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Synthesis of 2-(1-Arylcarbonyl-1-arylazomethylidene)-imidazolidines by the Reaction of 2-(Arylcarbonyl-methylidene)imidazolidines with Diazobenzenes

Min-De Ruan [a] , Wei-Qiang Fan [a] , Yun-Zhu Gu [a] , Hua-Jiang Jiang [a] & Yi-Fei Bu [a]

[a] Department of Chemistry , Hangzhou University , Hangzhou, Zhejiang, 310028, China

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SYNTHESIS OF 2-(1-ARYLCARBONYL-1-ARYLAZOMETHYLIDENE)-IMIDAZOLIDINES BY THE REACTION OF 2-(ARYLCARBONYL-METHYLIDENE)IMIDAZOLIDINES WITH DIAZOBENZENES

Min-De Ruan,* Wei-Qiang Fan,* Yun-Zhu Gu,
Hua-Jiang Jiang and Yi-Fei Bu

Department of Chemistry, Hangzhou University, Hangzhou,
Zhejiang 310028, China

ABSTRACT: A variety of 2-(1-arylcarbonyl-1-arylazomethylidene)-imidazolidines **3** were prepared by the reaction of 2-(arylcarbonylmethylidene)-imidazolidines **1** with diazobenzenes **2** in moderate to excellent yields.

Heterocyclic ketene aminals are versatile synthetic intermediates for various fused heterocycles.[1] A variety of ketene aminals containing an imidazolidine or a hexahydropyrimidine ring have been reported.[2-4] The carbon-carbon double bond of these ketene aminals are electron rich because of the conjugation with two nitrogen atoms. Therefore they readily undergo cyclocondenzation with α,β-unsaturated esters[5], nitro derivatives and azodicarboxylates[6] to give various heterocycles. However, reactions of ketene aminals with other electrophiles, such as diazo compounds, have only rarely been reported.[7] We now report the reaction

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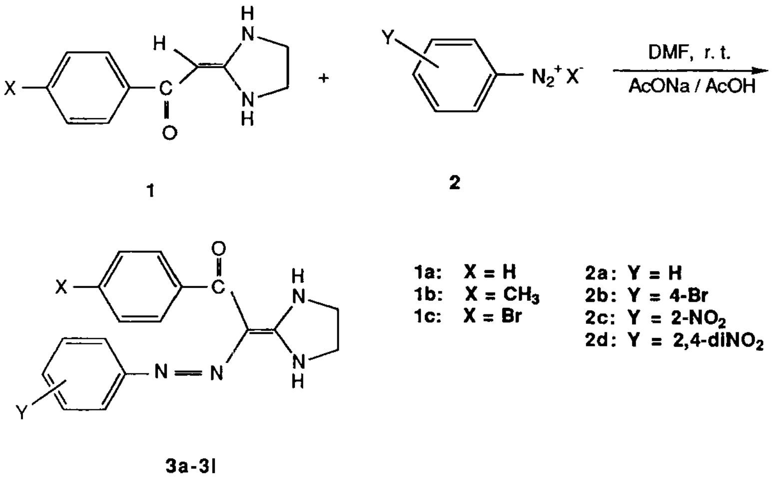
* To whom correspondence should be addressed.

of benzoyl substituted ketene aminals **1** with diazobenzenes to form 2-(1-arylcarbonyl-1-arylazomethylidene)imidazolidines.

2-(Benzoylmethylidene)imidazolidines **1a-1c**, prepared from benzoyl substituted ketene mercaptals and 1,2-ethylenediamine as previously described,[8] reacted smoothly with substituted diazobenzenes **2** in DMF in the presence of sodium acetate and acetic acid at room temperature to give 2-(1-arylcarbonyl-1-arylazomethylidene)imidazolidines **3a - 3l** in 35-99% yield. The coupling reaction took place at the α-position of the ketene aminals **1**. These reactions are shown in Scheme and listed in Table 1. The novel azo derivatives **3a - 3l**, ranging in color from yellow to purple, were characterized by their elemental analyses (Table 1) and by their ^{1}H- and ^{13}C-NMR spectra.



1

2

3a-3l

1a: X = H
1b: X = CH_3
1c: X = Br

2a: Y = H
2b: Y = 4-Br
2c: Y = 2-NO_2
2d: Y = 2,4-diNO_2

The ^{1}H- and ^{13}C-NMR chemical shifts of compounds **3a-3l** and their assignments are summarized in Tables 2 and 3. In the ^{1}H-NMR spectra, typical downfield singlets were observed at 9.83-10.13 ppm for NH groups, and CH_2 signals of imidazolidines appeared at 3.74-4.00 ppm. In the ^{13}C-NMR spectra, the carbonyl carbons appeared at from 189.0 to 191.2 ppm and CH_2 carbons at 42.3-42.9 ppm. The signals around 157 ppm were assigned as =C-NH carbons and those at around 117 ppm as =C-N=N carbons.

Table 1. Preparation of Azo Compounds 3a-3m and Their IR Spectra

No.	X	Y	crystal color	yield (%)	mp. (°C)	IR (ν, cm^{-1})		Calcd.			Found		
						NH	C=O	C	H	N	C	H	N
3a	H	H	yellow	40	169-170	3300	1590	69.86	5.47	19.17	69.71	5.44	18.79
3b	H	4-Br	orange	67	236-238	3280	1590	54.96	4.04	15.09	54.54	4.04	15.04
3c	H	2-NO_2	purple	35	217-218	3300	1610	60.03	4.45	20.77	59.84	4.39	20.60
3d	H	2,4-diNO_2	red	50	278-279	3370	1600	53.37	3.67	21.98	53.12	3.58	21.63
3e	4-CH_3	H	yellow	81	165-166	3300	1590	70.59	5.88	18.30	70.86	6.01	17.95
3f	4-CH_3	4-Br	yellow	97	208-209	3300	1600	56.16	4.45	14.55	55.95	4.44	14.43
3g	4-CH_3	2-NO_2	red	99	213-215	3300	1590	61.54	4.80	19.94	61.19	4.90	20.25
3h	4-CH_3	2,4-diNO_2	purple	61	> 350	3300	1600	54.54	4.04	21.21	54.47	4.17	20.81
3i	4-Br	H	yellow	64	199-201	3300	1590	54,98	4.04	15.09	54.58	4.08	14.73
3j	4-Br	4-Br	orange	90	196-198	3300	1685	45.33	3.11	11.44	44.95	3.03	11.80
3k	4-Br	2-NO_2	red	47	293-294	3350	1605	49.08	4.11	16.83	48.69	3.75	16.48
3l	4-Br	2,4-diNO_2	orange	44	321-322	3300	1600	44.25	2.81	18.22	44.21	2.80	17.92

Table 2. ^1H NMR Spectral Data of 2-(1-Arylcarbonyl-1-arylazomethylidene)imidazolidines 3 (δ, DMSO-d_6)

No.	NH (s, 2H)	CH_2CH_2 (s, 4H)	ArCO	ArN=N-
3a	9.93	3.75	7.58 (d, J=7.8, 2H), 7.45-7.35 (m, 3H)	7.40 (d, 2H), 7.31 (t, J=7.2, 2H, 7.12 (t, J=7.4, 1H)
3b	9.93	3.75	7.60 (d, J=7.5, 2H), 7.44-7.34 (m, 3H)	7.48 (d, J=8.5, 2H), 7.35 (d, J=8.5, 2H)
3c	10.03	3.81	7.62 (d, J=7.6, 2H), 7.50-7.40 (m, 3H)	7.92 (d, J=8.2, 1H), 7.54 (t, 1H), 7.36 (d, 1H), 7.26 (t, 1H)
3d	10.05	3.87	7.63 (d, J= 7.6, 2H), 7.49-7.38 (m, 3H)	8.80 (s, 1H), 8.40-8.20 (m, 2H)
3e	10.01	3.74	7.77 (d, J=7.8, 2H), 7.19 (d, J=7.8, 2H), 2.37 (s, CH_3)	7.44 (d, J=7.9, 2H), 7.30 (t, 2H), 7.11 (t, 1H)
3f	10.13	3.83	7.58 (d, J=7.9, 2H), 7.23 (d, J=7.9, 2H), 2.39 (s, CH_3)	7.90 (d, J=8.1, 1H), 7.54 (t, 1H), 7.44 (d, 1H), 7.24 (t, 1H)
3g	9.99	3.76	7.55 (d, J=7.9, 2H), 7.19 (d, J=7.9, 2H), 2.37 (s, CH_3)	7.44 (d, J=8.6, 2H), 7.35 (d, J=8.6, 2H)
3h	10.29	3.90	7.62 (d, J=8.1, 2H), 7.24 (d, J=8.1, 2H), 2.42 (s, CH_3)	8.75 (s, 1H), 8.34-8.23 (m, 2H)
3i	9.91	3.75	7.62-7.55 (A_2B_2 system, 4H)	7.50 (d, 2H), 7.34 (t, 2H), 7.14 (t, 1H)
3j	9.87	3.74	7.61 (d, J=8.4, 2H), 7.35 (d, J=8.4, 2H),	7.52 (d, J=8.5, 2H), 7.35 (d, J=8.5, 2H)
3k	10.03	3.85	7.56-7.38 (A_2B_2 system, 4H)	7.92 (d, 1H), 7.50 (d, 1H), 7.30 (t, 1H) a
3l	9.98	4.00	7.58-7.40 (A_2B_2 system, 4H)	8.87 (s, 1H), 8.37-8.20 (m, 2H)

a. signals overlapped with those of ArCO.

Table 3. ^{13}C NMR Spectral Data of 2-(1-Arylcarbonyl-1-arylazomethylidene)imidazolidines 3[a] (δ, DMSO-d_6)

No.	C=O	=C-NH	C=	CH_2	ArCO	ArN=N-
3a	190.6	157.7	117.7	42.7	141.7, 129.3, 127.0, 125.9	153.0, 129.2, 128.7, 120.4
3b	190.6	157.6	118.0	42.6	141.5, 129.3, 127.0, 122.7	152.2, 131.6, 122.2, 118.1
3c	191.2	157.8	117.6	42.3	140.9, 129.5, 127.3, 125.7	146.0, 143.8, 133.9, 130.0, 125.3, 120.4
3e	190.1	158.0	117.8	42.6	138.6, 129.6, 127.4, 125.7, 21.0 (CH_3)	152.9, 138.8, 128.6, 120.3
3f	190.2	157.8	117.9	42.6	138.4, 129.6, 127.4, 122.0, 21.0 (CH_3)	152.1, 138.9, 131.4, 122.1
3g	190.7	157.6	117.0	42.9	137.8, 129.6, 127.6, 124.7, 21.0 (CH_3)	145.9, 143.4, 139.6, 133.5, 124.7, 120.6
3i	189.0	157.7	117.7	42.7	140.7, 131.5, 128.8, 122.7	152.9, 130.0, 126.0, 120.4
3j	189.5	157.5	118.3	42.7	140.5, 131.5, 130.1, 122.9	152.1, 131.7, 131.4, 122.2

a. The ^{13}C NMR spectra of compounds **3d, 3h, 3k** and **3l** could not been recorded because of their sparing solubitity in DMSO-d_6.

Experimental

Melting points were determined with a X4 apparatus without correction. The ^1H- and ^{13}C-NMR spectra were recorded on a VXR-300 (FT-mode) spectrometer. IR spectra were measured on a IR-408 instrument. Elemental analyses were performed at a Carlo Erba-1106 analyzer. Compounds **1a** to **1c** were prepared as described in the literature.[8] The data for the novel compound **1c** is listed below.

2-(p-Bromobenzenecarbonylmethylidene)imidazolidine 1c.

33%, mp. 236-237°C. ^1H-NMR (DMSO-d_6): δ 9.20 (br, 2H, 2 x NH), 7.63 (A_2B_2 system, 4H), 5.36 (s, 1H, =CH), 3.35 (s, 4H, 2 x CH_2). Anal. Calcd. for $C_{11}H_{11}BrN_2O$: C, 49.44; H, 4.12; N, 10.49. Found: C, 49.18; H, 4.11; N, 10.80.

Preparation of Diazobenzenes, General Procedure:

To an aniline (25 mmol) in a mixture of acetic acid (30 ml) and concentrated sulfuric acid (3 ml) was added butyl nitrite at below 15°C. After standing for 1 hr the butyl nitrite had completely dissolved and then the solution was poured into diethyl ether (100 ml). The resulting solid was collected and kept in glacial acetic acid at below 5°C.

Reaction of 2-(Benzoylmethylidene)imidazolidine 1 and Diazobenzene 2.

To compound **1** (3 mmol) in a mixture of DMF (10 ml) and ethanol (2 ml) in the presence of sodium acetate (0.5 g) was added freshly prepared diazobenzene **1** [4 mmol in glacial acetic acid (4.5 ml)]. The mixture was stirred for 30 min at room temperature. The precipitate was collected by filtration, washed with water and ethanol and dried to give compound **3** (Tables 1-3).

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