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NOTE

Reaction of Benzaldehyde Hydrazones with 2-Diazo-1,2-diphenylethanone

G..S SINGH
Chemistry Department, University of Botswana, Private Bag 0022, Gaborone, Botswana
E-mail: singhgs@mopipi.ub.bw

An equimolar reaction of benzaldehyde hydrazones with 2-diazo-1,2-diphenylethanone affords benzaldehyde N-diphenylacyl hydrazones as a result of reaction of diphenyl ketene, generated *in situ* from the thermal decomposition of 2-diazo-1,2-diphenylethanone, with NH_2 of hydrazones.

Ketenes are well-known reactive intermediates in organic chemistry. Their reactions with compounds containing heteroatoms especially nitrogen have led to the synthesis of a wide variety of compounds including β-lactam heterocycle as a result of ketene-imine cycloaddition[1–3]. The reactions of ketenes with compounds containing C═N often depend on structural environment of the molecule. The reaction of diphenyl ketene with florenone N-benzoyl (acyl) hydrazone and with N-diphenylacetyl benzophenone hydrazones are reported to occur at C═N leading to the formation of azetidinone and 1,3,4-oxadiazoline derivatives, respectively[4, 5]. The reaction of diphenyl ketene with N-benzhydylidene-N′-phenyl urea has also been reported to yield azetidinone derivative showing that the reaction of diphenyl ketene occurred at C═N present in the substrate[6]. Phenoxy ketene however has been reported to react with N—H of benzophenone N-phenylhydrazone[7]. The present paper reports the reaction of diphenyl ketene, generated *in situ* from the thermal decomposition of 2-diazo-1,2-diphenylethanone (**1**) with benzaldehyde hydrazones (**2a–c**) leading to the formation of benzaldehyde N-diphenylacyl hydrazones (**3a–c**). The products have been characterised on the basis of satisfactory analytical (C, H and N) and spectral (IR, NMR and mass) data. Though N-unsubstituted benzaldehyde hydrazones themselves are not very stable their N-diphenylacyl derivatives are stable and can be used as synthons for various other organic compounds.

Melting points have been recorded on a Stuart scientific melting point SMP1 apparatus and are uncorrected. IR spectra have been recorded on a Perkin-Elmer 781 spectrophotometer. The NMR spectra have been recorded on a Bruker™ 300 MHz spectrometer in a $CDCl_3$ solution. The mass spectra are recorded on a Mat SSQ 7000 spectrometer using EI method.

2-Diazo-1,2-diphenylethanone (**1**) was prepared by the oxidation of benzil monohydrazone using bis-(acetylacetonato) copper(II)[8].

Benzaldehyde hydrazones (2a–c): Into a 100 mL round-bottomed flask containing 5.0 mmole of appropriate aldehyde in 20 mL of ether, 7.0 mmole of hydrazine hydrate was added. The solution was stirred at room temperature for 10 min and extracted with water to remove any unreacted hydrazine hydrate. Ether layer was dried over anhydrous magnesium sulfate. Evaporation of ether at room temperature under reduced pressure afforded hydrazone which was used immediately without any further purification.

General Reaction Procedure

An equimolar amount (1 mmole) of 2-diazo-1,2-diphenylethanone (**1**) and benzaldehyde hydrazones (**2a–c**) in 20 mL of dry benzene was refluxed under nitrogen for 6 h. The removal of solvent under reduced pressure and trituration of the residue with ethanol afforded white crystalline solid characterized as benzaldehyde N-diphenylacyl hydrazones (**3a–c**).

An equimolar reaction of 2-diazo-1,2-diphenylethanone (**1**) with benzaldehyde hydrazone (**2a**) followed by treatment with ethanol afforded a white crystalline solid with m.p. 190°C in 66% yield characterised as benzaldehyde N-diphenylacyl hydrazone (**3a**) on the basis of satisfactory analytical and spectral data given below: $C_{21}H_{18}N_2O$ req: C, 80.25; H, 5.7 and N, 8.90%; found: C, 80.00; H, 5.83 and N, 8.65%; IR (KBr, cm^{-1}): 3175, 3032, 1660, 1646 and 1601; ^1H NMR ($CDCl_3$, δ ppm): 8.78–8.53 (bs, 1H, NH, D_2O exchangeable), 7.90 (s, 1H, CH═N), 7.63 (*m*, 2H, arom), 7.35 (m, 13H, arom), 6.09 (s, 1H, $CHPh_2$); ^{13}C NMR ($CDCl_3$, δ ppm): 174.35 (sd, J = 6.10 Hz), 143.72 (dt, $J_{3C—H} = 4.27$ Hz), 139.00, 133.50. 130.15, 129.11, 128.71, 128.47, 127.16, 126.99 (all aromatic carbons) and 53.02 (CH); MS (m/z, r.i.): 314 (M^+ 65), 211 (30), 194 (10), 167 (100), 152 (15), 77, 65.

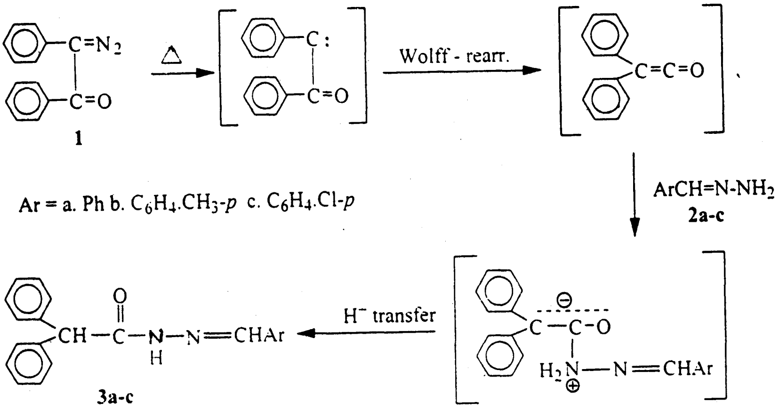
Similar reactions of **1** with 4-methylbenzaldehyde hydrazone (**2b**) and 4-chlorobenzaldehyde hydrazone (**2c**) afford crystalline compounds characterised as 4-methylbenzaldehyde N-diphenylacyl hydrazone (**3b**, m.p. 145°C, yield 72%) and 4-chlorobenzaldehyde N-diphenylacyl hydrazone (**3c**, m.p. 121°C, yield 58%), respectively on the basis of satisfactory analytical and spectral data given below:

3b. Mol. formula: $C_{22}H_{20}N_2O$, elemental analysis req: C, 80.48; H, 6.10 and N, 8.50%; found: C, 80.25; H, 6.38 and N, 8.30%; IR (KBr, cm^{-1}): 3180, 3050, 1660, 1645 and 1610; ^1H NMR ($CDCl_3$, δ ppm): 8.78–8.53 (bs, 1H, NH, D_2O exchangeable), 7.80 (s, 1H, CH═N), 7.58–7.30 (m, 14H, arom), 2.35 (s, 3H, methyl).

3c. Mol. formula: $C_{21}H_{17}N_2OCl$, elemental analysis req: C, 72.40; H, 4.90 and N, 8.04%; found: C, 72.15; H, 5.15 and N, 7.80%; IR (KBr, cm^{-1}): 3170, 3050, 1656, 1640 and 1610; ^1H NMR ($CDCl_3$, δ ppm): 8.75–8.50 (bs, 1H, NH, D_2O exchangeable), 7.75 (s, 1H, CH═N), 7.55–7.25 (m, 14H, arom).

The spectroscopic data are in agreement with the assigned structure. The bands at 1660 and 1646 cm^{-1} in the IR spectrum of **3a** are assigned to amide carbonyl and imino linkages, respectively. The singlets at δ 7.90 and 6.09 ppm have been attributed to azomethine and acyl protons, respectively. ^{13}C NMR spectrum shows two downfield carbon signals at δ 174.35 and 143.72 ppm. The study of ^{13}C—H coupling showed them as singlet of doublet and doublet of triplet, respectively. The former one is thus assigned to carbonyl carbon while the latter one is attributed to imino carbon.

The plausible mechanism for the formation of products **3a–c** is shown in Scheme I. Thermal decomposition of 2-diazo-1,2-diphenylethanone (**1**) is now a well-known method for *in situ* generation of diphenylketene *via* Wolff-rearrangement of benzoylphenyl carbene[2]. The reaction of diphenyl ketene with amino nitrogen of hydrazones **2a–c** may lead to a *zwitterionic* intermediate. Similar intermediates have been proposed earlier in the reactions of diphenyl ketene with amines[9]. A proton transfer in this intermediate explains the formation of the products **3a–c**.



SCHEME I

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