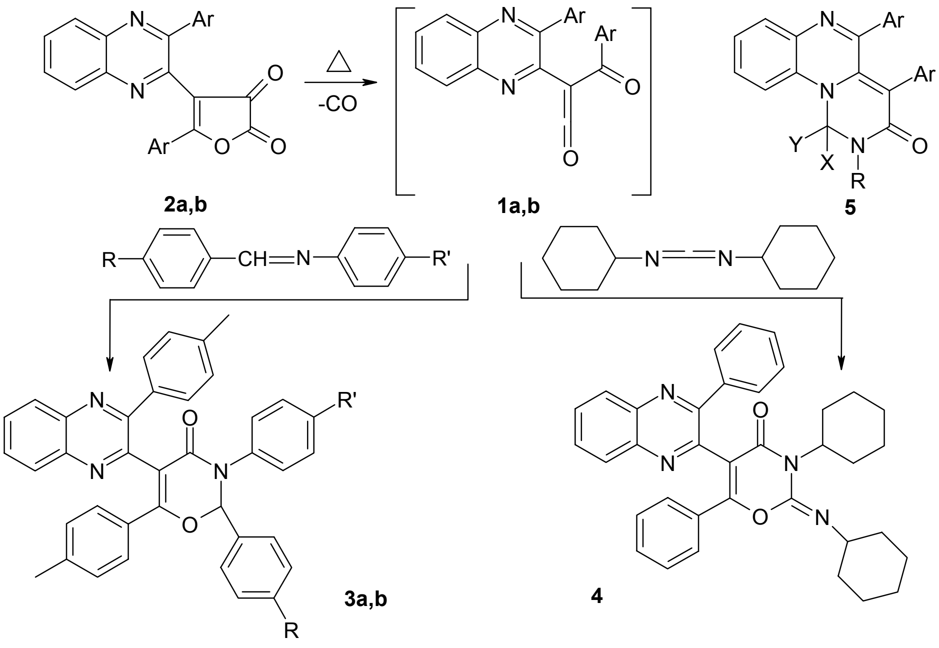
*Chemistry of Heterocyclic Compounds, Vol. 40, No. 2, 2004*

# REGIOSELECTIVE CYCLOADDITION OF AZOMETHINES AND CARBODIIMIDES TO AROYL(QUINOXALINYL)KETENES

**N. Yu. Lisovenko and A. N. Maslivets**

**Keywords:** aroyl(imidoyl)ketenes, 2,3-dihydro-2,3-furandiones, 1,3-oxazin-4-ones, cycloaddition.

3-Aryl-2-quinoxalinyl(aroyl)ketenes **1a,b**, generated in thermolysis of 3-aryl-2-(2-aryl-4,5-dioxo-4,5-dihydro-3-furyl)quinoxalines **2a,b**, in the absence of other partners undergo the reaction of [4+2] cyclodimerization, where one ketene molecule participates in the reaction as the dienophile by means of the C=C bond of the ketene moiety, while another ketene molecule participates as the diene by means of the conjugated C=C–C=N bond system of the imidoylketene moiety [1]. In contrast to the cyclodimerization reaction, attempts at "capturing" the aroyl(imidoyl)ketenes **1a,b** by cyclic ketones lead to formation of the corresponding [4+2] cycloadducts with participation of the C=O bond of the ketones in the conjugated system of bonds C=C–C=O of the aroylketene moiety [2]. Both of the reactions described, judging from TLC data for the reaction mixture, occur practically regioselectively.



**1**, **2** **a** Ar = Ph, **b** Ar = $p$-MeC$_6$H$_4$; **3** **a** R = Br, R' = OMe, **b** R = OMe, R' = Br

---

Perm State University, Perm 614990, Russia; e-mail: koh2@psu.ru. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 288-289, February, 2004. Original article submitted June 20, 2003.

0009-3122/04/4002-0247©2004 Plenum Publishing Corporation

We have found that "capture" of aroyl(imidoyl)ketenes **1a,b** by Schiff's bases or dicyclohexylcarbodiimide also leads practically regioselectively to formation of the corresponding [4+2] cycloadducts **3a,b,4**.

The spectral characteristics of compounds **3a,b, 4**, in particular the characteristic form of the multiplet for the four protons of the quinoxaline moiety, practically coinciding with that for model cycloaddition products of cyclic ketones in [2], the structure of which has been confirmed by X-ray diffraction, allow us to reject the isomeric structure **5** for compounds **3a,b, 4** and suggest that the C=N bond of azomethines or carbodiimides and the conjugated system of bonds C=C–C=O of aroyl(imidoyl)ketenes **1a,b** participate in the [4+2] cycloaddition reaction.

**2-(2-*p*-Bromophenyl-3-*p*-methoxyphenyl-4-oxo-6-*p*-tolyl-3,4-dihydro-2H-1,3-oxazin-5-yl)-3-*p*-tolylquinoxaline (3a).** A solution of furandione **2b** (1 mmol) and N-*p*-bromobenzylidene-*p*-anisidine (1.1 mmol) in absolute *p*-xylene (5 ml) was held for 20 min at 138-140°C and then cooled down, and the precipitate was filtered out. Yield 78%; mp 210-211°C ($CH_3CN$). IR spectrum (vaseline oil), ν, $cm^{-1}$: 1665 (C=O). $^1H$ NMR spectra (400 MHz, DMSO-$d_6$, HMDS), δ, ppm: 2.19 (3H, s, $CH_3$); 2.38 (3H, s, $CH_3$); 3.71 (3H, s, $OCH_3$); 6.81-7.68 (17H, m, $4C_6H_4$+CH); 7.86 (2H, m, 6-, 7-$H_{quinox}$); 8.07, 8.11 (2H, m, 5-, 8-$H_{quinox}$). Found, %: C 70.01; H 4.66; Br 12.07; N 6.21. $C_{39}H_{30}BrN_3O_3$. Calculated, %: C 70.06; H 4.52; Br 11.95; N 6.28.

**2-(3-*p*-Bromophenyl-2-*p*-methoxyphenyl-4-oxo-6-*p*-tolyl-3,4-dihydro-2H-1,3-oxazin-5-yl)-3-*p*-tolylquinoxaline (3b).** Obtained analogously. Yield 80%; mp 171-172°C ($CH_3CN$). IR spectrum (vaseline oil), ν, $cm^{-1}$: 1650 (C=O). $^1H$ NMR spectrum (400 MHz, DMSO-$d_6$, HMDS), δ, ppm: 2.19 (3H, s, $CH_3$); 2.38 (3H, s, $CH_3$); 3.77 (3H, s, $OCH_3$); 6.80-7.51 (17H, m, $4C_6H_4$+CH); 7.86 (2H, m, 6-,7-$H_{quinox}$); 8.06, 8.12 (2H, m, 5-,8-$H_{quinox}$). Found, %: C 70.07; H 4.09; Br 11.77. N 6.31. $C_{39}H_{30}BrN_3O_3$. Calculated, %: C 70.06; H 4.52; Br 11.95; N 6.28.

**2-(3-Cyclohexyl-2-cyclohexylimino-4-oxo-6-phenyl-3,4-dihydro-2H-1,3-oxazin-5-yl)-3-phenylquinoxaline (4).** Obtained analogously. Yield 92%; mp 168-170°C (acetonitrile). IR spectrum (vaseline oil), ν, $cm^{-1}$): 1675 (C=O). $^1H$ NMR spectrum (400 MHz, DMSO-$d_6$, HMDS), δ, ppm: 1.01-1.80 (20H, m, $10CH_2$); 3.70 (1H, m, NCH); 4.56 (1H, m, NCH); 7.00-7.45 (10H, m, 2Ph); 7.93 (2H, m, 6-,7-$H_{quinox}$); 8.12, 8.15 (2H, m, 5-,8-$H_{quinox}$). Found, %: C 77.90; H 6.67; N 10.25. $C_{36}H_{36}N_4O_2$. Calculated, %: C 77.67; H 6.52; N 10.06.

This research was done with the financial support of the Russian Foundation for Basic Research (grant No. 01-03-32641).

## REFERENCES

1. N. Yu. Lisovenko, O. P. Krasnykh, Z. G. Aliev, E. S. Vostrov, O. P. Tarasova, and A. N. Maslivets, *Khim. Geterotsikl. Soedin.*, 1429 (2001).
2. N. Yu. Lisovenko, A. N. Maslivets, and Z. G. Aliev, *Khim. Geterotsikl. Soedin.*, 140 (2003).