31) *cis* isomer m.p. 111–112°; and the *trans* isomer 89–90°.

Reaction of 3-Aroylaziridines with Aryl Isothiocyanates

General Method

The reaction method is exemplified by one reaction of each type in which [2 + 3] cycloaddition and nucleophilic ring opening predominated.

Reaction of 1-Cyclohexyl-2-phenyl-3-p-toluoylaziridine with p-Nitrophenyl Isothiocyanate

A solution of 2.16 g (0.0068 mole) of 1-cyclohexyl-2-phenyl-3-*p*-toluoyl-aziridine and 1.22 g (0.0068 mole) of *p*-nitrophenyl isothiocyanate in 30 ml of dry benzene was heated under reflux for 17 h when a deep orange color developed. The solution was concentrated *in vacuo* to ca. 12 ml and passed down a column of Grade 1 alumina (120 g). Elution with benzene afforded one main fraction which upon evaporation afforded 3-cyclohexyl-5-*p*-nitrophenylamino-2-phenyl-4-*p*-toluoyl-4-thiazoline as deep orange-red crystals 2.1 g (54% yield) m.p. 206–207° from ethyl acetate.

Anal. Calcd. for $C_{29}H_{29}N_3O_3S$ (mol. wt., 499.1930): C, 69.71; H, 5.85; N, 8.41; S, 6.42. Found (mol. wt. (mass spectrum) 499.1931): C, 69.44; H, 5.80; N, 8.38; S, 6.48.

Infrared spectrum: ν_{max} ($CHCl_3$), 1605(s) (C=O), 1589(s) (C=N), 1492(m) 3050 cm^{-1}(m) (broad, chelated hydrogen). Nuclear magnetic resonance spectrum ($CDCl_3$): 0.75–2.15 (11H, multiplet cyclohexyl protons), 2.32 (3H, singlet, aryl methyl), 6.02 (1H, singlet, 4-thiazoline proton), 7.10–8.4 (13H, multiplet, aryl protons), 13.23 (1H, singlet, exchangeable with D_2O, chelated NH proton).

Reaction of 3-Benzoyl-1-methyl-2-phenylaziridine with Phenyl Isothiocyanate

A solution of 1.39 g (0.0059 mole) of 3-benzoyl-1-methyl-2-phenylaziridine and 0.8 g (0.0059 mole) of phenyl isothiocyanate in 20 ml of dry benzene was heated under reflux for 12 h when a deep red-brown color developed. The cooled solution was subjected to chromatography on 70 g of Grade 1 alumina. Elution with benzene afforded one main fraction which upon evaporation of the solvent afforded an orange oil which crystallized upon trituration with ethyl acetate as golden–yellow plates of 4-benzoyl-3-methyl-2-phenylimino-5-phenyl-4-thiazoline, 0.68 g, (31% yield) m.p. 220–221° (from ethyl acetate).

Anal. Calcd. for $C_{23}H_{18}N_2OS$ (mol. wt., 370.1140): C, 74.57; H, 4.90; N, 7.56; S, 8.65. Found (mol. wt. (mass spectrum) 370.1140): C, 74.40; H, 4.69; N, 7.44; S, 8.31.

Infrared spectrum: ν_{max} ($CHCl_3$): 1615(s) (C=O), 1597(s) (C=N), 1497 cm^{-1}. Nuclear magnetic resonance spectrum ($CDCl_3$): 3.78 (3H, singlet N—CH_3 group), 7.13–8.40 (15H, multiplet, aryl protons).

Reaction of 3-Benzoyl-1-cyclohexyl-2-phenylaziridine with phenyl isothiocyanate

A solution of 6.35 g (0.0208 mole) of 3-benzoyl-1-cyclohexyl-2-phenylaziridine and 2.8 g (0.0208 mole) of phenyl isothiocyanate in 65 ml of dry benzene was heated under reflux for 7 h when a yellow-orange color developed. The cooled solution was concentrated to ca. 15 ml *in vacuo* and passed down a column of 200 g of Grade 1 alumina. Elution with benzene gave a yellow fraction which upon evaporation of the solvent gave a yellow solid, 1.74 g containing two products. Extraction with hot heptane allowed separation of the products:

(*a*) Insoluble in hexane was 4-benzoyl-3-cyclohexyl-2-phenylimino-5-phenylthiazolidine purified by recrystallization from benzene as pale-yellow crystals, 0.5 g, m.p. 204°.

Anal. Calcd. for $C_{28}H_{28}N_2SO$ (mol. wt., 440.1923): C, 76.33; H, 6.41; N, 6.36; S, 7.28. Found (mol. wt. (mass spectrum) 440.1927): C, 76.57; H, 6.78; N, 6.31; S, 7.34.

Infrared spectrum: ν_{max} ($CHCl_3$): 1673(s) (C=O); 1592(s) (C=N) 1490(m) cm^{-1}. Nuclear magnetic resonance spectrum ($CDCl_3$): 0.4–3.35 (11H, multiplet, cyclohexyl protons); AB quartet centered at 6.23 and 6.46 δ (J = 3Hz) (2H, 4,5 thiazolidine protons with *trans* geometry); 6.70–8.50 (15H, multiplet, aryl protons).

(*b*) Soluble in hexane was 4-benzoyl-3-cyclohexyl-2-phenyl-5-phenylamino-4-thiazoline 1.2 g, (20% yield) m.p. 156° (from benzene/hexane). Full details on this compound as well as the physical properties, analytical data and spectroscopic properties of the other 4-thiazolines synthesised may be found in Tables I to IV.

Reaction of 4-Benzoyl-3-cyclohexyl-2-phenylimino-5-phenyl-thiazolidine with 9,10-Phenanthrenequinone

A solution of 0.250 g (0.00057 mole) of the thiazolidine and 0.165 g (0.0008 mole) of 9,10-phenanthrenequinone in 3 ml of acetic acid was heated under reflux for 30 min, allowed to cool and diluted with 15 ml of ether and 15 ml of benzene and allowed to stand over 2.98 g of sodium carbonate overnight. The filtered solution was evaporated to dryness and the residual yellow solid taken up in 5 ml of benzene and subjected to chromatography on 15 g of Grade 1 alumina. Elution with benzene afforded two fractions:

(*a*) a white crystalline solid of 3-cyclohexyl-2-phenylimino-5-phenyl-1,3-thiazoline, 0.175 g (92% yield) m.p. 205° (from 1:1 benzene: petroleum ether).

Anal. Calcd. for $C_{21}H_{22}N_2S$ (mol. wt., 334.1504): C, 75.41; H, 6.63; N, 8.38; S, 9.59. Found (mol. wt. (mass spectrum) 334.1509): C, 75.57; H, 6.62; N, 8.41; S, 9.53.

Infrared spectrum: ν_{max} ($CHCl_3$): 1590(s) cm^{-1} (C=N). Nuclear magnetic resonance spectrum ($CDCl_3$): 0.83–2.48 (10H, multiplet, cyclohexyl protons), 4.57–5.19 (1H, broad multiplet, 1-cyclohexyl proton), 6.90 (1H, singlet, 4-proton) 6.8–7.50 (10H, multiplet, aryl protons).

Fraction (*b*) consisted of 9,10-phenanthrenequinone, 0.125 g m.p. 207°, mixture m.p. 207° with authentic material.

Reaction of 4-Benzoyl-3-cyclohexyl-2-phenylimino-5-phenyl-1,3-thiazolidine with Tetrachloro-1,2-benzoquinone

A solution of 0.421 g of the thiazolidine and 0.236 g of tetrachloro-1,2-benzoquinone in 20 ml of dry benzene was heated under reflux for 12 h during which time the red colour of the quinone was discharged. The cooled solution was passed down a column of 25 g of Grade 1 alumina and elution with benzene, affording one bright yellow fraction of 4-benzoyl-2-phenylamino-5-phenylthiazole 0.108 g (31% yield) m.p. 135° (from cyclohexane).

Anal. Calcd. for $C_{22}H_{16}N_2SO$ (mol. wt., 356.0984): C, 74.13; H, 4.52; N, 7.86; S, 9.00. Found (mol. wt. (mass spectrum) 356.0983): C, 73.95; H, 4.52; N, 7.87; S, 9.20.

Infrared spectrum: ν_{max} ($CHCl_3$): 1595 (C=O), 3150 (broad, NH). Nuclear magnetic resonance spectrum ($CDCl_3$): 6.91–8.52 (15H, multiplet, aryl protons), 11.92 (1H, exchangeable with D_2O, NH).

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