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Synthesis of 3-Acetyl-1-Aryl-4,5-Dihydro-5,5-Dimethyl-1H-Triazoles from the Reaction of Nitrilimines with Acetone Oxime

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A novel series of 3-acetyl-1-aryl-4,5-dihydro-5,5-dimethyl-1H-triazoles (7a–c) have been prepared *via* direct interaction between acetone oxime (3) and the appropriate hydrozonoyl chlorides (1) in presence of triethylamine.

INTRODUCTION

Nitrilimines are known to react mainly with three modes, namely, 1,3-dipolar cycloaddition with multiple bonds[1], cyclocondensation reactions with nucleophiles incorporating suitably located electrophilic centre[2] and 1,3-electrophilic addition with nucleophiles[3].

The reaction of nitrilimines (2) generated *in situ* from the respective hydrazonoyl chlorides (1) with acetone oxime (3) is expected to proceed by any one of the above mentioned modes leading to different products (4–6).

This study aims to investigate this reaction and characterize the resulting products.

EXPERIMENTAL

Melting points were determined on Electrothermal Mel. Temp. apparatus and are uncorrected. IR spectra were obtained by using Perkin-Elmer 237 infrared spectrometer in KBr discs. Mass spectra (electron impact) were performed with a Prospec 3000 instrument from Fisons Company at 70 eV. ^1H and ^{13}C NMR spectra were recorded on Bruker-AM 300 and 500 MHz instruments for solutions in $CDCl_3$ at 21°C, using TMS as an internal reference. Chemical shifts are expressed in δ (ppm) downfield from TMS and coupling constants are in Hertz (Hz). Acetone oxime[4] and hydrazonoyl chlorides[5] were prepared as previously described in the literature.

Synthesis of 3-Acetyl-1-Aryl-4,5-Dihydro-5,5-Dimethyl-1H-Triazoles (7a–c)

Triethylamine (5.0 g, 0.05 mol) in absolute tetrahydrofuran (10 mL) was dropwise added to a stirred solution of hydrazonoyl chlorides (0.015 mol) and acetone oxime (1.5 g, 0.03 mol) in tetrahydrofuran (100 mL) between –10 and

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0°C. The temperature of the reaction mixture was then allowed to rise slowly to room temperature and stirring was continued overnight. The solvent was then evaporated in *vacuo*, and residual solid was washed with water to get rid of the triethylamine salt. The crude product was recrystallized from ethanol. The following compounds were synthesized using the above mentioned method.

3-Acetyl-4,5-dihydro-5,5-dimethyl-1-phenyl-1H-triazole (7a)

^{1}H NMR ($CDCl_3$): δ/ppm = 7.00–7.31 (m, 5H, aromatic protons), 4.84 (s, 1H, NH), 2.48 (s, 3H, CH_3CO), 1.64 (s, 6H, $C(CH_3)_2$). ^{13}C NMR: δ/ppm = 189.53 (CH_3CO), 147.34 (C=N), 142.52, 128.98 (2C), 122.30 (2C) and 117.73 (aromatic carbons), 85.29 (ring spiro carbon), 27.69 ($C(CH_3)_2$), 24.80 (CH_3CO). IR cm^{-1} = 3327 ν(NH), 1668 ν(C=O).

3-Acetyl-4,5-dihydro-5,5-dimethyl-1-(4-methylphenyl)-1H-triazole (7b)

^{1}H NMR ($CDCl_3$): δ/ppm = 7.00–7.40 (m, 4H, aromatic protons), 4.82 (s, 1H, NH), 2.44 (s, 3H, CH_3CO), 2.29 (4-CH_3—C_6H_4), 1.55 (s, 6H, $C(CH_3)_2$). ^{13}C NMR: δ/ppm = 189.48 (CH_3CO), 147.41 (C=N), 140.12, 132.41, 129.50 (2C) and 118.61 (2C) (aromatic carbons), 85.68 (ring spiro carbon), 27.59 ($C(CH_3)_2$), 23.24 (CH_3CO); 20.69 (4-CH_3—C_6H_4), IR cm^{-1} = 3317 ν(NH), 1656 ν(C=O).

3-Acetyl-1-(4-chlorophenyl)-4,5-dihydro-5,5-dimethyl-1H-triazole (7c)

^{1}H NMR ($CDCl_3$): δ/ppm = 7.23–7.26 (m, 4H, aromatic protons), 4.92 (s, 1H, NH), 2.47 (s, 3H, CH_3CO), 1.62 (s, 6H, $C(CH_3)_2$). ^{13}C NMR: δ/ppm = 189.52 (CH_3CO), 147.48 (C=N), 141.22, 128.98 (2C), 127.13 and 118.61 (2C) (aromatic carbons), 85.22 (ring spiro carbon), 27.62 ($C(CH_3)_2$), 24.86 (CH_3CO). IR cm^{-1} = 3366 ν(NH), 1664 ν(C=O).

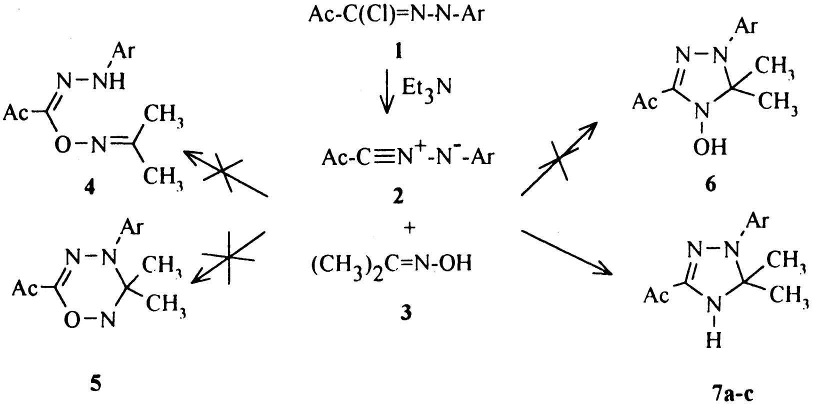
RESULTS AND DISCUSSION

In the present work, we found that acetone oxime (3) reacts readily with nitrilimines (2a–c) generated *in situ* from the action of triethylamine onto the respective hydrazonoyl chlorides (1a–c) yielding the unexpected triazoles (7a–c) in moderate yields (Scheme-1).

Structural assignment of the resulting triazoles (7a–c) is based on elemental analysis (Table-1) and spectra data. The electron impact (EI) spectra of com-

TABLE-1
PREPARATION AND PHYSICAL DATA FOR COMPOUNDS (7a–c)

Compound No.	Yield (%)	m.p. (°C)	Mol formula (mol weight)	Analysis, found (calcd) % C	H	N
7a	50	126–127	$C_{12}H_{15}N_3O$ (217.27)	66.31 (66.34)	6.68 (6.96)	19.22 (19.34)
7b	48	105–106	$C_{13}H_{17}N_3O$ (231.30)	67.41 (67.51)	7.55 (7.41)	17.95 (18.17)
7c	52	130–131	$C_{12}H_{14}ClN_3O$ (251.70)	57.00 (57.26)	5.63 (5.61)	16.59 (16.69)



7a Ar = C_6H_5
7b Ar = $4(CH_3)C_6H_4$
7c Ar = $4(Cl)C_6H_4$

Scheme-I

pounds 7a–c (Table-1) display the correct molecular ions in accordance with the suggested molecular formulae. The base peak is always the (M^+-15) peak. The IR spectra of 7a–c in KBr exhibit strong absorption bands in the regions 3370–3310 cm^{-1} ν(NH), and 1670–1650 cm^{-1} ν(C═O).

The ^{1}H NMR of 7a–c show singlets for the CH_3 of the acetyl group (δ *ca.* 2.4 ppm), the two methyl groups at C-5 (δ *ca.* 1.6 ppm) and the NH (δ *ca.* 4.8 ppm). The signals of the aromatic protons appear between $\delta = 7.0$ and 7.5 ppm.

The ^{13}C NMR spectra display the characteristic signals of the suggested structure. Thus, compounds 7a–c exhibit one signal for the methyl carbon of the acetyl group at about 24 ppm. The intense signal at about 27 ppm is assigned to the two equivalent methyl groups attached to C-5. The signal at about 147 ppm is attributed to the C-3 carbon of the ring. The C═O signal appears at about 190 ppm. The C-5 spiro carbon appears at about 85 ppm and this is similar to reported values of the spiro carbon flanked by two hetero-atoms in five-membered heterocycles[6].

Another piece of evidence in support of the suggested structure of 7a–c is the ^{15}N NMR spectrum of 7a (Fig. 1) which displays a doublet for the NH at 284.26 ppm relative to nitromethane ($^1J_{N-H} = 85$ Hz; $^4J_{N-CH_3} = 2.5$ Hz).

It is noteworthy that the reaction of the similar 1,3-dipoles nitrile oxides with oximes is reported to give the cycloaddition product 4-hydroxy-Δ^2-1,2,4-oxadiazolines[7].

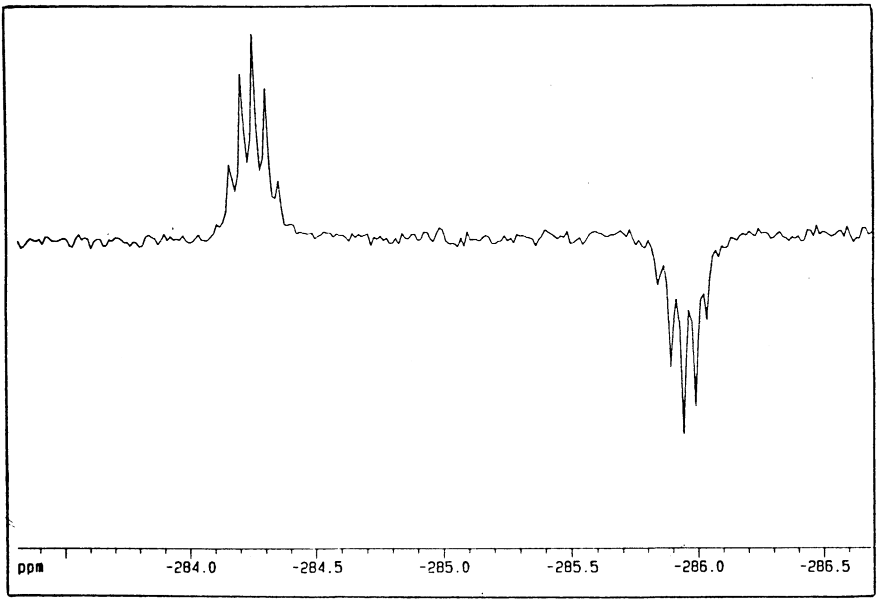


Fig. 1 ^{15}N-NMR Spectrum of compound **7a**

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