Indian Journal of Chemistry
Vol. 36B, November 1997, pp. 1071-1073

Note

Nitration of nitrogen heterocycles using microwaves

Mazaahir Kidwai* & Seema Kohli
Department of Chemistry, University of Delhi,
Delhi 110 007, India

Received 14 July 1997; accepted (revised) 17 October 1997

A comparative study of reaction time and yields for nitration of nitrogeneous heterocyclic compounds using $Cu(NO_3)_2$,KNO_3 and $NaNO_3$ under microwave irradiation as well as by conventional heating is reported.

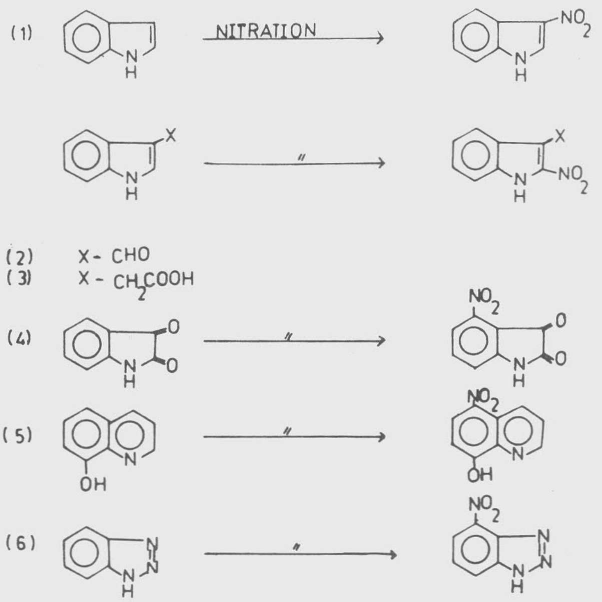
Nitro compounds are not only used as reactive intermediates[1] but also in nuclear nitration[2-5]. Recently reported studies on the use of domestic microwave oven for the synthesis of heterocycles[6-10] show that it is a safe and practically convenient methodology. Keeping in view the potential of microwave irradiation in organic synthesis we undertook the study on the nitration of some heterocyclic compounds using commonly available reagents under microwave irradiation and also by conventional heating.

Results and Discussion

Nitration of selected heterocycles using $Cu(NO_3)_2$, $Pb(NO_3)_2$, KNO_3 and $NaNO_3$ in gl. acetic acid under microwave irradiation and also by conventional heating method furnished products as are given in Scheme I. The results are reported in Tables I and II. The comparative study reveals that $Cu(NO_3)_2$ in gl. acetic acid is superior reagent over others. KNO_3 and $NaNO_3$ are the least reactive nitrants while $Pb(NO_3)_2$ is moderately reactive. The products were obtained in fairly good yields with enhanced rate of reaction using microwave irradiation. IR and mass spectra confirm the presence of mono nitro group in the products. This procedure provides an easier and safer method for nitration of heterocycles.

Experimental Section

Melting points were taken on electrothermal melting point apparatus and are uncorrected. IR spectra (ν_{max} in cm^{-1}) were recorded on 1710 Perkin Elmer FTIR spectro-photometer using KBr discs, ^1H NMR on FT NMR Hitachi R-600 using TMS as internal reference (chemical shifts in δ, ppm) and mass spectra on Jeol, JMS DX303 at 70eV. Reaction monitoring and the purity of compounds were checked on TLC (silica gel coated plates). Cupric nitrate, lead nitrate, potassium nitrate and sodium nitrate used were of laboratory reagent grade. All the sequences of irradiation were carried out in Padmini essentia microwave oven model Brownie using high as the cook level



Scheme I

Nitration of Compounds

Method A. Indole (0.01 mole) was dissolved in a minimum quantity of gl. acetic acid (6 mL) and to it was added a solution of $Cu(NO_3)_2$ (0.011 mole) in water (5 mL). The contents were subjected to microwave irradiation for an appropriate time. It was diluted and extracted with ethyl acetate (10 mL). The product obtained was recrystallized from ethyl acetate-pet. ether (10-15 mL).

Method B. Indole (0.01 mole) was dissolved in a minimum quantity of gl. acetic acid (6 mL) and

Table I—Nitration of heterocyclic compounds using microwave irradiation method (A) and by conventional heating method (B)

Compd	Heterocycles	$Cu(NO_3)_2$				$Pb(NO_3)_2$				KNO_3				$NaNO_3$				m.p. (°C)	Lit m p (°C)
		Yield %		Time		Yield %		Time		Yield %		Time		Yield %		Time			
		A	B	A (Sec)	B (hr)	A	B	A (Sec)	B (hr)	A	B	A (Sec)	B (hr.)	A	B	A (Sec)	B (hr.)		
1	Indole	92	70	30	3	60	51	90	8	53	40	180	20	50	40	210	22	214	210[4]
2	Formyl Indole	80	50	45	6	50	40	150	16.5	40	31	300	28	41	29	360	31	213	
3	Carboxyl Indole	70	45	55	7	45	38	180	23	39	25	330	32	35	26	360	35	213	
4	Isatin	68	30	90	5	57	48	210	11.5	45	35	360	31.5	40	30	330	29	251	248-50[11]
5	8-Hydroxy Quinoline	70	60	30	3.5	55	43	120	10	39	30	300	25	32	22	360	38	182-3	180[12]
6	Benzo- Triazole	50	35	120	8	42	35	210	15	30	18	360	36	28	20	360	40	216	220[13]

A—Using microwave irradiation
B—Using conventional heating

Table II—Spectral data of Compounds **1-6**

Compd	IR (V_{max} in cm^{-1})	^1H NMR ($CDCl_3$)
1	3220 (NH), 1520 (NO_2 asym), 1330 (NO_2 sym, deform)	7.5-7.7 (m, 4H, Ar-H), 8.2 (s, 1H 2CH), 9.0 (br, 1H NH)
2	3180 (NH), 1647 (C+O str.),1512 (NO_2 asym), 1310 (NO_2 sym)	7.2-7.5 (m, 4H Ar-H), 8.50 (br 1H NH), 9.8 (s, 1H, CHO)
3	3200 (NH), 1695 (C=O), 3480 (OH), 1510, 1360 (NO_2)	3.3-3.4 (s, 2H, CH_2), 7.3-7.6 (m, 4H, Ar-H), 8.7 (br, 1H, NH)
4	3280 (NH), 1750 (C=O), 1710 (C=O), 1520, 1350 (NO_2)	7.3-7.8 (m, 3H, Ar-H), 8.6 (br, 1H, NH)
5	3400 (OH), 1495, 1330 (NO_2)	6.0 (s, 1H, OH), 7.2-7.4 (m, 3H Ar-H), 7.6 (d, 1H, 6H), 7.9 (d, 1H, 7H)
6	3180 (NH), 1590 (N=N), 1490, 1320 (NO_2)	7.3-7.6 (m, 3H, Ar-H), 8.7 (br, 1H, NH)

to it was added a solution of $Cu(NO_3)_2$ (0.011 mole) in water (5 mL). It was refluxed for an appropriate time, and worked-up as described in Method A.

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