

## Preliminary Note

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Novel cycloaddition products from the reaction of 2,5-dichloro-1,1,1,6,6,6-hexafluoro-3,4-diazahexa-2,4-diene with cycloalkenes, cyclodienes and cycloheptatriene, and of hexafluoroacetone azine with cycloheptatriene

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(Received September 11, 1992; accepted November 3, 1992)

### Abstract

Thermal reaction (20–70 °C) of the dichloroazine  $\text{CF}_3\text{CCl}=\text{N}=\text{N}=\text{CClCF}_3$  (**2**) with cyclopentene (in  $\text{CH}_2\text{Cl}_2$  solvent), cycloheptene, indene, acenaphthylene, 2,3-dihydrofuran, 2,3-dihydropyran, norbornadiene, cyclopentadiene and dicyclopentadiene gives as the major product in each case the rearranged [3+2] cycloadduct (**3**) containing a  $\text{CF}_3\text{CCl}_2$  group; hydrolysis ( $\text{CF}_3\text{CCl}_2 \rightarrow \text{CF}_3\text{CO}$ ) to give the amide (**4**) takes place on attempted chromatographic purification on silica gel. With cyclopentene the rearranged cyclopentadiene [3+2] cycloadduct (**3b**) is also formed, while other products obtained by chromatographic separation from the 2,3-dihydropyran reaction are the 5,6-dihydropyran-3-yl azine (**5**), the hydrazone  $\overline{\text{CH}_2(\text{CH}_2)_2\text{OCH}=\text{C}-\text{C}(\text{CF}_3)=\text{NNH}_2}$  (**8**) and equimolar quantities of 5,6-dihydropyran-3-yl trifluoromethyl ketone (**6**) and the chlorohydrazone  $\overline{\text{O}(\text{CH}_2)_4\text{CHNHN}=\text{CClCF}_3}$  (**7**) possibly arising via hydrolysis of the 1:2 adduct (**16**). The reaction of azine **2** with cycloheptatriene at 70 °C gives a complex mixture, in which the major products are the rearranged [3+6] cycloadduct (**31**) and the dehydrochlorinated [3+2] cycloadducts (**10**) and (**11**) containing a  $\text{CF}_3\text{CHCl}$  group. The corresponding reaction with hexafluoroacetone azine (**1**) at 70 °C affords the criss-cross [3+2] cycloadduct (**22**), the bis-ene adduct (**23**) and its oxidation product, the azo compound (**24**), and the [3+6] cycloadduct diaziridine (**25**).

1,3-Dipolar cycloadditions of hexafluoroacetone azine (**1**) with a wide variety of alkenes, alkynes and dienes have been reported, e.g. refs. 1 and 2. In a preliminary investigation to determine whether the dichloroazine **2** [3] would react analogously, it was observed that reaction did not take place with the dipolarophiles  $\text{H}_2\text{C}=\text{CHEt}$ ,  $\text{H}_2\text{C}=\text{CMe}_2$ ,  $(\text{NC})_2\text{C}=\text{C}(\text{CN})_2$  or  $\text{HC}\equiv\text{CH}$ , but with cyclopentene a thick black multicomponent oil was formed; attempted separation of the components was unsuccessful [4].

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In the present work, the reaction of azine **2** with cyclopentene was repeated at 70 °C in CH<sub>2</sub>Cl<sub>2</sub> as the solvent and the results obtained prompted an investigation of the reactions of **2** with a range of cyclic alkenes, dienes and trienes as summarized in Table 1.

The rearranged 1:1 adducts **3** formed in the alkene and diene reactions arise by initial [3 + 2] cycloaddition to give the azomethine imines **14** followed by elimination of chloride ion and then addition of chloride ion to the resulting immonium ion **15**. Cycloadducts **3** were found to undergo facile hydrolysis on attempted purification on silica gel by dry column flash chromatography (DCFC) to afford the amides **4** (Scheme 1).

The cycloadducts did not contain a strong absorption in their IR spectra at *c.* 1500 cm<sup>-1</sup> as expected for azomethine imines **14** and observed for azomethine imines derived from azine **1** [1, 2]. Also, the <sup>13</sup>C NMR spectra contained an absorption in the range *c.* 90 ppm, as expected for N–CCl<sub>2</sub>CF<sub>3</sub> and an absence of an absorption at *c.* 140 ppm (or even lower field) expected for the immonium carbon in the  $\text{>N}^+\text{=CClCF}_3$  grouping of compounds **14** and **15**, thus confirming that the adducts had structure **3**.

An unexpected product formed in the cyclopentene reaction was the cyclopentadiene adduct **3b** which was isolated as amide **4b**. It is presumed

TABLE 1  
Reaction of azine **2** with unsaturated carbocycles

Carbocycle	Molar ratio 2:carbocycle	Conditions		Azine <b>2</b> recovered (%)	1:1 Adducts formed	Separated products (%)
		Temp. (°C)	Time (d)			
Cyclopentene <sup>a</sup>	1:1.1	70	21	23	<b>3a</b> <b>3b</b>	<b>4a</b> 31 <b>4b</b> 24
Cycloheptene	1:2	70	36	82	<b>3c</b>	<b>4c</b> 60
Indene	1:1	70	4	22	<b>3d</b>	<b>4d</b> 93
Acenaphthylene	2:1	70	12	88	<b>3e</b>	<b>4e</b> 67
2,3-Dihydrofuran	1:2	50	3 <sup>h</sup>	23	<b>3f</b>	<b>4f</b> 93
2,3-Dihydropyran	1:1	70	3	35	<b>3g</b>	<b>4g</b> 32; <b>5</b> 29; <b>6</b> 18; <b>7</b> 18; <b>8</b> 4
Norbornadiene	1:2	70	14	67	<b>3h</b> <b>3i</b>	<b>4h</b> 80 <b>4i</b> 12 <b>9</b> 4
Cyclopentadiene	1:1	20	8	43	<b>3b</b> <b>3j/3k</b>	<b>4b</b> 71 <b>4j/4k<sup>b</sup></b> 5
Dicyclopentadiene	1:1	40	16	32	<b>3j/3k</b>	<b>4j/4k<sup>b</sup></b> 76
Cycloheptatriene <sup>a</sup>	1:2	70	20	77	<b>3l</b>	<b>4l</b> 18 <b>10</b> 28; <b>11</b> 23 <b>12</b> 1; <b>13<sup>c</sup></b> 4

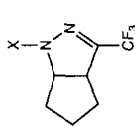
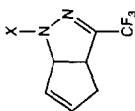
<sup>a</sup>In CH<sub>2</sub>Cl<sub>2</sub> as the solvent.

<sup>b</sup>Present in a 1:1 ratio.

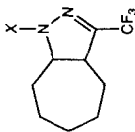
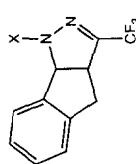
<sup>c</sup>Mixture of two isomers (3.4:1 ratio).



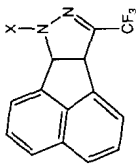
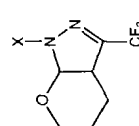
(1)

(3a) X =  $\text{CCl}_2\text{CF}_3$ (4a) X =  $\text{COCF}_3$ (3b) X =  $\text{CCl}_2\text{CF}_3$ (4b) X =  $\text{COCF}_3$ 

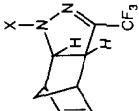
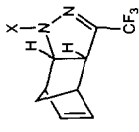
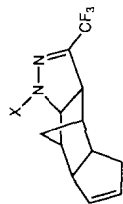
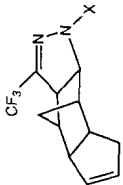
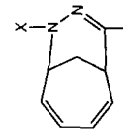
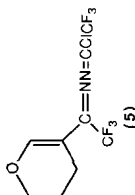
(2)

(3c) X =  $\text{CCl}_2\text{CF}_3$ (4c) X =  $\text{COCF}_3$ (3d) X =  $\text{CCl}_2\text{CF}_3$ (4d) X =  $\text{COCF}_3$ 

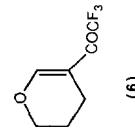
(17) X = H

(3e) X =  $\text{CCl}_2\text{CF}_3$ (4e) X =  $\text{COCF}_3$ (3g) X =  $\text{CCl}_2\text{CF}_3$ (4g) X =  $\text{COCF}_3$ 

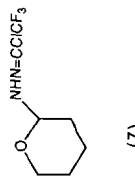
(18) X = H

(3h) X =  $\text{CCl}_2\text{CF}_3$ (4h) X =  $\text{COCF}_3$ (3i) X =  $\text{CCl}_2\text{CF}_3$ (4i) X =  $\text{COCF}_3$ (3j) X =  $\text{CCl}_2\text{CF}_3$ (4j) X =  $\text{COCF}_3$ (3k) X =  $\text{CCl}_2\text{CF}_3$ (4k) X =  $\text{COCF}_3$ (3l) X =  $\text{CCl}_2\text{CF}_3$ (4l) X =  $\text{COCF}_3$ 

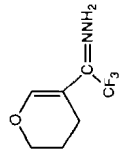
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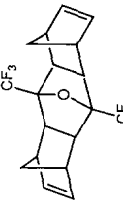
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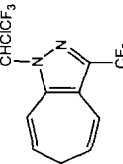
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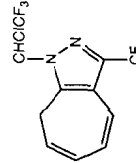
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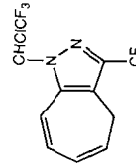
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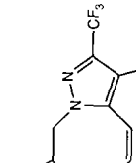
(10)



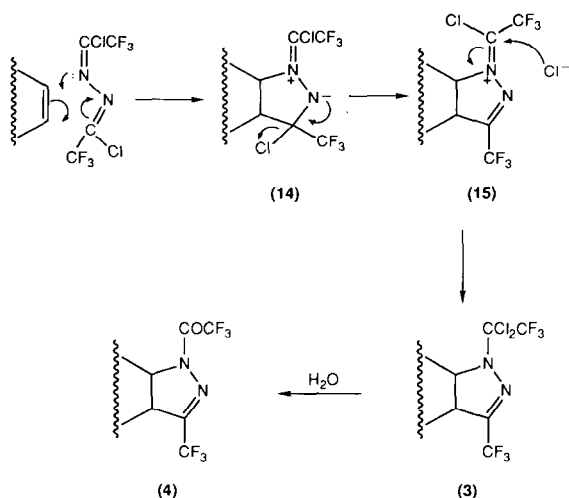
(11)



(12)



(13)



Scheme 1.

that compound **3b** arose via oxidation of cyclopentene to cyclopentadiene followed by reaction with azine **2**, but the nature of the oxidizing agent is not known.

The cycloadditions involving the unsymmetrical alkenes and dienes were all regiospecific and the direction of addition in each case was consistent with the reactions being LUMO(azine)–HOMO(dipolarophile) controlled.

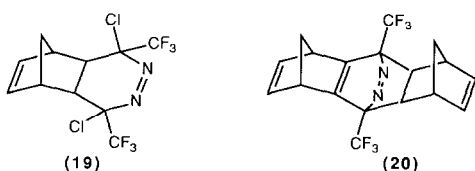
Apart from amide **4g**, four other products **5–8** were isolated from the 2,3-dihydropyran reaction and these are considered to have arisen as shown in Scheme 2.

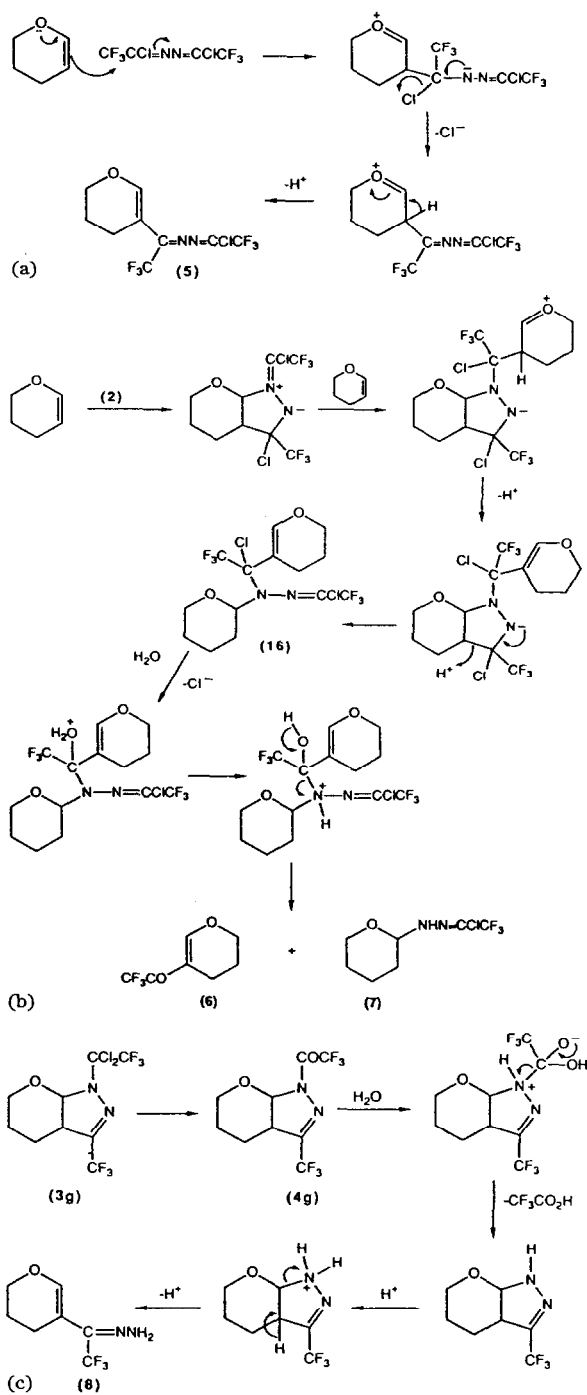
Nucleophilic attack by the pyran on azine **2** followed by elimination of hydrogen chloride gave the substituted azine **5**, while compounds **6** and **7** (1:1 molar ratio) are formed by hydrolysis (on silica) of the 2:1 adduct **16**. Amide **4g** was observed to undergo slow hydrolysis and elution after 4 h contact with silica gel gave hydrazone **8** (93%).

Elimination of the trifluoroacetyl group from the amides **4** was achieved by treatment with an ethanolic solution of methylamine, e.g. **4d**  $\rightarrow$  **17** (94%) and **4h**  $\rightarrow$  **18** (88%).

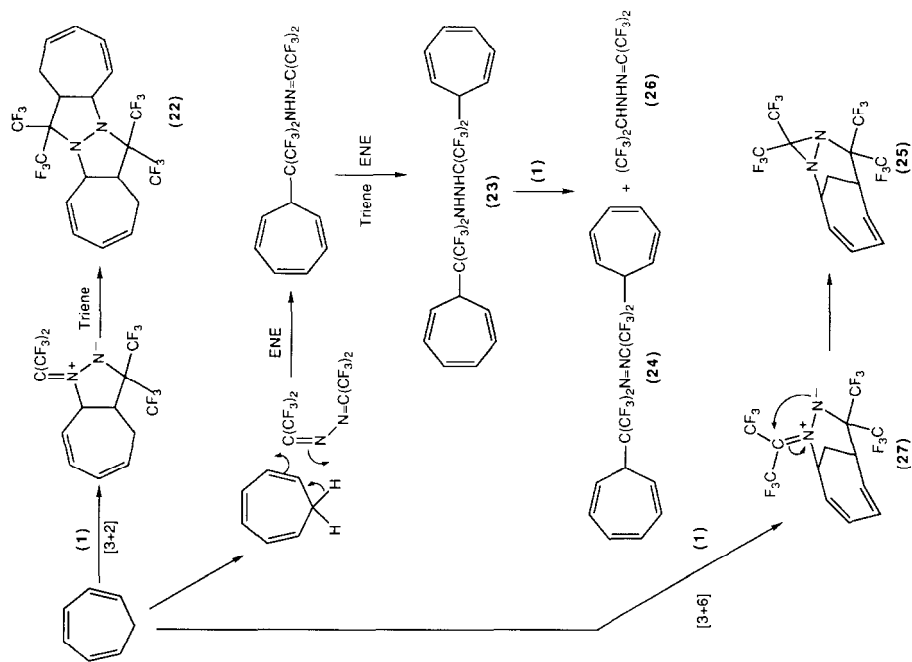
The minor product **9** isolated from the norbornadiene reaction is presumed to arise via the Diels–Alder [4+2] cycloadduct **19**, which after dehydrochlorination underwent a second [4+2] cycloaddition; the resulting adduct **20** then lost nitrogen and underwent hydrolysis.

The cycloheptatriene reaction afforded a complex mixture from which only the major products were isolated (DCFC). The only amide detected was

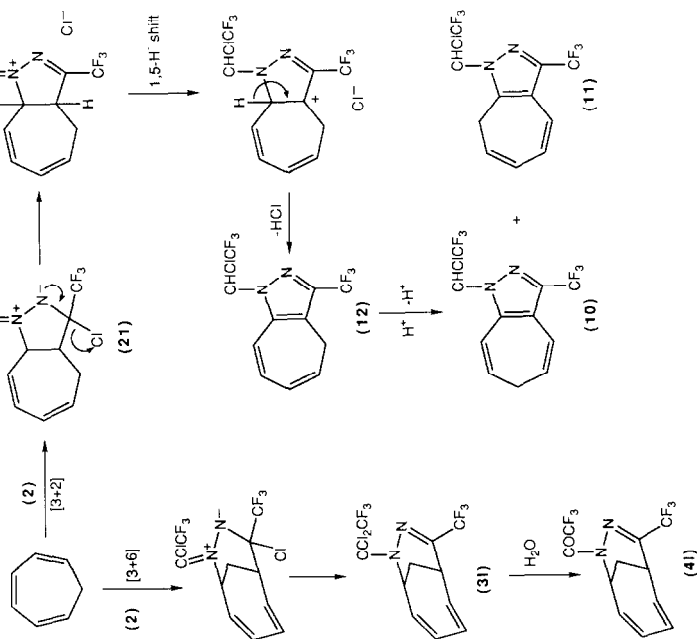




Scheme 2.



Scheme 4.

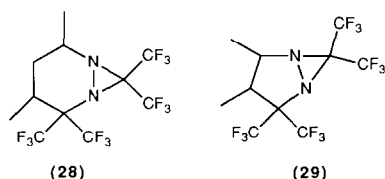


Scheme 3.

**41**, resulting from hydrolysis of the rearranged [3+6] cycloadduct **31** and compounds **10–12** are formed from the [3+2] cycloadduct **21** which, rather than rearranging by a chloride shift, underwent elimination of chloride ion followed by a 1,5-hydrogen shift and loss of a proton (Scheme 3). The formation of 1:1 adduct **13** requires considerable skeletal rearrangement and it is not apparent how this occurred.

The corresponding reaction of cycloheptatriene with azine **1** in the absence of solvent at 70 °C (2:1 molar ratio) was much cleaner and afforded the [3+2] criss-cross adduct **22** (15%), the bis-ene adduct **23** (17%), the azo compound **24** (21%) and the [3+6] cycloadduct, the diaziridine **25** (7%) as well as unchanged triene (47% recovered) and a mixture of unchanged azine **1** (30% recovered) and the reduced azine, hydrazone **26** (20%). The products are postulated to be formed as shown in Scheme 4.

The most noteworthy feature of the reaction was the formation of the diaziridine **25** by cyclization of the initial [3+6] cycloadduct, azomethine imine **27**. Azomethine imines formed by [3+2] cycloaddition involving azine **1** and alkenes or dienes do not cyclize to diaziridines, which illustrates the greater stability of the bicyclo[3.1.0]diazahexane system **28** relative to the bicyclo[2.1.0]diazahexane system **29**.



A satisfactory elemental analysis was obtained for the mixture of norbornadiene adducts **3h** and **3i**, and an accurate mass measurement was carried out on the cycloheptene adduct **3c**; the remaining adducts of type **3** were identified in the crude reaction product mixture from their IR, NMR and mass spectra. The other products gave satisfactory elemental analyses or accurate mass measurements and the spectral data obtained were consistent with the structures proposed.

## Acknowledgment

We thank the committee of Vice Chancellors and Principals for an O.R.S. award (to M. A-G.).

## References

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