Chemistry of Heterocyclic Compounds, Vol. 36, No. 5, 2000

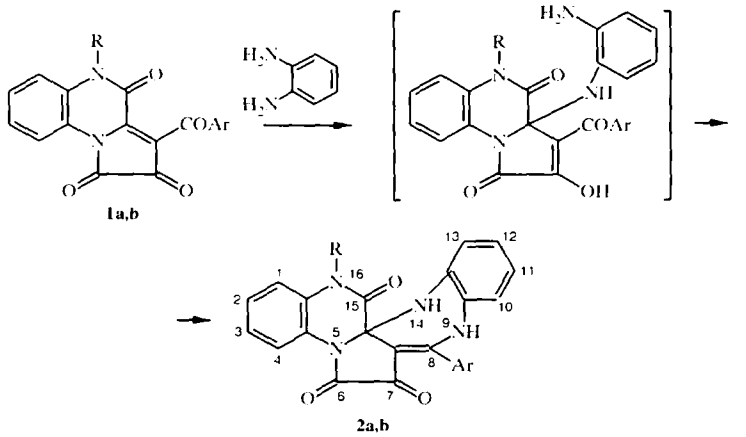
UNUSUAL REACTION OF CONDENSED 2,3-DIHYDRO-2,3-PYRROLEDIONES WITH *o*-PHENYLENEDIAMINE

I. V. Mashevskaya, A. V. Duvalov, S. V. Kol'tsova, and A. N. Maslivets

Keywords: 2,3-dihydro-2,3-pyrroledione, pyrrolo[1,2-*a*]quinoxaline, *o*-phenylenediamine, quinoxalino-[1,2-*a*]pyrrolo[2,3-*b*][1,5]benzodiazepine.

4-Unsubstituted 4-dialkylaminocarbonyl-2,3-dihydro-2,3-pyrroledione, condensed at the [*a*] side with an isoquinoline ring, react with *o*-phenylenediamine with initial addition of the amino group of the reagent to the carbon atom in the 3 position of the pyrroledione ring, followed by recyclization to 2-quinoxalones and then to pyrroloquinoxalines or cyclization to pyrrolospirobenzimidazolines [1]. 4-Aroyl-2,3-dihydro-2,3-pyrrolediones condensed at the [*a*] side with a 1,4-benzoxazin-2-one ring react with *o*-phenylenediamine with initial addition of the amino group of the reagent to the carbon atom in the 5 position of the pyrroledione ring, followed by recyclization with opening of the benzoxazine ring [2].

Reaction of 4-aroyl-2,3-dihydro-2,3-pyrrolediones condensed at the [*a*] side with a 2-quinoxalone ring (the 3-aroyl-5-unsubstituted and 5-phenyl-1,2,4,5-tetrahydropyrrolo[1,2-*a*]quinoxaline-1,2,4-triones (**1a,b**) [3]) with *o*-phenyldiamine proceeds in an unusual way, with sequential nucleophilic attack by the amino groups of the reagent on the carbon atoms in the 5 position and the carbonyl group of the aroyl moiety in the 4 position of the pyrroledione ring, i.e., with closure of the benzodiazepine ring, and formation of 16-unsubstituted and 8-aryl-16-phenyl-6,7,9,14,15,16-hexahydroquinoxalino[1,2-*a*]pyrrolo[2,3-*b*][1,5]-benzodiazepine-6,7,15-triones (**2a,b**).



1a,b

2a,b

1, 2 a R = H, Ar = Ph; **b** R = Ph, Ar = *p*-MeC_6H_4

This reaction is the first method reported for making the previously unavailable functionalized condensed heterocyclic system of quinoxalino[1,2-*a*]pyrrolo[2,3-*b*][1,5]benzodiazepine.

Perm State University, Perm 614000, Russia; e-mail: info@psu.ru. Translated from Khimiya Geterotsiklicheksikh Soedinenii, No. 5, pp. 701-702, May, 2000. Original article submitted March 3, 2000.

0009-3122/00/3605-0617$25.00©2000 KluwerAcademic/Plenum Publishers

8-Phenyl-6,7,9,14,15,16-hexahydroquinoxalino[1,2-*a*]pyrrolo[2,3-*b*][1,5]benzodiazepine-6,7,15-trione (2a). A solution of *o*-phenylenediamine (1.08 g, 10 mmol) in absolute dioxane (20 ml) was added to a solution of compound **1a** (3.18 g, 10 mmol) in absolute dioxane (50 ml). The reaction mixture was boiled for 3 min and then cooled down. The precipitate was filtered off. Yield 3.88 g (95%); mp 385-387°C (with decomposition, from DMF). IR spectrum: 3060 br. (N–H), 1685 ($C_{(6)}$=O), 1670, 1656 cm^{-1} ($C_{(7)}$=O, $C_{(15)}$=O). ^{1}H NMR spectrum (250 MHz, DMSO-d_6); 6.90 (1H, s, $N_{(14)}$H); 7.15-7.80 (11H, m, $2C_6H_4$ + C_6H_3); 7.96 (2H, d, J = 7.3 Hz, 2 *o*-CH in the C_6H_5 group); 12.58 (2H, br. s, $N_{(9)}$H + $N_{(16)}$H). UV spectrum, nm (log ε): 341 (3.83), 432 (3.81). Mass spectrum, *m/z*: 408 [M^+]. Found, %: C 70.56; H 3.90; N 13.72. $C_{24}H_{16}N_4O_3$. Calculated, %: C 70.58; H 3.95; N 13.72.

16-Phenyl-8-*p*-tolyl-6,7,9,14,15,16-hexahydroquinoxalino[1,2-*a*]pyrrolo[2,3-*b*][1,5]benzodiazepine-6,7,15-trione (2b). *o*-Phenylenediamine (1.08 g, 10 mmol) in absolute dioxane (20 ml) was added to a solution of compound **1b** (4.08 g, 10 mmol) in absolute dioxane (50 ml). The reaction mixture was boiled for 3 min and then cooled down. The precipitate was filtered off. Yield 3.98 g (80%); mp 315-317°C (with decomposition, from DMSO). IR spectrum: 3070 br. (N—H), 1686 ($C_{(6)}$=O), 1665 cm^{-1} ($C_{(7)}$=O, $C_{(15)}$=O). ^{1}H NMR spectrum (250 MHz, DMSO-d_6): 2.36 (3H, s, CH_3); 6.65 (1H, d, J = 7.3 Hz, *o*-CH in the C_6H_5 group); 6.90 (1H, s, $N_{(14)}$H); 7.10-7.67 (14H, m, $3C_6H_4$ + C_6H_2); 7.90 (2H, d, J = 8.2 Hz, 2 *o*-CH in the *p*-$C_6H_4CH_3$ group); 12.55 (1H, br. s, $N_{(9)}$H). Mass spectrum, *m/z*: 498 [M^+]. Found, %: C 74.67; H 4.40; N 11.23. $C_{31}H_{22}N_4O_3$. Calculated, %: C 74.69; H 4.45; N 11.24.

REFERENCES

1. A. G. Mikhailovskii and V. S. Shklyaev, *Khim. Geterotsikl. Soedin.*, No. 3, 291 (1997).
2. A. N. Maslivets, I. V. Mashevskaya, and Yu. S. Andreichikov, *Zh. Org. Khim.*, **31**, 616 (1995).
3. A. N. Maslivets, O. V. Golovnina, O. P. Krasnykh, and Z. G. Aliev, *Khim. Geterotsikl. Soedin.*, No. 1, 113 (2000).