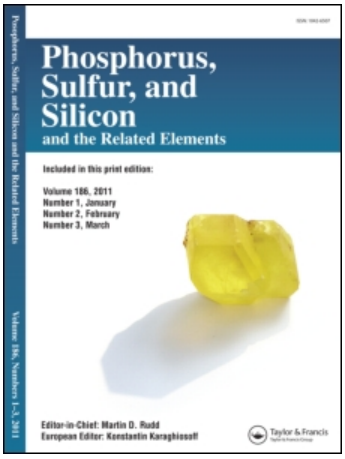


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

NEW RESULTS OF SULFUR CHEMISTRY OF 1,6-METHANO[10] ANNULENE AND 1H-CYCLOPROPABENZENE

Richard Neidlein[a]; Take Constantinescu[a]; Matthias Kohl[a]
[a] Pharmazeutisch - Chemisches Institut der Universität, Heidelberg, Germany

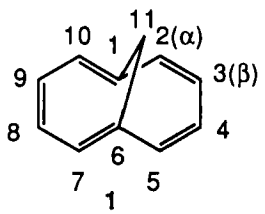
To cite this Article Neidlein, Richard , Constantinescu, Take and Kohl, Matthias(1991) 'NEW RESULTS OF SULFUR CHEMISTRY OF 1,6-METHANO[10] ANNULENE AND 1H-CYCLOPROPABENZENE', Phosphorus, Sulfur, and Silicon and the Related Elements, 59: 1, 165 — 168
To link to this Article: DOI: 10.1080/10426509108045715
URL: http://dx.doi.org/10.1080/10426509108045715

Phosphorus, Sulfur, and Silicon, 1991, Vol. 59, pp. 165–168
Reprints available directly from the publisher
Photocopying permitted by license only

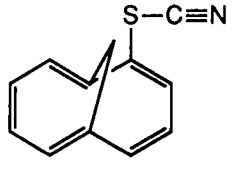
NEW RESULTS OF SULFUR CHEMISTRY OF 1,6-METHANO[10] ANNULENE AND 1H-CYCLOPROPABENZENE

RICHARD NEIDLEIN, TAKE CONSTANTINESCU AND MATTHIAS KOHL
Pharmazeutisch - Chemisches Institut der Universität,
Im Neuenheimer Feld 364, D - 6900 Heidelberg/Germany

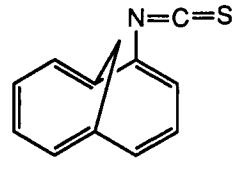
Literature data about the stereochemistry of electrophilic attack on 1,6 - methano[10] - annulene (**1**) appear to be conflicting. In an earlier report on the protonation of **1**, the π-electron density was assumed to be greater on the *endo* side of the annulene ring. In order to see how decisive is the steric factor, we tried to obtain an adduct of **1** with bulky electrophile. Thiocyanogen $(SCN)_2$, was chosen as reaction partner, not only for its large steric requirements, but also for its low electrophilicity. The reagent could thus be expected to discriminate between the *exo* and the *endo* region, if an unequally distributed electron density, and not the steric hindrance of the bridge, controls the stereochemistry. At the same time thiocyanogen was used hoping to obtain a stable addition product, displaying only a low re-aromatization tendency (by HNCS elimination), since - SCN



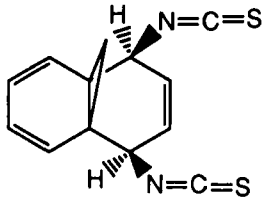
1



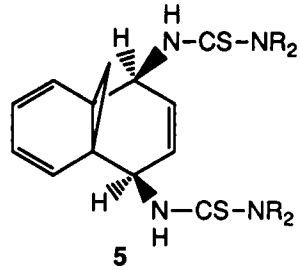
2



3



4



5

is a relatively poor leaving group.

The reaction of **1** with $(SCN)_2$ yields the normal substitution product - the thiocyanate **2** - and there were found two unusual products: the aromatic isothiocyanate **3** and the diisothiocyanate adduct **4**.

The syn - configuration of the two - N=C=S - groups in adduct **4** indicates that the *exo* - addition is the preferred stereochemical course of the electrophilic attack on **1**, in spite of a possible steric interference with the methylene bridge.

Similar results are obtained in the reaction of **1** with thiocyanogen generated in situ from ammonium thiocyanate and bromine. However, the low yield of isolated adduct **4** does not reflect the actual composition of the reaction mixture, being rather due to the difficulty of separation from **2** as well as to decomposition during workup. In a crude mixture the ratio **2/4** was found, by means of NMR, to be 1.8, which would correspond to a 29 % yield of adduct **4.**

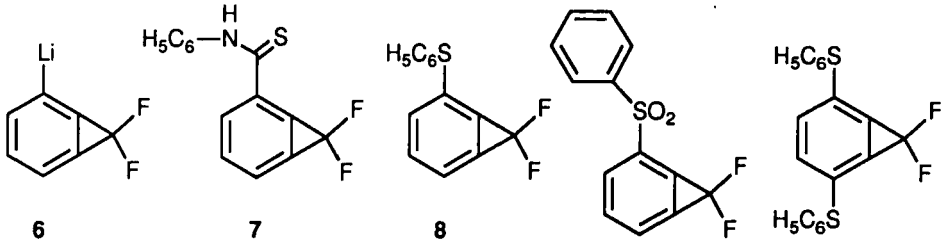
The presence of the two unexpected isothiocyanates **3** and **4** prompted us to investigate the influence of several reaction parameters upon the course of thiocyanation of **1**. Since the yields of isolated compounds did not afford reliable information concerning the product distribution, the reaction was monitored by means of thin-layer chromatography. Adduct **4** was just found, together with thiocyanate **2** (major product) and isothiocyanate **3** (minor product), under a wide range of reaction conditions.

TLC monitoring carried out at short reaction times showed that the first products formed are thiocyanate **2** and adduct **4**, isothiocyanate **3** appearing only in later stages of the reaction.

It is interesting to note that the presence of iron (which reacts with $(SCN)_2$, affording ferric thiocyanate), although repressing partially the formation of adduct **4**, could not prevent it entirely in favour of a substitution course. However, when stronger electrophilic catalysts were used ($AlCl_3$, $FeCl_3$ or $SnCl_4$), **4** was no longer found in the reaction mixture. In the presence of $FeCl_3$ or $SnCl_4$ small amounts of isothiocyanate **3** were still isolated, but with $AlCl_3$ only traces of it could be detected. (Anhydrous $AlCl_3$ was found to cause decomposition of 1 as well as polymerization of thiocyanogen. In order to prevent this, the catalyst was partially deactivated with diethyl ether).

The above observations show that the "abnormal" products **3** and **4** are not the result of a particular combination of reaction conditions, but constant components of the thiocyanation mixture. The formation of a relatively high proportion of **4** is significant in view of its possible intervention as intermediate in an addition-elimination mechanism.

As an explanation for the formation of the unexpected isothiocyanate **3** the possibility of an isomerization of the normal product **2** was first taken into consideration. In the aliphatic series the isomerization of thiocyanates into the thermodynamically more stable isothiocyanates is a wellknown transformation. With aromatic derivatives, however, isomerization appears to require strong electron-attracting groups (e.g. NO_2), which allow a nucleophilic attack of thiocyanate ions. Our control experiments showed that thiocyanate **2** cannot isomerize to isothiocyanate **3.**



6 **7** **8** **9** **10**

With the help of NMR-spectroscopic measurements could be shown unequivocally that the deprotonation of the 1,1-difluorocyclopropabenzene takes place only in position **2** under creation of lithium- 1,1-difluorocyclopropabenzene **6.**

The intense dark red lithiumorganic compound **6** generated in situ from 1,1-difluorocyclopropabenzene, 1,2-equivalents n-butyl-lithium, TMEDA and THF (-100 to -90 ° C, 2-3 h) had been intercepted at low temperature with a high surplus of perdeuterated methanol. From the ^{1}H-NMR-data a deprotonation of at least 90 - 95 per cent of the 1,1-difluorocyclopropabenzene can be obtained.

6 reacts as well with arylisocyanates as with arylisothiocyanates already under a temperature of - 100 ° C. The solution, intensely red coloured in the beginning by the anion **6**, changes during the addition of the heterocumulenes to a yellow-brown colouring. After a careful hydrolysis at low temperatures and column-chromotography purification the corresponding amides and thioamides, e.g. **7**, are obtained.

The experiments of metallations of 1,1-difluorocyclopropabenzene had been accomplished as well with N-containing bases as with the very much stronger lithium- and potassium-tert.-butylates in presence of different solvents.

In fact, lithiumorganic compound **6** could be changed to arylthioether **8** with the help of diphenyldisulfide at - 100 ° C to RT. For the production of **6**, TMEDA doesn´t have necessarily to be added, but its addition reduces 1 - 2 h the reaction time.

Aromatic thioether can be changed to the corresponding sulfones in presence of 30 per cent H_2O_2 and acetic acid at higher temperatures, the real O-containing reagent being the intermediarily formed peroxyacetic acid. To complete the oxidation of the thioether additional oxidations, for example with m-chloroperbenzoic acid at room temperature were accomplished and a high output of sulfones **9** could be obtained.

After the demonstration of monosubstituted 1,1-difluorocyclopropabenzene had been metallated with 2 equivalents of lithiumdiisopropylamide at low temperatures (-85 to -60 ° C) and interspersed with the 2,5-fold amount of diphenyldisulfide under - 90 ° C. After careful preparation and column - chromatography purification apart from **8** - the mono - aryl - thioether - could be isolated a low output of bis-aryl-thioether **10** in colourless crystals.

At least - if it is enough time - there will be shortly reported about DIELS-ALDER-reactions of 1H-cyclopropabenzene with electronpoor dienes, leading to substituted 1,6-methano [10] annulenes; intermediate cycloaddition-products could be isolated and also transformed to the 1,6-methano [10] annulene - derivatives. -