

Reaction of C-Aroyl-N-Aryl Nitrilimines with Selected Aliphatic Keto-Hydrazones and Keto-Methylhydrazones

EMTITHAL A. EL-SAWI†, ADEL M. AWADALLAH*, ABDEL-RAHMAN S. FERWANAH‡ and HANY M. DALLOUL†

*Chemistry Department, Faculty of Science, Islamic University of Gaza
P.O. Box 108, Gaza, Palestine
E-mail: awada@mail.iugaza.edu*

C-Benzoyl- and C-2-naphthoyl nitrilimines (**2**) react with methylhydrazones of aliphatic ketones (**3**, $R^1 = CH_3$) to afford the cyclocondensation products 1,2,4,5-tetrazines (**4**, **5**). The reaction of simple hydrazones (**3**, $R^1 = H$) with the same nitrilimines gives the acyclic electrophilic addition products (**6**, **7**), rather than the cyclocondensation tetrazine products.

Key Words: Reaction, C-aroyl-N-aryl nitrilimines, Aliphatic keto hydrazones, Keto-methyl hydrazones.

INTRODUCTION

The reactive 1,3-dipole nitrilimines undergo different types of reactions. They add to multiple bonds producing five-membered cycloaddition products¹. Their cyclocondensation reactions with nucleophiles incorporating suitably located electrophilic centres afford five or six-membered ring heterocycles². They also undergo 1,3-electrophilic addition with nucleophiles³.

The reaction of nitrilimines with hydrazones shows the above three types of reactions. Methylhydrazones of aliphatic ketones⁴ and aldehydes⁵ react with nitrilimines providing tetrahydro-1,2,4,5-tetrazines cyclocondensation products. In contrast, hydrazones of aliphatic aldehydes and ketones react with nitrilimines producing the acyclic addition products, which upon treatment with palladium-carbon cyclize to dihydro-1,2,4,5-tetrazines⁶. This study aims to investigate the reaction of C-benzoyl and C-2-naphthoyl nitrilimines with different hydrazones and methylhydrazones of aliphatic ketones.

†Chemistry Department, University College for Women, Ain Shams University, Heliopolis, Cairo, Egypt.

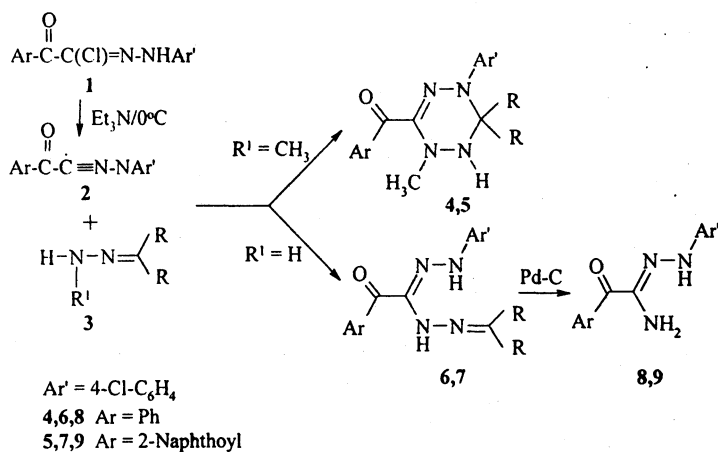
‡Chemistry Department, Faculty of Science, Al-Azhar University of Gaza, P.O. Box 1277, Gaza, Palestine.

EXPERIMENTAL

Melting points were determined on Electrothermal Mel. Temp. apparatus and are uncorrected. IR spectra were obtained by using Perkin-Elmer 237 infrared spectrometer (KBr discs). ^1H - and ^{13}C -NMR spectra were recorded on a Bruker 300 MHz instrument for solutions in CDCl_3 at 21°C , using TMS as an internal reference. Electron impact mass spectra were run on Finnigan Mat 8200 and 8400 spectrometers at 70 eV. C-Benzoyl-⁷ and C-2-naphthoyl-hydrazoneyl halides⁸ (1), hydrazones⁶ and methylhydrazones⁴ (3) were prepared as previously described.

Reaction of Nitrilimines (2) with hydrazones (3)

Triethylamine (5.0 g, 0.05 mol) in tetrahydrofuran (20 mL) was dropwise added to a stirred solution of the appropriate hydrazoneyl halides (1) (0.01 mol) and hydrazones (0.01 mol) in tetrahydrofuran (100 mL) at -5 to 0°C . The reaction temperature was allowed to rise slowly to room temperature and stirring was continued for 4-6 h. The precipitated triethylammonium salt was filtered off, and the solvent was evaporated under reduced pressure. The residue was washed with water, and in a few cases the oily or gummy products were triturated with ethanol, collected and recrystallized from the appropriate solvent.



	a	b	c	d	e
R, R	Me, Me				

SCHEME-1

RESULTS AND DISCUSSION

The reaction of nitrilimines (2) with hydrazones (3) was carried out by the addition of triethylamine to a 1 : 2 equivalent mixture of hydrazoneyl halides—(precursors of nitrilimines) and the appropriate hydrazones in tetrahydrofuran at 0°C .

Methylhydrazones (**3**) are found to afford cyclocondensation products (**4**, **5**).

The assignment of structures (**4**, **5**) is based on analytical and spectral data (Tables 1 and 2). The electron impact (EI) mass spectra (Table-1) display the correct molecular ions in accordance with the suggested structures. The IR spectra show characteristic signals for the $\nu(\text{N-H})$ (ca. 3250 cm^{-1}), $\nu(\text{C=O})$ (ca. 1640 cm^{-1}) and $\nu(\text{C=N})$ (ca. 1590 cm^{-1}).

TABLE-1
PHYSICAL DATA AND MOLECULAR ION PEAKS FOR COMPOUNDS.(4-9)

Compd.	m.p. (°C)	Yield (%)	m.f.	M ⁺
4a	130-2	83	C ₁₈ H ₁₉ N ₄ OCl	342/344
4b	104-6	85	C ₂₀ H ₂₁ N ₄ OCl	368/370
4c	130-2	87	C ₂₁ H ₂₃ N ₄ OCl	382/384
4d	110-2	82	C ₂₂ H ₂₅ N ₄ OCl	396/398
4e	108-10	80	C ₂₃ H ₂₇ N ₄ OCl	410/412
5a	134-6	85	C ₂₂ H ₂₁ N ₄ OCl	392/394
5b	116-8	88	C ₂₄ H ₂₃ N ₄ OCl	418/420
5c	140-2	90	C ₂₅ H ₂₅ N ₄ OCl	432/434
5d	132-4	83	C ₂₆ H ₂₇ N ₄ OCl	446/448
5e	123-5	82	C ₂₇ H ₂₉ N ₄ OCl	460/462
6a	98-101	65	C ₁₇ H ₁₇ N ₄ OCl	328/330
6b	107-9	70	C ₁₉ H ₁₉ N ₄ OCl	354/356
6c	120-2	72	C ₂₀ H ₂₁ N ₄ OCl	368/370
6d	103-5	62	C ₂₁ H ₂₃ N ₄ OCl	382/384
6e	103-5	60	C ₂₂ H ₂₅ N ₄ OCl	396/398
7a	91-3	67	C ₂₁ H ₁₉ N ₄ OCl	378/380
7b	144-6	71	C ₂₃ H ₂₁ N ₄ OCl	404/406
7c	118-20	75	C ₂₄ H ₂₃ N ₄ OCl	418/420
7d	152-4	66	C ₂₅ H ₂₅ N ₄ OCl	432/434
7e	120-2	65	C ₂₆ H ₂₇ N ₄ OCl	446/448
8	192-4	60	C ₁₄ H ₁₂ N ₃ OCl	273/275
9	186-8	62	C ₁₈ H ₁₄ N ₃ OCl	323/325

The ¹H NMR shows characteristic signals for the N-H at about (4.3, s, 1H), and N-CH₃ (3.2, s, 3H) in addition to the multiplets resulting from the aliphatic and aromatic hydrogens. The entire ¹H NMR data are presented in the experimental part.

The ¹³C NMR spectra display the characteristic signals of the suggested structures. The signal for C₆ (quaternary or spiro carbon) appears in the range of 80-90 ppm. This is similar to reported values of quaternary and spiro carbons flanked by two nitrogens in six-membered heterocycles¹⁰⁻¹². This provides a strong evidence in support of structures (**4**, **5**) rather than acyclic structures.

TABLE-2
CHARACTERISTIC IR, ^1H NMR AND ^{13}C NMR SPECTRAL DATA
OF COMPOUNDS 4-9

Compd.	IR (cm^{-1})		^1H NMR		^{13}C NMR		
	$\nu(\text{N}-\text{H})$	$\nu(\text{C}=\text{O})$	N-H	N- CH_3	C=O	C_6	N- CH_3
4a	3238	1654	4.40	3.20	187.7	68.6	42.9
4b	3248	1644	4.30	3.30	187.7	86.7	42.9
4c	3238	1654	4.30	3.20	187.7	80.0	42.9
4d	3251	1660	4.20	3.20	187.3	87.6	42.2
4e	3233	1653	4.50	3.10	187.5	86.6	42.0
5a	3274	1644	4.50	3.20	187.5	68.6	43.0
5b	3284	1643	4.40	3.30	187.4	80.0	43.0
5c	3271	1648	4.20	3.30	187.5	70.0	42.6
5d	3264	1645	4.50	3.20	187.1	84.9	42.4
5e	3272	1642	4.30	3.20	187.3	83.5	42.0
	$\nu(\text{NH}_2)$	$\nu(\text{C}=\text{O})$	N-H	N-H	C=O	N= CR_2	
6a	3247/3192	1643	11.71	8.63	186.9	146.3	
6b	3322/3191	1642	11.60	8.40	186.8	159.2	
6c	3325/3190	1634	11.80	8.80	187.0	152.2	
6d	3306/3171	1645	11.90	8.70	186.9	155.3	
6e	3348/3192	1639	11.90	8.80	186.9	155.1	
7a	3328/3229	1638	11.80	8.70	186.5	146.3	
7b	3324/3221	1638	11.60	8.70	186.4	159.3	
7c	3323/3222	1638	11.90	8.90	186.7	152.3	
7d	3306/3171	1638	11.90	8.70	186.6	155.3	
7e	3326/3174	1638	11.90	8.90	186.6	155.1	
8	3432/3341/3310	1632	9.90	5.60	187.2		
	$\nu(\text{NH}, \text{NH}_2)$			(NH_2)			
9	3434/3343/3312	1629	9.00	5.60	187.0		
	$\nu(\text{NH}, \text{NH}_2)$			(NH_2)			

On the other hand, the reaction with simple hydrazones is found to afford the acyclic adducts (6, 7), which give a complicated mixture of products upon heating with Pd-C from which amidrazones (8, 9) were separated, respectively. The assignment of structures (6-9) is based on spectral and analytical data.

ACKNOWLEDGEMENT

The authors wish to thank Dr. W. Schrader, Max-Planck Institut fuer Kohlenforschung, Muelheim, Germany, for obtaining the mass spectra.

REFERENCES

1. A.S. Shawali and P. Parkanyi, *J. Heterocycl. Chem.*, **17**, 833 (1980); A.S. Shawali, *Chem. Rev.*, **93**, 2733 (1933).
2. A.Q. Hussein, M.M. El-Abadelah and A.S. Ferwanah, *Dirasat*, **21B**, 71 (1994); M.M. El-Abadelah, M.Z. Nazer, N.S. El-Abadlah and H. Meier, *J. Prakt. Chem.*, **339**, 90 (1997); M.M. El-Abadelah, S.A. Saleh and A.M. Awadallah, *Asian J. Chem.*, **9**, 474 (1997).
3. M.R. El-Haddad, A.R.S. Ferwanah and A.M. Awadallah, *J. Prakt. Chem.*, **340**, 623 (1998); P.D. Crace, P. Debuttero, E. Licandro and S. Maiorana, *Synthesis*, **4**, 299 (1979).
4. M.M. El-Abadelah, A.Q. Hussein, M.R. Kamal and K.H. Al-Adhami, *Heterocycles*, **27**, 917 (1988).
5. A.Q. Hussein, M.M. El-Abadelah, K. Al-Adhami, and A.S. Abushamla, *Heterocycles*, **29**, 1163 (1989).
6. A.Q. Hussein, *J. Chem. Research (S)*, 174 (1996); *J. Chem. Research (M)*, 949 (1996).
7. K.C. Joshi, V.N. Pathak and S. Sharma, *Indian J. Chem.*, **24B**, 124 (1985).
8. H.M. Hassaneen, A.S. Shawali, N.M. Elwan and N.M. Abounada, *Sulfur Lett.*, **13**, 273 (1992).

(Received: 13 February 2002; Accepted: 5 April 2002)

AJC- 2671

2ND EURASIAN MEETING ON HETEROCYCLIC CHEMISTRY "Heterocycles in Organic and combinatorial Chemistry"

NOVGOROD THE GREAT, RUSSIA

14-17September 2002

Contact:

DR. EUGENE V. BABAEV

Chemistry Department

Moscow State University

Moscow 119899, Russia

Tel: +7-(095)-932-8846

Fax: +7-(095)-939-3020

E-mail: babaev@org.chem.msu.su

Websites:

<http://www.org.chem.msu.su/~babaev/eurasia/>

<http://www.chem.msu.su/eng/misc/~babaev/eurasia/>