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BECKMANN FRAGMENTATION OF DIPHENYLCARBAMOYLATED *N*-ARYLDIPHENACYLAMINE DIOXIMES. NEW METHOD FOR THE SYNTHESIS OF IMIDAZOOXADIAZOLONES

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Abstract: *N*-Aryl-*N,N*-diphenacylamine dioximes were prepared by the reaction of corresponding arylamines with α-bromoacetophenone oxime in ethanol-water at room temperature. These compounds reacted with aryl isocyanates in acetonitrile to give imidazooxadiazolones **9**. The probable mechanism of the reaction is discussed.

Although Beckmann fragmentation of some α-substituted oximes including α-amino oxime derivatives is a well known process,[1,2] studies on high-order use of its intermediates have been reported recently. [3-10]

Here we report on the fragmentation reaction of *N*-aryl-*N,N*-diphenacylamine dioximes which will serve as an useful tool for the construction of imidazooxadiazolone ring system.[11]

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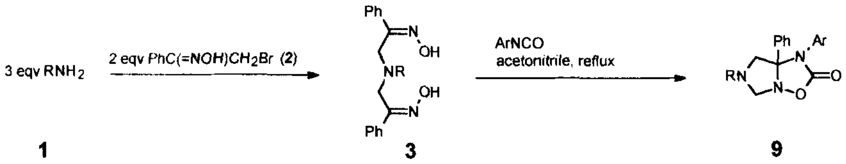
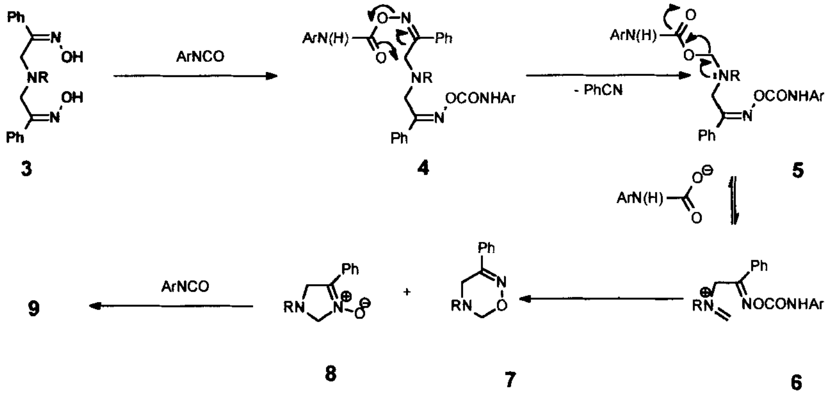
Compounds **3** were readily prepared by the reaction of aniline derivative **1** with *syn* α-bromoacetophenone oxime in ethanol-water (1:1) at room temperature in almost quantitative yields.[12] The treatment of compounds **3** with excess of aryl isocyanate in acetonitrile at reflux lead to the formation of imidazooxadiazolones **9**. To our knowledge these are the first examples of Beckmann fragmentation used in the synthesis of imidazole derivatives.



Scheme 1

Table 1. Compounds **3a-c**; **7b-c** and **9a-e**.

	R	Ar	Yield (%)	mp (°C)	molec.formula or lit mp
3a	4-MeC_6H_4		98	176	$C_{23}H_{23}N_3O_2$
3b	4-MeO C_6H_4		97	168-169	$C_{23}H_{23}N_3O_3$
3c	Ph		100	174.8-175.2	$C_{22}H_{21}N_3O_2$
7b	4-MeO C_6H_4		50	127	lit[13] 127
7c	Ph		49	99-100	lit[13] 100
9a	4-MeC_6H_4	Ph	56	159-160	lit[11] 159-160
9b	4-MeO C_6H_4	Ph	50	161	lit[11] 161.5
9c	Ph	Ph	51	143	$C_{22}H_{19}N_3O_2$
9d	4-MeC_6H_4	4-$MeOC_6H_4$	49	80-81	lit[11] 80-81
9e	4-$MeOC_6H_4$	4-$MeOC_6H_4$	52	113-114	lit[11] 114-115



Scheme 2

We assume that carbamoylated dioxime **4** undergo Beckmann fragmentation to give intermediates **5** and **6** which could cyclize to give both imidazoline 3-oxide **8** and oxadiazine 7. The formed *N*-oxide **8** undergo 1,3-dipolar cycloaddition with aryl isocyanate to give compound **9**.

EXPERIMENTAL

Compounds **1a-e** were commercial reagents, **2** was prepared according to known procedure.[14] Aryl isocyanates were purchased from Aldrich and used without additional purification. Melting points were determined on an Electrothermal digital melting point apparatus. IR spectra of the compounds were taken on a Mattson FTIR. ^{1}H NMR spectra of the compounds were recorded on a Bruker instrument (200 MHz). Elemental analyses were performed at Marmara Research Center-TUBITAK.

***N*-Aryl-*N*,*N*-diphenacylamine dioximes (3); General Procedure.** To a solution of amine **1** (15 mmol) in 20 mL of ethanol (50%) α-bromoacetophenone oxime was added portionwise within 5 min. The reaction mixture was stirred at room temperature for 6 h. The formed precipitate was filtered and recrystallized from ethanol.

3a. IR ν_{OH} 3250 cm^{-1} $\nu_{C=N}$ 1615 cm^{-1}; ^{1}H NMR (DMSO-d$_6$) δ 2.20 (3H, s), 4.20, 4.30, 4.48 (4H, three s), 6.55 (2H, d, J = 8), 6.85 (2H, d, J = 8), 7.25-7.40 (10H, m), 10.80 (1H, s), 11.50 (1H, s). Anal. Calcd for $C_{23}H_{23}N_3O_2$: C, 73.97; H, 6.21; N, 11.25. Found: C, 74.11; H, 6.30; N, 11.01. **3b**. IR ν_{OH} 3250 cm^{-1} $\nu_{C=N}$ 1615 cm^{-1}; ^{1}H NMR (DMSO-d$_6$) δ 3.63 (3H, s), 4.19, 4.22, 4.43 (4H, three s), 6.60-6.70 (4H, m), 7.20-7.45 (10H, m), 10.75 (1H, s), 11.40 (1H, s). Anal. Calcd for $C_{23}H_{23}N_3O_3$: C, 70.93; H, 5.95; N, 10.79. Found: C, 70.42; H, 6.11; N, 10.36. **3c**. IR ν_{OH} 3250 cm^{-1} $\nu_{C=N}$ 1615 cm^{-1}; ^{1}H NMR (DMSO-d$_6$) δ 4.27 (2H, s), 4.54 (2H, s), 6.40- 6.70 (3H, m), 7.09 (2H, t, J = 8), 7.20-7.40 (10H, m), 10.75 (1H, s), 11.44 (1H, s). Anal. Calcd for $C_{22}H_{21}N_3O_2$: C, 73.52; H, 5.89; N, 11.69. Found: C, 73.68; H, 6.23; N, 11.58.

3,5-Diphenyl-5,6-dihydro-1,2,5-oxadiazines 7b-c; General Procedure. To a solution of compound **3** (0.5 mmol) in acetonitrile (10 mL) phenyl isocyanate (1 mmol) was dropped at room temperature. The reaction mixture was refluxed for 3.5 h. The organic solvent was removed on a rotary-evaporator and the residue extracted with petroleum ether (40-60, 4 x 10mL) then with ether (2 x 10 mL). The combined extracts were filtered and concentrated and left to crystallize at room temperature. The formed crystals were collected by filtration and recrystallized from ether-petroleum ether (1 : 2).

Imidazooxadiazolones 9; General Procedure. To a solution of dioxime **3** (0.24 mmol) in acetonitrile (7 mL) phenyl isocyanate was added (1.2 mmol) and the mixture stirred at reflux for 21 h. The reaction was monitored by TLC. The solvent was evaporated and the residue subjected on a preparative TLC plate. The mixture of methanol chloroform and ether in a ratio 1:2:5 was used as an eluent. The isolated product was recrystallized from acetonitrile. The IR spectra of the compounds were superimposed with the spectra of those obtained by the reaction of imidazoline 3-oxides with aryl isocyanates.

9a. The compound was recrystallized from ethanol. Mp 143 °C. IR (KBr) $\nu_{C=O}$ 1750 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 3.60 (1H, d, J = 10.80), 4.20 (1H, d, J = 10.80), 4.50 (1H, d, J = 10.20), 5.05 (1H, d, J = 10.20), 6.65 (5H, m), 7.20-7.45 (10H,m).

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