1,3,4-Oxadiazolines from the reaction of diphenylketene with benzophenone N-diphenylacyl hydrazones. A reinvestigation

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Received 24 September 1998; accepted (revised) 27 March 2000

An equimolar reaction of diphenylketene with benzophenone N-diphenylacyl hydrazones 2a-c affords 5,5-diaryl-4-(diphenylacyl)-2-(diphenylmethyl)-1,3,4-oxadiazol-2-enes 5a-c which have been characterized on the basis of analytical and spectroscopic studies (IR, ¹H and ¹³C NMR and MS). A plausible mechanism of their formation has been suggested.

An equimolar reaction of diphenylketene, generated in situ from the thermal decomposition of 2-diazo-1,2-diphenylethanone 1, with benzophenone N-diphenylacyl hydrazones 2a-c has been reported to give 1-diphenylacylazo-1,1-diaryl-3,3-diphenyl-2-propanones 3a-c as a result of interaction of ketene with imino carbon of hydrazones followed by a 1,5-proton transfer in respective intermediates. Later on Sharma et al. reported that the reaction of phenoxy ketene with benzophenone N-H bond of hydrazones 2a-c, azopropanone structure 3a-c was proposed mainly on the basis of CH NMR spectrum which showed signals for two methine protons at different positions indicating their dissimilar environment which was impossible in 6a-c.

The present study, especially ¹³C NMR spectroscopy combined with the previous IR and ¹H NMR spectral data, reveals that the products formed from the reaction of diphenylketene with benzophenone N-diphenylacyl hydrazones 2a-c are actually 5,5-diaryl-4-(diphenylacyl)-2-(diphenylmethyl)-1,3,4-oxadiazol-2-enes 5a-c. Acyl hydrazones and their silver salts are reported earlier to give similar oxadiazolines by their cyclization with Ac₂O and with acyl chlorides, respectively.

The ¹³C NMR spectrum of 5a showed two signals at δ 168.25 and 157.15 ppm which have been assigned to carbonyl (C₈) and imino carbon (C₉), respectively. The remaining heterocyclic ring carbon (C₉), appeared at δ 103.47 ppm. Although only one carbonyl carbon and one imino carbon are also involved in oxadiazinones 4a-c and hydrazones 6a-c the latter is easily discarded because of (i) no carbon corresponding to signal at δ 103.47 ppm in it and (ii)

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diphenylketene on azatautomers of hydrazones 2a-c similar to the reaction of olefins with azatrienylbenzoyl Japan, leading to oxadiazines and of 1,3,4-oxadiazolines 5a-c.

With regard to the azopropanones structure 3a-c, the IR spectra were observed to have only one absorption band (at 1670 cm⁻¹ in 3a and at 1665 cm⁻¹ in 3b and 3c) in usual carbonyl absorption region despite of two functional groups (one keto carbonyl and one azo carbonyl) in 3a-c. It was also difficult to explain the absorption at 1600 cm⁻¹ due to N=N linkage. Though the IR data were in agreement with N,N-bis(diphenylacyl)benzophenone hydrazones 6a-c, the products expected from the reaction of diphenylketene with N-H bond of hydrazones 2a-c, azopropanone structure 3a-c was proposed mainly on the basis of ¹H NMR spectrum which showed signals for two methine protons at different positions indicating their dissimilar environment which was impossible in 6a-c.

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dissimilar nature of methine protons observed in \(^1\)H NMR spectrum. The study of \(^{13}\)C-H coupling constants rules out the former structure \(4a-c\). The signals at 168.25 and 157.15 ppm appear as singlets of doublet with \(J = 7.32\) and 9.16 Hz, respectively. These constants are only in agreement with structure \(5a\) in which carbonyl and imino carbons are having C-H in their vicinity. Since in oxadiazinones \(4a-c\) the carbon adjacent to carbonyl carbon is lacking proton no such high \(J_{C-H}\) is possible. The two singlet signals in \(^1\)H NMR spectrum at 5.77 and 5.02 ppm are assigned to methine protons adjacent to carbonyl and imino carbons, respectively. The strong absorption bands at 1670 and 1600 cm\(^{-1}\) in \(5a\) and at 1665 and 1600 cm\(^{-1}\) in \(5b,c\) can be well attributed to N-C=O and C=N-N linkages, respectively.

The most plausible mechanism for the formation of oxadiazolines \(5a-c\) is the reaction of diphenylketene with imino nitrogen of hydrazones \(2a-c\) leading to a zwitterionic intermediate (Scheme I) as proposed by various authors in ketene-imine cycloaddition\(^7\). An initial attack of diphenylketene at more electronegative nitrogen with a lone pair of electrons is more logical in comparison to that at imino carbon as proposed earlier\(^1\). A proton transfer in the zwitterion and subsequent cyclization of the resulting 1,3-dipolar intermediate may lead to the formation of oxadiazolines \(5a-c\).

**Experimental Section**

The IR spectra were recorded in KBr on a Perkin–Elmer 983 spectrophotometer; \(^1\)H and \(^{13}\)C NMR spectra on a Varian EM-390 and Bruker AM-360 spectrometers in a CDCl\(_3\) solution using TMS as an internal standard, and mass spectra on a Jeol DX-303 HF spectrometer.

2-Diazoketone \(1\), hydrazones \(2a-c\) and the products \(5a-c\) were obtained by exactly following the same procedure as described previously\(^1\). The physical and spectral data are given below.

**5,5-Dipheny 1-(4-(diphenylacyl)-2-(diphenylmethy l)-1,3,4-oxadiazol-2-ene 5a.** Yield 77 %; mp 177 °C; \(^1\)H NMR (CDCl\(_3\), ppm): 7.22 (m, 30H, arom), 5.77 (s, 1H, O=C-CH), 5.02 (s, 1H, -N=C-CH); \(^{13}\)C NMR (CDCl\(_3\)): 168.25 (sd, \(2J_{C-H} = 7.32\) Hz), 157.15 (sd, \(2J_{C-H} = 9.16\) Hz), 138.87, 137.83, 137.61, 129.27, 129.01, 128.60, 128.52, 128.23, 127.91, 127.70, 127.43, 126.75, 103.47 (C\(_6\)), 55.64 (dt, \(3J_{C-H} = 3.66\) Hz, CH) and 48.80 (dt, \(3J_{C-H} = 3.66\) Hz, CH); MS: m/z (rel. int.) 584 (4, M\(^+\)), 404 (4), 390 (55, M\(^+\)-Ph\(_2\)C=C=O), 223 (60), 194 (40, Ph\(_2\)C=C=O), 180 (37), 167 (100, Ph\(_2\)CH), 152 (14), 139 (4), 115 (4), 77 (8, Ph) and 51 (3); found: C, 84.37; H, 5.71; N, 4.75 %; \(C\(_6\)H\(_5\)N\(_2\)O\(_2\)) req.: C, 84.85; H, 5.48; N, 4.79 %.

**5,5-Bis(4-methoxyphenyl)-1-(4-(diphenylacyl)-2-(diphenylmethyl)-1,3,4-oxadiazol-2-ene 5b.** Yield 83 %; mp 140 °C; \(^1\)H NMR (CDCl\(_3\), ppm): 7.17 (m, 30H, arom), 6.75 (dd, 4H, o-arom), 5.76 (s, 1H, O=C-CH), 5.01 (s, 1H, -N=C-CH) and 3.79 (s, 6H, two methoxy); \(^{13}\)C NMR (CDCl\(_3\), ppm): 168.13 (sd, \(2J_{C-H} = 8.94\) Hz), 159.92 (st, CH\(_3\)O-C), 157.02 (sd, \(2J_{C-H} = 9.76\) Hz), 139.00, 137.94, 130.05, 129.32, 129.29, 128.60, 128.50, 128.21, 127.38, 126.71, 112.98, 103.54 (C\(_6\)), 55.62, (dt, \(3J_{C-H} = 3.50\) Hz, CH), 55.23
(q, J_{C-H} = 144 \text{ Hz}, \text{ methoxy carbon}) and 48.85 (dt, J_{C-H} = 3.50 \text{ Hz}, \text{ CH}); MS: m/z (r. i.) 644 (2, M'), 450 (98, M' - Ph_2C=\text{C}=O), 432 (2), 283 (30), 255 (100), 240 (55), 225 (10), 211 (5), 194 (28, Ph_2C=\text{C}=O), 165 (60), 152 (10), 139 (5), 115 (5), 82 (5) and 63 (2); found: C, 80.21; H, 5.79; N, 4.38 %; C_{43}H_{36}N_2O_4 req.: C, 80.10; H, 5.63; N, 4.34 %.

5-(4-Chlorophenyl)-5-phenyl-4-(diphenylacy1)-2-(diphenylmethyl)-1,3,4-oxadiazol-2-ene 5c. Yield 63 %; mp 148 °C; \textsuperscript{1}H NMR (CDCl\textsubscript{3}): δ 7.16 (m, 29H, arom), 5.75 (s, 1H, O=\text{C}-\text{CH}), 5.02 (s, 1H, -\text{N}≡\text{C}-\text{CH}); \textsuperscript{13}C NMR (CDCl\textsubscript{3}): δ 168.42 (sd, J_{C-H} = 7.32 Hz), 157.15 (sd, J_{C-H} = 9.16 Hz), 138.70, 137.69, 137.21, 136.25, 135.08, 129.45, 129.27, 129.21, 128.61, 128.57, 128.32, 128.28, 127.91, 127.73, 127.54, 126.88, 102.04 (C_6), 55.62 (dt, J_{C-H} = 3.55 \text{ Hz}, \text{ CH}) and 48.80 (dt, J_{C-H} = 3.55 \text{ Hz}, \text{ CH}); MS: m/z (r. i.) 618 (7, M'), 424 (30, M' - Ph_2C=\text{C}=O), 406 (8), 257 (30), 229 (10), 214 (15), 194 (50, Ph_2C=\text{C}=O), 167 (100, Ph_2CH), 152 (10), 139 (1) and 77 (2); found: C, 79.15; H, 5.26; N, 4.46 %; C_{41}H_{36}N_2O_4Cl req.: C, 79.54; H, 5.01; N, 4.52 %.

References