

Compounds Related to Acridine. XIII.¹⁾ Reactions of 9-Vinyl- and 9-Ethynylacridine with *C,N*-Diarylnitrones

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The reaction of 9-vinylacridine (**1**) with *C,N*-diarylnitrones (**3**) in xylene under reflux afforded 5-(9-acridinyl)-2,3-diarylisoxazolidines (**4**) and/or 9-acridinyl styryl ketones (**5**). On heating isoxazolidines **4** were readily converted into the styryl ketones **5** with the elimination of anilines: this is a new type of thermal decomposition of isoxazolidine ring. However, thermal decomposition of 3-(9-acridinyl)-2,5-diarylisoxazolidines (**9**) which were prepared from *N*-(9-acridinylmethylene)aniline *N*-oxide (**7**) and styrene (**8**), did not observed. On the other hand, the reaction of 9-ethynylacridine (**2**) with nitrones **3** in ethanol under the influence of hydrochloric acid proceeded smoothly to give the reversed 4-(9-acridinyl)-4-isoxazolines (**11**), which on heating were converted into the corresponding 4-oxazolines **12**.

It is known that the reactions of *C*-aryl-*N*-alkyl(or aryl)nitrones with mono-substituted alkenes proceed regioselectively to give only the 5-substituted isoxazolidines.²⁻⁶⁾ However, Huisgen, *et al.*^{7,8)} observed diminished regioselectivity in the cycloaddition reaction of *C*-phenyl-*N*-methylnitrone with methyl propiolate. Recently, it has been reported that *C*-phenyl-*N*-methylnitrone added to electron-deficient monosubstituted dipolarophiles such as nitroethylene and cyanoacetylene to yield only the reversed 4-substituted cycloadducts.⁹⁾

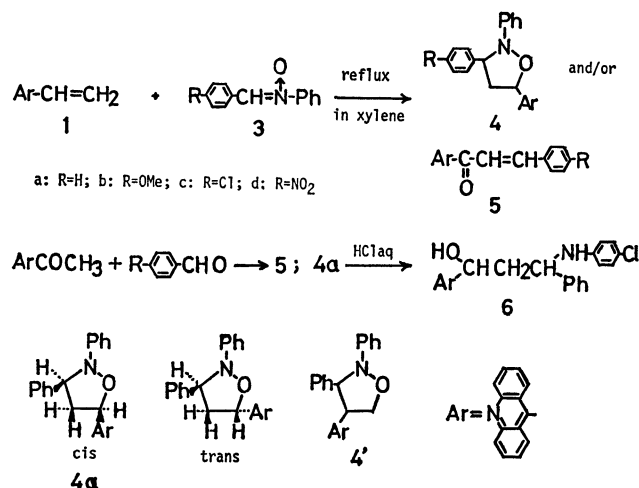
Thus, it seemed of interest to investigate the reactions of 9-vinyl- (**1**) and 9-ethynylacridine (**2**) with nitrones, because the 9-acridinyl group is rather bulky and electron-withdrawing. In this paper we wish to report the reactions of **1** and **2** with *C,N*-diarylnitrones which revealed some unusual phenomena.

Results and Discussion

The reaction of 9-vinylacridine (**1**) with *C,N*-diphenylnitrone (**3a**) in boiling benzene did not take place. When a solution of equimolar quantities of **1** and **3a** in xylene was refluxed for 1.5 h, an 1 : 1 adduct **4a**, mp 188—189 °C, and 9-acridinyl styryl ketone (**5a**)¹⁾ were obtained in 11 and 1% yields respectively, together with tarry materials.

On the basis of the chemical conversion and spectral data, **4a** was assigned to be 5-(9-acridinyl)-2,3-diphenylisoxazolidine (normal cycloadduct). Hydrolysis of **4a** with 20% aqueous hydrochloric acid at room temperature for 1.5 h afforded 1-(9-acridinyl)-3-(*p*-chloroanilino)-3-phenyl-1-propanol (**6**), mp 216—217 °C, in 60% yield. However, the configuration of **6** could not be determined, because the measurement of NMR spectrum of **6** was unsuccessful owing to its insolubility in solvents. Previously,¹⁰⁾ we have reported that hydrolysis of *cis*-2,3,5-triphenylisoxazolidine gave 1,3-diphenyl-3-(*p*-chloroanilino)-1-propanol. Thus, the reversed 4-(9-acridinyl) isomer **4'** can be excluded from the possibility for the structure of **4a**.

An inspection of Dreiding models indicates that there is a significant steric interaction between the acridinyl and *N*-phenyl groups in *trans*-isoxazolidine, but not in *cis*-isoxazolidine. Therefore, *cis*-configura-



Scheme 1.

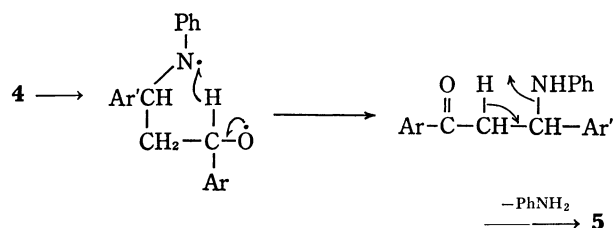
tion seems to be favorable to **4a**.

Under similar conditions, **1** reacted with *C-p*-anisyl-*N*-phenylnitrone (**3b**) to afford a normal cycloadduct **4b**, mp 202—203 °C, in 11% yield. However, the reaction of **1** with *C-p*-chlorophenyl- (**3c**) and *C-p*-nitrophenyl-*N*-phenylnitrone (**3d**) did not give the cycloadducts, but only acridinyl styryl ketones **5c**, mp 241—242 °C, and **5d**, mp 284 °C, were obtained in 27 and 13% yields respectively. The structures of **5c** and **5d** were confirmed by comparison with the authentic samples prepared from 9-acetylacridine and the corresponding benzaldehydes.

When heated in boiling xylene, isoxazolidines **4a** and **4b** were quantitatively converted into the corresponding acridinyl styryl ketones **5a** and **5b**, mp 200—201 °C. Thus, the formation of styryl ketones **5** in the reaction of **1** with **3** may be explained as arising from the corresponding isoxazolidines **4**. Little attention has been paid to the thermal decomposition of isoxazolidines. To our knowledge, the only one example has been reported on thermal isomerization of a bicyclic isoxazolidine.¹¹⁾

The transformation of isoxazolidines **4** into α,β -unsaturated ketones **5** is noteworthy as a new type of thermal decomposition of isoxazolidine ring. Although the exact pathway for the formation of **5** from **4** is not clear, we tentatively proposed the potential one as

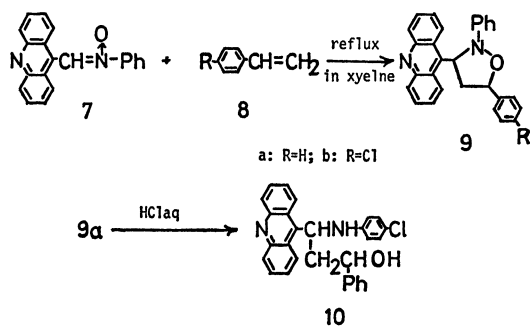
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Ar=9-acridinyl; Ar'=p-substituted phenyl

depicted below. The cleavage of N-O bond of **4**, followed by the hydrogen shift gives 1-(9-acridinyl)-3-anilino-3-(p-substituted phenyl)propanone. Subsequent elimination of aniline from the propanone yields the final acridinyl styryl ketone **5**.

In this context, it appeared of interest to know whether a positional isomer of **4** is thermally decomposed or not. The reaction of *N*-(9-acridinylmethylene)-aniline *N*-oxide (**7**) with styrene (**8a**) in xylene under reflux afforded the expected 3-(9-acridinyl)-2,5-diphenylisoxazolidine (**9a**), mp 202–203 °C, in 37% yield. The structure of **9a** was confirmed by the spectral data as well as by the result of hydrolysis.



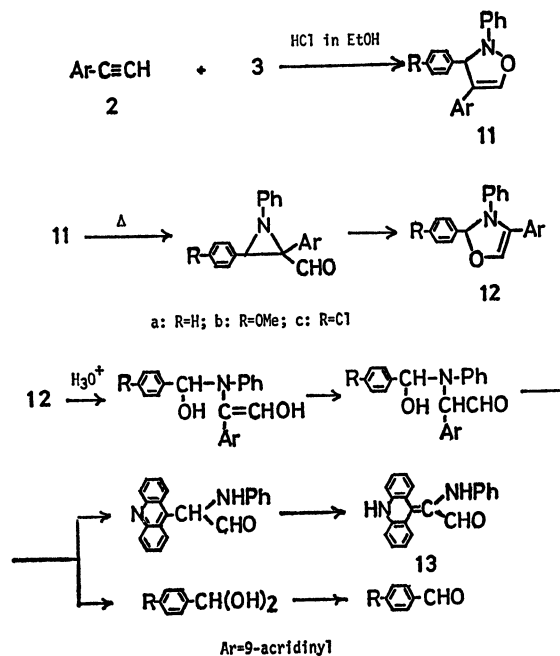
Scheme 2.

Hydrolysis of **9a** with 20% aqueous hydrochloric acid gave 3-(9-acridinyl)-3-(p-chloroanilino)-1-phenyl-1-propanol (**10**), mp 112–113 °C, in 68% yield. Similarly, p-chlorostyrene (**8b**) reacted with nitrone **7** to give 3-(9-acridinyl)-5-(p-chlorophenyl)-2-phenylisoxazolidine (**9b**), mp 205–206 °C, in 41% yield. Even when heated in boiling xylene for a long while, isoxazolidines **9a** and **9b** were recovered quantitatively.

On the other hand, the reaction of 9-ethynylacridine (**2**) with nitrones **3** in xylene under reflux yielded only tarry materials. However, we found that **2** reacted with *C,N*-diphenylnitron (**3a**) in ethanol under the influence of hydrochloric acid at room temperature to afford a 1:1 cycloadduct **11a**, mp 115–115 °C (dec); whose yield depended on the amounts of

hydrochloric acid used as shown in Table 1.

On the basis of the spectral data and chemical conversion, the structure of **11a** was deduced to be a reversed cycloadduct, 4-(9-acridinyl)-2,3-diphenyl-4-isoxazoline. The NMR spectrum (CS₂) of **11a** exhibited two doublets (each 1H, *J*=2 Hz) at δ 5.83 (3-H) and 6.83 ppm (5-H), besides aromatic protons (18H). As will be described below, **11a** was readily converted into the corresponding 4-oxazoline. These observations agreed with the assigned structure **11a**, but not with a normal cycloadduct, 5-(9-acridinyl) isomer **11'** (Scheme 3).



Ar=9-acridinyl

Scheme 3.

Similarly, the reaction of **2** with nitrones, **3b** and **3c** afforded the corresponding 4-(9-acridinyl)-4-isoxazoline compounds **11b**, mp 119 °C (dec), and **11c**, mp 85–86 °C (dec), in fairly good yields.

Previously, we have found that hydrochloric acid is an extremely effective catalyst for the reactions of 9-alkyl-,^{12–14} 9-vinyl-,¹⁵ and 9-ethynylacridine¹⁶ with nitrosobenzenes. Although the reaction of **1** with *C,N*-diarylnitrones in the presence of hydrochloric acid afforded only tarry materials, hydrochloric acid was also very effective for the reaction of **2** with **3**. Catalytic behaviour of hydrochloric acid in the above reactions is not clear at the present stage.

Baldwin, *et al.*¹⁷ demonstrated the existence of the facile thermal valence rearrangement of 4-isoxazoles to 2-acylaziridines, and subsequently to 4-oxazoles. Although attempts to isolate an acylaziridine intermediate were unsuccessful, heating of 4-isoxazoline **11a** in boiling benzene afforded 4-(9-acridinyl)-2,3-diphenyl-4-oxazoline (**12a**), mp 142–143 °C (dec), in 70% yield. Under similar conditions, 4-isoxazoles **11b** and **11c** were converted into the corresponding 4-oxazoles **12b**, mp 168 °C (dec), and **12c**, mp 114–115 °C (dec), in 85 and 50% yields respectively.

TABLE 1. REACTION OF **2** WITH **3a**^a

HCl, ml	11a , Yield (%)	HCl, ml	11a , Yield (%)
0.01	37	0.1	33
0.02	59	0.3	30
0.05	45	0.5	21

a) A mixture of **2** (1.0 g), **3a** (1.0 g), and the specified amount of hydrochloric acid (*d*₂₇ 1.1748) in ethanol (20 ml) was stirred at room temperature for 10 min.

The structures of 4-oxazolines **12** were deduced on the basis of the spectral data and chemical conversion. Hydrolysis of **12a** with 20% aqueous hydrochloric acid at room temperature afforded violet prisms **13** ($C_{21}H_{16}N_2O$), mp 192–193 °C, in a good yield, and from the reaction mixture benzaldehyde was identified as its 2,4-dinitrophenylhydrazone. Similarly, **12b** and **12c** yielded **13** and *p*-methoxy- or *p*-chlorobenzaldehyde.

The IR spectrum of **13** displayed the absorption bands at 3360, 3280 (NH) and 1620 cm^{-1} (conjugated C=O), and a strong absorption band appeared at 523 nm in the UV spectrum. The NMR spectrum (DMSO- d_6) exhibited signals at δ 6.7–8.3 (14H, NH and aromatic protons), 9.1 (1H, s, CHO) and 11.95 ppm (1H, s, NH). The above observations indicated that **13** was (9,10-dihydro-9-acridinylidene)anilinoacetaldehyde.

The pathway for the formation of **13** from **12** is shown in Scheme 3. Previously,¹⁸⁾ we have reported that 9-methyleneacridine compounds were easily transformed into 9,10-dihydro-9-acridinylidene compounds. Thus, hydrolysis of **12** gives 9-acridinylanilinoacetaldehyde with the elimination of benzaldehyde, and then isomerization yields the stable 9,10-dihydro-9-acridinylidene compound **13**. The formation of **13** from **12** strongly supported the assigned structure **12**.

Although hydrolysis of 4-isoxazoline **11a** under similar conditions afforded **13** and benzaldehyde, this result may be understood in terms of an initial isomerization of **11a** to **12a**, followed by hydrolysis of **12a**.

Experimental

All the melting points are uncorrected. The NMR spectra were determined with a Hitachi R-20 Model spectrometer, with TMS as the internal standard. The IR spectra were measured as KBr disks, and the mass spectra were obtained on a Hitachi RMS-4 mass spectrometer with a direct inlet and an ionization energy of 70 eV.

Reaction of 9-Vinylacridine (1) with C,N-Diphenylnitron (3a). A solution of **1**¹⁹⁾ (1.0 g) and **3a** (1.0 g) in xylene (10 ml) was refluxed under a stream of nitrogen for 1.5 h. Then, the reaction mixture was evaporated *in vacuo*, and the residue was chromatographed on alumina using benzene as the eluent, giving 0.32 g (11%) of 5-(9-acridinyl)-2,3-diphenylisoxazolidine (**4a**), mp 188–189 °C, as pale yellow needles, and 20 mg (1%) of 9-acridinyl styryl ketone (**5a**), mp 258 °C (lit.¹⁾ mp 258 °C), as pale yellow prisms. The NMR spectrum (CDCl₃) of **4a**: δ ppm 2.93 (1H, ddd, 4-H (*cis*), $J=9$, 12, and 13 Hz), 3.3 (1H, ddd, 4-H (*trans*), $J=7$, 9, and 13 Hz), 5.15 (1H, t, 3-H, $J=9$ Hz), 6.55 (1H, dd, 5-H, $J=7$ and 12 Hz), 7.0–8.7 (18H, m, aromatic protons). Mass spectrum: m/e 402 (M^+). Found: C, 84.81; H, 5.61; N, 6.01%. Calcd for $C_{28}H_{22}N_2O \cdot C_6H_6$: C, 84.97; H, 5.87; N, 5.83%.

Similarly, the reaction of **1** with *C-p*-anisyl-N-phenylnitron (**3b**) afforded 5-(9-acridinyl)-3-(*p*-anisyl)-2-phenylisoxazolidine (**4b**), mp 202–203 °C, as pale yellow prisms in 11% yield. NMR spectrum (CDCl₃): δ ppm 2.9, 3.3 (each 1H, m, 4-H), 3.85 (3H, s, OCH₃), 4.92 (1H, dd, 3-H, $J=6$ and 9 Hz), 6.8–8.8 (18H, m, $\geq$ CH and aromatic protons). Mass spectrum: m/e 416 (M^+). Found: C, 83.64; H, 5.80; N, 6.93%. Calcd for $C_{29}H_{24}N_2O$: C, 83.47; H, 5.94; N, 7.15%.

On the other hand, the reaction of **1** with *C-p*-chlorophenyl- (**3c**) or *C-p*-nitrophenyl-N-phenylnitron (**3d**) for 0.5 h

under similar conditions afforded only the corresponding styryl ketone **5c** or **5d** in 27 or 13% yield respectively. The styryl ketones **5c** and **5d** were identical with the authentic samples prepared from the reaction of 9-acetylacridine with *p*-chloro- and *p*-nitrobenzaldehyde in the presence of sodium hydroxide in ethanol.

9-Acridinyl *p*-chlorostyryl ketone (**5c**): mp 241–241 °C, yellow prisms. IR spectrum: 1680 cm^{-1} (C=O). Mass spectrum: m/e 345, 343 (M^+). Found: C, 77.17; H, 4.04; N, 4.17%. Calcd for $C_{22}H_{14}NOCl$: C, 76.86; H, 4.08; N, 4.08%.

9-Acridinyl *p*-nitrostyryl ketone (**5d**): mp 284 °C, yellow prisms. IR spectrum: 1680 cm^{-1} (C=O). Mass spectrum: m/e 354 (M^+). Found: C, 74.80; H, 3.80; N, 7.91%. Calcd for $C_{22}H_{14}N_2O_3$: C, 74.56; H, 3.98; N, 7.91%.

Thermal Decomposition of Isoxazolidine 4b. A solution of **4b** (0.1 g) in xylene (10 ml) was refluxed under a stream of nitrogen for 2 h. Then, the mixture was evaporated *in vacuo* to leave yellow crystals, which on recrystallization from benzene gave 80 mg (ca. 100%) of 9-acridinyl *p*-methoxystyryl ketone (**5b**), mp 200–201 °C, as pale yellow prisms. This compound was identical with the authentic sample prepared from 9-acetylacridine and *p*-anisaldehyde. Found: C, 82.55; H, 5.02; N, 3.94%. Calcd for $C_{23}H_{17}NO_2$: C, 82.39; H, 5.05; N, 4.13%.

Similarly, thermal decomposition of isoxazolidine **4a** afforded **5a** quantitatively.

Hydrolysis of Isoxazolidine 4a. A suspension of **4a** (50 mg) in 20% aqueous hydrochloric acid (2 ml) was stirred at room temperature for 1.5 h. Then, the mixture was neutralized with aqueous ammonia to give yellow prisms, which on recrystallization from benzene afforded 30 mg (60%) of 1-(9-acridinyl)-3-(*p*-chloroanilino)-3-phenyl-1-propanol (**6**), mp 216–217 °C, as yellow prisms. IR spectrum: 3200–3400 (OH and NH), 830 cm^{-1} . Mass spectrum: m/e 440, 438 (M^+), 422, 420 ($M^+ - H_2O$), 311 ($M^+ - H_2NC_6H_4Cl$), 222 (acridinyl-CH-CH₂), 218, 216 (Ph⁺CHNH-

C_6H_4Cl), 208 (9-acridinyl-CHOH), 205, 193, 178. Found: C, 76.30; H, 5.42; N, 6.06%. Calcd for $C_{28}H_{23}N_2OCl$: C, 76.27; H, 5.67; N, 6.35%.

Reaction of N-(9-Acridinylmethylene)aniline N-oxide (7) with Styrene (8a). A solution of nitron **7**²¹⁾ (0.2 g) and **8a** (0.1 g) in xylene (3 ml) was refluxed under a stream of nitrogen for 1.5 h. Then, the mixture was evaporated *in vacuo* to leave yellow crystals, which on recrystallization from benzene afforded 50 mg (37%) of 3-(9-acridinyl)-2,5-diphenylisoxazolidine (**9a**), mp 202–203 °C, as pale yellow prisms. NMR spectrum (CDCl₃): δ ppm 2.9–3.5 (2H, m, $\geq$ CH), 5.45 (1H, dd, $\geq$ CH, $J=6$ and 12 Hz), 6.3 (1H, dd, $\geq$ CH, $J=10$ and 12 Hz), 6.9–8.5 (18H, m, aromatic protons). Mass spectrum: m/e 402 (M^+). Found: C, 83.26; H, 5.33; N, 6.67%. Calcd for $C_{28}H_{22}N_2O$: C, 83.55; H, 5.51; N, 6.92%.

Similarly, the reaction of **7** with *p*-chlorostyrene (**8b**) afforded a 41% yield of 3-(9-acridinyl)-5-(*p*-chlorophenyl)-2-phenylisoxazolidine (**9b**), mp 205–206 °C, as pale yellow needles. NMR spectrum (CDCl₃): δ ppm 2.6–3.4 (2H, m, $\geq$ CH), 5.4 (1H, dd, $\geq$ CH, $J=5$ and 13 Hz), 6.1–6.4 (1H, m, $\geq$ CH), 6.7–8.5 (17H, m, aromatic protons). Mass spectrum: m/e 438, 436 (M^+). Found: C, 76.89; H, 4.61; N, 6.65%. Calcd for $C_{28}H_{21}N_2OCl$: C, 76.97; H, 4.81; N, 6.14%.

Hydrolysis of Isoxazolidine 9a. A suspension of **9a** (0.25 g) in 20% aqueous hydrochloric acid (10 ml) was

stirred at 90 °C for 1 h. The mixture was neutralized with aqueous ammonia to give yellow crystals, which on recrystallization from a mixture of benzene and petroleum ether (bp 60–85 °C) afforded 0.17 g (68%) of 3-(9-acridinyl)-3-(*p*-chloroanilino)-1-phenyl-1-propanol (**10**), mp 112–113 °C, as yellow prisms. IR spectrum: 3200–3400 (OH and NH), 830 cm⁻¹. Mass spectrum: *m/e* 440, 438 (M⁺), 422, 420 (M⁺–H₂O), 319, 317 (M⁺–PhCH(OH)CH₂), 206, 204, 193, 178. Found: C, 78.80; H, 5.58; N, 5.58%. Calcd for C₂₈H₂₃N₂OCl·C₆H₆: C, 78.99; H, 5.61; N, 5.42%.

Reaction of 9-Ethynylacridine (2) with C₆N-Diphenylnitron (3a). A solution of **2**¹⁶ (1.0 g) and **3a** (1.0 g) in ethanol (20 ml) containing concd hydrochloric acid (0.02 ml) was stirred at room temperature for 10 min. Filtration gave yellow crystals, which were washed with ethanol (20 ml×3) to leave 4-(9-acridinyl)-2,3-diphenyl-4-isoxazoline (**11a**), mp 115–116 °C (dec), as pale yellow prisms. Isoxazoline **11a** was subjected to microanalysis without further purification. NMR spectrum (CS₂): δ ppm 5.83 (1H, d, >CH, *J*=2 Hz), 6.83 (1H, d, >CH, *J*=2 Hz), 7.0–8.1 (18H, m, aromatic protons). Mass spectrum: *m/e* 400 (M⁺). Found: C, 83.77; H, 5.24; N, 6.71%. Calcd for C₂₈H₂₀N₂O: C, 83.97; H, 5.03; N, 7.00%.

The results of other reactions under varying amounts of hydrochloric acid are shown in Table I.

Similarly, the reaction of **2** with *C-p*-anisyl- (**3b**) and *C-p*-chlorophenyl-*N*-phenylnitron (**3c**) gave the corresponding 4-isoxazolines **11b**, mp 119 °C (dec), **11c**, mp 85–86 °C (dec), in 73 and 41% yields respectively.

4-(9-Acridinyl)-3-(*p*-anisyl)-2-phenyl-4-isoxazoline (**11b**). NMR spectrum (CS₂): δ ppm 3.51 (3H, s, OCH₃), 5.8 (1H, d, >CH, *J*=2 Hz), 6.8 (1H, d, =CH, *J*=2 Hz), 6.4–8.1 (17H, m, aromatic protons). Mass spectrum: *m/e* (M⁺). Found: C, 81.09; H, 5.09; N, 6.30%. Calcd for C₂₆H₂₂N₂O: C, 80.90; H, 5.15; N, 6.51%.

4-(9-Acridinyl)-3-(*p*-chlorophenyl)-2-phenyl-4-isoxazoline (**11c**). NMR spectrum (CS₂): δ ppm 5.82 (1H, d, >CH, *J*=2 Hz), 6.84 (1H, d, =CH, *J*=2 Hz), 6.6–8.1 (17H, m, aromatic protons). Mass spectrum: *m/e* 436, 434 (M⁺). Found: C, 77.16; H, 4.37; N, 6.34%. Calcd for C₂₈H₁₉N₂OCl: C, 77.16; H, 4.16; N, 6.05%.

Thermal Isomerization of 4-Isoxazoline 11a. A solution of **11a** (0.2 g) in benzene (5 ml) was refluxed for 5 min. Then, the mixture was evaporated *in vacuo* to leave orange crystals, which on recrystallization from petroleum ether (bp 60–85 °C) afforded 0.14 g (70%) of 4-(9-acridinyl)-2,3-diphenyl-4-oxazoline (**12a**), mp 142–143 °C (dec), as orange prisms. NMR spectrum (CS₂): δ ppm 6.6–8.1 (18H, m, aromatic protons), 8.6, 8.73 (each 1H, d, *J*=2 Hz). Mass spectrum: *m/e* 400 (M⁺), 371 (M⁺–CHO), 323 (M⁺–Ph), 294 (M⁺–PhCHO), 281 (9-acridinyl-C≡N–Ph, base peak). Found: C, 84.26; H, 4.93; N, 6.83%. Calcd for C₂₈H₂₀N₂O: C, 83.97; H, 5.03; N, 7.00%.

Similarly, other 4-isoxazolines **11b** and **11c** were easily isomerized into the corresponding 4-oxazolines. 4-(9-Acridinyl)-2-(*p*-anisyl)-3-phenyl-4-oxazoline (**12b**), mp 168 °C (dec), as orange prisms (from petroleum ether). Yield, 85%. NMR spectrum (CS₂): δ ppm 3.81 (3H, s, OCH₃), 6.6–8.2 (17H, m, aromatic protons), 8.64, 8.75 (each 1H, d, *J*=2 Hz). Mass spectrum: *m/e* 430 (M⁺), 401 (M⁺–CHO), 323 (M⁺–MeOC₆H₄), 294 (M⁺–MeOC₆H₄CHO), 281 (base peak). Found: C, 80.90; H, 4.99; N, 6.36%. Calcd for C₂₉H₂₀N₂O₂: C, 80.90; H, 5.15; N, 6.51%.

4-(9-Acridinyl)-2-(*p*-chlorophenyl)-3-phenyl-4-oxazoline (**12c**), mp 114–115 °C (dec), as orange prisms (from benzene). Yield, 50%. NMR spectrum (CS₂): δ ppm 6.6–8.2 (17H, m, aromatic protons), 8.55, 8.68 (each 1H, d, *J*=2 Hz). Mass spectrum: *m/e* 436, 434 (M⁺), 407, 405 (M⁺–CHO), 323 (M⁺–ClC₆H₄), 294 (M⁺–ClC₆H₄CHO), 281 (base peak). Found: C, 78.25; H, 4.81; N, 5.75%. Calcd for C₂₈H₁₉N₂OCl·1/2C₆H₆: C, 78.48; H, 4.62; N, 5.91%.

Hydrolysis of 4-Oxazoline 12b. A solution of **12b** (0.3 g) in ethanol (5 ml) was stirred with 20% hydrochloric acid (5 ml) at room temperature for 2 h, and then the mixture was neutralized with aqueous ammonia. Filtration gave violet crystals, which on recrystallization from chloroform afforded 0.21 g (96.7%) of (9,10-dihydro-9-acridinylidene)-anilinoacetaldehyde (**13**), mp 192–193 °C, as violet prisms. UV spectrum (EtOH): λ_{max} nm (log ε) 252 (4.9), 362 (3.8), 380 (3.9), 399 (3.8), 523 (3.1). Found: C, 80.50; H, 5.04; N, 8.98%. Calcd for C₂₁H₁₆N₂O: C, 80.75; H, 5.16; N, 8.97%.

From the filtrate *p*-anisaldehyde was identified as its 2,4-dinitrophenylhydrazone.

Similarly, hydrolysis of 4-oxazolines **12a** and **12c** gave **13** and the corresponding benzaldehydes.

References

- 1) Part XII of this series: A. Torii and O. Tsuge, *Heterocycles*, **3**, 557 (1975).
- 2) R. Huisgen, R. Grashey, H. Hauck, and H. Seidl, *Chem. Ber.*, **101**, 2043 (1968).
- 3) R. Huisgen, R. Grashey, H. Hauck, and H. Seidl, *Chem. Ber.*, **101**, 2548 (1968).
- 4) R. Huisgen, R. Grashey, H. Seidl, and H. Hauck, *Chem. Ber.*, **101**, 2559 (1968).
- 5) R. Huisgen, H. Hauck, R. Grashey, and H. Seidl, *Chem. Ber.*, **101**, 2568 (1968).
- 6) R. Huisgen, H. Seidl, and I. Brünig, *Chem. Ber.*, **102**, 1102 (1969).
- 7) H. Seidl, R. Huisgen, and R. Knorr, *Chem. Ber.*, **102**, 904 (1969).
- 8) R. Huisgen, H. Seidl, and J. Wulff, *Chem. Ber.*, **102**, 915 (1969).
- 9) J. Sims and K. N. Houk, *J. Am. Chem. Soc.*, **95**, 5798 (1973).
- 10) O. Tsuge, M. Tashiro, and Y. Nishihara, *Nippon Kagaku Zasshi*, **92**, 72 (1971).
- 11) G. R. Delpierre and M. Lamchen, *J. Chem. Soc.*, **1963** 4693.
- 12) O. Tsuge, M. Nishinohara, and M. Tashiro, *Bull. Chem. Soc. Jpn.*, **36**, 1477 (1963).
- 13) O. Tsuge, M. Nishinohara, and K. Sadano, *Bull. Chem. Soc. Jpn.*, **38**, 2037 (1965).
- 14) A. Torii, H. Higashiuchi, and O. Tsuge, *Heterocycles*, **2**, 615 (1974).
- 15) O. Tsuge and A. Torii, *Bull. Chem. Soc. Jpn.*, **45**, 3187 (1972).
- 16) O. Tsuge and A. Torii, *Bull. Chem. Soc. Jpn.*, **43**, 2920 (1970).
- 17) J. E. Baldwin, R. G. Pudussery, A. K. Qureshi, and B. Sklarz, *J. Am. Chem. Soc.*, **90**, 5325 (1968).
- 18) O. Tsuge and A. Torii, *Bull. Chem. Soc. Jpn.*, **46**, 283 (1973).
- 19) O. Tsuge, A. Torii, and T. Tomita, *Nippon Kagaku Zasshi*, **90**, 1263 (1969).