Novel Cycloadducts from the Reactions of 2,5-Dichloro-1,1,1,6,6,6-hexafluoro-3,4-diazahexa-2,4-diene, Hexafluoroacetone Azine and the Azomethine Imide, 2-Hexafluoroisopropylidene-3-methyl-3-phenyl-5,5-bis(trifluoromethyl)-tetrahydropyrazol-2-ium-1-ide with Quadricyclane

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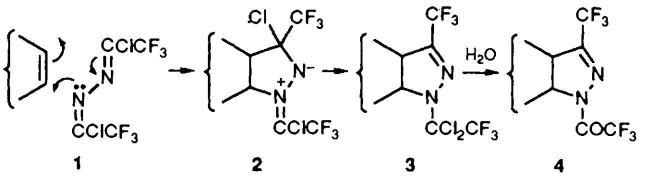
Reaction of quadricyclane with the azine $CF_3CCl{=}NN{=}CClCF_3$ **1** in dichloromethane at 70 °C gives a mixture of two 1 : 1 adducts, the $[{}_{\sigma}2_s + {}_{\sigma}2_s + {}_{\pi}2_s]$ cycloadduct **9a**, and an unexpected and hitherto unreported product, the 1,3-dipolar cycloadduct **10**, in the ratio 70 : 19 (*i*) an analogous reaction with the azine $(CF_3)_2C{=}NN{=}C(CF_3)_2$ **5** at 70 °C affords the corresponding [2 + 2 + 2] cycloadduct **9b**, which reacts further to some extent with quadricyclane to give the 2 : 1 adduct **11** and (*ii*) with azine **5** to afford the intermediate azomethine imide **17** and hence the 2 : 2 adduct **12**.

Azines are masked 1,3-dipolar reagents and they react with alkenes and alkynes to give [3 + 2] cycloadducts, *i.e.* azomethine imides, which undergo further reaction with the dipolarophile, to afford 2 : 2 'criss-cross' adducts; in certain cases the intermediate azomethine imides can be isolated. Reactions of the dichloroazine $CF_3CCl{=}NN{=}CClCF_3$ **1** with cycloalkenes and cyclodienes have been investigated recently, and it was found that the intermediate azomethine imides **2** underwent rearrangement to the dihydropyrazoles **3**, which were hydrolysed readily to the amides **4**[1] (Scheme 1). Although treatment of hexafluoroacetone azine **5** with acetyl chloride and triethylamine gave the β-lactam **6**,[2] cycloadditions across the C=N bond of the azine **1** have not been reported.



Scheme 1

$(CF_3)_2C{=}NN{=}C(CF_3)_2$

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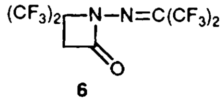

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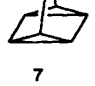

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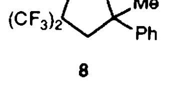

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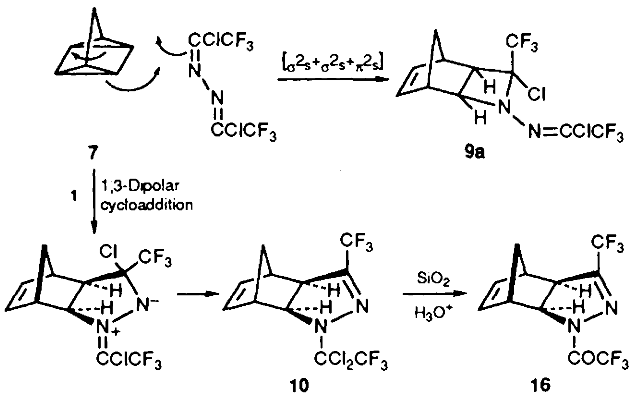
Since quadricyclane **7** undergoes facile reaction with a variety of alkenes and alkynes by a $[{}_{\sigma}2_s + {}_{\sigma}2_s + {}_{\pi}2_s]$ process to afford the *exo*-1 : 1 cycloadducts,[3] its reaction with azine **1** was investigated initially, to determine if cycloaddition across the C=N bond would occur. The results obtained prompted a study of the reactions of the azine **5** and the azomethine imide **8** with quadricyclane **7**, which are summarised in Table 1.

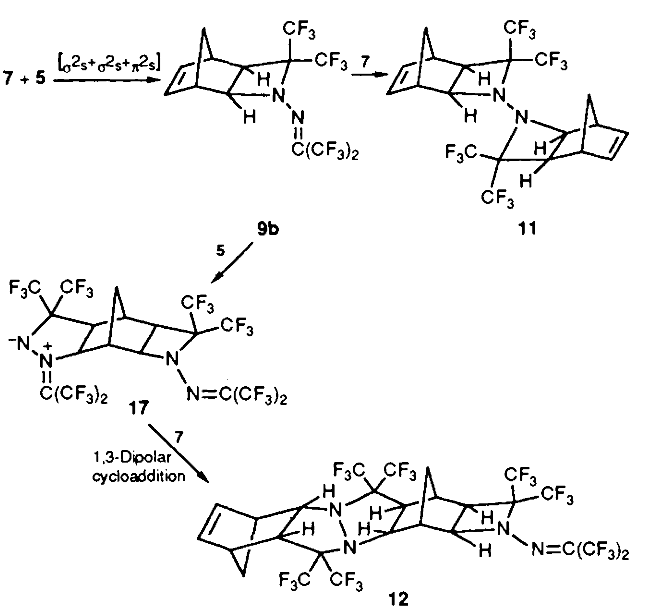
The reaction involving the azine **1** gave the expected *exo*-cycloadduct **9a** by a concerted $[{}_{\sigma}2_s + {}_{\sigma}2_s + {}_{\pi}2_s]$ pathway in good yield, but, surprisingly, the *exo*-1,3-dipolar cycloadduct

Table 1 Reactions of 1,3-dipolar reagents with quadricyclane in dichloromethane at 70 °C

1,3-Dipole	Ratio 1,3-Dipole : 7	Time/day	Products (%)
1	1.24	2	**9a**(70); **10**(19)
5	0.54	2	**9b**(54); **11**(8); **12**(31)
8	0.83	6	**13a**(17); **13b**(12); **14** or **15**(32)



Scheme 2

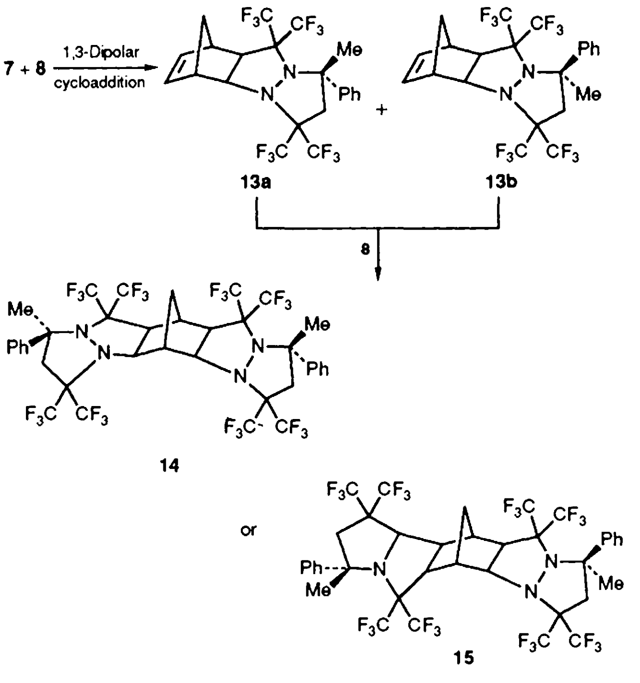


Scheme 3

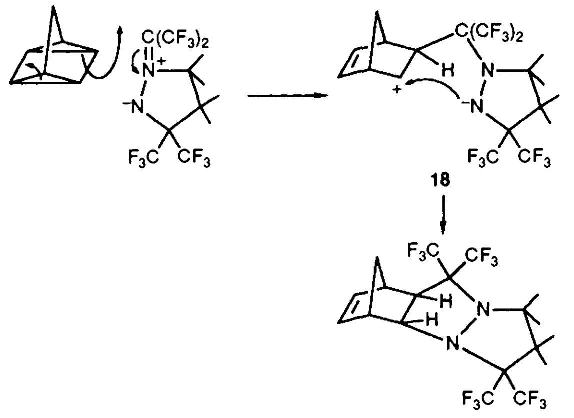
10 was also produced. A mixture (94%) of the adduct **9a** and its *endo*-isomer in the ratio 82 : 12 was formed in the slow reaction of the azine **1** with norbornadiene at 70 °C over an extended period (33% conversion of **1** in 14 days).[1] It was considered possible that adduct **10** was formed in the present reaction by addition of azine **1** to norbornadiene, which arose from isomerisation of quadricyclane **7**, although this isomerisation is reported not to occur below 120 °C.[4] In a control experiment, a solution of **7** in dichloromethane was heated at 70 °C (7 days) and a quantitative recovery of **7** was obtained; norbornadiene was not detected (^{1}H NMR).

Adduct **10** is believed therefore to arise *via* 1,3-dipolar cycloaddition of azine **1** to **7**, and on attempted separation from compound **9a** by dry column flash chromatography on silica gel, it was hydrolysed to the amide **16** (Scheme 2).

The reaction of azine **5** with **7**, under the same conditions, gave a single 1 : 1 adduct **9b**, the bis $[_{\sigma}2_s + {}_{\sigma}2_s + {}_{\pi}2_s]$ cycloadduct **11**, formed by reaction of the C=N bond in adduct **9b** with **7**, and a 2 : 2 adduct **12**. The latter compound was formed from the initial adduct **9b** by reaction with the azine **5** at the C=C bond to give an intermediate azomethine imide **17**, which underwent 1,3-dipolar cycloaddition to **7** (Scheme 3); the structure of the compound **12** was established by X-ray crystallography.[5]



Scheme 4



Scheme 5

1,3-Dipolar cycloaddition of the azomethine imide **8** (prepared by treatment of the azine **5** with the alkene $CH_2{=}CMePh$[6]) to quadricyclane **7** gave the two diastereoisomeric adducts **13a** and **13b**, and a symmetrical 1 : 2 adduct **14** or **15** (^{1}H, ^{13}C and ^{19}F NMR), formed by further 1,3-dipolar cycloaddition to **13a** and **13b** (Scheme 4).

No mention was made in the two reference volumes on 1,3-dipolar cycloaddition by Padwa[7] of such a reaction involving quadricyclane **7**, and a search of the literature has also failed to uncover any such report.

Concerted 1,3-dipolar cycloaddition to quadricyclane **7** would involve a suprafacial $[_{\sigma}2 + {}_{\sigma}2 + {}_{\pi}4]$ process, which is symmetry forbidden under thermal conditions. We therefore propose that such additions reported in the present work are two-step reactions, which involve initial electrophilic attack on quadricyclane **7** to give a zwitterion **18**, where the positive charge is associated with a norbornenyl cation and the negative charge is on nitrogen, which ring closes to give the *exo*-adduct (Scheme 5).

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