25. ^{17}O-NMR Spectra of Mesoionic Compounds: The Polarized Carbonyl Group

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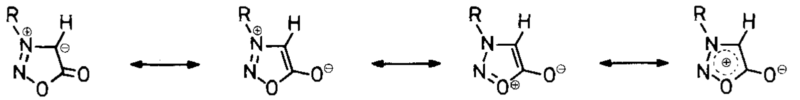
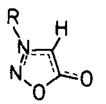
The ^{17}O-NMR spectra of 5 mesoionic compounds have been measured; in two cases, the peak attribution between endo- and exocyclic O-atoms has been made unambiguous by synthesizing specifically O-labelled samples. The signal of the exocyclic O-atom appears at particularly high field, closer to the values of enolate than of carbonyl O-atoms. The cyclic O-atom resonates close to values of furans (or isoxazol, if bound to N). The exocyclic O-atom is much more susceptible to structure and substituent variations than the endocyclic, an observation which is in favour of a chain-conjugated (non-aromatic) structure **1E**.

Introduction. – Mesoionic compounds, *e.g.* sydnones **1** [1], cannot be characterized by any single covalent formula, but are represented as resonance hybrids of several di-(and tetra-)polar formulae (**1A–C** and others) [2]. As a consequence, the carbonyl group of **1** is presented as intermediate between that of a lactone (see **1A**) and an enolate (see **1B**). Mesoionic compounds are often considered as dipolar aromatics, as symbolized by **1D**. Aromaticity has, however, never been unambiguously demonstrated, though the existence of electrophilic substitution reactions [2], the UV spectra, the ^{1}H-NMR signal (δ *ca.* 6.8 ppm [3]) of the ring proton and the magnetic susceptibility [4] have been interpreted in this sense. On the other hand, the IR vibrations (1740–1760 cm^{-1} [2]) and X-ray determined bond length (1.218 Å [5]) are close to the values expected for a true C=O double bond. Furthermore, the same X-ray structure determinations indicate a particularly long C(5)–O(1) distance, significantly longer than in furans; as a consequence, the displacement of π and p electrons has been considered to be restricted as shown in **1E**, excluding a true aromatic ring current, a formulation first proposed on the basis of ESCA spectra combined with MO calculations [6].

We have shown earlier [7] that the chemical-shift values of ^{17}O-NMR give a good indication of the electron density around O-atoms, distinguishing clearly between doubly



1A **1B** **1C** **1D**

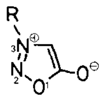


1E

bonded (=O) and singly (–O–) bonded O-atoms and allowing for intermediate, resonance-determined situations, in which the =O attracts π-electron density from a donator group. For instance, carbonyl O-atoms show $\delta_O = 550–580$ ppm in aldehydes and ketones, 360 ppm in carboxylic esters, and 300 ppm in carboxamides [8]; in the highly polarized cyclopropenones, δ_O is found at *ca.* 240 ppm [9]. Singly bonded O-atoms as in alcohols and ethers resonate at still higher field, δ_O *ca.* -50 to $+100$ ppm, δ_O values can be easily measured to within ±0.5 ppm [8].

Kintzinger and *Nguyen* [10] in this laboratory, and *Tanaka* and *Yokoi* [11] have, independently, applied the tool of ^{17}O-NMR spectroscopy to the problem of bonding in sydnones. They found two signals for *N*-methylsydnone (**1b**, R = Me) at 387 and 232 ppm. Both groups assigned the higher-field resonance to the exocyclic ('carbonyl') O-atom, essentially on the basis of the argument that qualitative valence-bond-type considerations as well as MO calculations [12] indicate that the exocyclic O presents the higher electron density and, thus, better shielding. It is this same signal which is most affected by complexation with lanthanide type shift reagents [10] and by H-bond formation [11][1]).

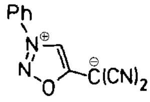
This assignment is, however, in contradiction with the general experience [7] that =O resonates at lower field than –O–. In view of the importance for the interpretation of the bonding state in mesoionic compounds, a strict attribution of the signals appears necessary. This could, in principle, be furnished by a mesoionic compound containing one O-atom only. *Stefaniak et al.* [13] have measured the ^{17}O-NMR spectrum of *N*-methylsydnon-imine hydrochloride (**2c**, X=Cl). The value reported, δ_O 590 ppm, however, is too


1a 388 244 ppm
b 387' 232 ppm

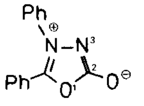
1a R = Ph
b R = Me


2a 348 ppm
b 350 ppm

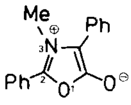
2a R = Ph, R' = H
b R = Me, R' = i-Pr
c R = Me, R' = H


339 ppm

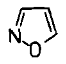
3


266 181 ppm

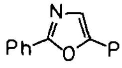
4


278 191 ppm

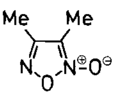
5


350 ppm

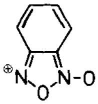
8


247 ppm

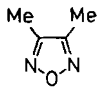
9


475 350 ppm

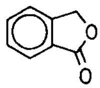
6


490 380 ppm

7


460 ppm

10


168 ppm
325 ppm

11

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[1]) The value of the nuclear quadrupole coupling constants can be interpreted in the same sense [10].

different from both δ_O values of **1b** to be useful for signal attribution; furthermore, it is practically out of the range of δ_O values for C-bound O-atoms; so it seems to need confirmation.

In order to assess the signal attribution for sydnones **1**, we have 1) synthesized and measured specifically labelled **1a** (R = Ph) and 2) measured mesoionic compounds containing only one O-atom. Furthermore, we have determined the influence of the ring N-atoms in mesoionic compounds by comparing with different heterocycles, including specifically labelled **5** and furans.

Results. – *^{17}O-Labelling of* **1a**. Many carbonyl compounds exchange their O-atom with water by a mechanism of nucleophilic addition plus elimination [14]. It is known [2] that sydnones can undergo nucleophilic attacks on C(5), mostly followed by ring opening. When we heated **1a** in $H_2[^{17}O]$ in the presence of *ca.* 0.01N H_2SO_4 for 2 days at 40°, recovered **1a** contained no tracer; clearly $k_{\text{ring opening}} > k_{\text{elimination}}$.

To synthesize specifically labelled **1a**, we applied its normal synthesis using (nitroso-labelled) *N*-nitroso-*N*-phenylglycine; as *N*-nitroso compounds exchange their O-atom only very sluggishly [15], nitrosation has to be done with labelled HNO_2. In order to avoid the preparation and isolation of $HN[^{17}O_2]$ in a separate step, we decided to chose nitrosation conditions in which the O-exchange of a nitrosating agent with water, *via* its attack on the nucleophile H_2O, is more rapid than its attack on a (more nucleophilic) amine. This is the case if one choses an agressive, little discriminating reagent: as water molecules are far more abundant than amine in aqueous solution, the exchange reaction prevails; furthermore, at low pH, most of the amine is present in the form of unreactive ammonium ion. It is known that among the nitrosating species, the $H_2NO_2^+$ ion, present at low pH, and NOCl, formed in the presence of Cl^-, are much more agressive than N_2O_3, prevalent at pH *ca.* 4. For $H_2NO_2^+$, we can apply the rate laws established for the reactions with water [16] and with *N*-phenylglycine [17], respectively[2]):

$$v_{\text{exchange}} = 230\,[H^+][HNO_2]$$
$$v_{\text{nitrosation}} = ca.\ 100\,[PhNHCH_2COOH][H^+][HNO_2]$$

Under the conditions chosen ($[H^+] = 2$N; $[HNO_2] = 0.9$M; $[PhNHCH_2COOH$ (stoich.)$] = 1.3$M), one can estimate that $v_{\text{exchange}}/v_{\text{nitrosation}} \approx 2 \cdot 10^5$, which means complete incorporation of tracer[3]). Nitrosating in aqueous HCl solution containing 1.38% of ^{17}O (enrichment 37-fold) and 10% of ^{18}O, and cyclising the isolated labelled *N*-nitroso compound (see *Scheme 1*), we obtained [1-^{17}O]-**1a** in which the tracer incorporation had taken place at ≥ 99% (evaluation by MS on the peak $M^{+\cdot} + 2$, less submitted to noise than $M^{+\cdot} + 1$).

From the way of formation, it is clear that the nitroso O-atom can persist only in the ring position O(1) of **1a**; the presence of tracer proves at the same time that the path of cyclisation is nucleophilic attack of the nitroso O-atom on the carboxyl C (as opposite to the *a priori* less probable attack of carbonyl O on nitroso N).

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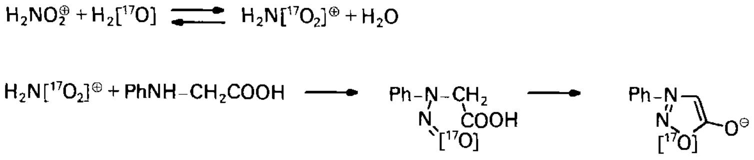
[2]) The 3rd-order rate constant has been estimated from known values for aromatic amines [18]; for details, see [19].

[3]) The nitrosating species NOCl is as little discriminating as $H_2NO_2^+$ [17]. On the other hand, at pH *ca.* 4, *i.e.* with N_2O_3 as nitrosating species, the strong discrimination by the weak electrophile would play in disfavour of exchange: $v_{\text{exchange}}/v_{\text{nitrosation}} \approx 4 \cdot 10^{-4}$.

Scheme 1



[1-¹⁷O]-**1a**

The *¹⁷O-NMR spectrum* showed two signals for **1a**, at 388 and 242 ppm, very close to those of **1b** (387 and 232 ppm [10]). In [1-¹⁷O]-**1a**, the signal at 388 ppm was greatly enhanced, proving that it belongs to the ring O-atom; this confirms the earlier, more intuitive attribution [10] [11] of the higher shielding to the carbonyl O-atom (see *Table*).

¹⁷O-NMR Spectra of Other Mesoionic Compounds. As a second way to identify the signals of **1**, we chose mesoionic compounds containing only one O-atom. The sydnon-imines **2a,b** [20] (in aqueous solution) showed signals at 350 and 348 ppm, resp., reasonably close to the ring O of **1a** (at 388 ppm). The δ_O value reported earlier for sydnon-imine **2c** (590 ppm [13]) is very different; we doubt the identity and/or purity of the substrate[4]. For confirmation, we chose the mesoionic compound **3** [21], in which the negative charge can be formulated on the exocyclic C-atom: we found δ_O 339 ppm, in good agreement with **2a,b**.

In order to test the variability of the mesoionic ¹⁷O-NMR signals, including the influence of N(2) on the ring O(1) atom, we measured the isosydnone **4** [22], which showed δ_O 266 and 181 ppm, and the oxazole derivative **5** (a 'Münchnon' [23]), δ_O 278 and 191 ppm. As the position of the signals does not allow an unambiguous attribution, we

Table. *¹⁷O-NMR Data of Mesoionic Compounds.* δ_O in ppm from H_2O (= 0 ppm); in parentheses: line width in Hz.

Compound	O(1) δ_O (line width)	Exocyclic O-atom δ_O (line width)	Ref.
1a	388 (370)	244 (250)	[a]
[1-¹⁷O]-**1a**	388 (260)	242	[a]
1b	387 (330)	232 (150)	[10]
	389	234	[11]
2a	348 (310)	–	[b]
2b	350 (350)	–	[b]
3	339 (360)	–	[c]
4	266 (430)	181 (390)	[c]
5	278 (1000)	191 (580)	[d]
[1-¹⁷O]-**5**	278 (850)		[d]
6	475 (700)	350 (700)	[7]
7	490	380	[24]
8	350 (90)	–	[26]
9	247 (900)	–	[e]
10	460 (700)	–	[7]
Furan	228		[27]

[a] In C_6D_6 at 85°. [b] In $H_2{}^{16}O$ at 80°. [c] In CH_3CN at 80°. [d] In $CDCl_3$ at 72°. [e] In CCl_4 at r.t. (result of Dr. *V. Toan*).

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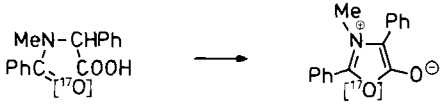
[4] The authors report an extremely broad peak, covering more than one third of the spectral window. The starting material for (and decomposition product of) **2c**, a *N*-nitroso compound, resonates at *ca.* 700 ppm [13].

Scheme 2



[1-^{17}O]-**5**

prepared specifically labelled [1-^{17}O]-**5** by cyclizing, by the method of *Huisgen et al.* [23], *N*-[^{17}O]benzoyl-*N*-methyl-2-phenylglycin (^{17}O *ca.* 1%, see *Scheme 2*). By this reaction the tracer is confined to the O(1) position of **5**. In the ^{17}O-NMR spectrum, the peak at 278 ppm was enhanced, proving that the ring O-atom in **5** resonates at lower field than the carbonyl O. Because of close structural analogy, we admit that this is the case for **4**, too. Again, the subsistence of tracer in **5** furnishes a proof for the reaction path of cyclisation. In **4** and **5**, the exocyclic O-atoms appear at even higher field (181 and 191 ppm, resp.) than in **1a,b** (244, 232 ppm).

Discussion. – *Furoxans.* A further group of mesoionic compounds are the furoxans (furazan oxides), in which the exocyclic O-atom is bound to N instead of C; compounds **6** and **7**, measured earlier [7] [24], show δ_O at 475, 350 and 490, 380 ppm, respectively. Comparing naïvely with ordinary carbonyl compounds, the low-field signal had been attributed to the exocyclic O-atom. On the basis of the results with other mesoionic compounds, we can now assume that the N^+–O^- is the one resonating at higher field (350 and 380 ppm, resp.). An experimental verification by labelling is not feasible because of rapid tautomeric interchange of the two O-atoms[5]; the attribution is, however, corroborated by a comparison with pyridine *N*-oxides, showing for N^+–O^- a δ_O of *ca.* 350 ppm [25], as well as by considerations concerning the ring O-atom (see below).

The Ring O-Atom. The endocyclic O(1) appears at lower field when it is bound to N (**1**–**3**, δ_O *ca.* 370 ppm) rather than to C only (**4**, **5**, δ_O *ca.* 270 ppm). This deshielding is not an effect specific to mesoionic compounds nor to heterocycles at all: it reappears in the difference between isoxazole **8** (δ_O 350 ppm [26]) and furan (δ_O 228 ppm [27]) as well as in that between *O*-methylhydroxylamine (δ_O +35 ppm [7]) and dimethyl ether (δ_O −52 ppm [28]). In the furoxans **6** and **7**, O(1) is deshielded by the influence of two N-atoms, and the shift difference $\Delta\delta_O$ is doubled yielding δ_O 475 ppm [7] and 490 ppm, respectively [24], confirming the attribution of the lower-field resonance to O(1).

The charge character has only a slight influence on the δ_O value of the ring O-atom: comparisons of **4** and **5** (δ_O 266 and 278 ppm, resp.) with the oxazole **9** (247 ppm), or of the sydnones **1**–**3** (388, 348 and 339 ppm, resp.) with isoxazole **8** (350 ppm) show only minor differences. The same is true for the low-field resonance of the furoxans **6**, **7** (475 and 490 ppm, resp.) as compared with the furazan **10** (460 ppm [7]), thus confirming the assignment of the resonance of O(1) in **6**.

An N-atom in the β-position also has only a small influence on the δ_O value of O(1), as shown by a comparison of the oxazole **9** (247 ppm) and furan (228 ppm), as well as of **4** (266 ppm) and **5** (278 ppm); smallness of influence on O(1) is equally found for the character of the exocyclic group (O, N, or C in **1**, **2**, or **3**, resp.), as well as for the substituents on N(3) (see **1a** and **1b**). This brings all these O-heterocycles into comparison with furans. Indeed, it has been stated that the furan O-atom is rather insensitive to ring

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[5] This exchange is, however, slow on the NMR time scale.

substituents: δ_O 220–250 ppm [29][6]; it has not been possible to correlate the small shift differences observed to any of the *Hammett*-type substituent constants [29] [19]. This behaviour contrasts with *e.g.* that of substituted pyridine *N*-oxides [25] and aromatic carbonyl compounds [30]. It is interesting to note, however, that in spite of the similarity of shielding of O(1) with that of furans, the bond lengths of O(1) with its neighbours are longer in **1** [5].

The Exocyclic O-Atom. In **1**, **4**, and **5**, the signal of the C-bonded exocyclic O-atom (δ_O 180–240 ppm) appears at much higher field than those of carbonyl compounds. Only the cyclopropenones, presenting also a highly polarized carbonyl group, resonate at such a high field: δ_O *ca.* 240 ppm [9]. In ordinary esters, C=O is found at *ca.* 360 ppm [7]; cyclisation exerts only a moderate influence [7] [31]; we found, *e.g.*, δ_O (benzene, 85°; in parenthesis: linewidth in Hz) for benzyl benzoate at 343 (300; =O) and 157 (160; –O–), and for phthalide (**11**) at 325 (90; =O) and 168 (50; –O–). On the other hand, completely polarized formulae like **1B–D** present an enolate-type structure for the exocyclic O-atom; we have shown that the enolate $PhC(O^-)=CHMe$ resonates at 137, phenolate PhO^- at 158, and *p*-nitrophenolate at 210 ppm [9]. Even though it is difficult to account for the influence of the ring O-atom on the exocyclic enolate O, the δ_O values found for the mesoionic compounds fit better a highly shielded exocyclic O-atom, as symbolized by formula **1B**.

The δ_O values are compatible, too, with formula **1E**, which restricts resonance to the chain extending from N(2) or C(2) to the exocyclic O-atom, and which had been suggested by X-ray and ESCA measurements. Our results furnish further arguments in favour of such a non-aromatic formula. 1) Replacing C(2) by N (oxazole oxide **5** *vs.* sydnone **1**) deshields not only the immediately neighbouring O(1) ($\Delta\delta_O$ = 110 ppm), but is important too on the exocyclic O($\Delta\delta_O$ *ca.* 50 ppm), in spite of the long distance of 4 bonds. 2) Changing the substituents on N(3) (**1a** *vs.* **1b**) gives a (small) difference on the exocyclic O and none on the less distant O(1). Thus, the exocyclic O-atom seems to be more susceptible to electronic influences than O(1); formula **1E** can be considered an expression of this observation.

Conclusions. – In mesoionic compounds as well as in cyclopropenone [9], the high-field ^{17}O shift values correspond well with the established polarisation of the carbonyl group. On the other hand, polarization of the carbonyl group, expressed as π-bond order [32] [8], is considered to influence also the C–O bond length. We have found that (high) shielding and (high) bond length go parallel in the cyclopropenones [9]. In the sydnone-type compounds, however, high shielding of the exocyclic O-atom goes with normal C=O bond length (and normal IR vibrations); at the same time, the ring O-atom of these compounds shows normal furan-type shielding, but a weakened bond to its neighbour. For an interpretation, the specific interactions of the heterocycle with the C=O dipole, acting not only on π but also on σ bonds, should certainly be considered. Furthermore, one has to take into account that ^{17}O-shielding is, in the first place, determined by a paramagnetic term [8], which might respond in a different way to changes in electron distribution than do force-oriented properties like bond lengths and vibrations.

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[6] We have confirmed [19] several of the published values [29] and added further compounds: 2-(diethoxymethyl)furan, δ_O 236 (230) and 47 ppm; 3-bromofuran, δ_O 239 ppm (60); 3,4-bis(hydroxymethyl)furan, δ_O 226 (470) and 9 ppm (in parenthesis: line widths in Hz; all spectra measured in $CDCl_3$ at r.t.).

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Experimental Part

General. See [9].

^{17}O-NMR Spectra. The spectra were recorded on a *Bruker WH-360* spectrometer operating at 48.8 MHz. The temperature was stabilized by a *Bruker B-VT* unit and controlled by a *Hewlett-Packard 2802 A* thermistance Pt thermometer placed in the interior of the 10 mm sample tube. Shimming of the magnetic field was done with a D_2O lock; the spectra were recorded with sample spinning and without lock. The instrumental settings were: 40 kHz spectral width; 2 K data points; 90° pulse length: 33 µs; quadrature phase detection; acquisition time $T_{acq} \geqslant 4\ T_2$; preacquisition delay *Δt:* 50 µs; no relaxation delay T_d; zero filling up to 8 K before FT; *ca.* 10^6 scans for non-enriched samples. The signal-to-noise ratio was improved by applying 100–200 Hz exponential broadening factor to the FID prior to FT. The chemical-shift error was ±0.2 ppm. The chemical-shift data are reported relative to $\delta(H_2O) = 0.00$ ppm; dioxane ($\delta = 0.0$ ppm) was used as an external reference standard [33].

3-Phenyl-1,2,3-oxadiazolylium-5-[^{17}O]olate (= *3-Phenyl[1-^{17}O]sydnone;* [1-^{17}O]-**1a**). To a soln. of *N*-phenylglycine (1.0 g, 6.6 mmol) in conc. HCl soln. (1.0 ml) and $H_2[^{17}O]$ (4.0 ml; 1.4% ^{17}O, 10% ^{18}O) at 0°, $NaNO_2$ (0.32 g, 4.6 mmol) was added within 10 min. After 2 h, the precipitate was filtered, washed with 2 × 2 ml of cold $H_2{}^{16}O$ and dried: 0.72 g (61%) of *N*-[^{17}O]nitroso-*N*-phenylglycine. The latter (0.71 g, 3.9 mmol) and Ac_2O (3.8 ml) were heated under reflux. After 2 h, the mixture was cooled, 20 ml of cold $H_2{}^{16}O$ were added, and [1-^{17}O]-**1a** was isolated following [34]: 0.43 g (68%), m.p. 136°. ^1H-NMR and ^{13}C-NMR: identical with [34]. MS: 164 (10.7, $M^{+\cdot} + 2$), 162 (100, $M^{+\cdot}$); non-enriched sample: 164 (0.8), 162 (100); ^{18}O content: 9.9%, corresponding to *ca.* 99% tracer incorporation.

5-Amino-3-phenyl-1,2,3-oxadiazolylium Iodide (= *3-Phenylsydnon-imine Hydroiodide;* **2a**) was prepared from 2-(phenylamino)acetonitrile [35] by nitrosation [36] and cyclisation with 95% HNO_3 [20]. The nitrate of **2a** obtained (1.0 g, 4.5 mmol) was treated with KI (2.6 g) in H_2O (30 ml); the precipitate was isolated and recrystallized from H_2O: 0.8 g (60%), m.p. 177–178°. ^1H-NMR ((D_6)DMSO): 7.65–8.28 (*m*, Ph); 8.68 (*s*, CH); 9.77 (br. *s*, NH_2). MS (nitrate, CI); 162 (5, M^+), 132 (33), 104 (38), 77 (100). Anal. calc. for $C_8H_8IN_3O$ (289.1): N 14.53; found: N 14.51.

5-Amino-4-isopropyl-3-methyl-1,2,3-oxadiazolylium Chloride (= *4-Isopropyl-3-methylsydnon-imine Hydrochloride;* **2b**) was prepared following [37]; m.p. 185°. ^1H-NMR ((D_6)DMSO): 1.35 (*d*, *J* = 7, 2 Me); 3.09–3.38 (*m*, CH); 4.38 (*s*, MeN); 9.64 (br. *s*, NH).

4,5-Diphenyl-1,3,4-oxadiazolylium-2-olate (= *4,5-Diphenylisosydnone;* **4**) was prepared following [22] [37]; properties and spectra identical with those given in literature.

3-Methyl-2,4-diphenyl-1,3-oxazolylium-5-[^{17}O]olate ([1-^{17}O]-**5**). [^{17}O]Benzoic acid, prepared by hydrolysis of benzoyl chloride with $H_2[^{17}O]$ (2.66% ^{17}O, 39.0% ^{18}O) in dioxane, was transformed into [^{17}O]benzoyl chloride, which was used to prepare [1-^{17}O]-**5** following the procedure of [23]. ^1H-NMR and ^{13}C-NMR identical with those described; ^{17}O *ca.* 20 times enriched (by NMR).

Other Compounds. 3-Phenyl-1,2,3-oxadiazolylium-5-dicyanomethylide (**3**): by courtesy Prof. *Araki*, Nagoya. 'Münchnon' **5**: by courtesy Prof. *Huisgen*, München. Oxazole **9**: *Fluka*. Phthalide (**11**), benzyl benzoate, and substituted furans: *Aldrich*.

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