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1,3-Dipolar Cycloaddition Reactions of α-Diazocarbonyl Compounds, Organoazides, and Ethynyl(phenyl)iodonium Triflate Salts

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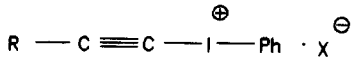
Abstract: The electron-poor triple bond of R-C≡C-I^+-Ph·TfO$^-$ (**1**, R = H, $SiMe_3$, *t*BuCO) undergoes [2+3] cycloaddition with α-diazocarbonyl compounds. Whereas 1:1 cycloadducts (**4a-d,6**) are obtained for R = $SiMe_3$ or *t*BuCO (X-ray structure analysis of **4b**), diazoacetic esters react with two equivalents of the parent alkyne (**1**, R = H) to form bis-iodonium salts **9**. Cycloaddition of methyl or phenyl azide to **1** yields (1,2,3-triazolyl-4-yl)iodonium salts (**13,14**) in low yield.

Alkynyl(phenyl)iodonium salts **1** represent highly activated, electron-deficient alkynes with a strongly polarized[1] C≡C bond. By virtue of their ability to couple with a wide range of nucleophiles (e.g. diketonates[2,3], 2-lithio-furan and -thiophene[4a], organocuprates[5], Cl^- [2], N_3^- [6], trialkoxyphosphanes[7], as well as anionic sulfonates[8], carboxylates[9], and phosphates[10], they have recently become valuable synthetic building blocks[11,12]. However, the cycloaddition behavior of **1** towards 1,3-dipoles, except for some nitrile oxides and nitrones[13] (with **1**, R = aryl, X = TsO^-), has not been explored. It is expected that the strong electron-withdrawing effect of the iodonium substituent renders alkynes of type **1** comparable in reactivity to neutral alkynes bearing electron-withdrawing substituents such as COOR, CN, or CF_3. We wish to report here our results concerning some 1,3-dipolar cycloadditions of α-diazocarbonyl compounds and organic azides to ethynyl(phenyl)iodonium triflates **1a-d**.



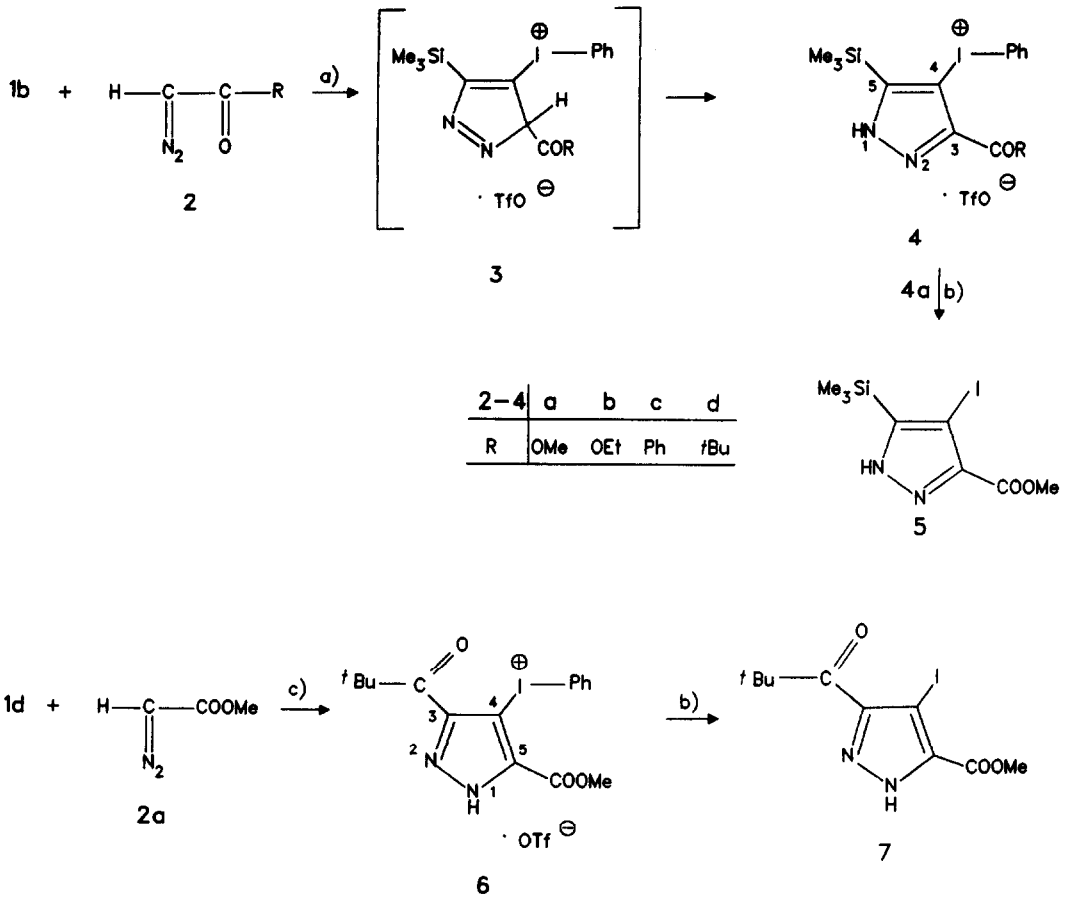
1

1	a	b	c	d
R	H	Me_3Si	*t*Bu	*t*BuC(=O)
X	TfO	TfO	TfO	TfO

RESULTS AND DISCUSSION

Cycloaddition reactions of Diazo Compounds

α-Diazocarbonyl compounds such as **2** undergo [3+2] cycloaddition to a number of electron-poor alkynes[14]. Similarly, **2a-d** behave as 1,3-dipoles towards **1b**. In a slow reaction (reaction time **2a,b<2c<2d**), (4-pyrazolyl)-phenyliodonium salts **4** are obtained as colorless, air-stable crystalline compounds, wich arise from precursor [3+2] cycloaddition products **3** by a fast hydrogen shift.



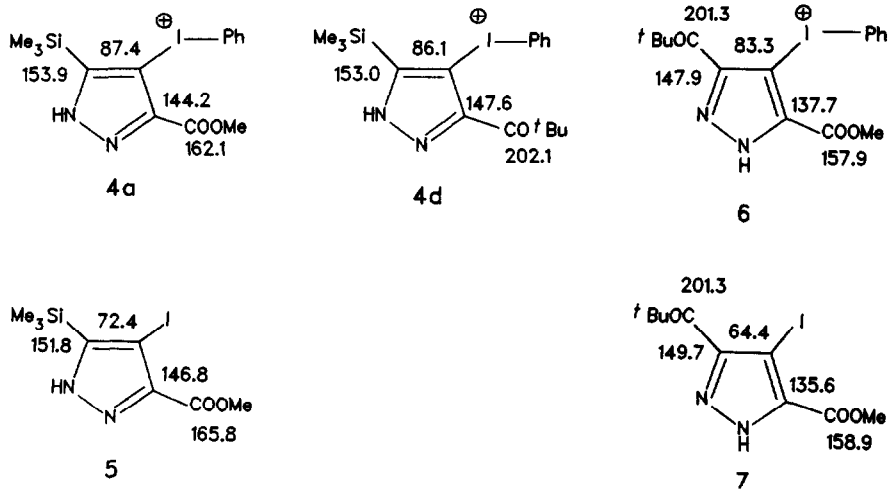
Scheme 1. Reaction conditions: a) CH_2Cl_2, r.t., 4-8 days, 14-49 %; b) NaI/CH_3CN, then 160 °C / 2 min; c) CH_2Cl_2, r.t., 17 h, 43 %.

Although the isolated yields of **4a-d** are low, the second possible regioisomeric cycloaddition product was not detected in any of the reaction mixtures. The constitution of **4a-d** is established by an X-ray structure analysis of **4b** (see below) and the similarity of ^{13}C NMR data for the heterocyclic ring carbon atoms of all four compounds [δ(C-3) 144.3-149.5, δ(C-4) 86.1-87.4, δ(C-5) 153.0-154.0 ppm; the assignment of δ(C-3) is based on the greater variance between **4a-d** as compared to δ(C-5)].

Diazoester **2a** adds to the particularly electron-poor triple bond of **1d** to give **6** in moderate yield; this cycloaddition is distinctly faster than those described above for **1b**. Again, only one regioisomer is isolated; based on the close similarity of the ^{13}C chemical shift for C-4 with the values obtained for pyrazoles **4**, the cycloaddition is likely to have the same regiochemistry in all these cases.

Pyrazolyl(phenyl)iodonium salts **4** and **6** can be converted into the neutral 4-iodopyrazoles **5** and **7**, resp., according to a literature procedure[13] (anion exchange $TfO^- \rightarrow I^-$, followed by thermal[15] elimination of iodobenzene). For all NH pyrazoles presented here, the question of annular tautomerism arises[16]. For **4a**, an answer is given by the X-ray structure analysis, and it seems justified to assume the same constitution for both, the solid state and the solution. As already mentioned, ^{13}C NMR data suggest the same tautomeric structure for all pyrazoles **4a-d**. Furthermore, since the chemical shifts of

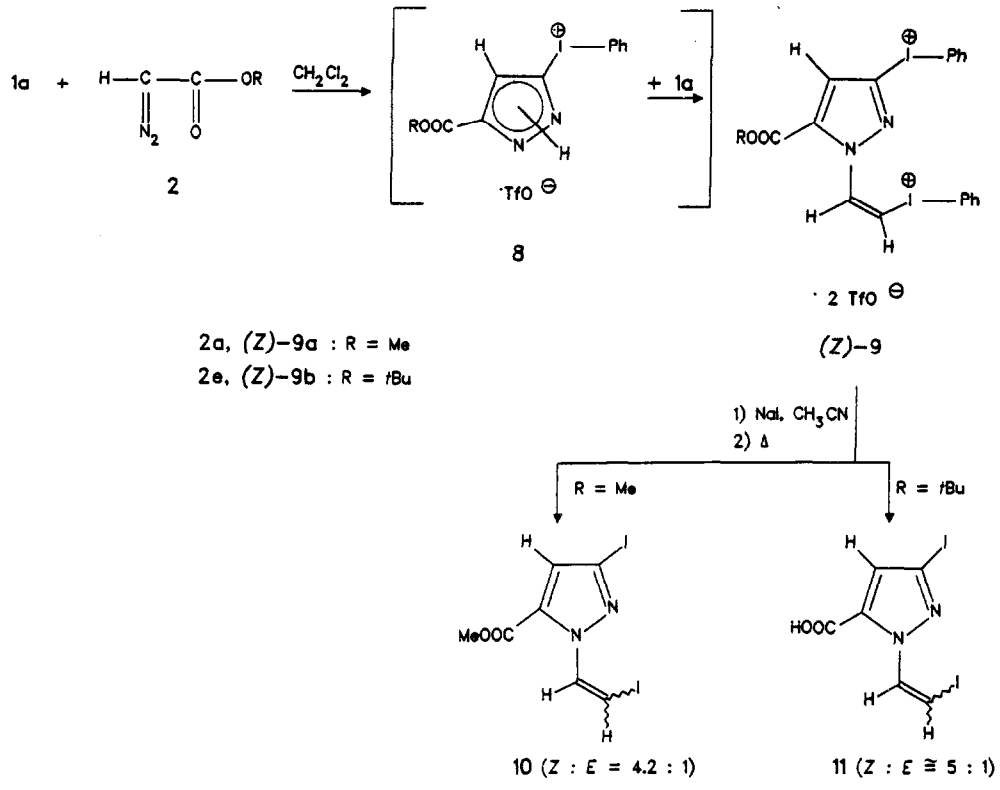
the ring carbon atoms C-3 and C-5 change by ≤ 3 ppm when going from **4a** to iodopyrazole **5**, the latter is likely to have the same ring constitution, too (Scheme 2). In contrast, ^{13}C NMR spectra suggest the constitution with the ester group attached to ring position 5 for pyrazoles **6** and **7**. If **6**(**7**) had the same tautomeric structure as **4a**(**5**), replacement of Me_3Si by *t*BuCO would not be expected to entail a high-field shift of the COOR signal of 4.2(6.9) ppm (Scheme 2). On the other hand, if one formally derives **6** from the 3-pivaloylpyrazole **4d** and replaces 5-$SiMe_3$ by 5-COOMe, it is expected that only δ(C-5) changes significantly, and the predicted high-field shift[17] is indeed observed. The preceeding discussion does not touch the question, whether pyrazoles **4**-**7** exist in solution exclusively as the tautomers shown in the formulae or as the major components of a tautomeric equilibrium. No investigations on this matter have been undertaken.



Scheme 2. Comparison of ^{13}C NMR chemical shifts for some (4-pyrazolyl)-iodonium salts and 4-iodopyrazoles [δ values, ppm; solvent CD_3CN (**4a**,**4d**,**6**) or $CDCl_3$ (**5**,**7**)].

From the reaction of ethynyl(phenyl)iodonium salt **1a** with diazoacetate **2a**, only a 2:1 adduct ((*Z*)-**9a**) could be isolated. This dicationic salt was transformed into the neutral diiodide **10** by the method described above, whereby a partial *Z*→*E* isomerization occurs at the vinylic double bond [^1H NMR assignment of configuration: $^3J(H,H)_{cis} < {}^3J(H,H)_{trans}$]. For a definite proof of the pyrazole substitution pattern, an X-ray structure analysis was intended, but no suitable crystals were obtained. Therefore, the reaction sequence was repeated with *t*-butyl diazoacetate **2e** instead of **2a**. At the temperature required for the transformation of (*Z*)-**9b** into the neutral diiodide, the ester function is converted into the carboxylic acid, and an X-ray crystal structure analysis of the pyrazole carboxylic acid (*Z*)-**11a** could be carried out (see below). Based on the comparison of ^1H NMR spectra, the constitution of all pyrazoles **9**-**11** could now be assigned beyond doubt. ^{13}C NMR chemical shifts of the ring carbon atoms correspond reasonably well to those of model compounds[18].

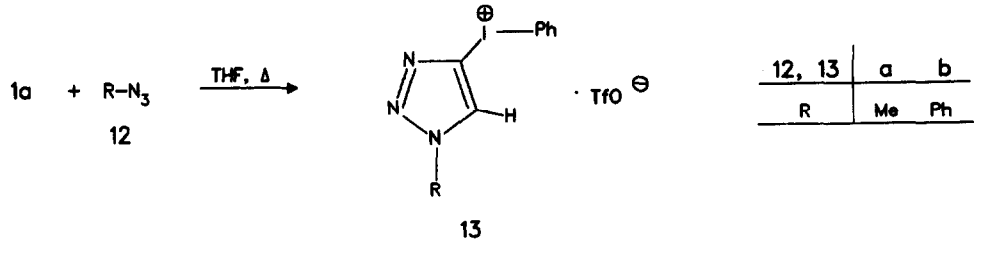
In mechanistic terms it is reasonable to assume that the initially formed [3+2] cycloaddition product **8** (note that the regiochemistry of this addition is opposite to that observed for the internal alkynes **1b**-**d**) undergoes a fast Michael addition to excess alkyne **1a**. We did not succeed in obtaining the 1:1 adduct **8** by appropriate reaction conditions (slow addition of diazo compound to **1a**, overall 1:1 stoichiometry, see Experimental Part).



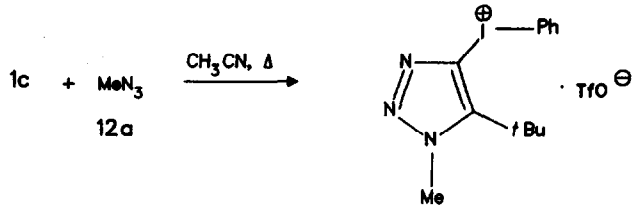
Scheme 3

Cycloaddition of organoazides to ethynyl(phenyl)iodonium salts

In contrast to a report[13] that no products were isolated from the reaction of **1** (R =Ph, X=TsO) with tosyl azide or NaN_3, methyl azide (**12a**) adds to **1a** and **1c** under forcing conditions in the [3+2] mode to give (1,2,3-triazol-4-yl)phenyliodonium salts **13a** and **14**, resp. (Scheme 4; **13a**: 85 °C, 50 h, 25 %; **14**: 75 °C, 28 h, 26 %). Under analogous conditions, phenyl azide (**12b**) does not react with **1c**, whereas cycloaddition to the terminal triple bond of **1a** yields triazole **13b** in low yield (17 %). Similar to the cycloaddition reactions with the diazo 1,3-dipoles, formation of only one regioisomer was observed in all cases.



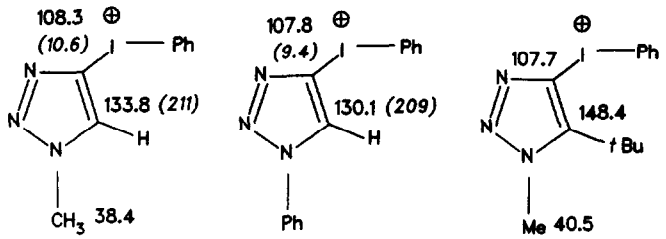
12, 13	a	b
R	Me	Ph



14

Scheme 4

The constitution of **13a,b**, and **14** is derived from ^{13}C NMR assignments (Scheme 5). One notes that replacement of N-Me by N-Ph (**13a**→**13b**) causes a shift of δ(C-5) by -3.7, and of δ(C-4) by -0.5 ppm. These changes correspond qualitatively to the differences found between 1-methyl- and 1-phenyl-1,2,3-triazole[19] [Δ(C-5) -2.6, Δ(C-4) +0.5 ppm]. On the other hand, if our triazoles were of the 2H-1,2,3-triazole type, replacement of N-Me by N-Ph would cause a very similar change of δ(C-4) and δ(C-5) (+1.4 ppm for 2-methyl- → 2-phenyl-1,2,3-triazole[19]).



Scheme 5. ^{13}C NMR data (δ, in CD_3CN) for triazoles **13a,b**, and **14**. Values in italics represent coupling constants [Hz].

Regioselectivity of the cycladdition reactions

In each of the cycloaddition reactions described above, only one heterocyclic product (pyrazole or triazole derivative) was isolated. Although the yields were low and the material balance was far from complete, it is unlikely that cycloaddition products resulting from the opposite orientation of the reactants have been lost during the work-up procedure or have escaped our attention during NMR spectroscopic analysis (detection limit ca. 2 %). Hence, we consider these cycloaddition reactions to be at least highly regioselective.

In discussing the reasons for the regioselectivity observed in every case, we begin with the observation that the pyrazoles derived from the parent ethynyliodonium salt **1a** (*i.e.* **9a,b**) stem from a cycloaddition orientation opposite to that leading from disubstituted alkynes **1b,d** to pyrazoles **4** and **6**. As we have already stated in the introduction, ethynyliodonium salts **1** are expected to display dipolarophilic qualities similar to those of other, more familiar electron-deficient alkynes. Cycloaddition of diazo dipoles to the triple bond of H-C≡C-CO-R yields the corresponding 3,5-disubstituted pyrazole with high or complete regioselectivity[14,20], in agreement with both, the FMO approach to the theory of 1,3-dipolar cycloaddition reactions[21-23], and the charge distribution in the reactants. The formation of

pyrazoles **9** indicates a fully analogous behavior between acylated terminal alkynes and ethynyliodonium salt **1a**, and one may wonder what factors cause the reversal of regiochemistry, when alkynes **1c,d** are used as dipolarophiles. Since neither frontier orbital energies nor orbital coefficients are known, an FMO treatment can be done merely in a qualitative way. The regioselectivity observed in the cycloaddition of diazo acetates to monosubstituted electron-poor alkynes is to be attributed to the dominant HOMO(dipole)-LUMO(dipolarophile) interaction (see lit.[21] for the reaction involving olefinic dipolarophiles). Introduction of a second electron-withdrawing substituent at the alkyne will lower both the HOMO and the LUMO and, therefore, strengthen the HOMO(dipole) control. Furthermore, the replacement of the acetylenic hydrogen by an acyl group (**1a**→ **1d**) will very much diminish, if not reverse, the difference in magnitude of the LUMO(C≡C) coefficients. In either case, one expects that **1d** accepts the diazo dipole (HOMO coefficients of **1a**[21]: 0.68 at the diazo carbon, -0.50 at the terminal nitrogen) with a regioselectivity opposite to that displayed by **1a**. If the LUMO(C≡C) orbital coefficient at the carbon atom adjacent to the iodonio group becomes larger than that at the ß carbon, the observed regiochemistry[24] would correspond to the principle of maximum orbital overlap; if the two orbital coefficients are of similar magnitude, this principle is of reduced importance due to the not very pronounced difference between the HOMO coefficients at the dipole termini, and steric effects can take over. In that case, the COOMe group of the dipole is predicted to develop less steric interaction with the phenyliodonio substituent (the bond length C-I is 2.03 Å, see below) than with the pivaloyl group.

The arguments trying to explain the dipole orientation leading to the formation of **4** are similar to the preceding ones. The $SiMe_3$ group is known as a π-withdrawing substituent[25]. Hence, it has the same directing effect in 1,3-dipolar cycloaddition reactions as other electron-withdrawing groups, but its influence is easily overridden by more strongly conjugating substituents[25,26]. For example, in the cycloaddition of monosubstituted diazoalkanes and of ethyl diazoacetate to 3-trimethylsilyl-propenoates the diazo carbon invariantly adds to the olefinic carbon atom adjacent to the silyl group, and steric hindrance between $SiMe_3$ and a bulky diazo substituent does not seem to be of importance[27]. Therefore, ethynyliodonium salts **1a** and **1b** should accept the diazoester **1a** under the same orientation. Since electronic factors definitely do not explain the observed reversal of the regiochemistry, we invoke steric factors. In the "two-plane orientation complex" describing the transition state of 1,3-dipolar cycloadditions[21,22], the extent of repulsive interactions between substituents at the carbon atoms which will become C3 and C4 in the resulting 1-pyrazoline (or 3H-pyrazole) is different for olefinic and acetylenic dipolarophiles. Whereas in the former case, bulky substituents at these positions will arrange themselves in a *trans* geometry in order to avoid steric repulsion, the acetylenic case brings the two substituents in a *gauche* relationship. Thus, the dipole orientation expected on electronic grounds for the reaction of **1a,b** with diazocarbonyl compounds **2a-d** would create considerable steric interaction between the $SiMe_3$ and the acyl groups, even in an early transition state. Once again, the opposite cycloaddition direction (i.e. the one leading to **3**) does not suffer from severe steric interactions, because the C-I bond is still longer than the C-Si bond and the (I-)phenyl group does not interfere with the acyl group of **2**.

Cycloaddition of phenyl or alkyl azides to monosubstituted electron-deficient acetylenes usually yields a mixture of 1,4- and 1,5-disubstituted 1,2,3-triazoles, in which the 1,4-isomer predominates[21,28,29]. HOMO(azide) control is considered to account for the major regioisomer. Insofar, the formation of (1-R-1,2,3-triazol-4-yl)iodonium salts **13a,b**, and **14** is in line with the expectations. The second possible regioisomer has been formed either not at all or only in trace amounts and was therefore not detected; eventually, it may even have decomposed thermally under the harsh reaction conditions. The fact that the disubstituted alkyne **1c** reacts with methyl azide, but not with phenyl azide, should be attributed to steric hindrance; if so, this further supports the assignment of the constitution of **14**.

Crystal structure analysis of **4b** *and* **(Z)-11**

An ORTEP plot of salt **4b** in the solid state is shown in Fig. 1, selected values for the intramolecular bond geometry are given in Table 1. The steric strain between the three neighboring substituents at the pyrazole ring is relieved partly by torsions around the C3-C1 and C3-C2 bond, resp., and partly by the enlargement of the C3-C2-Si and (to a lesser extent) C3-C1-C4 bond angles. The angle C3-I-C7 (98.1°) is significantly (*i.e.* by ca. 6°) larger than in several diaryliodonium salts[30,31] or in an aryl(hetaryl)iodonium salt[13], whereas the almost perpendicular arrangement of the phenyl and pyrazole rings meets expectations. Besides the two primary I-C bonds (2.032 and 2.121 Å), two secondary I··O bonds (2.786 and 2.938 Å, the oxygen atoms involved belong to different anions) are found. The latter contacts are in between the sum of the covalent radii (1.99 Å) and the sum of the van der Waals radii of I and O (3.5 Å). Similar contacts have been found in other structures containing iodonium cations and oxygen-containg anions, e.g. ethynyl(phenyl)iodonium triflate[1a] (2.620, 2.915 Å, both oxygen atoms in the same anion), (3-mesityl-5-phenyl-1,2-oxazol-4-yl)phenyliodonium tosylate[13] (2.691, 2.735 Å), and diphenyliodonium nitrate[32] (2.768, 2.877 Å). The I··O contacts in **4b** are aligned (Table 2) with the C-I bonds so as to form a planar tetragonal coordination around the iodine atom; the iodine atom is displaced by only 0.036 Å from the least-squares plane defined by C3-C7-O4-O5' (deviations of the defining atoms from this plane are ≤0.012 Å). We leave it open to speculation, whether the intramolecular distance I··O1 [3.217(6) Å] is to be taken for an additional coordination site around the iodine atom.

The basic unit of the crystal structure is a centrosymmetric dimer built up from two cations and two anions and held together by the I··O interactions, in which the atoms I, O4, S, O5 and their centrosymmetric equivalents form a chair-shaped eight-membered ring. Such a coordination has been observed in a related salt before[13]. In the crystal structure of **4b**, however, a further intermolecular coordination exists. Whilst two oxygen atoms of the triflate anion maintain I··O contacts, the third one is involved in an O··H-N hydrogen bond. Since one triflate anion bridges not only two cations via coordination to the iodine atoms, but also associates with a third cation by a hydrogen bond to the pyrazole ring (Fig. 2), a linear polymeric chain is built up.

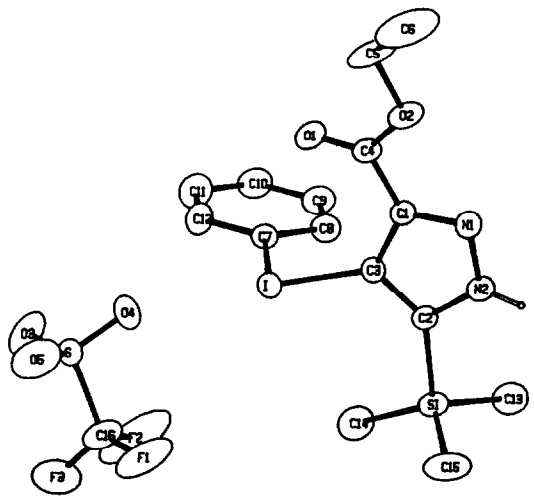


Fig.1 ORTEP plot of **4b**. The size of the ellipsoids of thermal vibration corresponds to a 20% probability.

The coordinating properties of the triflate anion described here -i.e. involvement of O-S-O in an eight-menbered coordination dimer and use of the third oxygen for extended coordination - may reflect a general behavior in a suitable solid environment; further examples are provided by the crystal structure of trifluoromethanesulfonic acid monohydrate[33] and the Cu(I)triflate- cyclohexene complex[34]. It is interesting to note that, despite of its function in holding together the coordination polymer, the triflate anion is subject to some oriental or vibrational disorder. This fact is at least partly responsible for the observed scatter of the S-O and C-F bond distances.

Table 1. Selected Bond Lengths, Bond Angles, and Torsion Angles in **4b**

	bond lengths [Å]	
I - C3 2.032(5)	N1 - N2 1.341(7)	C3 - C1 1.403(7)
I - C7 2.121(6)	N2 - C2 1.336(7)	S - O3 1.391(5)
I - O4 2.786(8)	C2 - Si 1.892(6)	S - O4 1.344(6)
N1 - C1 1.312(7)	C2 - C3 1.387(7)	S - O5 1.367(6)
	bond angles [°]	
C3-I-C7 98.1(2)	I -C3-C1 126.4(4)	Si-C2-N2 120.9(4)
C3-I-O4 171.1(2)	I -C3-C2 125.3(4)	C3-C1-C4 126.7(6)
C7-I··O4 90.6(3)	Si-C2-C3 137.2(4)	N1-C1-C4 122.8(5)
	torsion angles [°]	
C7-I-C3-C2 -97.6	C3-C1-C4-O1 -10.8	Si-C2-C3-I 9.9
C4-C1-C3-I -11.1		

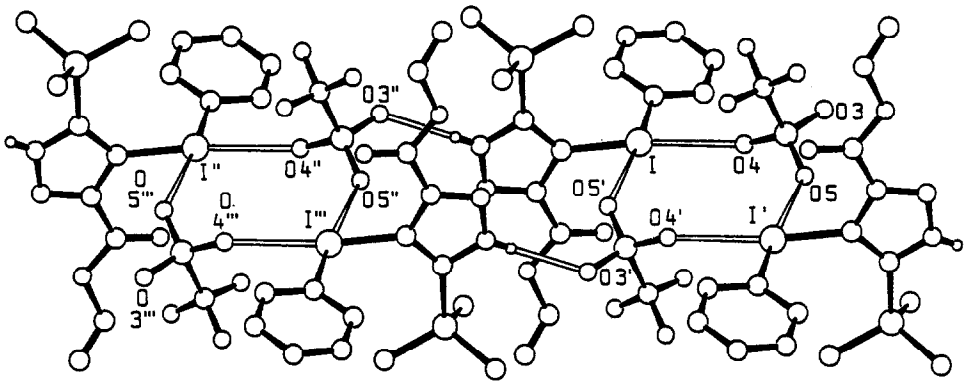


Fig. 2. Cation-anion coordination in the crystal structure of **4b**. Symmetry code: atom, x,y,z; atom', 2-x,-y,1-z; atom", x-1,y,z; atom"', 1-x,-y,1-z. Shown is the repeating unit of an infinite chain extending in the direction of the *x*-axis.

Table 2. Cation-Anion Coordination in the Crystal Structure of **4b** (Distances [Å] and Angles[°]; for Symmetry Code, see Fig. 2)

I··O4	2.786(8)	I··O5'	2.938(6)	N2··O3"	2.809(10)	H(N2)··O3"	2.10(5)
C3- I··O4	171.1(2)	C3- I··O5'	76.3(2)	I'·· O5-S	138.6(5)		
C7- I··O4	90.6(3)	C7- I··O5'	174.4(3)	N2-H(N2)··O3"	171(5)		
O4 I··O5'	95.0(3)	I·· O4-S	155.7(6)				

Fig.3 shows the molecular structure of (*Z*)-**11a** in the solid state. Selected values for the bond geometry are given in Table 3. The carboxyl group is nearly coplanar with the pyrazole ring, whereas the vinyl group assumes an approximately perpendicular conformation with respect to the latter. In this

manner, and by widening of the exocyclic angle C3-N2-C4, steric hindrance between the vicinal substituents at the N2-C3 bond is greatly reduced. Another remarkable feature of the structure is the unusually short C4-C5 double bond (1.28 Å).

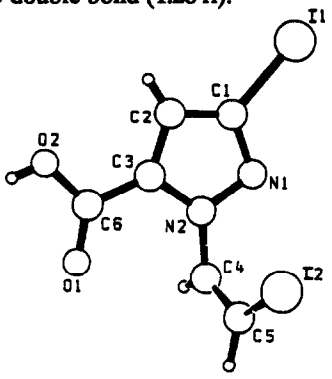


Fig. 3. SCHAKAL plot of (*Z*)-**11a** in the solid state. Two COOH groups are connected by an inversion center, so that a carboxylic acid dimer is formed; O2-H(O1) 0.75(14) Å, H(O1)···O1' 1.90(14) Å, angle O2-H(O1)···O1' 170(12) °.

Table 3. Selected Bond Lengths, Bond Angles, and Torsion Angles in (*Z*)-**11a**.

		bond lengths [Å]			
I1 - C1	2.057(8)	C3 - N2	1.36(1)	N2 - C4	1.41(1)
C1 - C2	1.35(1)	N1 - C1	1.33(1)	C4 - C5	1.28(1)
C2 - C3	1.37(1)	N1 - N2	1.345(9)	I2 - C5	2.072(9)
		bond angles [°]			
C2-C3-C6	132.6(8)	N1-N2-C3	110.7(6)	N2-C4-C5	124.1(8)
N2-C3-C6	121.3(7)	C3-N2-C4	130.0(7)	C4-C5-I2	122.6(7)
		torsion angles [°]			
N2-C3-C6-O1	-3.1(1.2)	C3-N2-C4-C5	-116.2(1.0)		
C4-N2-C3-C6	4.2(1.2)	N2-C4-C5-I2	8.5(1.2)		

EXPERIMENTAL

General information. ^{1}H NMR spectra: Varian EM 390 (90 MHz) and Bruker AM 400 (400 MHz); TMS as internal standard. ^{13}C NMR spectra: Bruker AM 400 (100.6 MHz); TMS as internal standard. IR spectra: Perkin-Elmer IR 397; wavenumbers [cm^{-1}] are given. Elemental analyses: Perkin-Elmer EA 2400. Melting points: Mettler FP5 and FP51 (3° min^{-1}). Single-crystal X-ray diffraction: Enraf-Nonius CAD4 diffractometer.

Compounds **1a**[1a], **1b,c**[35], **1d**[36], **2a**[37], **2b**[38], **2c,d**[39], and **2e**[40] were prepared according to published procedures.

*Cycloaddition of **2a-d** to **1b**; general procedure*

A solution of diazocarbonyl compound **2a-d** (1.2 mmol) and salt **1b** (0.45 g, 1.0 mmol) in dichloromethane (5 ml) is stirred until the diazo compound has disappeared (IR control; **2a,b**: 4 days, **2c**; 6 days,

2d: 8 days). After evaporation of the solvent, the residue is triturated with dry ether (2x 5 ml), and the remaining solid is recrystallized form dry acetonitrile (**4b,d**) or dry dichloromethane (**4a,c**) at -20 °C.

(3-Methoxycarbonyl-5-trimethylsilyl-4-pyrazolyl)-phenyliodonium trifluoromethanesulfonate (4a): From **2a** and **1b**; yield: 49 %, m.p. 175 °C. - IR (KBr): 3170 (br, NH), 1715 (s, C=O); 1280-1220 (br, vs), 1165 (s), 1030 (s) ($CF_3SO_3^-$). - ^1H NMR (CD_3CN): δ = 0.40 ($SiMe_3$). 3.92 (OMe), 13.1 (NH). - ^{13}C NMR (CD_3CN): δ = -1.1 ($SiMe_3$), 53.4 (OMe), 87.4 (C-4), 116.5(s), 121.7 (q, $^1J_{C,F}$ = 320 Hz, CF_3), 133.1(d), 133.4(d), 134.6(d), 144.2 (C-3), 153.9 (C-5), 162.1 (C=O). - Anal. Calcd. for $C_{15}H_{18}F_3IN_2O_5SSi$ (550.4): C, 32.74; H, 3.29; N, 5.09. Found: C, 31.4; H, 3.15; N, 4.8.

(3-Ethoxycarbonyl-5-trimethylsilyl-4-pyrazolyl)-phenyliodonium trifluoromethanesulfonate (4b): From **2b** and **1b**; yield: 25 %, m.p. 201 °C. - IR (KBr): 3170 (br, NH), 1704 (s, C=O), 1280-1240 (br, vs), 1175 (vs), 1038 (s) ($CF_3SO_3^-$). - ^1H NMR (CD_3CN): δ = 0.36 ($SiMe_3$). - ^{13}C NMR (CD_3CN): δ = -1.1 ($SiMe_3$), 14.3 ($CH_2\mathit{CH}_3$), 63.0 (OCH_2), 87.2 (C-4), 116.4(s), 121.8 (q, $^1J_{C,F}$ = 320 Hz, CF_3), 133.1(d), 133.4(d), 134.4(d), 144.3 (C-3), 154.0 (C-5), 161.6 (C=O). - Anal. Calcd. for $C_{16}H_{20}F_3IN_2O_5SSi$ (564.4): C, 34.05; H, 3.57; N, 4.96. Found: C, 34.0; H, 3.59; N, 4.9.

(3-Benzoyl-5-trimethylsilyl-4-pyrazolyl)-phenyliodonium trifluoromethanesulfonate (4c): From **2c** and **1b**; yield: 23 %, m.p. 208 °C. - IR (KBr): 3220 (s, NH), 1640 (s, C=O), 1270-1250 (br, vs), 1165/1152 (s), 1035 (s) ($CF_3SO_3^-$). - ^1H NMR (CD_3CN): δ = 0.40 ($SiMe_3$). - ^{13}C NMR (CD_3CN): δ = -1.1 ($SiMe_3$), 85.6 (C-4), 116.4(s), 121.8 (q, $^1J_{C,F}$ = 320 Hz, CF_3), 129.4-134.9 (C_{phenyl}), 149.5 (C-3), 153.6 (C-5), 188.1 (C=O). - Anal. Calcd. for $C_{20}H_{20}F_3IN_2O_4SSi$ (596.4): C, 40.28; H, 3.38; N, 4.69. Found: C, 40.0; H, 3.35; N, 4.5.

[3-(2,2-Dimethyl-1-oxopropyl)-5-trimethylsilyl-4-pyrazolyl]-phenyliodonium trifluoromethanesulfonate (4d): From **2d** and **1b**; yield: 14 %, m.p. 210 °C. - IR (KBr): 3210 (s, NH), 1665 (s, C=O), 1270-1245 (br, vs), 1175/1160 (vs), 1035 (vs) ($CF_3SO_3^-$). - ^1H NMR (CD_3CN): δ = 0.38 ($SiMe_3$), 1.28 (CMe_3), 12.4 (NH). - ^{13}C NMR (CD_3CN): δ = -1.0 ($SiMe_3$), 27.2 ($C\mathit{Me}_3$), 45.5 ($\mathit{C}Me_3$), 86.1 (C-4), 116.3(s), 121.6 (q, $^1J_{C,F}$ = 320 Hz, CF_3), 133.1(d), 133.4(d), 134.4(d), 147.6 (C-3), 153.0 (C-5), 202.1 (C=O). - Anal. Calcd. for $C_{18}H_{24}F_3IN_2O_4SSi$ (576.4): C, 37.50; H, 4.19; N, 4.86. Found: C, 37.3; H, 4.14; N, 4.7.

4-Iodo-3-methoxycarbonyl-5-trimethylsilyl-pyrazole (5)

A solution of NaI (1.59 g, 10.6 mmol) in acetonitrile (10 ml) is added at 0 °C to a solution of **4a** (2.39 g, 4.3 mmol) in acetonitrile (10 ml). After stirring for 1 h at 0 °C, the now yellow solution is concentrated to ca. 5 ml. Dichloromethane (20 ml) is added, and the precipitated salts (excess NaI and sodium trifluoromethanesulfonate) are filtered off and washed with CH_2Cl_2 (10 ml). Addition of petroleum ether (30-75 °C) to the combined filtrates precipitates a yellow solid, which is then thermolyzed at 160 °C (oil bath) for 2 min. The resulting dark-brown material is dissolved in CH_2Cl_2 (30 ml), filtered over silica gel (4 g), and the eluate is concentrated to a volume of 2 ml. Addition of petroleum ether (10 ml) yields **5** as a beige powder (0.47 g, 34 %), m.p. 198 °C. - IR (KBr): 3100 (br, s, NH), 1705 (s, C=O). - ^1H NMR ($CDCl_3$); δ = 0.33 ($SiMe_3$), 3.77 (OMe), 13.45 (broad, NH). - ^{13}C NMR ($CDCl_3$): δ = 2.0 ($SiMe_3$), 55.5 (OMe), 72.4, (C-4), 146.8 (C-5), 151.8 (C-3), 165.8 (C=O). - Anal. Calcd. for $C_8H_{13}IN_2O_2Si$ (324.2): C, 29.64; H, 4.04; N, 8.64. Found: C, 29,1; H, 3.9; N, 8.5.

[3-(2,2-Dimethyl-1-oxopropyl)-5-methoxycarbonyl-4-pyrazolyl]-phenyliodonium trifluoromethanesulfonate (6)

A solution of **1d** (0.61 g, 1.3 mmol) and **2a** (0.13 g, 1.3 mmol) in CH_2Cl_2 (20 ml) is stirred for 20 h, then concentrated to a volume of 5 ml, and cooled to -35 °C. The colorless crystals formed are collected

and washed with a small amount of cold ether; yield 0.32 g (43 %), m.p. 112-114 °C. - IR (KBr): 3300-3030 (NH), 1725 (s, C=O, ketone), 1670 (s, C=O, ester), 1280-1210 (br, vs), 1160 (vs), 1025 (vs) ($CF_3SO_3^-$). - ^{1}H NMR (CD_3CN): δ = 1.34 (CMe_3), 3.98 (OMe), 7.3-8.2 (m, 5 H). - ^{13}C NMR (CD_3CN): δ = 27.0 (*C*Me_3), 45.3 (*C*Me_3), 54.0 (OMe), 83.3 (C-4), 116.3(s), 121.5 (q, $^1J_{C,F}$=320 Hz, CF_3), 132.8(d), 133.7(d), 136.2(d), 137.7 (C-5), 147.9 (C-3), 157.9 (COOMe), 202.1 (CO*t*Bu). - Anal. Calcd. for $C_{17}H_{18}F_3IN_2O_6S$ (562.3); C, 36.31; H; 3.23; N, 4.98. Found: C, 36.2; H, 3.3; N, 4.9.

3-(2,2-Dimethyl-1-oxopropyl)-4-iodo-5-methoxycarbonyl-pyrazole (7)

Synthesis from **6** (0.85 g, 1.5 mmol) in analogy to that of **5**; the thermolysis mixture is separated by column chromatography (Merck Lobar column, LiChroprep Si-60, 40-63 µm, ether / petroleum ether (1:2)); yield: 0.31 g (61 %), m.p. 94 °C. - IR (KBr); 3220 (br, s, NH), 1730 (s, C=O, ketone), 1650 (s, C=O, ester). - ^{1}H NMR ($CDCl_3$): δ = 1.38 (CMe_3), 3.98 (OMe), 11.66 (broad, NH). - ^{13}C NMR ($CDCl_3$): δ = 26.8 (*C*Me_3), 44.6 (*C*Me_3), 52.5 (OMe), 64.4 (C-4), 135.6 (C-5), 149.7 (C-3), 158.9 (COOMe), 201.3 (CO*t*Bu). - Anal. Calcd. for $C_{10}H_{13}IN_2O_3$ (336.1): C, 35.73; H, 3.90; N, 8.33. Found: C, 36.0; H, 3.9; N, 8.3.

{5-Methoxycarbonyl-1-[(Z)-2-(phenyliodonio)vinyl]-3-pyrazolyl}-phenyliodonium bis(trifluoromethanesulfonate) ((Z)-9a)

A solution of **2a** (1.16 g, 11.6 mmol) in CH_2Cl_2 (10 ml) is added dropwise at 0 °C to a suspension of **1a** (4.07 g, 10.8 mmol) in CH_2Cl_2 (20 ml). After 24 h at room temperature, the solvent is replaced by ethyl acetate. At -30 °C, a solid is obtained which is filtered off, washed with cold ethyl acetate until the filtrate becomes colorless, and dried at 50 °C /0.01 mbar; yield: 1.89 g (41 %); m.p. 95-97 °C. - IR (KBr): 1720 (s, C=O), 1625 (w, C=C), 1290-1230 (br, vs), 1170 (br, vs), 1030 (vs) ($CF_3SO_3^-$). - ^{1}H NMR (CD_3CN, 400 MHz): δ = 3.92 (OMe), 6.80 (d, ^3J=6.5 Hz), 7.60-7.81 (m, 3 H_{phenyl} and NH), 8.10 and 8.27 (2 H_{phenyl}), 9.06 (d, ^3J=6.5 Hz). - ^{13}C NMR (D_6-acetone/$CDCl_3$ (2:1)): δ = 52.0 (OMe), 90.7 (d, ^1J=198 Hz, =CHI$^+$), 113.0(s), 114.3(s), 116.9 (s, probably C-3), 119.5 (d, ^1J=194.5 Hz, C-4), 119.6 (q, $^3J_{C,F}$=321 Hz, CF_3), 129.7 (d, ^1J=144 Hz, NCH=), 134.3 (C-5), 130.9-134.9 (C_{phenyl}), 156.1 (C=O). - Anal. Calcd. for $C_{21}H_{16}F_6I_2N_2O_8S_2$ (856.3): C, 29.46; H, 1.88; N, 3.27. Found: C, 29.2; H, 2.1; N, 3.1.

3-Iodo-1-[(Z)- and (E)-2-iodovinyl]-5-methoxycarbonyl-pyrazole ((Z)-10, (E)-10)

A solution of NaI (1.26 g, 8.4 mmol) in acetonitrile (10 ml) is added at 0 °C to a solution of **(Z)-9a** (1.89 g, 2.2 mmol) in acetonitrile (20 ml). After stirring for 1 h at 0 °C, the now yellow solution is concentrated to ca. 10 ml. Dichloromethane (20 ml) is added, and the precipitated salts (excess NaI and sodium trifluoromethanesulfonate) are filtered off. The remaining solution is evaporated to dryness to leave a yellow-brown powder, which is heated to 160 °C (oil bath) for 3 min. A dark red-brown liquid is obtained which after cooling to room temperature is dissolved in ether (20 ml). Filtration over silica gel (4 g) and separation by column chromatography (Merck Lobar column, silica gel LiChroprep Si-60, 40-63 µm; eluation with ether / petroleum ether, 1:5) yields first **(*E*)-10**, then **(*Z*)-10**.

(*E*)-10: Pale-yellow powder, yield: 0.082 g (10 %); m.p. 83 °C. - IR (KBr): 3162, 3108 (=CH), 1735 (C=O). - ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.84 (OMe), 7.00 (s, 4-H), 7.03 (d, ^3J=13.2 Hz, =CHI), 8.40 (d, ^3J=13.2 Hz, NCH=). - ^{13}C-NMR ($CDCl_3$): δ = 52.5 (OMe), 68.9 (d, ^1J=192 Hz, =CHI), 97.1 (C-3), 120.8 (d, ^1J=188 Hz, C-4), 132.3 (C-5), 134.2 (d, ^1J=190 Hz, NCH=), 158.4 (C=O). - Anal. Calcd. for $C_7H_6I_2N_2O_2$ (404.0): C, 20.81; H, 1.50; N, 6.94. Found: C, 21.0, H, 1.4; N; 6.8.

(*Z*)-10: Yellow crystals from ether; yield: 0.356 g (42 %); m.p. 48 °C. - IR (KBr); 3150, 3090 (=CH), 1730 (C=O). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.88 (OMe), 6.58 (d, ^3J=7.2 Hz, =CHI), 7.08 (s, 4-H), 8.15 (d, ^3J=7.6 Hz). - ^{13}C NMR ($CDCl_3$): δ = 52.5 (OMe), 72.7 (d, ^1J=190 Hz, =CHI), 95.4 (C-3), 120.8 (d, ^1J=187 Hz, C-4), 133.5 (d, ^1J=188 Hz, NCH=), 134.4 (C-5), 158.2 (C=O). - Anal. Calcd. for $C_7H_6I_2N_2O_2$ (404.0); C, 20.81, H, 1.50; N, 6.94. Found: C, 20.8; H, 1.5; N, 6.8.

5-Carboxy-3-iodo-1-[(Z)- and (E)-2-iodovinyl]-pyrazole ((Z)-11, (E)-11)

A solution of **2e** in CH_2Cl_2 (10 ml) is added dropwise at 0 °C to a suspension of **1a** (4.15 g, 11.0 mmol) in CH_2Cl_2 (15 ml). After 22 h at room temp., the solvent is evaporated, and the residue is triturated with ether until a beige microcrystalline solid is obtained (2.05 g of crude bis(phenyliodonium) salt (*Z*)-**9b**). The solid is dissolved in CH_3CN (20 ml), and anhydrous NaI (1.37 g, 9.1 mmol) is added at 0 °C. After 1 h at 0 °C, the solution is concentrated to a volume of 5 ml. Upon addition of CH_2Cl_2 (25 ml) a white precipitate forms which is washed with more CH_2Cl_2 (20 ml). The combined filtrates yield a yellow-brown powder (1.32 g) which is kept for 1 min at 190 °C (oil bath). Column chromatography (as described above for **10**) of the resulting brown-violet oil yields first (*Z*)-**11**, then (*E*)-**11**; both compounds are recrystallized from chloroform.

(*Z*)-**11**: Pale-yellow crystals; yield; 0.117 g (5.5 %); m.p. 187 °C. - IR (KBr): 3200-2700 (COOH), 1680 (C=O). - ^{1}H-NMR (D_6-DMSO): δ = 6.69 (d, ^3J=6.0 Hz, =CHI), 7.14 (s, 4-H), 8.18 (d, ^3J=6.0 Hz, NCH=). - ^{13}C-NMR (D_6-DMSO): δ = 75.6 (d, ^1J=191 Hz, =CHI), 97.5 (C-3), 120.0 (d, ^1J=187 Hz, C-4), 134.2 (d, ^1J=189 Hz, NCH=), 135.8 (C-5), 158.9 (C=O). - Anal. Calcd. for $C_6H_4I_2N_2O_2$ (389.9); C, 18.48; H, 1.03; N, 7.18. Found: C, 19.2; H, 1.4; N, 6.8.

(*E*)-**11**: Yellowish crystals; yield: 0.023 g (1 %); m.p. 210-212 °C. - ^{1}H-NMR (D_6-DMSO): δ = 6.44 (d, ^3J=13.5 Hz, =CHI), 6.61 (s, 4-H), 7.85 (d, ^3J=13.5 Hz, NCH=).

(1-Methyl-1,2,3-triazol-4-yl)-phenyliodonium trifluoromethanesulfonate (13a)

Methyl azide (**12a**) (3 mmol) is added to a solution of **1a** (1 mmol) in dry THF (5 ml), and the mixture is heated at 85 °C for 50 h. Back at room temperature, the solvent and excess azide are removed at 20 °C /0.005 mbar. The solid residue is washed with CH_2Cl_2 (3x5 ml), then recrystallized from anhydrous acetonitrile; colorless crystals, m.p. 138 °C; yield: 25 %. - ^{1}H NMR (CD_3CN): δ = 4.20 (s, NMe), 7.3-8.3 (m, 5H), 8.60 (s, 5-H). - ^{13}C-NMR (CD_3CN): δ = 38.4 (NMe), 108.3 (d, ^2J=10.6 Hz, C-4), 116.2(s), 121.7 (q, $^1J_{C,F}$=320 Hz, CF_3), 133.2(d), 133.8 (d, ^1J=211 Hz, C-5), 134.0(d), 136.0(d). - Anal. Calcd. for $C_{10}H_9F_3IN_3O_3S$ (435.0): C, 27.61; H, 2.06; N, 9.65. Found: C, 27.5; H, 2.1; N, 9.5.

(1-Phenyl-1,2,3-triazol-4-yl)-phenyliodonium trifluoromethanesulfonate (13b)

A solution of **1a** (0.56 g, 1.5 mmol) and phenyl azide (**12b**) (0.54 g, 4.5 mmol) in dry acetonitrile (10 ml) is heated at 75 °C for 40 h. Work-up as described above for **13a** yields **13b** as a colorless powder (0.13 g, 17 %), m.p. 120 °C. - ^{1}H NMR (CD_3CN): δ = 7.35-8.15 (m, 10 H), 8.95 (s, 5-H). - ^{13}C-NMR (CD_3CN); δ = 107.8 (d, ^2J=9.4 Hz, C-4), 144.4(s), 120.3(d), 121.6 (q, $^1J_{C,F}$=320 Hz, CF_3), 129.3 (d) 130.1 (d, ^1J=209 Hz, C-5), 131.4(d), 132.2(d), 134.6(d), 135.1(s), 135.4(d). - Anal. Calcd. for $C_{15}H_{11}F_3IN_3O_3S$ (497.1); C, 36.24; H, 2.21; N, 8.44. Found: C, 35.2; H, 2.2; N, 8.3.

[5-(1,1-Dimethylethyl)-1-methyl-1,2,3-triazol-4-yl]-phenyliodonium trifluoromethanesulfonate (14)

From methyl azide (4.5 mmol) and **1c** (1.5 mmol) as described above for **13a**; 28 h at 75 °C; yield: 26 %; colorless crystals, m.p. 125 °C. - ^{1}H NMR (CD_3CN): δ = 1.50 (s, CMe_3), 4.25 (s, NMe), 7.3-8.3 (m, 5H). - ^{13}C-NMR (CD_3CN): δ = 29.9 (CMe_3), 32.6 (CMe_3), 40.5 (NMe), 107.7 (C-4), 118.3(s), 121.5 (q, $^1J_{C,F}$=321 Hz, CF_3), 133.2(d), 133.8(d), 135.5(d), 148.4(C-5). - Anal. Calcd. for $C_{14}H_{17}F_3IN_3O_3S$ (491.1): C, 24.23; H, 3.46; N, 8.55. Found: C, 24.0; H, 3.6; N, 8.2.

X-ray crystal structure analyses[41,42]

4b: *Crystal data*: $C_{16}H_{20}F_3IN_2O_5SSi$, monoclinic, space group $P2_1/c$; a = 11.501(6), b = 19.819(12), c = 11.519(5) Å, ß = 118.99(4) °; Z = 4, D_{calc} = 1.63 g cm^{-3}. - *Data collection*: Crystal size 0.5x0.3x0.5 mm, monochromatized Mo-K_α radiation, 3822 independent reflections with 2.0° ≤ θ ≤ 23.0°, ω/2θ scan, scan width (1.20 + 0.35 tan θ)°. Data were corrected for a linear loss of intensity (maximum loss 3.9 %). An empirical absorption correction was applied (μ = 15.7 cm^{-1}). - Structure solution by direct methods (MULTAN), refinement by a full-matrix least-squares method (SHELX-76). Hydrogen atom HN2 was located in a ΔF map and refined, positions of all others were calculated and not refined.

Refinement converged at R = 0.043, $R_w = [\Sigma\Delta^2F/\Sigma F_o^2]^{1/2}$ = 0.43 (3220 reflections with $I > 2\,\sigma(I)$, 285 variables, unit weights); residual electron density 0.59 e Å^{-3}, shift/error ratio ≤ 0.51.

(Z)-11a: *Crystal data*: $C_6H_4I_2N_2O_2$, monoclinic, space group $P2_1/n$; a = 5.784(2), b = 22.384(13), c = 7.670(2) Å, ß = 100.34(4) °; Z = 4, D_{calc} = 2.65 g cm^{-3}. - *Data collection*: Crystal size 0.35x0.13x0.55 mm, monochromatized Mo-Kα radiation, 1600 independent reflections with 2.0° ≤ θ ≤ 25.0°, ω/2θ scan, scan width (1.00 + 0.35 tan θ)°. Data were corrected for a linear loss of intensity (maximum loss 3.0 %). An empirical absorption correction was applied (μ = 63.4 cm^{-1}). - Structure solution by direct methods (MULTAN), refinement by a full-matrix least-squares method. Hydrogen atoms were located in a difference Fourier map and included in the refinement with isotropic B's. Refinement converged at R = 0.043, $R_w = [\Sigma w\Delta^2F / \Sigma wF_o^2]^{1/2}$ = 0.56 [1385 reflections with $I > 2\,\sigma(I)$, 125 variables, $w = 4{\cdot}F_{obs}^2/\sigma^2(F_{obs}^2)$]. The residual electron density was 0.65 e Å^{-3}.

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41. Calculations were done with the *Structure Determination Package* (Enraf-Nonius, Delft, The Netherlands) and with the *SHELX* program package.
42. Tables of atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, England. The data are available on request from the Director of CCDC by quoting the full literature citation of this paper.