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The reactions of tosyl isocyanate with diethyl diphenylsulfuranylidenemalonate, 2-dimethylsulfuranylidenedimedone, and 2-dimethylsulfuranylideneindane-1,3-dione afforded 1,3-ditosyl-5,5-diethoxycarbonylimidazolidine-2,4-dione and tosylimination products at the keto groups, respectively. Phenyliodonium ylides derived from diethyl malonate and ethyl acetate react with 3,4-dichlorophenyl isocyanate to form substituted oxazolin-2-ones.

Key words: distabilized β -dicarbonyl sulfonium and iodonium ylides, aryl isocyanates, tosyl isocyanate, tosylimination, 1,3-ditosyl-5,5-dicarbethoxyimidazolidine-2,4-dione, oxazolin-2-one, X-ray diffraction study.

Distabilized cycloimmonium, sulfonium, and iodonium ylides derived from β -dicarbonyl compounds have attracted considerable attention as functional nucleophilic reagents.¹⁻³ The electronic structures of these compounds give promise that interesting results will be obtained in comparative studies of the reactions of distabilized ylides with isocyanates.

As part of our research on the reactions of carbanions with isocyanates,⁴ we qualitatively correlated the reactivities of distabilized β -dicarbonyl cycloimmonium, iodonium, and sulfonium ylides with the Mulliken charges on the ylide carbon atoms calculated by the quantum chemical DFT B3LYP/LanL2DZ method.

$$\begin{array}{c} -0.748 & -0.571 \\ \hline \\ N - \overline{C}[C(O)OMe]_2 & Ph - \overline{I} - \overline{C} \\ C(O)OMe \\ \hline \\ C(O)OMe \end{array}$$

 $\begin{array}{ccc} -0.261 & & -0.361 \\ & & & -0.361 \\ R_2 S - C \\ C(0) OMe \end{array} & & R_2 S - C [C(0) COMe]_2 \end{array}$

As can be seen from the above data, the highest negative charge is concentrated on the carbon atom of pyridinium ylide, the ylide carbon atom of the iodine derivative bears a somewhat lower negative charge, and the anionic charges are delocalized to the greatest extent in sulfur ylides. The nucleophilic reactivity of the ylides under consideration can correlate with the negative charges on the ylide carbon atoms. However, the scheme of interactions can also be influenced by the strength of the bond between the ylide carbon atom and the heteroatom. Apparently, this type of compounds have the weakest C—I bond. Therefore, in summary of the above-mentioned factors, pyridinium and phenyliodonium ylides would be expected to exhibit the highest reactivity toward isocyanates. However, the schemes of their interactions can be substantially differrent due to the above-mentioned structural features.

Actually, pyridinium ylide 1 reacts with aryl isocyanates at room temperature in a solution in CH_2Cl_2 providing the $C \rightarrow N$ migration of the ethoxycarbonyl group in the second step of the reaction. This rearrangement affords new pyridinium ylide 3 containing the carbamate function⁵ (Scheme 1).

The reaction according to Scheme 1 is a special case of the reactions of carbanions derived from esters with alkyl and aryl isocyanates giving rise to new types of carbamates through the insertion of the isocyanate molecule at the C—CO₂Alk bond of the starting carbanion.⁶ Taking into account the above-mentioned reactivity of nitrogen ylides toward aryl isocyanates and with the aim of comparing the reactivities of different distabilized ylides, we performed the reactions of isocyanates with iodonium and sulfonium derivatives, for which only scarce examples were documented.^{7,8}

The reactivity of iodonium ylides **4** toward aryl isocyanates was demonstrated to be comparable to that of pyridinium ylide **1**. The reactions of iodonium ylides with 3,4-dichlorophenyl isocyanate proceed at 0 °C but afford oxazolin-2-ones **7** rather than lead to the insertion of the isocyanate molecule at the C–C bond (*cf.* lit. data;⁷ Scheme 2). In addition, it should be emphasized that "dimers" **8a** and **8b** were found among the products of

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Scheme 1



these reactions (see Scheme 2). The structure of tetraethyl ethylenetetracarboxylate **8b** was established by X-ray diffraction.

Scheme 2



R = Me (a), OEt (b)Ar = 2,4-Cl₂C₆H₃

Since the bond between the iodine and carbon atoms in the assumed betaine **5** is weak and the formation of the aromatic system of iodobenzene is energetically favorable (*cf.* lit. data⁹), the C—I bond cleavage in the second step of the reaction leads, apparently, to α -elimination of iodobenzene and isocyanate and the formation of carbene **6**, which can undergo both dimerization and transformation into heterocycle **7** occurring as 2+3 cyclization.

The structure of oxazolin-2-one **7b** was established by elemental analysis, IR and NMR spectroscopy, and X-ray diffraction. It should be noted that the Raman spectra of compounds **7a,b** and **8a** show intense bands in the $1650-1670 \text{ cm}^{-1}$ region (C=C). There are four indepen-



Fig. 1. Molecular structure of compound 7b in the crystal.

dent structurally identical molecules in the crystal structure of **7b** (Fig. 1). In the crystals, molecules **7b** are nonplanar. The dichlorophenyl ring is twisted by 60° about the N(1)–C(9) bond. The oxazolinone ring, the CO₂Et group, and the O(3) and N(1) atoms are coplanar. The Et substituent of the ethoxy group is in an orthogonal orientation.

The structure of tetraethyl ethylenetetracarboxylate **8b** was established by X-ray diffraction. The crystal structure consists of the centrosymmetric isolated molecules (Fig. 2). The overall molecular conformation is characterized by the coplanar arrangement of two carboxylate substituents and the ethylenic bond, whereas two other carboxylate substituents are orthogonal to this bond (Table 1).

Taking into account that the basicity (and, apparently, the nucleophilicity) of distabilized sulfonium ylides is much lower than that of nitrogen and iodonium analogs,¹⁰ the reactivity of distabilized sulfonium ylides toward isocyanates would be expected to be lower. Actually, ylide 9 reacts with aryl isocyanates only at about 100 °C to



Fig. 2. Orientation of the CO_2Et groups relative to the ethylenic bond in molecule **8b**.



Scheme 3

form a complex mixture of nonidentified products. By contrast, the reaction with substantially more electrophilic tosyl isocyanate (TsNCO) smoothly proceeds in CH_2Cl_2 at 20 °C to give hydantoin **12** (Scheme 3).

Presumably, due to the high electron-withdrawing ability of the tosyl group, anion 10 generated in the first step is weakly nucleophilic. As a result, it cannot efficiently attack the carbonyl C atom of the ethoxycarbonyl group, which could lead to the rearrangement presented in Scheme 1. At the same time, the nucleophilicity of N-anion 10 is sufficiently high for this anion to react with the second tosyl isocyanate molecule to form anion 11. The latter undergoes cyclization giving rise to hydantoin 12 according to a known scheme.⁸ The structure of compound 12 was established by elemental analysis, IR and NMR spectroscopy, and X-ray diffraction. According to the X-ray diffraction data (Fig. 3), the central heterocycle is planar (within ± 0.03 Å) with the C(1) atom deviating from the plane through the other four atoms by only 0.132 Å. The sulfur and oxygen atoms also lie in this plane. Pairs of the benzene ring and the CO₂Et group are located on the opposite sides of the heterocycle. The bond lengths and bond angles (Table 2) in the heterocycle are typical of hydantoin rings.¹¹ The ¹H NMR spectroscopic study demonstrated that the methylene protons of the ethoxy groups in hydantoin 12 are magnetically nonequivalent, which is evidence for the

Table 1. Selected bond lengths (*d*), bond angles, and torsion angles (ω) in molecules **8b**

Bond	d∕Å	Angle	ω/deg
$\overline{C(1)-C(1A)}$	1.334(4)	C(2) - C(1) - C(5)	115.3(2)
C(1) - C(2)	1.513(2)	C(2) - C(1) - C(1A)	120.3(2)
C(1) - C(5)	1.511(2)	C(5) - C(1) - C(1A)	124.3(2)
C(2) - O(1)	1.203(2)	O(1)-C(2)-C(1)-C(1A)	1.6(4)
C(2) - O(2)	1.320(2)	O(3) - C(5) - C(1) - C(1A)	89.9(3)
C(5) - O(3)	1.199(2)		. ,
C(5) - O(4)	1.327(2)		
O(2) - C(3)	1.471(2)		
O(4) - C(6)	1.464(2)		
C(3) - C(4)	1.489(3)		
C(6) - C(7)	1.506(3)		

structural asymmetry of the molecule. Actually, X-ray diffraction study showed (Fig. 3) that the hydrogen atoms of both CH₂ groups are in a different intramolecular environment because the ethoxy groups have a different orientation relative to the heterocycle. The C(11)(=O(12))O(13)C(14)C(15) fragment is planar. The dihedral angle between this fragment and the plane of the heterocycle is 90.3°. The C(6)(=O(7))O(8)C(9)C(10)group is nonplanar (the C(6)O(8)C(9)C(10) torsion angle is 83.3°). The dihedral angle between the average plane of this group and the heterocycle is 28.3°. A consequence of the planar structure of the former ethoxy group is that both hydrogen atoms of the methylene group form intramolecular contacts with the carbonyl oxygen atom (O(12)...H(14a), 2.74 Å; O(12)...H(14b), 2.58 Å), whereas only one hydrogen atom of the nonplanar ethoxy group is involved in an analogous contact (O(7)...H(9a), 2.45 Å; O(7)...H(9b), 3.60 Å).

A comparison of the reactivities of distabilized sulfonium ylide (derivative of diethyl malonate) and distabilized sulfonium ylides containing the keto group at the ylide carbon atom is of considerable interest. Earlier,¹² we have described a new reaction of keto ylides **13** with tosyl isocyanate, which occurs at the keto group, the latter being transformed into the tosylimino group (Scheme 4).

Table 2. Bond lengths (*d*) and bond angles (ω) in molecule 12

Bond	d/Å	Bond	d∕Å
S(1)-N(3)	1.717(2)	N(5)-C(1)	1.470(4)
S(2) - N(5)	1.693(3)	N(5) - C(4)	1.385(4)
S(1) - C(16)	1.735(3)	C(4) - N(3)	1.412(4)
S(2)-C(23)	1.737(4)	N(3) - C(2)	1.400(4)
C(1) - C(2)	1.538(4)	C(2) - O(1)	1.191(3)
C(4)—O(2)	1.198(3)		
Angle	ω/deg	Angle	ω/deg
C(1) - N(5) - C(4)	112.3(2)	C(4) - N(3) - C(2)	111.2(3)
C(1) - N(5) - S(2)	124.8(2)	N(3) - C(2) - C(1)	106.6(3)
C(4) - N(5) - S(2)	121.9(2)	N(5) - C(1) - C(2)	101.6(2)
C(4) - N(3) - S(1)	121.5(2)	C(2) - N(3) - S(1)	126.8(2)
N(5)-C(4)-N(3)	107.0(3)		. ,



Fig. 3. Molecular structure of compound 12.

Scheme 4



R = C(O)Me(a), C(O)OEt(b)

Presumably, such an unusual behavior of keto ylides **13** is partly due to considerable delocalization of the nega-

tive charge resulting in a high negative charge on the oxygen atom of the keto group. As a result of this charge distribution, the attack occurs on the O atom. The X-ray diffraction data are consistent with this assumption. We demonstrated that the structure of keto ylide hemihydrate **13a** (see Ref. 13) consists of centrosymmetric H-bonded dimers formed by two ester molecules, which are linked together by strong C=O...H—O hydrogen bonds between the carbonyl groups and the water molecule (Fig. 4).

The hydrogen bond parameters are as follows: O(3)...O(3A), 2.730(2) Å; O(3)...H(1w), 1.88(2) Å;



Fig. 4. Centrosymmetric H-bonded dimer in the crystal structure of $13a \cdot 0.5H_2O$.

O(3)-H(1W)-O(1W), 169.4(8)°. The geometric parameters of ylide 13a are indicative of high polarization of the keto group due, evidently, to an efficient delocalization of the negative charge. The S(1)-C(2) bond length (1.737(1) Å) is substantially smaller than the typical $S-C_{sn^3}$ bond length, the C(3)-O(3) bond (1.257(2) Å) is substantially longer than the typical C=O bond in ketones and carboxylic acids (1.21 Å),¹⁴ and the C(2)-C(3) bond is stronger that the single C-C bond in ketones. This distribution of the bond lengths provides evidence for a substantial contribution of the betaine form Me_2S^+ -C(COOEt)=C(Me)-O⁻ along with the ylide form Me_2S^+ -C⁻(COOEt)C(Me)=O. Apparently, the betaine form is responsible for the formation of the strong hydrogen bond between the O(3) atom and the water molecule in the crystal structure.

The second step of the reaction (Scheme 4) is accompanied by the formation of energetically favorable carbon dioxide, which is the driving force of the process.

With the aim of extending tosylimination of keto ylides to other sulfonium keto ylides, we performed the reaction of TsNCO with cyclic diketo ylides **15** and **18**. In both processes, the first step of imination readily occurs to give monoylides **17** and **19**, respectively, in yields of about 70%. The replacement of the second keto group in keto ylide **16** occurs at high temperature.

By contrast, the reaction of cyclic diketo ylide **18** even with a large excess of TsNCO affords only monoylide. Apparently, such a large difference in the reactivity of keto ylides **15** and **18** in tosylimination is associated with

the total complex influence of the electronic and steric factors in the step of the replacement of the second keto group. The structures of the imination products were confirmed by elemental analysis, NMR spectroscopy, and IR spectroscopy. The three-dimensional structure of difficult difference of the solvate $17 \cdot \text{CHCl}_2$ was established by X-ray diffraction. The latter contains two crystallographically independent molecules, each being involved in an S=O...H(CHCl₃) hydrogen bond (O...H, 2.25 Å; CHO, 160°). The independent molecules are structurally identical (Fig. 5). The central ring adopts a sofa conformation with the C(3) atom deviating from the mean plane through the other atoms of the ring by 0.6 Å. The phenyl rings are orthogonal to the central ring and are located on the opposite sides of this ring. The geometric parameters of the molecules (Table 3) are indicative of the ylide structure. The C=N bond lengths in molecule 17 have typical values.¹⁴ The C(6)-C bond lengths (aver., 1.41 Å) are similar to the bond lengths in the benzene rings (1.39 Å). The C(6)-S(3) bond lengths (aver., 1.75 Å) are similar to the corresponding bond lengths in molecule 13a (1.737(1) Å) and the dication of bis(2-dimethylsulfoniocyclohexyl) sulfide.¹⁵

To summarize, the variety of the above-described transformations of isocyanates with nitrogen-, iodine-, and sulfur-substituted distabilized ylides is attributed both to the difference in the nucleophilicity and polarizability of these compounds and the structural features of the bonds between the heteroatoms and the ylide carbon atom.





Fig. 5. Molecular structure of compound 17.

Table 3. Selected bond lengths (*d*) and bond angles (ω) in two independent molecules (17A and 17B) in the crystal structure of $17 \cdot \text{CHCl}_3$

Parameter	Va	lue
	17A	17B
Bond	d,	/Å
C(1) - N(1)	1.274(7)	1.316(8)
C(5)-N(2)	1.313(7)	1.305(8)
N(1) - S(1)	1.635(6)	1.623(6)
N(2)-S(2)	1.634(6)	1.627(6)
C(6) - S(3)	1.767(6)	1.742(6)
S(3)-C(7)	1.787(7)	1.790(6)
S(3)-C(8)	1.769(6)	1.758(7)
C(1) - C(6)	1.411(8)	1.376(8)
C(1) - C(2)	1.550(8)	1.542(8)
C(2) - C(3)	1.503(8)	1.500(8)
C(3) - C(4)	1.525(8)	1.519(8)
C(4) - C(5)	1.513(8)	1.514(8)
C(5) - C(6)	1.405(8)	1.413(8)
Angle	ω/	deg
C(1) - C(6) - C(5)	126.1(6)	124.7(6)
C(6) - C(5) - C(4)	117.7(6)	117.7(6)
C(6) - C(1) - C(2)	112.9(6)	114.8(6)
C(1) - N(1) - S(1)	125.4(5)	125.0(5)
C(5)-N(2)-S(2)	120.8(5)	120.8(6)

Experimental

The NMR spectra were recorded on a Bruker AMX-400 spectrometer (400.26 MHz for ¹H and 100.68 MHz for ¹³C) in CDCl₃. The IR spectra were measured on a Magna-IR-750 (Nicolet) Fourier transform spectrometer (KBr pellets). The Raman spectra of solid samples were recorded on a LabRAM laser spectrometer (Jobin Yvou) at $\lambda = 632.8$ nm. The reactions were performed under dry nitrogen. The solvents were purified and dried before use.

Phenyliodonioacetylethoxycarbonylmethanide (4a) was synthesized according to a known procedure.¹⁶ ¹H NMR, δ : 1.19 (t,

3 H, C<u>H</u>₃CH₂, J = 7.2 Hz); 2.55 (s, 3 H, CH₃C(O)); 4.10 (q, 2 H, CH₃C<u>H</u>₂, J = 7.2 Hz); 7.32–7.75 (m, 5 H, H_{arom}).

Phenyliodoniodiethoxycarbonylmethanide (4b) was synthesized according to a known procedure.¹⁷ ¹H NMR, δ : 1.31 (t, 6 H, C<u>H</u>₃CH₂, J = 7.2 Hz); 4.31 (q, 4 H, CH₃C<u>H</u>₂, J = 7.2 Hz); 7.08–7.70 (m, 5 H, H_{arom}).

Ethyl 3-(3,4-dichlorophenyl)-5-methyl-2-oxooxazolin-4carboxylate (7a). A solution of 3,4-dichlorophenyl isocyanate (0.93 g, 4.95 mmol) in CH₂Cl₂ (20 mL) was added dropwise to a solution of 4a (0.55 g, 1.65 mmol) in CH₂Cl₂ (25 mL) at -10 °C. The reaction mixture was stirred at -10 °C for 1 h and then kept at 0 °C for 16 h. The precipitate was separated, the filtrate was concentrated in vacuo, and the residue was successively treated with hexane and ethyl ether. Diethyl acetylfumarate 8a was isolated from the hexane solution in a yield of 0.12 g (56.6%), m.p. 93-95 °C (cf. lit. data18: 94 °C). Found (%): C, 56.19; H, 6.25. C₁₂H₁₆O₆. Calculated (%): C, 56.24; H, 6.29. ¹H NMR, δ: 1.28 (t, 6 H, C \underline{H}_3 CH₂, J = 7.2 Hz); 2.45 (s, 6 H, CH₃C(O)); 4.25 (q, 2 H, CH₃C<u>H₂</u>, J = 7.2 Hz). IR, v/cm⁻¹: 1644 (C=C); 1713 (C(O)Me); 1724 (C(O)OEt). Raman spectrum, v/cm⁻¹: 1646 (C=C). Crystalline colorless product 7a was isolated from the ethereal solution in a yield of 0.15 g (28.8%), m.p. 136-137 °C. Found (%): C, 49.33; H, 3.41; N, 4.34; Cl, 22.17. C₁₃H₁₁Cl₂NO₄. Calculated (%): C, 49.39; H, 3.51; N, 4.43; Cl, 22.43. IR, v/cm⁻¹: 1644 (C=C); 1723 (C(O)OEt); 1776 (N-C(O)-O). Raman spectrum, v/cm⁻¹: 1596 (Ar); 1655 (C=C). ¹H NMR, δ : 1.18 (t, 3 H, C<u>H</u>₃CH₂, J = 7.2 Hz); 2.49 (s, 3 H, CH₃); 4.19 (q, 2 H, CH₃C \underline{H}_2 , ${}^{3}J$ = 7.2 Hz); 7.14 (dd, 1 H, H_{arom}, ${}^{3}J$ = 8.8 Hz, ${}^{4}J$ = 2.4 Hz); 7.40 (d, 1 H, H_{arom}, ${}^{4}J = 2.4 \text{ Hz}$; 7.50 (d, 1 H, H_{arom}, ${}^{3}J = 8.8 \text{ Hz}$). ${}^{13}\text{C}$ NMR, δ : 12.4 (<u>C</u>H₃CH₂); 13.8 (<u>C</u>H₃C-O-); 61.3 (CH₃<u>C</u>H₂); 115.6 (=<u>C</u>-C(O)OEt); 126.2, 128.9, 130.3, 132.5, 132.6, 133.7 (C_{arom}) ; 147.9 (=<u>C</u>-Me); 152.4 (OC=O); 158.2 (<u>C</u>(O)OEt).

Ethyl 3-(3,4-dichlorophenyl)-5-ethoxy-2-oxooxazolin-4carboxylate (7b). A solution of 3,4-dichlorophenyl isocyanate (2.73 g, 14.5 mmol) was added dropwise to a solution of 4b (1.75 g, 4.83 mmol) in CH₂Cl₂ (25 mL) at -10 °C. The reaction mixture was stirred at -10 °C for 1 h and then stored at 0 °C for 16 h. The precipitate was separated, the filtrate was concentrated, and the residue was successively treated with hexane and acetone. Ethyl ethylenetetracarboxylate 8b was isolated from the hexane solution in a yield of 0.39 g (51%), m.p. 44–46 °C (cf. lit. data¹⁹: 45–46 °C). Found (%): C, 53.21; H, 6.41; $C_{14}H_{20}O_8$. Calculated (%): C, 53.16; H, 6.37. ¹H NMR, δ : 1.27 (t, 12 H, CH_2CH_3 , J = 7.2 Hz); 4.27 (q, 8 H, CH_2CH_3 , J = 7.2 Hz). IR, v/cm⁻¹: 1657 (C=C); 1736 (C=O). Crystals of **7b** were isolated from the acetone solution in a yield of 0.4 g (24%), m.p. 132–134 °C. Found (%): C, 48.65; H, 3.74; N, 4.07; Cl, 20.59. $C_{14}H_{31}Cl_2NO_5$. Calculated (%): C, 48.58; H, 3.78; N, 4.05; Cl, 20.48. IR, v/cm⁻¹: 1786 (OC=O); 1723, 1707 (O=C–OEt), 1669 (C=C). Raman spectrum, v/cm⁻¹: 1667 (C=C). ¹H NMR, δ : 1.17 (t, 3 H, CH_3CH_2 , J = 6.8 Hz); 1.48 (t, 3 H, CH_3CH_2O , J = 7.2 Hz); 4.16 (q, 2 H, CH_3CH_2O , $^3J = 7.2$ Hz); 4.46 (q, 2 H, CH_3CH_2 , $^3J = 6.8$ Hz); 7.17 (dd, 1 H, H_{arom} , $^3J = 8.8$ Hz, $^4J = 2.4$ Hz); 7.40 (d, 1 H, H_{arom} , $^4J = 2.4$ Hz); 7.49 (d, 1 H, H_{arom} , $^3J = 8.8$ Hz).

Diethyl 2-diphenylsulfuranylidenemalonate (9) was synthesized by analogy with the known procedure.²⁰ A mixture of diethyl diazomalonate (1.23 g, 6.6 mmol), Ph₂S (5 mL), and CuSO₄ (20 mg) was heated at 90 °C for 5 h. Toluene (10 mL) was added, the precipitate was separated, and the filtrate was chromatographed on a silica gel column (toluene was used as the eluent for the separation of impurities, and the product was eluted with the use of CH₂Cl₂). The yield of ylide **9** was 0.57 g (25%), m.p. 106–108 °C. Found (%): C, 66.36; H, 5.76; S, 9.02. C₁₉H₁₀O₄S. Calculated (%): C, 66.25; H, 5.85; S, 9.31. IR, v/cm⁻¹: 1672, 1648 (C=O). ¹H NMR, δ : 1.15 (t, 6 H, ³*J* = 7.2 Hz); 4.12 (q, 4 H, CH₂, ³*J* = 7.2 Hz); 7.39–7.60 (m, 10 H, H_{arom}). ¹³C NMR, δ : 14.37 (CH₂CH₃); 59.40 (CH₂CH₃); 59.93 (C_{ylide}); 129.10, 129.23, 130.50, 131.04 (C_{arom}); 166.12 (C=O).

5,5-Diethoxycarbonyl-1,3-ditosylimidazolidine-2,4-dione (12). Tosyl isocyanate (0.89 g, 4.5 mmol) was added to a solution of ylide 9 (0.7 g, 2 mmol) in CH₂Cl₂ (2 mL). The reaction mixture was kept at 20 °C for 3 days, and then hexane was added. The target product was separated and recrystallized from a 1:5 CH₂Cl₂—hexane mixture. The yield was 0.67 g (62%), m.p. 168-170 °C. Found (%): C, 50.08; H, 4.57; S, 11.63. C₂₃H₂₄N₂O₁₀S₂. Calculated (%): C, 50.00; H, 4.35; S, 11.59. IR, v/cm⁻¹: 1758, 1764, 1777 (C=O). ¹H NMR, (CDCl₃), δ : 1.25 (t, 6 H, CH_2CH_3 , ${}^3J = 7.2$ Hz); 2.45 and 2.46 (both s, 3 H each, CH₃ in Ts); 4.30 (H_A), 4.33 (H_B) (C<u>H_AH_BCH₃, 4 H</u>, ${}^{3}J_{\text{H}_{\text{A}},\text{H}} = {}^{3}J_{\text{H}_{\text{B}},\text{H}} = 7.2 \text{ Hz}, {}^{2}J_{\text{H}_{\text{A}},\text{H}_{\text{B}}} = 10.8 \text{ Hz}); 7.36, 7.38, 7.96, and 8.08 (all d, 4 H, Ts, {}^{3}J = 7.6 \text{ Hz}). {}^{13}\text{C NMR (CDCl}_{3}), \delta:$ 13.54 (C(10), C(15)); 21.69, 21.73 (C(22), C(29)); 64.38 (C(9), C(14)); 73.65 (C(1)); 128.62, 129,35 (C(18), C(20), C(25), C(27)); 129.99, 130.11 (C(17), C(21), C(24), C(28)); 133.36, 133.87 (C(16), C(23)); 146.38, 146.43 (C(19), C(26)); 147.32 (C(4)); 156.95 (C(2)); 159.99 (C(6), C(11)).*

2-Dimethylsulfuranylidene-5,5-dimethylcyclohexane-1,3dione (15) and 2-dimethylsulfuranylideneindane-1,3-dione (18) were synthesized according to a known procedure.²¹

2-Dimethylsulfuranylidene-5,5-dimethyl-3-tosyliminocyclohexanone (16). A solution of ylide **15** (0.4 g, 3 mmol) in CHCl₃ (5 mL) was added to a solution of TsNCO (0.6 g, 3 mmol) in CHCl₃ (5 mL). The reaction started immediately and was accompanied by extensive elimination of CO₂. The reaction mixture was stirred at 20 °C for 12 h and then poured into hexane. The precipitate was separated and recrystallized from a 4 : 1 acetone—CHCl₃ mixture. The colorless product was obtained in a yield of 0.52 g (67%), m.p. 226–227 °C. Found (%): C, 57.68; H, 6.64; N, 4.00; S, 17.85. $C_{17}H_{23}NO_3S_2$. Calculated (%): C, 57.77; H, 6.56; N, 3.96; S, 18.14. IR, v/cm⁻¹: 1605 (C=O). ¹H NMR, δ : 0.97 (s, 6 H, CH₃); 2.22 (s, 2 H, CH₂); 2.38 (s, 3 H, Me_{Ts}); 2.91 (s, 6 H, Me₂S); 2.93 (s, 2 H, CH₂); 7.24 and 7.78 (both d, 2 H each, H_{arom}, ³J = 8 Hz).

2-Dimethylsulfuranylidene-5,5-dimethyl-1,3-bis-tosyliminocyclohexane (17). Ylide 15 (0.26 g, 1.3 mmol) was added to a solution of TsNCO (0.53 g, 2.6 mmol) in toluene (5 mL). The reaction was accompanied by extensive elimination of CO₂ and the formation of a precipitate. The reaction mixture was heated at 100 °C for 5 min and then stirred at 20 °C for 12 h. The precipitate was separated and recrystallized from toluene. A colorless product was obtained in a yield of 0.45 g (68%), m.p. 238-239 °C. Found (%): C, 56.93; H, 6.04; N, 5.41; S, 18.91. C₂₄H₃₀N₂O₄S₃. Calculated (%): C, 56.89; H, 5.98; N,5.53; S, 18.98. The IR spectrum shows no absorption bands of the CO groups in the 1600–1750 cm⁻¹ region. ¹H NMR, δ : 0.96 (s, 6 H, Me); 2.39 (s, 6 H, Me_{Ts}); 2.89 (s, 6 H, Me₂S); 2.94 (s, 4 H, CH_2 ; 7.25 and 7.76 (both d, 4 H each, Ar, J = 8 Hz). ¹³C NMR, δ: 21.36 (Me_{Ts}); 25.04 (Me–S); 27.69 (Me); 31.26 (CMe₂); 44.29 (CH₂); 87.06 (C_{vlide}); 126.28, 129.25, 140.31,142.42 (C_{arom}); 175.95 (C=N).

2-Dimethylsulfuranylidene-3-tosyliminoindanone (19). Ylide **18** (0.42 g, 2 mmol) was added to a solution of TsNCO (1 g, 5 mmol) in toluene (10 mL). The reaction mixture was heated at 100 °C for 5 h and then cooled. The crystalline precipitate was separated and crystallized. Bright-yellow crystals were obtained in a yield of 0.35 g (80%), m.p. 230–232 °C (decomp., from toluene). Found (%): C, 60.05; H, 4.71; N, 3.68; S, 17.78. C₁₈H₁₇NO₃S₂. Calculated (%): C, 60.14; H, 4.77; N, 3.89; S, 17.84. IR, v/cm⁻¹: 1649 (C=O), 1605 (Ar); 1523 v.s. ¹H NMR, δ : 2.42 (s, 3 H, Me_{Ts}); 3.13 (s, 6 H, Me₂S); 7.30–7.94 (m, 8 H, Ar). ¹³C NMR, δ : 21.41 (Me_{Ts}); 26.73 (Me–S); 75.64 (C_{ylide}); 120.07, 121.46, 128.09, 129.11, 131.38, 131.92, 135.40, 140.34, 141.12, 142.32 (C_{arom}); 168.59 (C=N); 189.96 (C=O).

Quantum chemical calculations. The charges were calculated with the use of the Gaussian-98 program package.²²

X-ray diffraction study. The crystallographic data, details of X-ray data collection, and parameters of the structure refinement for compounds **8b**, **12**, **13b** \cdot 0.5 H₂O, and **17** \cdot CHCl₃ are given in Table 4.

The intensities of reflections were integrated and the equivalent reflections were merged using the SAINT²³ and SAINTPlus programs.²⁴ Absorption corrections were applied using the SADABS program.²⁵

The structures were solved by direct methods. All nonhydrogen atoms were located in difference electron density maps and refined anisotropically against F_{hkl}^2 . All hydrogen atoms were placed in geometrically calculated positions and refined using a riding model with U(H) = nU(C), where n = 1.2 and 1.5 for the methylene and methyl groups, respectively, and U(C) are the equivalent thermal parameters of the C atoms to which the corresponding H atoms are bound. All calculations were carried out using the SHELXTL PLUS 5 program package.²⁶ For compounds **12**, **13a**, and **17**, semiempirical absorption corrections were applied based on equivalent reflections.

Colorless plate-like crystals of compound **7b** were obtained as twins. Numerous attempts to find a single-crystalline fragment (or to perform additional recrystallization) were unsuccesfull. We also failed to separate the X-ray intensity data (14441 reflections), which were collected on a Bruker SMART

^{*} The atomic numbering scheme for C atoms is given in Fig. 3.

Compound	8b	12	13a • 0.5(H ₂ O)	17 • CHCl ₃		
Molecular formula	C ₁₄ H ₂₀ O ₈	C ₂₃ H ₂₄ N ₂ O ₁₀ S ₂	C ₈ H ₁₅ O ₃₅ S	C ₂₅ H ₃₁ Cl ₃ N ₂ O ₄ S ₃		
Molecular weight	316.30	552.56	199.26	626.05		
Space group	$P\overline{1}$	$P\overline{1}$	C2/c	$P\overline{1}$		
T/K	140(2)	293(2)	110(2)	120(2)		
a/Å	7.7502(14)	8.561(2)	11.087(2)	5.831(2)		
b/Å	7.9240(15)	10.747(2)	10.484(2)	22.680(9)		
c/Å	8.0293(15)	14.376(3)	18.529(3)	23.077(10)		
α/deg	72.984(4)	81.934(5)	_	71.370(10)		
β/deg	67.102(4)	80.651(5)	100.874(4)	82.889(10)		
γ/deg	61.963(3)	82.212(5)	_	82.645(8)		
$V/Å^3$	397.3(1)	31283.7(5)	2115.1(7)	2857(2)		
Ż	1	2	8	4		
$d_{\rm calc}/{\rm g}~{\rm cm}^{-3}$	1.322	1.430	1.251	1.455		
Crystal color	Colorless	Colorless	Colorless	Colorless		
and shape	prism	plate	plate	plate		
Dimensions/mm	0.60×0.40×0.30	0.20×0.15×0.03	0.60×0.45×0.30	0.25×0.20×0.15		
Diffractometer		Bruker S	MART			
Radiation		Mo-K α (λ =	0.71073 Å)			
μ/cm^{-1}	1.0979	2.66	2.83	5.75		
$T_{\rm min}/T_{\rm max}$	_	0.962/0.677	0.3470/1.000	0.962/0.677		
Scanning mode		, φ/σ	ώ	,		
$2\theta_{\rm max}/{\rm deg}$	52.00	56.10	60.06	46.52		
Total number of reflections	3076	13318	18096	13840		
Number of independent	1347	6160	3082	8069		
reflections (R_{int})	(0.0969)	(0.0625)	(0.0192)	(0.0939)		
R_1 (based on F for reflections	0.0737	0.0554	0.0467	0.0682		
with $I \ge 2\sigma(I)$)	(1089 refl.)	(2124 refl.)	(2801 refl.)	(2754 refl.)		
wR_2 (based on F^2 for	0.1419	0.1401	0.1334	0.1078		
all reflections)						
Number of parameters in refinement	102	408	118	619		
Weighing scheme	$w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$ where $P = 1/3(F^2 + 2F^2)$					
a	0.0013	0.0532	0.0988	0.0011		
b	0.2500	0	0.7839	0		
GOOF	0.966	0.771	1.022	0.910		
<i>F</i> (000)	168	576	856	1304		

Table 4. Crystallographic data and details of the structure refinement for compounds 8b, 12, 13a • 0.5H₂O, and 17 • CHCl₃

diffractometer at 140 K, into single-crystalline sets with the use of the GEMINI program.²⁷ Crystals of **7b** (C₁₄H₁₃Cl₂NO₅, M = 346.15) are triclinic, at 140 K a = 7.921(15) Å, b =14.47(3) Å, c = 25.78(5) Å, $\alpha = 81.94(3)^{\circ}$, $\beta = 85.55(3)^{\circ}$, $\gamma = 89.67(3)^{\circ}$, V = 2916(9) Å³, space group $P\overline{1}$, Z = 8, $d_{calc} = 1.577$. The refinement by the least-squares method converged to a high *R* factor ($R_1 = 0.1981$; calculated based on 3339 reflections with $I > 2\sigma(I)$); 626 parameters were refined. All four crystallographically independent molecules are structurally identical. The errors in bond lengths and bond angles were high (0.01–0.03 Å and 1–2°, respectively) and did not allow us to compare these parameters. These data should be considered as preliminary results, which provide a reliable insight into the overall molecular structure of compound **7b**.

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