Synthesis and Thermal Reactions of Perfluoroalkylsulphonyl Substituted Ylides

Jürgen Hackenberg and Michael Hanack*

Institut für Organische Chemie, Lehrstuhl für Organische Chemie II, Auf der Morgenstelle 18, D-7400 Tübingen 1, Federal Republic of Germany

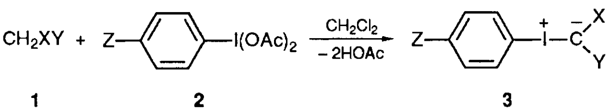
The synthesis of several perfluoroalkylsulphonyl substituted ylides is described; thermal decomposition of the phenyliodonio(cyanononafluorobutylsulphonyl)methanide **3a** in cyclohexene yields the bicyclo[4.1.0]heptane derivative, while the phenyliodoniobis(nonafluorobutylsulphonyl)methanide **3c** gives an insertion reaction.

In continuation of our work on perfluoroalkyl sulphones[1] we have been interested in the synthesis and reactions of perfluoroalkylsulphonyl substituted ylides. We have already obtained[2] the dimethylsulphoniobis(nonafluorobutylsulphonyl)methanide **8c** by reaction of bis(nonafluorobutylsulphonyl)bromomethane with dimethyl sulphide and subsequent dehydrobromination. We report here on the synthesis and some reactions of a variety of bis(perfluoroalkylsulphonyl) and cyanoperfluoroalkylsulphonyl ylides **3**, **6**, **8**, **10** and **11**.

Our earlier attempts[2] to decompose the ylide **8c** with formation of the corresponding bis(nonafluorobutylsulphonyl)carbene were not successful. In search of a better source of these carbenes we turned our attention to phenyliodonioperfluoroalkylsulphonyl and related methanides **3a–f**. A recent publication[3] on phenyliodoniobis(perfluoroalkylsulphonyl)methanides prompts us to report our own results in this field.

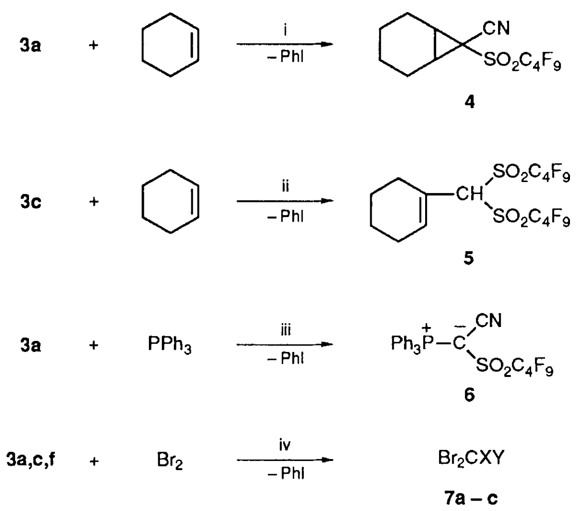
All iodine ylides **3** are easily prepared in high yield from the corresponding methylene compounds **1**[4] and the diacetoxyiodobenzenes **2**, containing different substituents in the *para*-position, Scheme 1. The reaction conditions for preparation, yields and melting points of **3a–f** are given in Table 1. The ylides **3a–f** are stable compounds at room temperature, but **3a**, **b** are somewhat less stable than **3c–f**, and for use over a longer period of time they should be stored in a refrigerator.

All spectra of the ylides **3** are in accordance with the given structure. The ^{13}C NMR spectra of **3** show the typical downfield shift of the aromatic carbon atom attached to the positively charged iodine atom.[5] The *para* substituent of the



	X	Y	Z
a:	CN	$SO_2C_4F_9$	H
b:	CN	SO_2CF_3	H
c:	$SO_2C_4F_9$	$SO_2C_4F_9$	H
d:	$SO_2C_4F_9$	$SO_2C_4F_9$	OCH_3
e:	$SO_2C_4F_9$	$SO_2C_4F_9$	NO_2
f:	SO_2CF_3	SO_2CF_3	H

Scheme 1



Scheme 2 *Conditions and yields*: (i) $Cu(acac)_2$ (0.5 mol%), benzoyl peroxide (0.1 mol%), 55 °C, 3 h, 65%; (ii) see (i), autoclave, 140 °C, 1.5 h, 10%; (iii) $ClCH_2CH_2Cl$, $Cu(acac)_2$ (0.5 mol%), 80 °C, 1.5 h, 69%; (iv) CH_2Cl_2, 20 °C, 24 h, 66–79%

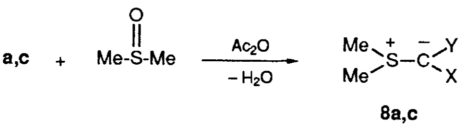
Table 1 Preparation of **3**

Compound	T/°C	t/h	Yield (%)	M.p./°C
3a	0	1	77	135 (decomp.)
3b	0	1	75	116 (decomp.)
3c	20	24	87	129[a]
3d	20	24	83	139 (decomp.)
3e	20	36	90	217
3f	20	24	80	140

[a] Contrary to literature,[3] compound **3c** shows no decomposition up to 190 °C.

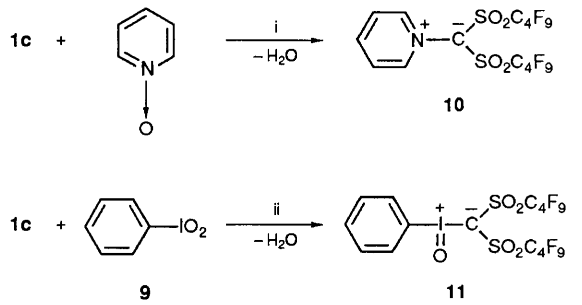
phenyl ring in **3c–e** has no effect on the chemical shift of the methanide carbon atom.†

The cyanononafluorobutylsulphonyl ylide **3a** is decomposed with pentane-2,4-dionato copper(II) as catalyst and traces of peroxide[6] in the presence of cyclohexene to form the cyclopropane compound **4** in 65% yield, Scheme 2. The almost exclusive formation of **4** under the conditions given in Scheme 2 points to a carbene or carbenoid intermediate which subsequently reacts with cyclohexene. Only one isomer of **4** is formed; the stereochemistry of the product is under investigation. The bis(nonafluorobutylsulphonyl) ylide **3c** does not react to afford the corresponding cyclopropane product, only the vinylic insertion product **5** could be isolated in low yield, Scheme 2. When **3a** is heated with $Cu(acac)_2$ (Hacac = pentane-2,4-dione) and triphenylphosphine in 1,2-dichloroethane a transylidation occurs and the phosphorous ylide **6** is formed, Scheme 2.



	X	Y
8a	CN	$SO_2C_4F_9$
8c	$SO_2C_4F_9$	$SO_2C_4F_9$

Scheme 3 *Conditions and yields:* 20 °C, 24 h, **8a**: 75%, **8c**: 86%



Scheme 4 *Conditions and yields*: (i) Ac_2O, 20 °C, 72 h, 62%; (ii) CH_2Cl_2, molecular sieves 4 Å, 20 °C, 48 h, 72%

Contrary to the recent report[3] we have not been able to decompose compounds **3** photolytically using a 150 W low-pressure mercury lamp, since their absorption maxima lie between λ 206 and 224 nm.‡ Even after 48 h under these conditions no carbene formation is observed. However, bromination of **3a**, **c**, **f** with bromine in dichloromethane without illumination produces the dibromides **7** in high yields, Scheme 2.

The easy formation of ylides from the methylene compounds **1** can also be demonstrated by a series of additional reactions. Sulphur ylides **8** result from the reaction of the methylene compounds **1a**, **c** and dimethyl sulphoxide in acetic anhydride, Scheme 3. The bis(nonafluorobutylsulphonyl)methane **1c** reacts with pyridine *N*-oxide and iodylbenzene **9** to yield the pyridinium ylide **10** and the pentavalent iodine ylide **11** respectively, Scheme 4.

The preparative aspects of the new ylides **8**, **10** and **11**, as well as further reactions of ylide **3**, are under investigation in our laboratory.

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† ^{13}C NMR ([$^2H_6$] acetone); methanide carbon shift, δ 55.2 (**3c**), 55.8 (**3d**), 56.0 (**3e**).

‡ With **3e** [λ_{max}(MeOH) 292 nm] the reaction mixture quickly turned black and the reaction was interrupted.