

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 phenyliodonibis(nonafluorobutylsulphonyl)methanide **3c** gives an insertion reaction.

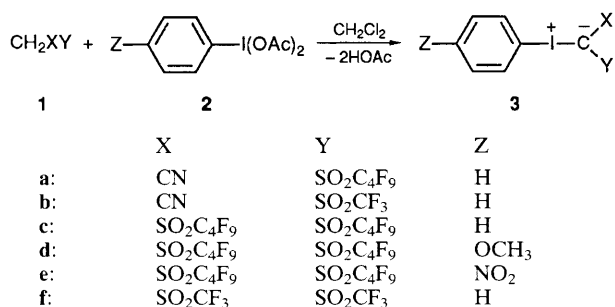
In continuation of our work on perfluoroalkyl sulphones¹ we have been interested in the synthesis and reactions of perfluoroalkylsulphonyl substituted ylides. We have already obtained² the dimethylsulphoniobis(nonafluorobutylsulphonyl)methanide **8c** by reaction of bis(nonafluorobutylsulphonyl)bromomethane 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 attempts² 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 phenyliodonio(perfluoroalkylsulphonyl) and related methanides **3a-f**.

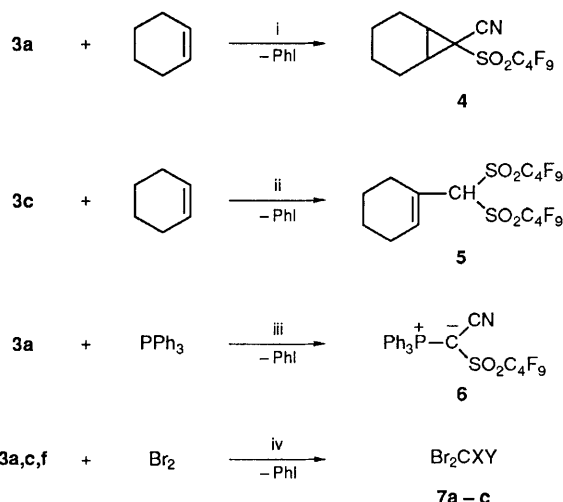
A recent publication³ on phenyliodonibis(perfluoroalkylsulphonyl)methanides prompts us to report our own results in this field.

All iodine ylides **3** are easily prepared in high yield from the corresponding methylene compounds **1**⁴ and the diacetoxiodobenzenes **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 ¹³C 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



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) ClCH₂CH₂Cl, Cu(acac)₂ (0.5 mol%), 80 °C, 1.5 h, 69%; (iv) CH₂Cl₂, 20 °C, 24 h, 66–79%

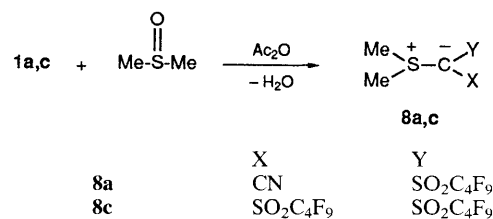
Table 1 Preparation of 3

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

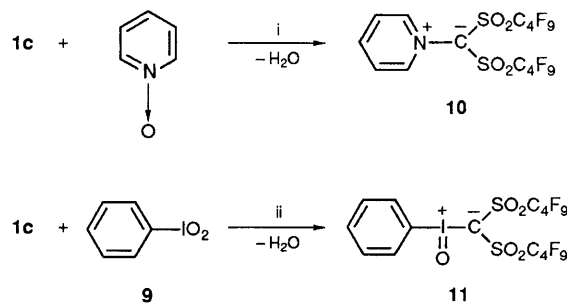
^a Contrary to literature,³ compound 3c shows no decomposition up to 190 °C.

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 peroxide⁶ 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 =



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



Scheme 4 Conditions and yields: (i) Ac₂O, 20 °C, 72 h, 62%; (ii) CH₂Cl₂, molecular sieves 4 Å, 20 °C, 48 h, 72%

pentane-2,4-dione) and triphenylphosphine in 1,2-dichloroethane a transylidation occurs and the phosphorous ylide 6 is formed, Scheme 2.

Contrary to the recent report³ 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 sulfoxide 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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[†] ¹³C NMR ([²H₆] 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.