EXPEDITENT ROUTES TO 1,2,4-TRIAZOLINIUM SALTS

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Abstract – Concomitant S-alkylation and ketazonation of thiosemicarbazide in acetone eventually led to unanticipated ring closure and formation of (3-alkylthio)-1,2,4-triazolinium salts. This initial finding was complemented by employing another three representative aldehydes and ketones. Supplementarily, some respective intermediates have been isolated by stepwise synthetic procedures. In addition to the usual spectroscopic characterization, the structures of six 1,2,4-triazolinium heterocycles, as well as two unexpected by-products thereof have been characterized by single-crystal X-ray diffraction.

INTRODUCTION

The reaction of thiosemicarbazide with organic carbonyl compounds is well known and has been used extensively in traditional qualitative analysis by capitalizing on the sharp melting points of their highly crystalline thiosemicarbazone derivatives,1 which moreover form the related aldazines and ketazines straightforwardly. Later research brought about the various possibilities offered by thiosemicarbazides and thiosemicarbazones as starting materials for organic synthesis,2 which also led to the discovery of countless pharmaceutical active principles.3-5 One of the main topics of research was the preparation of heterocycles such as imidazole and 1,2,4-triazole derivatives.6-7 By using neutral S-alkylated isothiosemicarbazones as starting materials for cyclization reactions, remarkable achievements have been contributed by several groups, particularly Yamazaki and coworkers.8-17 Interestingly, hardly any research has been published on the cyclization of ionic S-alkylated isothiosemicarbazone hydroiodides (S-alkyl isothiosemicarbazonium iodides).18 In the present contribution, we wish to report on 1,2,4-triazoline substructures bearing an iminium functionality as shown by the structures (1-6) in Figure 1. To the best of our knowledge only one similar structural motif (7) stemming from the reaction of a 2-azaallenium compound with an aziridine co-reactant,19 has been reported in the literature so far (see Figure 1).
Figure 1. Structures of (1-6), purpose of this research and (7), both bearing the 1,2,4-triazolinium motif with iminic N(1) ($R^1, R^2, R^4, R^5 = \text{Me, H or C}_6\text{H}_5$; $R^3 = \text{Me or C}_2\text{H}_4(\text{CF}_2)_5\text{CF}_3$).

Heterocyclic cores are relevant to both, biochemistry and materials science since they exhibit very distinct biological and physicochemical profiles, such as anti-fungal activity, or for their applicability as high energy density materials.

**RESULTS AND DISCUSSION**

In a non-targeted explorative effort to synthesize affordable fluorosurfactants, thiosemicarbazide was treated with the industrial starting material 1$H,1H,2H,2H$-perfluorooctyl iodide by refluxing these key reactants in acetone overnight (see Scheme 1).

![Scheme 1](image)

**Scheme 1.** Formation of anticipated $S$-alkyl isothiosemicarbazone hydroiodide (10a) and heterocyclic byproduct (1)

In addition to the expected product (10a), a highly crystalline fraction (1) could be separated during workup and its structure was unequivocally confirmed by single crystal X-ray diffraction. Evidently, after thiosemicarbazone formation along with the well-established ease of $S$-alkylation of thiourea substructures, in a final sequence, a second acetone molecule underwent aminalization of the anticipated preformed isothiuronium salt (10a) to yield the 1,2,4-triazolinium end-product (1).

In this context it should be interposed that triazolines (dihydrotriazoles) are generally unstable and thus have not been subjected to extensive studies. Structures which are disubstituted at the C(3) or C(5) atom (see Figure 1) are more stable than the mono- or unsubstituted analogues.
Since to the best of our knowledge this serendipitously discovered pathway has not yet been described, our efforts shifted towards obtaining better insight as to its conditions and mechanisms of formation. To that purpose the three reaction steps, namely thiosemicarbazone condensation, S-alkylation and cyclization, occurring in the one-pot synthesis were performed separately and intermediate products were isolated. Furthermore, for a more principled approach to the topic, iodomethane was chosen as the alkylating agent.

Over the course of our experiments, it became evident that the first reaction that occurred was the formation of the thiosemicarbazone (11a), followed by S-alkylation to yield the S-methyl isothiosemicarbazone hydroiodide (10b). Both species were readily accessible in excellent yields and purity. The last step, the condensation of the second carbonyl functionality under subsequent ring closure turned out to be significantly more challenging, but acceptable conversions could be achieved using molecular sieves to remove cumulating water from the condensation steps and by buffering the pH at approximately 5. Different buffer systems, such as 2:1 mixtures of pyridine and methanolic hydrochloric acid or pyridine and p-toluenesulfonic acid, were tested. However, both buffer pairs led only to a partial formation of the desired product, which is attributable to a known reaction of S-methylisothiuronium iodides with pyridine. Fortunately, the utilization of a 2:1 mixture of pivalic acid and N,N-diisopropyl-N-ethylamine led to complete conversion of the S-methyl isothiosemicarbazone hydroiodide to (2) as shown in Scheme 2.

**Scheme 2.** Stepwise preparation of 1,2,4-triazolinium iodide 2 from isolated intermediates 11a and 10b

After appropriate reaction conditions had been determined, additional experiments were conducted in order to expand the scope of the cyclization from aliphatic ketones (acetone) to other carbonyl compounds such as aliphatic aldehydes (acetaldehyde), aromatic aldehydes (benzaldehyde) and aromatic ketones (acetophenone), which were met with varying success. The syntheses of the thiosemicarbazones (11b-d) and their corresponding S-methyl isothiosemicarbazone hydroiodides (10c-e) again proceeded with good to excellent yields (see Table 1, entries 2-4 for 11b-d and entries 7-9 for 10c-e).
Table 1. Substitution patterns of compounds 1-6 and 10-11

(8) \[ \text{HN-} \text{NH}_2 \] \[ \rightarrow \] \[ \text{HN-} \text{NH}_2 \] \[ \rightarrow \] \[ \text{HN-} \text{NH}_2 \] \[ \rightarrow \] \[ \text{I}^- \text{S-R}^3 \] \[ \rightarrow \] \[ \text{N}^+ \text{S-R}^3 \] \[ \rightarrow \] \[ \text{N}^+ \text{S-R}^3 \] \[ \rightarrow \] \[ \text{1-6} \]

(a) ketone or aldehyde in EtOH/EtOAc reflux 16 h; (b) R^3 in MeCN; (c) ketone or aldehyde in i-PrOH, molecular sieves (3 Å), pivalic acid - N,N-diisopropyl-N-ethylamine buffer solution (0.4 M)

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However, the ring closure turned out to be surprisingly dependent on the reaction temperature. At moderate temperatures, no product was formed, whereas at excessive temperatures, an additional side-reaction occurred, leading to substituent scrambling via the exchange of the carbonyl compound condensed in the preceding syntheses of the thiosemicarbazones (11a-d) through the carbonyl compound introduced in step 3. This observed interchangeability of the aldehydes and ketones in the reaction as outlined in scheme 3 was evidenced by ^1H NMR monitoring of the reaction products. (see Scheme 3).
Therefore, we invested some effort into finding optimum reaction conditions. In the experiments conducted with acetophenone, only the exchange reaction took place, most likely due to the low reactivity of the aromatic ketone. As a consequence, harsher reaction conditions like higher temperatures are needed to achieve any conversion at all. Acetaldehyde, as the most reactive investigated carbonyl compound, readily reacted at low temperatures as expected. However, the formation of a highly reactive ethylidene-iminium functionality rapidly led to dissociation, and, according to $^1$H NMR monitoring, polymerization. Hence, work-up and isolation turned out to be extremely challenging. Furthermore, due to adsorption phenomena, no molecular sieves could be used during these experiments. Owing to these difficulties, only one target product (6) was isolated in traces (see Table 1, entry 15). Experiments with other, less reactive aliphatic aldehydes are the subject of current research.

In the case of benzaldehyde, three out of four desired 1,2,4-triazolinium iodides (see Table 1, entries 12-14) could be synthesized (3, 4, 5). Cyclization reactions of aldehyde S-methyl isothiosemicarbazone hydroiodides (10c, 10d, entries 7 and 8) with acetone led to the metathesis-side product. In the conversion of 10e (entry 9) with acetone, the desired product was detected in the $^1$H NMR spectra of the reaction mixture. However, isolation of the product has not yet been achieved.

Based on previous findings described in literature, we initially assumed that the final condensation would occur at the terminal NH$_2$-functionality of the S-methyl isothiosemicarbazone hydroiodide, resulting in an imine that in turn would form a mesomeric 2-azaallenium intermediate (see Scheme 4). However, during experiments with mixed carbonyls (3, 5, 6), the likelihood of such a reaction mechanism sharply decreased. In all cases, the cyclization only took place with the derivative of which the carbonyl was introduced in the first step of the reaction (see Table 1, entries 12, 14 and 15).
Scheme 4. Initially assumed reaction mechanism, concerning the formation of a 2-azaallenium intermediate as reported in literature\textsuperscript{19}

Interestingly, the lone pair of the iminic moiety appears to be the most nucleophilic position, probably because of a known delocalization of the positive charge over the isothiouronium substructure\textsuperscript{31,32} and the influence of the (admittedly disputed) alpha-effect.\textsuperscript{33-35}

Scheme 5. Proposed novel, reaction mechanism for the formation of compounds 1-6

Over the course of our experiments, two dissociation products were isolated and identified by single-crystal X-ray structure determination (see Figure 2). Compound 12, which has been synthesized in a similar way before,\textsuperscript{36} was obtained in an attempt to alkylate thiosemicarbazide in EtOH. Thiocarbamate 13 was obtained during an attempt to synthesize fluorosurfactant 1 upon acidification of the reaction mixture with hydrochloric acid, evidencing protic hydrolysis.
Lastly, it can be concluded, that, starting with thiosemicarbazone formation, a domino reaction, actually a sequence of condensation / S-alkylation / ring closing condensation, is operative. This finds additional support by the fact that, in contrast to S-alkylated isothiosemicarbazone hydroiodides, the S-alkylated isothiosemicarbazide hydroiodides are not trackable under the given reaction conditions. In addition, the assumption of an intermediate alkylation cascade is supported by the fact that the postulated intermediates could be isolated. Moreover the reaction worked most satisfactorily under sequential reactant addition.

CRYSTAL STRUCTURES
Crystal structures for compounds 1 – 6, 12 and 13 have been determined from single crystal data, including those of a monohydrate of 3 and an acetonitrile (MeCN) solvate of 4. The molecular geometries are unexceptional and consistent with relevant reference structures. The perfluoroctyl chain of 1 is disordered over two orientations. In 3 · H2O, the water molecule occupies two alternative positions. Each of 1, 2, 3 · H2O, 4 · MeCN, 5 and 6 display a single N–H···I bond between the triazole ring and the iodide ion (see Figure 3a) with an H···I distance in the range between 2.62 and 2.75 Å and an N–H···I angle between 150.2° and 173.7°. The asymmetric unit of 12, consists of two cations, one iodide ion located in a general position and another two iodide ions which are located in a special position on a two-fold axis. The cation of 12 displays three NH2 groups which can act as H-bond donor sites in addition to the NH group of the triazole ring. Neighboring cations of 12 are linked into N–H···N bonded dimers, whilst the NH2 groups are employed in N–H···I interactions. As a result, a complex H-bonded framework structure is formed between the cations and anions of 12 (see Figure 3b). The structure of 13 displays N–H···O bonded dimers (see Figure 3c).

CONCLUSIONS AND OUTLOOK
In this contribution, the synthesis and characterization of the first six examples of a unique class of 1,2,4-triazolinium salts are discoursed. The non-aromatic heterocyclic products are apparently formed through an unprecedented domino pathway with fair to good yields. As a first general outcome, it was shown that the ring closure is possible with different carbonyl compounds and even metathetical carbonyl exchange under ring re-opening can occur. In particular, the newly discovered cyclization may offer
interesting contributions to the currently revitalized chemistry of thiourea-based organocatalysis. Likewise, they could serve as aza-analogues of recently discovered allylic isothiouronium salts, a novel family of thiourea-based lead principles with antitumor activity. As a concluding example, possible dehydrohalogenations in order to obtain zwitterionic species may represent an inviting topic as well. Thus applies all the more, since 1,3-dipolar cyclizations and related vinylogous additions offer an entire synthetic playground for its own. These preliminary achievements should unfold new facets of

Figure 3. H-Bonded structures: a) N–H···I bonded cation and iodide ion of 2; b) N–H···N and N–H···I bonded framework of 12 (viewed along the b axis); c) N–H···O bonded dimer of 13
interesting follow-up chemistry, since a plethora of thiosemicarbazones, as well as the established pool of task-optimized alkylating agents are effortlessly accessible as starting materials.

EXPERIMENTAL
Reagents and solvents were purchased from Sigma-Aldrich and used as received unless stated otherwise. Thiosemicarbazones (11a-d) were prepared according to published procedures. Acetaldehyde and benzaldehyde were purified before application as described in literature. The buffer solution used throughout the experiments was prepared by dissolving 0.2 mol (20.4 g) of pivalic acid and 0.1 mol (12.9 g) of N,N-diisopropyl-N-ethylamine in 250 ml of iPrOH, yielding a 0.4 M pH 5 stock solution.

NMR spectra were recorded with a Bruker Avance DPX 300 spectrometer. Because of a reported ring-chain tautomerism in solution, the NMR-spectra of S-alkyl isothiosemicarbazone hydroiodides (10a-e) show more peaks with different shifts and coupling patterns than expected. IR spectra were obtained with a Bruker ALPHA Platinum FT-ATR instrument.

Diffraction intensity data were recorded with a Bruker D8 Quest Photon 100 diffractometer using MoKα (\(\lambda = 0.7107 \text{ Å}\)) radiation. The crystal structures were solved by Direct Methods and refined by full-matrix least-squares techniques.

1: (C15H17F13N3S)+ I−; monoclinic space group \(P2_1/c\); \(Z = 4\); unit cell \(a = 18.6686(9) \text{ Å}, b = 12.7077(5) \text{ Å}, c = 9.8171(4) \text{ Å}, \beta = 93.559(2)^\circ, V = 2324.47(17) \text{ Å}^3\); \(T = 183 \text{ K}\); 33950 reflections collected (\(R_{int} = 0.0340\)); 4580 independent reflections; 435 parameters; \(R1 [I > 2\sigma(I)] = 0.0328\); \(wR2 (all data) = 0.0819\); CCDC 1934885.

2: (CsH16N3S)+ I−; monoclinic space group \(C2/m\); \(Z = 4\); unit cell \(a = 14.7116(7) \text{ Å}, b = 7.4283(4) \text{ Å}, c = 12.8873(6) \text{ Å}, \beta = 114.9566(11)^\circ, V = 1276.85(11) \text{ Å}^3\); \(T = 223 \text{ K}\); 7145 reflections collected (\(R_{int} = 0.0206\)); 1352 independent reflections; parameters; \(R1 [I > 2\sigma(I)] = 0.0172\); \(wR2 (all data) = 0.0432\); CCDC 1934891.

3 · H2O: (C12H16N3S)+ I−·H2O; monoclinic space group \(C2/c\); \(Z = 8\); unit cell \(a = 15.9117(9) \text{ Å}, b = 14.2823(8) \text{ Å}, c = 13.6716(8) \text{ Å}, \beta = 96.284(2)^\circ, V = 3088.3(3) \text{ Å}^3\); \(T = 183 \text{ K}\); 31771 reflections collected (\(R_{int} = 0.0213\)); 3040 independent reflections; parameters; \(R1 [I > 2\sigma(I)] = 0.0204\); \(wR2 (all data) = 0.0518\); CCDC 1934891.

4 · MeCN: (C16H16N3S)+ I−·C2H3N; triclinic space group \(P\bar{1}\); \(Z = 2\); unit cell \(a = 8.8122(12) \text{ Å}, b = 11.0463(14) \text{ Å}, c = 11.0838(15) \text{ Å}, \alpha = 97.617(3)^\circ, \beta = 112.940(4)^\circ, \gamma = 95.854(4)^\circ, U = 970.8(2) \text{ Å}^3\); \(T = 183 \text{ K}\); 34241 reflections collected (\(R_{int} = 0.0288\)); 3983 independent reflection; 223 parameters; \(R1 [I > 2\sigma(I)] = 0.0171\); \(wR2 (all data) = 0.0449\); CCDC 1934888.
5: (C11H14N3S)+ I−; monoclinic space group P21/c; Z = 4; unit cell \(a = 10.2584(12)\) Å, \(b = 11.6726(13)\) Å, \(c = 11.4824(13)\) Å, \(\beta = 105.747(3)\) \(^\circ\), \(V = 1323.3(3)\) Å\(^3\); \(T = 183\) K; 15377 reflections collected (\(R_{\text{int}} = 0.0247\)); 2444 independent reflections; 149 parameters; \(R_1 [I > 2\sigma(I)] = 0.0368\); \(wR_2\) (all data) = 0.0840; CCDC 1934892.

6: (C7H14N3S)+ I−; orthorhombic space group Pnma; Z = 4; unit cell \(a = 12.1981(15)\) Å, \(b = 7.5554(8)\) Å, \(c = 12.7883(15)\) Å, \(\beta = 116.666(2)\) \(^\circ\), \(V = 2905.6(3)\) Å\(^3\); \(T = 183\) K; 10096 reflections collected (\(R_{\text{int}} = 0.0284\)); 1118 independent reflections; 74 parameters; \(R_1 [I > 2\sigma(I)] = 0.016\); \(wR_2\) (all data) = 0.0412; CCDC 1934890.

12, [89831-23-2]: (C2H7N6)+ I−; monoclinic space group C2/c; Z = 16; unit cell \(a = 23.0536(13)\) Å, \(b = 10.9148(6)\) Å, \(c = 12.9219(7)\) Å, \(\beta = 95.304(2)\) \(^\circ\), \(V = 3511.9(4)\) Å\(^3\); \(T = 173\) K; 18895 reflections collected (\(R_{\text{int}} = 0.0441\)); 2850 independent reflections; 221 parameters; \(R_1 [I > 2\sigma(I)] = 0.0204\); \(wR_2\) (all data) = 0.0506; CCDC 1934887.

13: C12H11F13N2OS; monoclinic space group C2/c; Z = 8; unit cell \(a = 33.616(2)\) Å, \(b = 20.1665(14)\) Å, \(c = 10.148(6)\) Å, \(\beta = 95.304(2)\) \(^\circ\), \(V = 3511.9(4)\) Å\(^3\); \(T = 183\) K; 13861 reflections collected (\(R_{\text{int}} = 0.0264\)); 3080 independent reflections; 269 parameters; \(R_1 [I > 2\sigma(I)] = 0.0302\); \(wR_2\) (all data) = 0.0733; CCDC 1934889.

**S-(1H,1H,2H,2H-Perfluoroctyl)-N’-(propan-2-ylidene)carbamohydrazonothioate hydroiodide, (S-(1H,1H,2H,2H-Perfluoroctyl)acetoneisothiosemicarbazone hydroiodide) (10a)**

Acetonethiosemicarbazone (11a, 5.00 g, 38 mmol) and 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8-iodooctane (19.8 g, 42 mmol) were dissolved in MeCN (20.0 mL). The mixture was refluxed for 18 h under stirring. During cooling to room temperature the solution turned to a slightly yellow solid, which was dissolved in acetone (60.0 mL). Petrolether (200 mL) was added and the suspension was kept at -32 °C for 16 h. The resulting white precipitate was filtered off, washed with petrolether (2 × 20 mL) and dried under reduced pressure to yield 17.9 g (78 %) of a white solid, Mp 117.5 °C. \(^1H\) NMR (300 MHz, DMSO-\(d_6\)) \(\delta = 11.62\) (s, 1H), 9.06 (s, 2H), 3.52 – 3.43 (m, 2H), 2.81 – 2.62 (m, 2H), 2.15 (s, 3H), 2.07 (s, 3H) ppm (visible ring-tautomerism peaks at: \(\delta = 3.36 – 3.27\) (m), 2.85 – 2.63 (m), 2.15 (s, 3H), 2.07 (s, 3H) ppm). \(^13C\) NMR (75 MHz, DMSO-\(d_6\)) \(\delta = 166.51, 163.54, 125-100\) (6C, m), 30.69 (t), 25.13, 22.58, 19.43 ppm (visible ring-tautomerism peak at: \(\delta = 81.16\) ppm). IR (neat): \(\nu = 3265\) (w), 3157 (w), 3090 (w), 1631 (s), 1576 (w), 1460 (w), 1442 (w), 1363 (m), 1316 (w), 1293 (w), 1233 (s), 1210 (s), 1186 (vs), 1166 (s), 1138 (vs), 1088 (m), 1071 (m), 1012 (w), 953 (m), 822 (w), 777 (m), 726 (s), 710 (s), 689 (m), 652 (s), 597 (m), 563 (m), 533 (m), 494 (w), 449 (w) cm\(^{-1}\).
Acetonethiosemicarbazone (11a, 9.84 g, 75 mmol) and iodomethane (11.2 g, 78.8 mmol) were dissolved in MeCN (35.0 mL) and MeOH (2.00 mL). The mixture was refluxed for 18 h under stirring. After cooling to room temperature Et₂O (100 mL) was added and the suspension was kept at -32 °C for 16 h. The resulting white precipitate was filtered off, washed with Et₂O (2 × 20 mL) and dried under reduced pressure to yield 20.1 g (98%) of a white solid, Mp 175 °C. ¹H NMR (300 MHz, DMSO-d₆) δ 11.67 (s, 1H), 9.23 (s, 2H), 2.66 (s, 3H), 2.07 (s, 3H), 2.02 (s, 3H) ppm (visible ring-tautomerism peaks at: δ 8.78 (s), 2.54 (s), 1.52 (s) ppm). ¹³C NMR (75 MHz, DMSO-d₆) δ 166.05, 164.53, 25.00, 18.93, 13.53 ppm (visible ring-tautomerism peaks at: δ 80.65, 24.71 ppm). IR (neat): ν 3223 (m), 3168 (m), 3078 (s), 2970 (m), 1653 (w), 1613 (vs), 1559 (vs), 1491 (m), 1432 (s), 1372 (m), 1321 (m), 1225 (m), 1108 (m), 1082 (m), 1021 (m), 984 (m), 861 (m), 770 (s), 651 (vs), 593 (m), 509 (m), 417 (m) cm⁻¹.

**S-Methyl-N’-(ethylidene)carbamohydrazonothioate hydroiodide, (S-Methylacetaldehydeisothiosemicarbazone hydroiodide) (10e)**

Acetaldehydethiosemicarbazone (11b, 11.7 g, 100 mmol) and iodomethane (14.9 g, 105 mmol) were dissolved in EtOH (50 mL). The mixture was refluxed for 30 minutes under stirring. After cooling to room temperature Et₂O (150 mL) was added and the suspension was kept at -32 °C for 16 h. The resulting white precipitate was filtered off, washed with Et₂O (2 × 20 mL) and dried under reduced pressure to yield 22.5 g (87%) of a white solid, Mp 141 °C. ¹H NMR (300 MHz, DMSO-d₆) δ 12.52 (s, 1H), 9.47 (s, 2H), 7.96 – 7.42 (m, 1H), 2.67 (s, 3H), 2.01 (dd, J = 5.4, 1.7, 3H) ppm. ¹³C NMR (75 MHz, DMSO-d₆) δ 165.34, 154.89, 18.53, 13.44 ppm. IR (neat): ν 3245 (w), 3187 (w), 3136 (m), 3085 (w), 3017 (w), 2929 (m), 2822 (m), 2767 (w), 1616 (vs), 1561 (vs), 1430 (s), 1380 (s), 1350 (s), 1317 (m), 1259 (s), 1153 (m), 1086 (m), 1031 (s), 987 (m), 884 (s), 783 (m), 693 (w), 616 (s), 597 (m), 487 (m), 448 (m) cm⁻¹.

**S-Methyl-N’-(benzylidene)carbamohydrazonothioate hydroiodide (S-Methylbenzaldehydeisothiosemicarbazone hydroiodide) (10d)**

Benzaldehydethiosemicarbazone (11c, 13.4 g, 75 mmol) and iodomethane (11.2 g, 78.8 mmol) were dissolved in MeCN (35 mL) and MeOH (10 mL). The mixture was refluxed for 30 minutes, followed by stirring at room temperature continued for another 18 h. The resulting yellow solution was treated with Et₂O (150 mL) and the suspension was kept at -32 °C for 16 h. The precipitate was filtered off, washed with Et₂O (2 × 20 mL) and dried under reduced pressure to yield 23.2 g (96%) of a slightly yellow solid, Mp 132.5 °C. ¹H NMR (300 MHz, DMSO-d₆) δ 12.93 (s, 1H), 9.62 (s, 2H), 8.36 (s, 1H), 7.98 – 7.92 (m, 2H), 7.50 (s, 3H), 2.76 (s, 3H) ppm (visible ring-tautomerism peaks at: δ 7.71 (s), 2.60 (s) ppm). ¹³C
NMR (75 MHz, DMSO-\textit{d}_6) \delta 166.09, 151.79, 132.44, 131.58, 128.78 (2C), 128.42 (2C), 13.69 ppm. IR (neat): \nu 3245 (w), 3168 (w), 3084 (m), 3031 (w), 2971 (w), 2938 (w), 2824 (w), 2788 (w), 1601 (vs), 1560 (vs), 1490 (m), 1448 (m), 1421 (m), 1374 (m), 1269 (m), 1226 (m), 1084 (m), 1057 (m), 952 (m), 803 (m), 757 (s), 688 (s), 641 (s), 618 (s), 516 (s), 482 (m) cm\textsuperscript{-1}.

\textit{S-Methyl-N'-(1-phenylethylidene)carbamohydrazonothioate hydroiodide (\textit{S-Methylacetophenone-isothiosemicarbazone hydroiodide}) (10e)}

Acetophenonethiosemicarbazone (11d, 14.5 g, 75 mmol) and iodomethane (11.2 g, 78.8 mmol) were dissolved in MeCN (35 mL) and MeOH (30 mL). The mixture was refluxed for 30 minutes, followed by stirring at room temperature continued for another 18 h. The resulting suspension was treated with Et\textsubscript{2}O (150 mL) and kept at -32 °C for 16 h. The precipitate was filtered off, washed with Et\textsubscript{2}O (2 \times 20 mL) and dried under reduced pressure to yield 24.6 g (98 %) of a white solid, Mp 176 °C (decomp.). \textit{1H NMR (300 MHz, DMSO-\textit{d}_6)} \delta 11.93 (s, 1H), 9.47 (s, 2H), 8.03 (d, \textit{J} = 7.2, 2H), 7.60 – 7.34 (m, 3H), 2.76 (s, 3H), 2.42 (s, 3H) ppm (visible ring-tautomerism peaks at: \delta 9.03 (s), 7.79 (s), 2.60 (s) ppm). \textit{13C NMR (75 MHz, DMSO-\textit{d}_6)} \delta 167.07, 159.11, 136.14, 130.65, 128.34 (2C), 127.39 (2C), 15.72, 13.94 ppm (visible ring-tautomerism peaks at: \delta 172.77, 155.98, 126.52, 105.16, 15.01, 13.17 ppm). IR (neat): \nu 3270 (m), 3159 (w), 3123 (m), 3050 (m), 2991 (w), 2931 (w), 1633 (vs), 1569 (s), 1496 (m), 1422 (s), 1365 (m), 1299 (m), 1119 (m), 1075 (m), 1034 (m), 953 (m), 919 (m), 778 (m), 750 (vs), 689 (s), 667 (vs), 557 (s), 532 (s), 468 (m) cm\textsuperscript{-1}.

\textit{5,5-Dimethyl-1-(propan-2-ylidene)-3-(1H,1H,2H,2H-perfluoroctylthio)-4,5-dihydro-1H-1,2,4-triazol-1-ium iodide (1)}

\textit{S-(1H,1H,2H,2H-Perfluoroctylthio) acetoneisothiosemicarbazone hydroiodide (10a), 3.00 g 5.00 mmol)}

activated molecular sieves (2.00 g; 3 Å) and acetone (1.45 g, 25.0 mmol) were suspended in MeCN (10 mL). After addition of 0.4 M pivalic acid – \textit{N,N-diisopropyl-N-ethylamine buffer solution (2.00 mL), the mixture was refluxed for 8 h without stirring and under exclusion of atmospheric moisture (CaCl\textsubscript{2}-filled drying tube). The molecular sieves were separated from the hot solution through filtration and washed with MeCN (15 mL). The filtrate was treated with Et\textsubscript{2}O (35 mL) and kept at -32 °C for 72 h. The crystalline product was filtered off, washed with Et\textsubscript{2}O (2 \times 10 mL) and dried under reduced pressure yielding 1.10 g (35%) of a white crystalline solid. Single-crystals were obtained by diffusion of Et\textsubscript{2}O into a methanolic solution of 1 at 4 °C, Mp 172 °C. \textit{1H NMR (300 MHz, Chloroform-\textit{d})} \delta 9.89 (s, 1H), 3.37 – 3.21 (m, 2H), 2.71 (s, 3H), 2.67 – 2.53 (m, 2H), 2.49 (s, 3H), 2.07 (s, 6H) ppm. \textit{13C NMR (75 MHz, Chloroform-\textit{d})} \delta 165.92, 165.75, 120-100 (6C, m), 90.32, 31.81 (t), 27.76 (2C), 25.81, 23.50, 22.74 (t)
ppm. IR (neat): \( \nu \) 3042 (m), 2938 (w), 2908 (w), 1649 (w), 1509 (s), 1480 (m), 1450 (m), 1434 (w), 1406 (w), 1377 (w), 1214 (vs), 1187 (vs), 1139 (vs), 1115 (vs), 1072 (m), 1040 (m), 990 (m), 960 (m), 846 (w), 799 (w), 734 (m), 707 (m), 685 (m), 628 (m), 601 (m), 564 (m), 530 (m) cm\(^{-1}\).

5,5-Dimethyl-3-(methylthio)-1-(propan-2-ylidene)-4,5-dihydro-1H-1,2,4-triazol-1-ium iodide (2)

S-Methyl-acetoneisothiosemicarbazone hydroiodide (10b, 1.36 g, 5.00 mmol) and activated molecular sieves (2.00 g, 3 Å) were put in a thick-walled glass vessel. Acetone (20 mL) and 0.4 M pivalic acid – \( \text{N,N-diisopropyl-N-ethylamine buffer solution (2.00 mL)} \) were added. Subsequently, the vessel was sealed and the mixture heated to 60 °C for 48 h without stirring. Over the course of the reaction, colorless product crystals formed on top of the molecular sieves. After cooling to room temperature, the solid matter was filtered off, washed with acetone (2 × 10 mL) and the product was separated manually from the molecular sieves to yield 1.05 g (67 %) of slightly yellow crystals. Single-crystals were obtained by diffusion of Et\(_2\)O into a methanolic solution of 2 at -32 °C, Mp 201 °C. \(^1\)H NMR (300 MHz, DMSO-\( d_6 \)) \( \delta \) 9.92 (s, 1H), 2.59 (s, 3H), 2.56 (s, 3H), 2.43 (s, 3H), 1.84 (s, 6H) ppm. \(^{13}\)C NMR (75 MHz, DMSO-\( d_6 \)) \( \delta \) 167.39, 166.20, 88.71, 26.32 (2C), 25.17, 22.20, 13.08 ppm. IR (neat): \( \nu \) 3231 (w), 3143 (m), 2997 (w), 2910 (w), 1643 (m), 1500 (s), 1476 (vs), 1444 (vs), 1420 (vs), 1393 (s), 1377 (s), 1296 (m), 1259 (m), 1203 (s), 1165 (m), 1113 (m), 1064 (m), 1035 (m), 986 (m), 964 (m), 891 (m), 872 (m), 715 (w), 677 (w), 559 (m), 491 (m), 476 (m) cm\(^{-1}\).

1-Benzylidene-5,5-dimethyl-3-(methylthio)-4,5-dihydro-1H-1,2,4-triazol-1-ium iodide (3)

S-Methyl-acetoneisothiosemicarbazone hydroiodide (10b, 1.36 g, 5.00 mmol) and activated molecular sieves (2.00 g, 3 Å) were put in a thick-walled glass vessel. Benzaldehyde (0.56 g, 5.25 mmol), i-PrOH and 0.4 M pivalic acid – \( \text{N,N-diisopropyl-N-ethylamine buffer solution (2.00 mL)} \) were added. Subsequently, the vessel was sealed and the mixture heated to 90 °C for 10 min to dissolve the educts before continuing the reaction for 4 h at 60 °C. After cooling to room temperature, the molecular sieves were filtered off and washed with i-PrOH (2 × 10 mL). The yellow filtrate was treated with Et\(_2\)O (150 mL) and kept at -32 °C for 16 h. The resulting precipitate was filtered off and dried under reduced pressure to yield 1.27 g of an orange crystalline solid as raw product, containing \( \text{N,N-diisopropyl-N-ethylammonium pivalate as impurity} \). The crude product was dissolved in boiling MeCN (10 mL) and kept at -32 °C for 16 h. The resulting crystals were filtered off, washed with cold MeCN (2 × 5.00 mL; -32°C) and dried under reduced pressure yielding 0.88 g (48%) of orange crystals. Single-crystals were obtained by diffusion of Et\(_2\)O into a methanolic solution of 3 at -32 °C, Mp 179 -181 °C. \(^1\)H NMR (300 MHz, DMSO-\( d_6 \)) \( \delta \) 10.91 (s, 1H), 8.84 (s, 1H), 8.48 – 8.44 (m, 2H), 7.89 – 7.58
(m, 3H), 2.74 (s, 3H), 1.89 (s, 6H) ppm. $^{13}$C NMR (75 MHz, DMSO-$d_6$) $\delta$ 170.59, 141.33, 134.67, 133.15 (2C), 129.28 (2C), 127.86, 90.92, 28.35 (2C), 127.16 (m), 2984 (m), 1628 (w), 1593 (w), 1467 (vs), 1445 (vs), 1399 (s), 1383 (s), 1363 (s), 1327 (s), 1270 (s), 1197 (s), 1051 (s), 996 (s), 977 (s), 940 (m), 902 (m), 874 (m), 839 (m), 762 (vs), 684 (vs), 605 (m), 549 (m), 504 (s), 483 (m), 429 (w) cm$^{-1}$.

1-Benzylidene-3-(methylthio)-5-phenyl-4,5-dihydro-1H-1,2,4-triazol-1-ium iodide (4)

S-Methylbenzaldehydeisothiosemicarbazone hydroiodide (10d, 1.61 g, 5.00 mmol) activated molecular sieves (2.00 g, 3 Å) and benzaldehyde (2.66 g, 25.0 mmol) were suspended in $i$-PrOH (10 mL). After addition of 0.4 M pivalic acid – $N,N$-diisopropyl-$N$-ethylamine buffer solution (2.00 mL), the mixture was heated to 90 °C for 5.5 h without stirring and under exclusion of atmospheric moisture (CaCl$_2$-filled trying tube). The molecular sieves were separated from the hot solution through filtration and washed with hot $i$-PrOH (15 mL). The orange filtrate was treated with Et$_2$O (150 mL) and kept at -32 °C for 18 h. The resulting precipitate was filtered off and dried under reduced pressure to yield 0.96 g of a yellow solid as raw product, containing $N,N$-diisopropyl-$N$-ethylammonium pivalate as impurity. The crude product was dissolved in boiling MeCN (10 mL) and kept at -32 °C for 3 h. The resulting crystals were filtered off, washed with cold MeCN (2 × 5.00 ml, -32 °C) and dried under reduced pressure yielding 0.59 g (29%) of orange crystals. Single-crystals were obtained by recrystallization from MeCN, Mp 150.5 °C (under decomposition). $^1$H NMR (300 MHz, MeOH-$d_4$ – slight dissociation) $\delta$ 8.40 (s, 1H), 8.38 (d, $J = 1.6, 1H$), 8.19 (d, $J = 2.5, 1H$), 7.74 – 7.56 (m, 8H), 7.41 (d, $J = 2.5, 1H$), 2.86 (s, 3H) ppm. $^{13}$C NMR (75 MHz, MeOH-$d_4$ – slight dissociation) $\delta$ 175.90, 145.91, 136.66, 136.41, 135.16 (2C), 133.10, 131.31 (2C), 130.68 (2C), 129.16 (2C), 128.99, 87.79, 14.66 ppm. IR (neat): $\nu$ 3045 (w), 2985 (w), 2900 (w), 1698 (m), 1629 (m), 1593 (m), 1466 (s), 1444 (vs), 1402 (vs), 1354 (m), 1312 (m), 1280 (m), 1239 (s), 1200 (s), 1182 (s), 1108 (w), 1083 (w), 1053 (m), 1026 (m), 990 (m), 962 (m), 942 (m), 873 (m), 843 (w), 827 (m), 796 (m), 765 (s), 742 (m), 697 (s), 685 (vs), 632 (m), 557 (m), 529 (s), 489 (m), 455 (m) cm$^{-1}$.

1-Benzylidene-5-methyl-3-(methylthio)-4,5-dihydro-1H-1,2,4-triazol-1-ium iodide (5)

S-Methylacetalddehydeisothiosemicarbazone hydroiodide (10e, 1.30 g, 5.00 mmol) and activated molecular sieves (2.00 g, 3 Å) were put in a thick-walled glass vessel. Benzaldehyde (0.58 g, 5.50 mmol), $i$-PrOH (10 mL) and 0.4 M pivalic acid – $N,N$-diisopropyl-$N$-ethylamine buffer solution (2.00 mL) were added. Subsequently, the vessel was sealed and the mixture heated to 40 °C for 4 h without stirring. The molecular sieves were separated from the warm solution through filtration and washed with hot EtOH (2 × 10 mL). The yellow filtrate was treated with Et$_2$O (100 mL) and kept at -32 °C for 72 h. The precipitate
was filtered off and dried under reduced pressure to yield 1.00 g of a yellow, crystalline solid as raw product, containing \(N,N\)-diisopropyl-\(N\)-ethylammonium pivalate as impurity. The crude product was dissolved in boiling MeCN (15 mL) and kept at -32 °C for 16 h. The resulting crystals were filtered off, washed with cold MeCN (2 × 5 mL, -32 °C) and dried under reduced pressure yielding 0.43 g (25%) of orange crystals. Single-crystals were obtained by recrystallization from MeCN, Mp 173 °C. \(^1\)H NMR (300 MHz, DMSO-\(d_6\) – slight dissociation) \(\delta\) 10.60 (s, 1H), 8.76 (d, \(J = 2.5\), 1H), 8.47 – 8.29 (m, 3H), 7.80 – 7.56 (m, 1H), 6.52 (dd, \(J = 6.3\), 3.1, 3H), 2.70 (s, 1H), 1.81 (d, \(J = 6.0\), 3H) ppm. \(^{13}\)C NMR (75 MHz, DMSO-\(d_6\) – slight dissociation) \(\delta\) 172.44, 142.65, 134.47 (2C), 133.03, 129.25 (2C), 127.51, 81.70, 22.37, 13.82 ppm. \(^1\)H NMR (300 MHz, MeOH-\(d_4\)) \(\delta\) 8.57 (d, \(J = 2.5\), 1H), 8.49 – 8.40 (m, 2H), 7.78 – 7.61 (m, 3H), 6.43 (qd, \(J = 6.0\), 2.2, 1H), 2.78 (s, 3H), 1.89 (d, \(J = 6.0\), 3H) ppm. IR (neat): \(\nu\) 3083 (m), 2990 (m), 2928 (w), 1641 (w), 1594 (w), 1574 (w), 1478 (vs), 1437 (vs), 1408 (vs), 1369 (s), 1311 (s), 1264 (s), 1239 (s), 1188 (m), 1136 (m), 1105 (m), 1011 (s), 993 (s), 939 (m), 921 (m), 884 (m), 842 (m), 757 (s), 720 (m), 687 (vs), 616 (w), 570 (s), 510 (s), 457 (w) cm\(^{-1}\).

1-Ethylidene-5,5-dimethyl-3-(methylthio)-4,5-dihydro-1\(^H\)-1,2,4-triazol-1-ium iodide (6)

\(S\)-Methylacetoneisothiosemicarbazone hydroiodide (10b, 1.36 g, 5.00 mmol) and acetaldehyde (0.44 g, 10.0 mmol) were dissolved in \(i\)-PrOH (10 mL), followed by the addition of 0.4 M pivalic acid – \(N,N\)-diisopropyl-\(N\)-ethylamine buffer solution (2.00 mL). Subsequently, the reaction mixture was ultra-sonicated for 4 h, during which time the water temperature of the ultra-sonication bath slowly rose to 40 °C. The resulting yellow solution was treated with Et\(_2\)O (200 mL) and kept at -32 °C for 72 h. The slightly yellow precipitate was filtered off and washed with Et\(_2\)O (2 × 10 mL). During warming to room temperature, the precipitate melted and formed a yellow oil, which was dried under reduced pressure. The crude product was dissolved in MeOH (3.00 mL) and purified through diffusion of Et\(_2\)O into the methanolic solution (4 °C, 72 h), which led to the formation of a white, crystalline phase, and a yellow oily phase. The residue was filtered off, and washed with cold EtOH (2 × 5 mL, -32 °C), effecting dissolution of the yellow oil. The white crystals where collected and dried under reduced pressure to yield 0.22 g as raw product, containing \(N,N\)-diisopropyl-\(N\)-ethylammonium pivalate as impurity. Attempts to isolate the desired product through recrystallization in different solvents led to dissociation. Single-crystals of 6 were obtained by diffusion of Et\(_2\)O into a methanolic solution of the raw product at 4 °C. Under these conditions \(N,N\)-diisopropyl-\(N\)-ethylammonium pivalate crystals formed as well. \(^1\)H NMR (300 MHz, MeOH-\(d_4\) – impurified with \(N,N\)-diisopropyl-\(N\)-ethylammonium pivalate) \(\delta\) 8.08 (q, \(J = 5.8\), 1H), 2.67 (s, 3H), 2.47 (d, \(J=5.9\), 3H), 1.81 (s, 6H) ppm.

4\(^H\)-1,2,4-Triazole-3,4,5-triamine hydroiodide (Guanazinium iodide 36) (12)
The compound was obtained as an occasional dissociation product. Thiosemicarbazide (8) (5.00 g, 54.9 mmol) and 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8-iodooctane (9) (31.2 g, 65.8 mmol) were dissolved in EtOH (50 mL) and refluxed for 18 h. During cooling to room temperature white crystals formed in the yellow, malodorous solution. The solid was filtered off, washed with EtOH (2 × 5 mL) and dried under reduced pressure. Single-crystals suitable for X-ray diffraction analysis were obtained through recrystallization from boiling EtOH, Mp 218 °C (under decomposition), Mp 194 °C.\(^{35}\) \(^1\)H NMR (300 MHz, DMSO-\(\text{d}_6\)) \(\delta\) 12.46 (s, 1H), 7.06 (s, 4H), 5.58 (s, 2H) ppm. \(^{13}\)C NMR (75 MHz, DMSO-\(\text{d}_6\)) \(\delta\) 149.87 (2C) ppm. IR (neat): \(\nu\) 3369 (w), 3306 (m), 3237 (s), 3127 (m), 1692 (s), 1656 (vs), 1597 (m), 1575 (m), 1546 (m), 1526 (w), 1437 (w), 1309 (w), 1294 (m), 1129 (w), 1019 (m), 909 (m), 803 (w), 690 (m), 633 (m), 425 (w) cm\(^{-1}\).

\(S\)-(1\(H\),1\(H\),2\(H\),2\(H\)-Perfluorooctyl) 2-(propan-2-ylidene)hydrazine-1-carbothioate (13)

The compound was obtained as an undesired dissociation product in an attempt to synthesize 1. Acetone-thiosemicarbazon (11a, 1.50 g 11.4 mmol), 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8-iodooctane (9) (5.70 g, 12.0 mmol) and acetone (1.30 g, 22.8 mmol) were dissolved in EtOH (20 mL, 90%). Then HCl in water (1M, 5.00 mL) were added and the solution was refluxed for 72 h. The resulting malodorous, yellow solution was treated with Et\(_2\)O (70 mL) and kept at -32 °C for 16 h. The precipitate was filtered off, washed with Et\(_2\)O (2 × 20 mL) and dried under reduced pressure yielding 100 mg of a white solid. Single-crystals suitable for X-ray diffraction analysis were obtained through slow evaporation of an ethanolic solution of 10 at 4 °C, Mp 124 °C. \(^1\)H NMR (300 MHz, Chloroform-\(d\)) \(\delta\) 9.38 (s, 1H), 3.05 – 2.91 (m, 2H), 2.50 – 2.26 (m, 2H), 1.97 (s, 3H), 1.83 (s, 3H) ppm. \(^{13}\)C NMR (75 MHz, Chloroform-\(d\)) \(\delta\) 171.03, 151.74, 125-100 (6C, m), 32.47 (t), 25.33, 20.00, 16.59 ppm. IR (neat): \(\nu\) 3173 (w), 3049 (w), 1644 (s), 1441 (w), 1416 (w), 1363 (m), 1317 (m), 1296 (m), 1232 (s), 1232 (s), 1213 (s), 1183 (vs), 1139 (vs), 1075 (s), 955 (w), 910 (w), 720 (s), 708 (s), 686 (s), 634 (s), 565 (m), 527 (s) cm\(^{-1}\).

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