Chemoselectivity in reactions of an α-diazo-β-diketone with some conjugative double-bond systems

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Reactions of 2-diazo-1,3-diphenylpropane-1,3-dione with α,β-unsaturated aldehydes and ketones, and keto-imines, in refluxing anhydrous toluene indicate that benzoyl(phenyl)ketene, which is generated by the thermal Wolff rearrangement of 2-diazo-1,3-diphenylpropane-1,3-dione, shows a pronounced tendency to form chemospecific [2 + 4] Diels–Alder adducts with the carbonyl group in α,β-unsaturated aldehydes and ketones, and the imine group in keto-imines. The reactivity in reactions of the α-diazo-β-diketone with these conjugative double-bond systems is C=N > C=O > C=C. However, benzoyl(phenyl)ketene reacts with α,β-unsaturated imines to produce chemospecific [2 + 2] cycloadducts: β-lactams.

Introduction

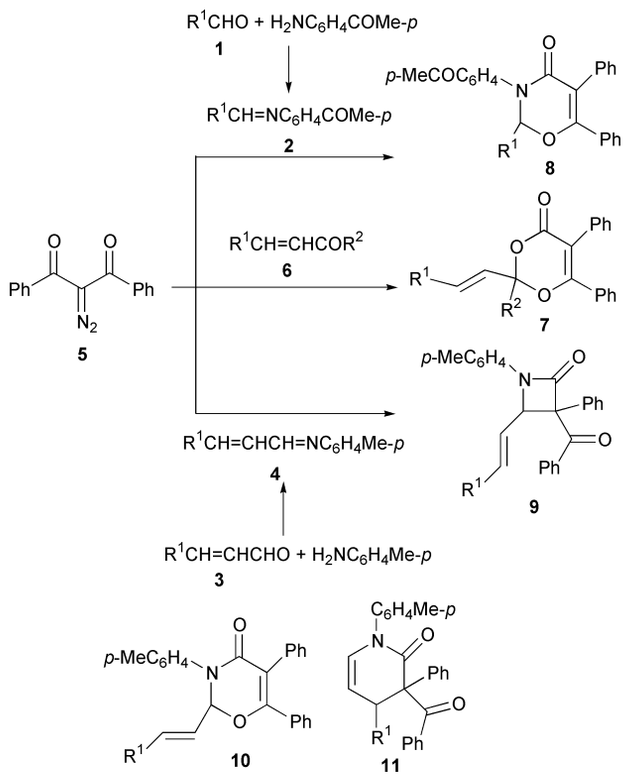
The acylketenes are highly reactive and useful synthons for the syntheses of oxygen-containing six-membered heterocyclic compounds.[1,2] They show a pronounced tendency to form [2 + 4] Diels–Alder adducts when trapped with dienophiles. They exhibit excellent and predictable regioselectivity, and as electron-deficient oxygen-containing dienes they participate preferentially as the 4π component in inverse (diene-LUMO-controlled) Diels–Alder reactions with electron-rich and/or dipolar dienophiles.[3–8] They are especially prone to undergo [2 + 4] cycloadditions with heterodienophiles, such as imines [3–6] or nitriles [7] for synthesis of 2,3-dihydro-4*H*-1,3-oxazin-4-one or 4*H*-1,3-oxazin-4-one derivatives, carbonyl groups for 4*H*-1,3-dioxin-4-one derivatives,[8,9] as well as electron-rich alkenes; or alkynes, for example, enamines [9] or enol ethers [10] for syntheses of 2,3-dihydropyran-4-one derivatives, alkoxyacetylenes [11] for synthesis of 1,4-pyrone derivatives. The acylketenes can also react with some heterocumulenes [12] such as carbodiimides and isocyanates, to yield 2,3-dihydro-1,3-oxazine derivatives.

α-Diazo-β-diketones, diacyldiazomethanes, are very important and suitable precursors for the generation of acylketenes *via* thermal, photolytic, or metal catalytic elimination of nitrogen accompanied by Wolff rearrangement.[1,2,13] The acylketenes are also generally generated *in situ* by flash vacuum pyrolysis of furan-2,3-diones.[14]

Recently we studied reactions of α-diazo-β-diketones with aldehydes and ketones,[8] and with imines in 1,5-benzodiazepines and 1,5-benzothiazepines.[5,6] In a continuation of this study, we investigate herein the chemoselectivity in reactions of α-diazo-β-diketones with α,β-unsaturated aldehydes and ketones, keto-imines, and α,β-unsaturated imines.

Results and discussion

α,β-Unsaturated aldehydes and ketones used in this study are commercially available. Keto-imines **2** were obtained from the reaction of *p*-aminoacetophenone and aromatic aldehydes **1** by dissolving them in benzene and azeotropically distilling for removal of water. α,β-Unsaturated imines **4a**,**b** were obtained from α,β-unsaturated aldehydes and *p*-toluidine. After equimolar amounts of α,β-unsaturated aldehydes **3** and *p*-toluidine were mixed in anhydrous diether ether, water separated from the resulting solution (visible at the bottom of the flask). After drying with anhydrous sodium sulfate and removal of solvent yellow unsaturated imines **2** were obtained (Scheme 1).



Scheme 1

First, our α-diazo-β-diketone, 2-diazo-1,3-diphenylpropane-1,3-dione **5**, reacted with α,β-unsaturated aldehydes and ketones **6**, substrates containing both C=O and C=C double bonds, in anhydrous toluene for 1–2 h to give colorless cycloadducts, 4*H*-1,3-dioxin-4-ones **7**, in yields of 49–99% (Table 1). The C=O double bond as dienophile participated in the cycloaddition due to the C=C double bond being electron deficient. α,β-Unsaturated aldehydes gave almost quantitative yields. Chalcone, with two phenyl groups, gave the lowest yield (49%). Secondly, α-diazo-β-diketone **5** reacted with keto-imines **2**, substrates containing both C=N and C=O double bonds,

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Table 1 Cycloadducts of 2-diazo-1,3-diphenylpropane-1,3-dione and compounds containing two double bonds

Cycloadduct	R^1	R^2	Yield (%)	Mp(°C)
7a	Ph	H	99	162–163
7b	Me	H	99	130–131
7c	Ph	Me	81	150–151
7d	Ph	Ph	49	144–145
7e	$[CH_2]_3$-		78	136–137
7f	H	Me	84	100–101
8a	Ph		85	178–179
8b	4-$O_2NC_6H_4$		82	218–220
8c	4-ClC_6H_4		76	182–184
8d	4-$MeOC_6H_4$		65	154–156
9a	Ph		45	172–173
9b	2-$MeOC_6H_4$		53	167–168

in the molar ratio 1.1 : 1 in anhydrous toluene for 1–2 h to give colorless cycloadducts, 4*H*-1,3-oxazin-4-ones **8**, in yields of 65–85%, and not 4*H*-1,3-dioxin-4-ones. Even when the molar ratio of compounds **5** : **2** was increased up to 2.2 : 1, no 4*H*-1,3-dioxin-4-one derivatives were found in the reaction mixture. We also attempted to force 4*H*-1,3-oxazin-4-ones **8** to react with α-diazo-β-diketone **5**, but still no 4*H*-1,3-dioxin-4-one derivatives were found in the reaction mixture. In a previous paper,[8] α-diazo-β-diketone **5** was shown to react with acetophenone to produce 2-methyl-2,5,6-triphenyl-4*H*-1,3-dioxin-4-one in a good yield. However, herein an excess of α-diazo-β-diketone **5** did not undergo cycloaddition with the carbonyl group in keto-imines. The reason could presumably be that α-diazo-β-diketone **5** prefers to react with C=N double bonds to yield stable adducts **8**. After 4*H*-1,3-oxazin-4-ones **8** had been formed, α-diazo-β-diketone **5** could not react with the C=O double bond in the product 4*H*-1,3-oxazin-4-ones **8** due to steric hindrance. Based on the results above, the reactivity of these double bonds with the α-diazo-β-diketone is C=N > C=O > C=C.

The reaction of α-diazo-β-diketone **5** and α,β-unsaturated imines **4**, substrates containing both C=N and C=C double bonds in conjugative form, was also carried out under the same reaction conditions. Only one set of colorless cycloadducts was obtained, in yields of 45–53%, without any by-product. The cycloadducts are 3-acyl-β-lactam derivatives **9**, and not 4*H*-1,3-oxazin-4-ones **10** or 3,4-dihydropyridin-2-ones **11**, based on their IR (1753–1751 cm^{-1} for C=O in β-lactam, 1672–1670 cm^{-1} for C=O in aromatic ketone) and ^{13}C NMR spectra (δ ≈162 for C=O in β-lactam, ≈ 194 for C=O in aromatic ketone).[15] Although both acylketene and α,β-unsaturated imine can serve as either a diene or dienophile in the Diels–Alder reaction,[2–12,16–18] no Diels–Alder reaction occurred under our reaction conditions when the reaction of α-diazo-β-diketone **5** and α,β-unsaturated imines **4** was attempted.

All cycloadducts described in the present study were fully characterized by ^1H NMR, MS and IR spectroscopy and elemental analyses. Cycloadducts **9** were also characterized by ^{13}C NMR spectroscopy.

In conclusion, chemoselectivity in reactions of an α-diazo-β-diketone, 2-diazo-1,3-diphenylpropane-1,3-dione, with some conjugative double-bond systems has been studied using α,β-unsaturated aldehydes and ketones, and keto-imines and α,β-unsaturated imines as two-double-bond systems. The results indicate that benzoyl(phenyl)ketene, which is generated by the thermal Wolff rearrangement of 2-diazo-1,3-diphenylpropane-1,3-dione, shows a pronounced tendency to form chemospecific [2 + 4] Diels–Alder adducts with the carbonyl group in α,β-unsaturated aldehydes and ketones, and with the imine group in keto-imines. The reactivity is C=N > C=O > C=C. However, benzoyl(phenyl)ketene reacts with α,β-unsaturated imines to produce chemospecific [2 + 2] cycloadducts, 3-acyl-4-vinyl-β-lactams.

Experimental

Mps were obtained on a Yanaco melting-point apparatus and are uncorrected. Elemental analyses were carried out on an Elementar Vario EL elemental analyzer. ^1H NMR spectra were recorded on a Varian Mercury 200 or a Varian Inova 300 spectrometer with $SiMe_4$ as internal standard in $CDCl_3$. ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer with $SiMe_4$ as internal standard in $CDCl_3$. IR spectra were taken on a Bruker Vector 22 FT-IR spectrophotometer for samples in KBr. Mass spectra were obtained on a VG ZAB-HS mass spectrometer. TLC separations were performed on silica gel G plates with petroleum ether (30–60 °C)–ethyl acetate (5 : 1) as developer, and the plates were visualized with UV light.

Synthesis of keto-imines

An aldehyde **1** (20 mmol) and *p*-aminoacetophenone (2.70 g, 20 mmol) were dissolved in anhydrous benzene (50 mL). The resulting solution was azeotropically refluxed for 3–5 h for removal of water. The solvent was evaporated off at reduced pressure, and the residue was crystallized from ethanol to give yellow crystals of the corresponding keto-imine **2**.

4-Acetyl-*N*-benzylideneaniline (PhCH=NC_6H_4COMe-4) 2a. Yellow crystals, yield 90%, mp 103–105 °C (lit.,[19] 99.5–100.5 °C).

4-Acetyl-*N*-(4-nitrobenzylidene)aniline (4-$NO_2C_6H_4$CH=NC_6H_4COMe-4) 2b. Yellow crystals, yield 95%, mp 146–147 °C (lit.,[20] 146 °C).

4-Acetyl-*N*-(4-chlorobenzylidene)aniline (4-ClC_6H_4CH=NC_6H_4COMe-4) 2c. Yellow crystals, yield 93%, mp 144–146 °C (lit.,[21] 145 °C).

4-Acetyl-*N*-(4-methoxybenzylidene)aniline (4-$MeOC_6H_4$CH=NC_6H_4COMe-4) 2d. Yellow crystals, yield 85%, mp 124–126 °C (lit.,[21] 124–125 °C).

Synthesis of α,β-unsaturated imines

An aldehyde **3** (20 mmol) and *p*-toluidine (2.14 g, 20 mmol) were dissolved in anhydrous diethyl ether (50 mL). The resulting mixture was stirred for 1 h and was dried over anhydrous sodium sulfate. The solvent was evaporated off at reduced pressure to give the corresponding yellow oil **4**.

***N*-Cinnamylidene-4-toluidine (PhCH=CHCH=NC_6H_4Me-4) 4a.** Yellow oil, yield 99% (becomes solid after storage in refrigerator for several days, mp 80–81 °C) (lit.,[22] mp 80–80.5 °C).

***N*-(2-Methoxycinnamylidene)-4-toluidine (2-$MeOC_6H_4$CH=CHCH=NC_6H_4Me-4) 4b.** Yellow oil, yield 99% (becomes solid after storage for several days, mp 54–56 °C); ^1H NMR (300 MHz; $CDCl_3$) δ 8.32–7.11 (9H, m, ArH and CH), 6.99 (1H, dd, *J* 7.5, 8.1 Hz, CH), 6.93 (1H, d, *J* 8.1 Hz, CH), 3.91 (3H, s, MeO), 2.37 (3H, s, Me); IR (KBr) ν (cm^{-1}) 3022.04, 2938.41, 2836.22, 1623.06, 1504.45, 1486.85, 1246.53; MS 251 (M^+) [Calc. for $C_{17}H_{17}NO$ (251.32): C, 81.24; H, 6.82; N, 5.57. Found: C, 81.00; H, 6.56; N, 5.37%].

Reaction of 2-diazo-1,3-diphenylpropane-1,3-dione 5 with α,β-unsaturated aldehydes and ketones, keto-imines, and α,β-unsaturated imines

General procedure. The substrate (α,β-unsaturated aldehyde or ketone **6**, keto-imine **2**, or α,β-unsaturated imine **4**) (1 mmol) and 2-diazo-1,3-diphenylpropane-1,3-dione **5** (0.275 g, 1.1 mmol) were dissolved in anhydrous toluene (10 mL). The resulting mixture was stirred for 1–2 h at 100 °C in an oil-bath, the

optimum reaction time being determined by TLC monitoring (silica gel). The solvent was evaporated off at reduced pressure, and the residue was crystallized from a mixture of petroleum ether and ethyl acetate or separated on a silica gel column with petroleum ether–ethyl acetate (5 : 1) as eluent to give colorless crystals of a product **7**, **8**, or **9**.

5,6-Diphenyl-2-styryl-4*H*-1,3-dioxin-4-one 7a. White solid; ^{1}H NMR (300 MHz; $CDCl_3$) δ 7.52–7.18 (15H, m, ArH), 7.11 (1H, d, J = 15.9 Hz, CH=), 6.48 (1H, dd, J 5.7, 15.9 Hz, CH), 6.37 (1H, d, J 5.7 Hz, CH); IR (KBr) ν (cm^{-1}) 1722; MS-FAB m/z 355 (MH^+, 26) [Calc. for $C_{24}H_{18}O_3$ (354.40): C, 81.34; H, 5.12. Found: C, 81.52; H, 5.34%].

5,6-Diphenyl-2-(prop-1-enyl)-4*H*-1,3-dioxin-4-one 7b. White solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36–7.15 (10H, m, ArH), 6.29 (1H, dt, J 22.5, 7.0 Hz, CH), 6.12 (1H, d, J 5.7 Hz, CH), 5.87 (1H, ddt, J 22.5, 5.7, 1.5 Hz, CH), 1.88 (3H, dd, J 1.5, 7.0 Hz, Me); IR (KBr) ν (cm^{-1}) 1717; MS-FAB m/z 293 (MH^+, 19) [Calc. for $C_{19}H_{16}O_3$ (292.33): C, 78.06; H, 5.52. Found: C, 78.32; H, 5.42%].

2-Methyl-5,6-diphenyl-2-styryl-4*H*-1,3-dioxin-4-one 7c. White solid; ^{1}H NMR (300 MHz; $CDCl_3$) δ 7.42–7.17 (15H, m, ArH), 6.98 (1H, d, J 16.2 Hz, CH), 6.43 (1H, d, J 16.2 Hz, CH), 2.00 (3H, s, Me); IR (KBr) ν (cm^{-1}) 1712; MS-FAB m/z 369 (MH^+, 24) [Calc. for $C_{25}H_{20}O_3$ (368.42): C, 81.50; H, 5.47. Found: C, 81.52; H, 5.33%].

2,5,6-Triphenyl-2-styryl-4*H*-1,3-dioxin-4-one 7d. White solid; ^{1}H NMR (300 MHz; $CDCl_3$) δ 7.75–7.02 (20H, m, ArH), 6.96 (1H, d, J 16 Hz, CH), 6.56 (1H, d, J 16 Hz, CH); IR (KBr) ν (cm^{-1}) 1728; MS-FAB m/z 431 (MH^+, 26) [Calc. for $C_{30}H_{22}O_3$ (430.49): C, 83.70; H, 5.15. Found: C, 87.52; H, 5.15%].

3,4-Diphenyl-1,5-dioxospiro[5.5]undeca-3,7-dien-2-one 7e. White solid; ^{1}H NMR (300 MHz; $CDCl_3$) δ 7.36–7.16 (10H, m, ArH), 6.30 (1H, d, J 10.8 Hz, CH=), 6.19 (1H, dt, J 10.8, 3.6 Hz, CH=), 2.46–2.30 (2H, m, CH_2), 2.27–2.20 (2H, m, CH_2), 2.02–1.95 (2H, m, CH_2); IR (KBr) ν (cm^{-1}) 1718; MS-FAB m/z 319 (MH^+, 34) [Calc. for $C_{21}H_{18}O_3$ (318.37): C, 79.22; H, 5.70. Found: C, 79.52; H, 5.58%].

2-Methyl-5,6-diphenyl-2-vinyl-4*H*-1,3-dioxin-4-one 7f. White solid; ^{1}H NMR (300 MHz; $CDCl_3$) δ 7.32–7.18 (10H, m, ArH), 6.13 (1H, dd, J 11.1, 17.4 Hz, CH), 5.68 (1H, d, J 17.4 Hz, H in CH_2), 5.49 (1H, d, J 11.1 Hz, H in CH_2), 1.89 (3H, s, Me); IR (KBr) ν (cm^{-1}) 1718; MS-FAB m/z 293 (MH^+, 29) [Calc. for $C_{19}H_{16}O_3$ (292.33): C, 78.06; H, 5.52. Found: C, 78.322; H, 5.42%].

3-(4-Acetylphenyl)-2,3-dihydro-2,5,6-triphenyl-4*H*-1,3-oxazin-4-one 8a. White solid; ^{1}H NMR (200 MHz; $CDCl_3$) δ 7.97–7.06 (19H, m, ArH), 6.92 (1H, s, CH), 2.58 (3H, s, CH_3); IR (KBr) ν (cm^{-1}) 1670; MS-FAB m/z 446 (MH^+, 38) [Calc. for $C_{30}H_{23}NO_3$ (445.51): C, 80.88; H, 5.20; N, 3.14. Found: C, 81.01; H, 5.06; N, 3.06%].

3-(4-Acetylphenyl)-2,3-dihydro-2-(4-nitrophenyl)-5,6-diphenyl-4*H*-1,3-oxazin-4-one 8b. White solid; ^{1}H NMR (200 MHz; $CDCl_3$) δ 8.35–7.06 (18H, m, ArH), 6.99 (1H, s, CH), 2.59 (3H, s, CH_3); IR (KBr) ν (cm^{-1}) 1673; MS-FAB m/z 491 (MH^+, 19) [Calc. for $C_{30}H_{22}N_2O_5$ (490.51): C, 73.46; H, 4.52; N, 5.71. Found: C, 73.13; H, 4.80; N, 5.58%].

3-(4-Acetylphenyl)-2-(4-chlorophenyl)-2,3-dihydro-5,6-diphenyl-4*H*-1,3-oxazin-4-one 8c. White solid; ^{1}H NMR (200 MHz; $CDCl_3$) δ 7.99–7.06 (18H, m, ArH), 6.89 (1H, s, CH), 2.59 (3H, s, CH_3); IR (KBr) ν (cm^{-1}) 1672; MS-FAB m/z 480 (MH^+, 24) [Calc. for $C_{30}H_{22}ClNO_3$ (479.95): C, 75.07; H, 4.64; N, 2.92. Found: C, 75.13; H, 4.82; N, 3.18%].

3-(4-Acetylphenyl)-2,3-dihydro-2-(4-methoxyphenyl)-5,6-diphenyl-4*H*-1,3-oxazin-4-one 8d. White solid; ^{1}H NMR (200 MHz; $CDCl_3$) δ 7.97–6.94 (18H, m, ArH), 6.87 (1H, s, CH), 3.84 (3H, s, OCH_3), 2.58 (3H, s, CH_3); IR (KBr) ν (cm^{-1}) 1671; MS-FAB m/z 476 (MH^+, 21) [Calc. for $C_{31}H_{25}NO_4$ (475.53): C, 78.30; H, 5.30; N, 2.95. Found: C, 78.08; H, 5.03; N, 2.74%].

3-Benzoyl-1-(4-methylphenyl)-3-phenyl-4-styrylazetidin-2-one 9a. White solid; ^{1}H NMR (300 MHz; $CDCl_3$) δ 8.00–7.09 (19H, m, ArH), 6.77 (1H, d, J 15.6 Hz, CH), 6.37 (1H, dd, J 8.4, 15.6 Hz, CH), 5.08 (1H, d, J 8.4 Hz, CH), 2.29 (3H, s, Me); ^{13}C NMR (400 MHz, $CDCl_3$) δ_C 194.1, 162.7, 136.7, 136.4, 136.3, 135.5, 134.6, 130.9, 130.5, 130.2, 129.9, 129.2, 129.0, 128.9, 128.5, 127.9, 127.2, 125.8, 118.1, 117.2, 78.8, 66.8, 23.1; IR (KBr) ν (cm^{-1}) 1753 (C=O in azetidinone), 1672 (C=O in PhCO); MS-FAB m/z 444 (MH^+, 21) [Calc. for $C_{31}H_{25}NO_2$ (443.54): C, 83.95; H, 5.68; N, 3.16. Found: C, 83.75; H, 5.79; N, 3.02%].

3-Benzoyl-1-(4-methylphenyl)-4-(4-methoxystyryl)-3-phenylazetidin-2-one 9b. White solid; ^{1}H NMR (300 MHz; $CDCl_3$) δ 7.98–6.82 (19H, m, ArH and CH), 6.32 (1H, dd, J 9.3, 16.2 Hz, CH), 5.16 (1H, J 9.3 Hz, CH), 3.80 (3H, s, OMe), 2.28 (3H, s, Me); ^{13}C NMR (400 MHz; $CDCl_3$) δ_C 194.3, 162.9, 157.3, 136.6, 136.3, 135.7, 134.4, 130.8, 130.5, 130.4, 130.0, 129.8, 129.7, 129.1, 128.6, 128.4, 127.8, 126.1, 125.4, 118.2, 117.9, 111.3, 78.5, 66.6, 55.9, 21.6; IR (KBr) ν (cm^{-1}) 1751 (C=O in azetidinone), 1670 (C=O in PhCO); MS-FAB m/z 474 (MH^+, 33) [Calc. for $C_{32}H_{27}NO_3$ (473.56): C, 81.16; H, 5.75; N, 2.96. Found: C, 81.00; H, 5.92; N, 3.06%].

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