Chemoselectivity in the Reaction of 2-Diazo-3-oxo-3-phenylpropanal with Aldehydes and Ketones

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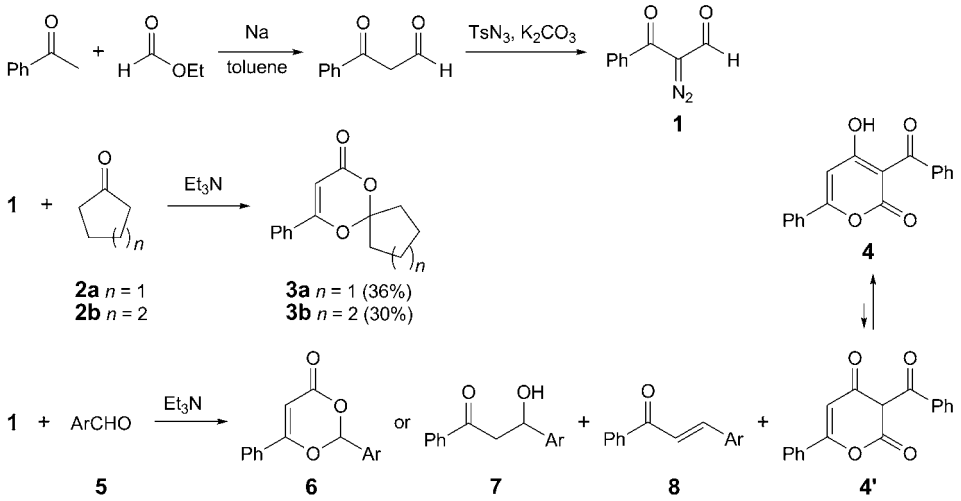
The chemoselectivity in the reaction of 2-diazo-3-oxo-3-phenylpropanal (**1**) with aldehydes and ketones in the presence of Et_3N was investigated. The results indicate that **1** reacts with aromatic aldehydes with weak electron-donating substituents and cyclic ketones under formation of 6-phenyl-4*H*-1,3-dioxin-4-one derivatives. However, it reacts with aromatic aldehydes with electron-withdrawing substituents to yield 1,3-diaryl-3-hydroxypropan-1-ones, accompanied by chalcone derivatives in some cases. It did not react with linear ketones, aliphatic aldehydes, and aromatic aldehydes with strong electron-donating substituents. A mechanism for the formation of 1,3-diaryl-3-hydroxypropan-1-ones and chalcone derivatives is proposed. We also tried to react **1** with other unsaturated compounds, including various olefins and nitriles, and cumulated unsaturated compounds, such as *N*,*N*′-dialkylcarbodiimines, phenyl isocyanate, isothiocyanate, and CS_2. Only with *N*,*N*′-dialkylcarbodiimines, the expected cycloaddition took place.

1. Introduction. – α-Diazo-β-dicarbonyl compounds react with various unsaturated bonds yielding different heterocyclic compounds [1–9]. Recently, we reported on the synthesis of a series of 2,3,6-trisubstituted 2*H*-1,3-oxazin-4(3*H*)-one derivatives in satisfactory-to-good yields by reaction of imines and 2-diazo-3-oxo-3-phenylpropanal (**1**) in the presence of the catalytic amount of Et_3N under mild conditions [9g][10]. The reaction is metal-free, mild, and highly regioselective. To extend the application of 2-diazo-3-oxo-3-phenylpropanal (**1**) to cycloaddition reactions with unsaturated compounds, we explored its reaction with aldehydes and ketones and found that the cycloaddition reaction shows a different chemoselectivity depending on the structural feature of aldehydes and ketones. The mechanism of the formation of 1,3-diaryl-3-hydroxypropan-1-ones and chalcone derivatives is also discussed.

2. Results and Discussion. – 2-Diazo-3-oxo-3-phenylpropanal (**1**) was previously prepared from 2-diazoacetophenone and the *Vilsmeier–Haack* reagent [9a], which was synthesized from DMF and $(COCl)_2$ [11]. However, the overall yield was low. The diazo transformation is a general method for the preparation of α-diazo-β-diketones and α-diazo-β-oxo alkanoates from the corresponding β-diketones and β-oxo alkanoates under basic conditions [2]. We attempted to synthesize 2-diazo-3-oxo-3-phenylpropanal (**1**) by this method. 3-Oxo-3-phenylpropanal was prepared from acetophenone and HCOOEt by *Claisen* condensation. It was converted to 2-diazo-3-

Scheme 1. *Reactions of 2-Diazo-3-oxo-3-phenylpropanal* (**1**) *with Ketones and Aldehydes*



oxo-3-phenylpropanal (**1**) by the treatment with TsN_3 in the presence of K_2CO_3 in a high yield (*Scheme 1*).

2-Diazo-3-oxo-3-phenylpropanal (**1**) was reacted with various ketones, however, only with cycloalkanones **2** (cyclopentanone (**2a**) and cyclohexanone (**2b**)), the corresponding spiro 6-phenyl-4*H*-1,3-dioxin-4-one derivatives **3a** and **3b** were formed in the presence of Et_3N (*Scheme 1*). On the other hand, aromatic ketones (acetophenone and benzophenone) and aliphatic linear ketones (acetone, heptan-2-one, and heptan-4-one) did not undergo the desired cycloaddition. Instead, the benzoylketene generated from **1** dimerized to 3-benzoyl-6-phenyl-2*H*-pyran-2,4(3*H*)-dione (**4′**), which tautomerized to give 3-benzoyl-4-hydroxy-6-phenyl-2*H*-pyran-2-one (**4**) [12].

The reaction of **1** with various aldehydes was attempted as well. No desired cycloaddition was observed with aliphatic aldehydes. However, diverse products were obtained with aromatic aldehydes **5**, depending on the electronic characters of the aromatic aldehydes (*Table*). We found that **1** reacted with aromatic aldehydes with weak electron-donating substituents to generate 6-phenyl-4*H*-1,3-dioxin-4-one derivatives **6**. However, it reacted with aromatic aldehydes with electron-withdrawing substituents to yield 1,3-diaryl-3-hydroxypropan-1-ones **7**, accompanied by chalcone derivatives **8** in some cases.

On the basis of the above results, we propose the mechanism of the chemoselective reaction of **1** with aromatic aldehydes as depicted in *Scheme 2*. Diazo compound **1** is converted in the presence of Et_3N to benzoylketene, which undergoes [4 + 2] or [2 + 2] cycloaddition chemoselectively with different aromatic aldehydes to give rise to 6-phenyl-4*H*-1,3-dioxin-4-one derivatives **6** or 3-benzoyl-β-lactones **9**, respectively. However, 3-benzoyl-β-lactones **9** are unstable under the reaction conditions and undergo elimination of CO_2 to afford chalcone derivatives **8**. Lactones **9** are hydrolyzed to β-oxo alkanoic acids **10** during workup, which undergo a decarboxylation to form 3-hydroxy-1-phenylalkan-1-ones **7**. The different cycloadditions result in the chemo-

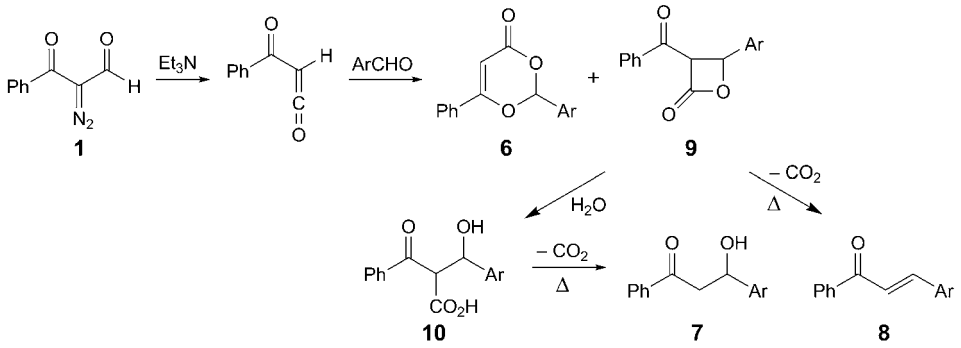
Table. *Reactions of 2-Diazo-3-oxo-3-phenylpropanal* (**1**) *with Aromatic Aldehydes*

Entry	ArCHO	Ar	Yield [%]			
			6	**7**	**8**	**4**
1	**5a**	4-MeO–C_6H_4	–	–	–	46
2	**5b**	4-Me_2N–C_6H_4	–	–	–	45
3	**5c**	4-Me–C_6H_4	80	–	–	n.d.[a])
4	**5d**	Ph	71	–	–	n.d.
5	**5e**	4-F–C_6H_4	21	–	–	37
6	**5f**	2-Cl–C_6H_4	–	10	14	36
7	**5g**	4-Cl–C_6H_4	–	11	–	44
8	**5h**	2,6-Cl_2–C_6H_3	–	10	–	40
9	**5i**	2-O_2N–C_6H_4	–	16	–	33
10	**5j**	4-O_2N–C_6H_4	–	27	–	35
11	**5k**	2-Cl-5-O_2N–C_6H_3	–	16	46	19
12	**5l**	Pyridin-4-yl	–	19	33	20

[a]) n.d. = Not determined.

selective formation of various products in the reaction. However, it is not completely clear so far why different aromatic aldehydes undergo [4 + 2] or [2 + 2] cycloaddition chemoselectively with benzoylketene.

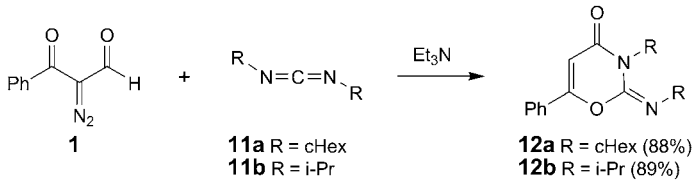
Scheme 2. *Proposed Reaction Mechanism of the Chemoselective Reaction of 2-Diazo-3-oxo-3-phenylpropanal* (**1a**) *and Aromatic Aldehydes*



To investigate the generality of the cycloaddition of **1** and other unsaturated compounds, we attempted to react **1** with olefins (such as styrene, cyclohexene, 1-phenylpropene, cyclopenadiene, 1,1-dichloroethene, vinyl acetate, and butyl vinyl ether) and nitriles (including benzonitrile, 2-chlorobenzonitrile, acetonitrile, and ethyl cyanoacetate). In all cases, no desired reaction occurred, only 3-benzoyl-6-phenyl-2*H*-pyran-2,4(3*H*)-dione, dimer of benzoylketene, was obtained in each of the reactions. The reaction of **1** with cumulated unsaturated compounds, including *N*,*N*′-dicyclohexylcarbodiimide (DCC; **11a**), *N*,*N*′-diisopropylcarbodiimide (DIC; **11b**), phenyl isocyanate, phenyl isothiocyanate, and CS_2, was also attempted. With **11a** and **11b**, the desired cycloadducts, 3-cyclohexyl-2-(cyclohexylimino)-6-phenyl-2*H*-1,3-oxazin-

4(3*H*)-one (**12a**) and 3-isopropyl-2-(isopropylimino)-6-phenyl-2*H*-1,3-oxazin-4(3*H*)-one (**12b**), respectively, were formed (*Scheme 3*). However, no desired reaction occurred with phenyl isocyanate, phenyl isothiocyanate, and CS_2.

Scheme 3. *Reaction of 2-Diazo-3-oxo-3-phenylpropanal* (**1**) *and* N,N′*-Dialkylcarbodiimides*



3. Conclusions. – The chemoselectivity of the reaction of 2-diazo-3-oxo-3-phenylpropanal (**1**) with aldehydes and ketones in the presence of Et_3N was investigated. The results indicate that 2-diazo-3-oxo-3-phenylpropanal (**1**) reacted with aromatic aldehydes with weak electron-donating substituents and cyclic ketones to generate 6-phenyl-4*H*-1,3-dioxin-4-one derivatives. With aromatic aldehydes with electron-withdrawing substituents, however, **1** furnished 1,3-diaryl-3-hydroxypropan-1-ones, accompanied by chalcone derivatives in some cases. For linear aliphatic and aromatic ketones, aliphatic aldehydes, and aromatic aldehydes with strong electron-donating substituents, no cycloaddition reaction was observed. A mechanism of the formation of 1,3-diaryl-3-hydroxypropan-1-ones and chalcone derivatives has been proposed (*Scheme 2*). 2-Diazo-3-oxo-3-phenylpropanal (**1**) was also attempted to react with other unsaturated compounds, such as different olefins and nitriles, and cumulated unsaturated compounds, including *N*,*N*′-dialkylcarbodiimides, phenyl isocyanate, phenyl isothiocyanate, and CS_2. Only *N*,*N*′-dialkylcarbodiimides undergo the expected cycloaddition reaction.

Experimental Part

General. Column chromatography (CC): silica gel (200–300 mesh) with petroleum ether (PE) and AcOEt as the eluent. M.p.: *Yanaco MP-500*; uncorrected. IR Spectra: *Nicolet Avatar 330* FT-IR spectrometer; in KBr; $\tilde{\nu}$ in cm^{-1}. ^1H- and ^{13}C-NMR spectra: *Bruker AV 400* at 400 MHz in $CDCl_3$; δ in ppm rel. to Me_4Si as internal standard, *J* in Hz. HR-ESI-MS: *LC/MSD TOF* mass spectrometer; in *m*/*z*.

Reaction of 2-Diazo-3-oxo-3-phenylpropanal (**1**) *with Unsaturated Compounds in the Presence of Et₃N: General Procedure.* To a soln. of **1** (87 mg, 0.5 mmol) and an aldehyde, ketone, or carbodiimide (0.5 mmol) in CH_2Cl_2 (1 ml) was added a drop of Et_3N (30 mg, 0.3 mmol) under stirring in an ice-water bath or at r.t. N_2 was liberated immediately, and TLC monitoring indicated that the reaction was complete. After stirring for 2 to 5 s, the residue was separated by CC (AcOEt/PE(60–90°) 1:10 to 1:20) to afford product(s).

9-Phenyl-6,10-dioxaspiro[4.5]dec-8-en-7-one (**3a**). Colorless oil. M.p. 54–56° ([13]). Yield: 42 mg (36%). IR: 1722 (C=O). ^1H-NMR: 1.51–2.31 (*m*, 4 CH_2); 5.93 (*s*, CH); 7.47–7.50 (*m*, 2 arom. H); 7.55 (*m*, arom. H); 7.71–7.73 (*m*, 2 arom. H). ^{13}C-NMR: 18.4; 23.2; 36.7; 58.5; 67.3; 71.0; 88.4; 92.3; 116.3; 126.4; 128.9; 132.2.

4-Phenyl-1,5-dioxaspiro[5.5]undec-3-en-2-one (**3b**). Colorless oil. M.p. 54–55° ([13]). Yield: 37 mg (30%). IR: 1721 (C=O). ^1H-NMR: 1.49–3.51 (*m*, 5 CH_2); 5.91 (*s*, CH); 7.47–7.55 (*m*, 2 arom. H); 7.56

(*m*, arom. H); 7.74 – 7.76 (*m*, 2 arom. H). ^{13}C-NMR: 22.5; 24.7; 33.8; 91.5; 107.3; 126.4; 128.9; 132.1; 162.0; 164.6.

*3-Benzoyl-4-hydroxy-6-phenyl-2*H-*pyran-2-one* (**4**). Yellow crystals. M.p. 169 – 170° ([12b]: 169 – 170°). Yield: 67 mg (46%). ^{1}H-NMR: 6.66 (*s*, CH); 7.43 – 7.92 (*m*, 10 arom. H); 15.94 (*s*, C=COH).

*2-(4-Methylphenyl)-6-phenyl-4*H-*1,3-dioxin-4-one* (**6c**). Yield: 106 mg (80%). Colorless crystals. M.p. 109 – 110°. IR: 1724 (C=O). ^{1}H-NMR: 2.45 (*s*, Me); 6.09 (*s*, C=CH); 6.56 (*s*, CH); 7.31 – 7.79 (*m*, 9 arom. H). ^{13}C-NMR: 21.4; 93.2; 100.5; 126.7; 128.9; 129.4; 130.2; 130.9; 132.5; 140.6; 163.2; 168.3. HR-ESI-MS: 267.1014 ($[M+H]^+$, $C_{17}H_{15}O_3^+$; calc. 267.1016).

*2,6-Diphenyl-4*H-*1,3-dioxin-4-one* (**6d**). Yield: 90 mg(71%). Colorless crystals. M.p. 103 – 105° ([13]: 103 – 105°). IR: 1680 (C=O). ^{1}H-NMR: 6.11 (*s*, C=CH); 6.60 (*s*, CH); 7.47 – 7.81 (*m*, 10 arom. H). ^{13}C-NMR: 93.3; 100.4; 126.7; 126.7; 128.7; 129.0; 130.5; 132.6; 163.0; 168.2.

*2-(4-Fluorophenyl)-6-phenyl-4*H-*1,3-dioxin-4-one* (**6e**). Yield: 28 mg (21%). Colorless crystals. M.p. 152 – 153°. IR: 1733 (C=O). ^{1}H-NMR: 6.08 (*s*, C=CH); 6.55 (*s*, CH); 7.16 – 7.77 (*m*, 9 arom. H). ^{13}C-NMR: 93.3; 99.7; 115.7; 116.0; 126.7; 128.8; 128.9; 129.0; 132.6; 162.8; 168.2; 172.1. HR-ESI-MS: 271.0771 ($[M+H]^+$, $C_{16}H_{12}FO_3^+$; calc. 271.0765).

3-(2-Chlorophenyl)-3-hydroxy-1-phenylpropan-1-one (**7f**). Yield: 13 mg(10%). Colorless crystals. M.p.: 78 – 80° ([14]: 80°). IR: 1677 (C=O), 3466 (OH). ^{1}H-NMR: 3.18 (*dd*, $J = 9.6, 17.6$, 1 H of CH_2); 3.59 (*dd*, $J = 2.4, 17.6$, 1 H of CH_2); 3.87 (*s*, OH); 5.72 (*dd*, $J = 2.4, 9.6$, CH); 7.25 – 8.00 (*m*, 9 arom. H). ^{13}C-NMR: 45.4; 66.9; 127.3; 128.2; 128.6; 128.8; 129.4; 131.2; 133.8; 136.5; 140.4; 200.3.

3-(4-Chlorophenyl)-3-hydroxy-1-phenylpropan-1-one (**7g**). Yield: 15 mg (11%). Colorless crystals. M.p. 99 – 100° ([15]: 99.4 – 100.4°). IR (KBr): 1724 (C=O), 3446 (OH). ^{1}H-NMR: 3.37 (*dd*, $J = 2.8, 17.2$, 1 H of CH_2); 4.04 (*dd*, $J = 9.6, 17.2$, 1 H of CH_2); 3.92 (*s*, OH); 6.19 (*dd*, $J = 2.8, 9.6$, CH); 7.45 – 8.00 (*m*, 8 arom. H). ^{13}C-NMR: 44.8; 66.5; 123.1; 123.4; 128.2; 128.9; 130.3; 134.1; 142.6; 199.6.

3-(2,6-Dichlorophenyl)-3-hydroxy-1-phenylpropan-1-one (**7h**). Yield: 15 mg (10%). Colorless crystals. M.p. 150 – 151°. IR: 1643 (C=O), 3243 (OH). ^{1}H-NMR: 7.71 (*d*, $J = 18.8$, ArCH); 7.66 (*d*, $J = 18.8$, COCH); 7.47 – 7.65 (*m*, 5 arom. H); 8.02 – 8.70 (*m*, 4 arom. H). HR-ESI-MS: 295.0288 ($[M+H]^+$, $C_{15}H_{13}Cl_2O_2^+$; calc. 295.0287).

3-Hydroxy-3-(2-nitrophenyl)-1-phenylpropan-1-one (**7i**). Yield: 22 mg (16%). Colorless crystals. M.p. 106 – 107° ([16]: 106 – 107°). IR: 1678 (C=O), 3509 (OH). ^{1}H-NMR: 3.21 (*dd*, $J = 9.2, 17.6$, 1 H of CH_2); 3.74 (*dd*, $J = 2.0, 17.6$, 1 H of CH_2); 4.01 (*s*, OH); 5.88 (*dd*, $J = 2.0, 9.2$, CH); 7.45 – 8.00 (*m*, 9 arom. H). ^{13}C-NMR: 45.4; 66.9; 127.3; 128.2; 128.6; 128.8; 129.4; 131.2; 133.8; 136.5; 140.4; 200.3.

3-Hydroxy-3-(4-nitrophenyl)-1-phenylpropan-1-one (**7j**). Yield: 37 mg (27%). Colorless crystals. M.p. 113 – 114° ([15]: 114 – 114.7°). IR: 1670 (C=O), 3499 (OH). ^{1}H-NMR: 3.38 (*dd*, $J = 9.6, 17.6$, 1 H of CH_2); 3.58 (*dd*, $J = 4.0, 17.6$, 1 H of CH_2); 3.90 (*s*, OH); 5.71 (*dd*, $J = 4.0, 9.6$, CH); 7.48 – 8.26 (*m*, 8 arom. H). ^{13}C-NMR: 47.0; 69.2; 123.8; 126.6; 128.2; 134.0; 136.2; 147.4; 150.3; 199.5.

3-(2-Chloro-5-nitrophenyl)-3-hydroxy-1-phenylpropan-1-one (**7k**). Yield: 25 mg (16%). Colorless crystals. M.p. 120 – 122°. IR: 1681 (C=O), 3466 (OH). ^{1}H-NMR: 3.17 (*dd*, $J = 9.6, 17.6$, 1 H of CH_2); 3.58 (*dd*, $J = 2.0, 17.6$, 1 H of CH_2); 4.01 (*s*, OH); 5.71 (*dd*, $J = 2.0, 9.6$, CH); 7.26 – 8.64 (*m*, 8 arom. H). ^{13}C-NMR: 42.8; 67.7; 128.3; 128.7; 129.32; 129.5; 133.6; 134.8; 136.3; 136.6; 198.9. HR-ESI-MS: 306.0528 ($[M+H]^+$, $C_{15}H_{13}ClNO_4^+$; calc. 306.0528).

3-Hydroxy-1-phenyl-3-(pyridin-4-yl)propan-1-one (**7l**) [17]. Yield: 22 mg (19%). Colorless oil. ^{1}H-NMR: 3.35 (*d*, $J = 6.0$, CH_2); 4.21 (*s*, OH); 5.36 (*t*, $J = 6.0$, CH); 7.37 (*d*, $J = 6.0$, 2 arom. H); 7.47 (*t*, $J = 7.6$, 2 arom. H); 7.60 (*t*, $J = 7.2$, arom. H); 7.95 (*dd*, $J = 7.2, 1.2$, 2 arom. H); 8.57 (*dd*, $J = 1.2, 4.4$, 2 arom. H). ^{13}C-NMR: 46.7; 68.6; 120.6; 128.1; 128.7; 133.7; 136.3; 149.7; 152.0; 199.4.

*(2*E*)-3-(2-Chlorophenyl)-1-phenylprop-2-en-1-one* (**8f**) [18]. Yield: 17 mg (14%). Colorless oil. M.p. 50 – 52°. IR: 1663 (C=O). ^{1}H-NMR: 8.21 (*d*, $J = 16.0$, ArCH); 7.52 (*d*, $J = 16.0$, COCH); 7.34 – 8.06 (*m*, 9 arom. H).

*(2*E*)-3-(2-Chloro-5-nitrophenyl)-1-phenylprop-2-en-1-one* (**8k**). Yield: 66 mg (46%). Colorless crystals. M.p. 152 – 155° ([19]: 151 – 152°). IR: 1670 (C=O). ^{1}H-NMR: 8.18 (*d*, $J = 17.2$, ArCH); 7.70 (*d*, $J = 17.2$, COCH); 7.65 – 8.65 (*m*, 8 arom. H).

*(2*E*)-1-Phenyl-3-(pyridin-4-yl)prop-2-en-1-one* (**8l**). Yield: 35 mg (33%). Colorless crystals. M.p. 74 – 75° ([20]: 73 – 74.5°). IR: 1667 (C=O). ^{1}H-NMR: 7.71 (*d*, $J = 18.8$, ArCH); 7.66 (*d*, $J = 18.8$, COCH);

7.47 – 7.65 (*m*, 5 arom. H); 8.02 – 8.70 (*m*, 4 arom. H). ^{13}C-NMR: 122.0; 125.9; 128.5; 128.6; 133.1; 137.2; 141.3; 141.9; 150.4; 189.6.

*3-Cyclohexyl-2-(cyclohexylimino)-6-phenyl-2,3-dihydro-4*H-*1,3-oxazin-4-one* (**12a**). Yield: 155 mg (88%). Colorless crystals. M.p. 123 – 125° ([21]: 119 – 120°). IR: 1670 (C=O). ^{1}H-NMR: 1.24 – 2.63 (*m*, 10 CH_2); 3.85 (*m*, CHN); 4.77 (*m*, CHN); 6.08 (*s*, CH); 7.48 – 7.54 (*m*, 3 arom. H); 7.70 – 7.73 (*m*, arom. H). ^{13}C-NMR: 22.4; 25.5; 26.1; 26.4; 28.0; 33.9; 53.6; 54.5; 97.1; 125.6; 129.0; 131.6; 159.5; 162.1.

*2,3-Dihydro-3-(1-methylethyl)-2-[(1-methylethyl)imino]-6-phenyl-4*H-*1,3-oxazin-4-one* (**12b**). Yield: 122 mg (89%). Colorless crystals. M.p. 47 – 48°. IR: 1670 (C=O). ^{1}H-NMR: 1.21 (*d*, $J = 6.4$, NCH*Me*$_2$); 1.48 (*d*, $J = 6.4$, NCH*Me*$_2$); 4.12 (*sept.*, $J = 6.4$, NC*H*Me$_2$); 5.15 (*sept.*, $J = 6.4$, NC*H*Me$_2$); 6.05 (*s*, CH); 7.45 – 7.71 (*m*, 5 arom. H). HR-ESI-MS: 272.1525 ($[M+H]^+$, $C_{16}H_{20}N_2O_2^+$; calc. 272.1525).

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