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CRISS-CROSS CYCLOADDITION REACTIONS WITH HEXAFLUOROACETONE AZINE. MECHANISM AND SOME SYNTHETIC APPLICATIONS

Klaus Burger,^{*a} Lothar Hennig,^a Olaf Zeika,^b and Andrea Lux^b

^a Department of Organic Chemistry, University of Leipzig, Johannisallee 29, D-04103 Leipzig, Germany

^b Novald GmbH, Tatzberg 49, D-01307 Dresden, Germany

E-mail: burger@organik.chemie.uni-leipzig.de

Abstract – Using hexafluoroacetone azine as model compound we have shown that azomethine imines are the [1.1]intermediates of the criss-cross cycloaddition. The readily available trifluoromethyl substituted azomethine imines are reactive species exhibiting considerable synthetic potential for the construction of partially fluorinated heterocycles and polymers.

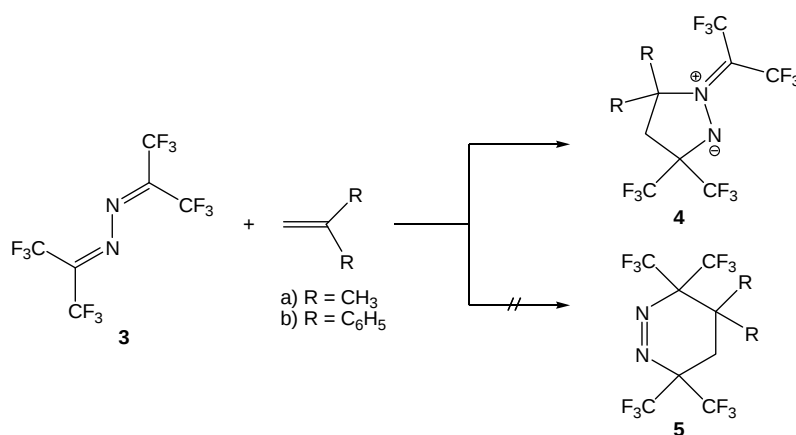
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^{*} Dedicated to Prof. Barry M. Trost on the occasion of his 65th birthday

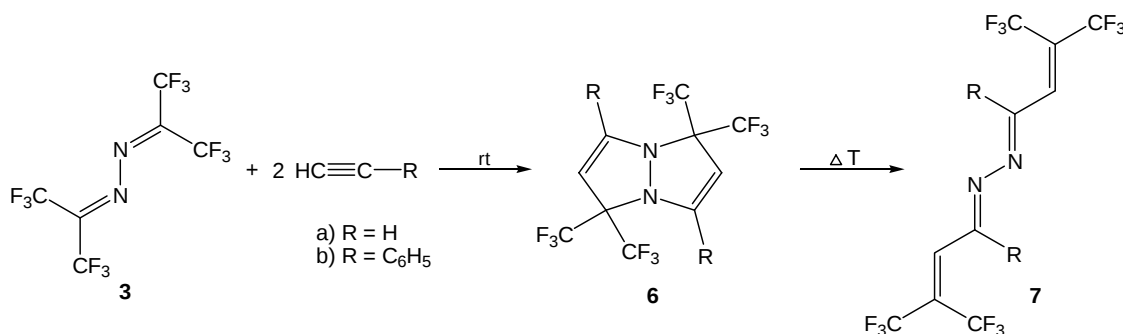
sublimation or recrystallization from hexanes. When the colorless crystals of the [1:1] adducts were dissolved in organic solvents yellow or green solutions were obtained. Above their melting points, the samples show a green color, changing back to colorless when the samples crystallize on cooling.

Based on the NMR spectroscopic data the structure of a Diels-Alder adduct (**5**) could be ruled out for the [1:1] adducts.⁶ Finally, X-Ray structure analysis unambiguously revealed that the intermediate of the criss-cross cycloaddition of azines is an azomethine imine (**4**)¹² confirming Huisgens postulat (Scheme 2).^{4,13} The dipolmoments of **4a** (R = CH₃, 5.04 D) and **4b** (R = C₆H₅, 5.13 D) were measured in benzene, the values are in agreement with a 1,3-dipolar species.



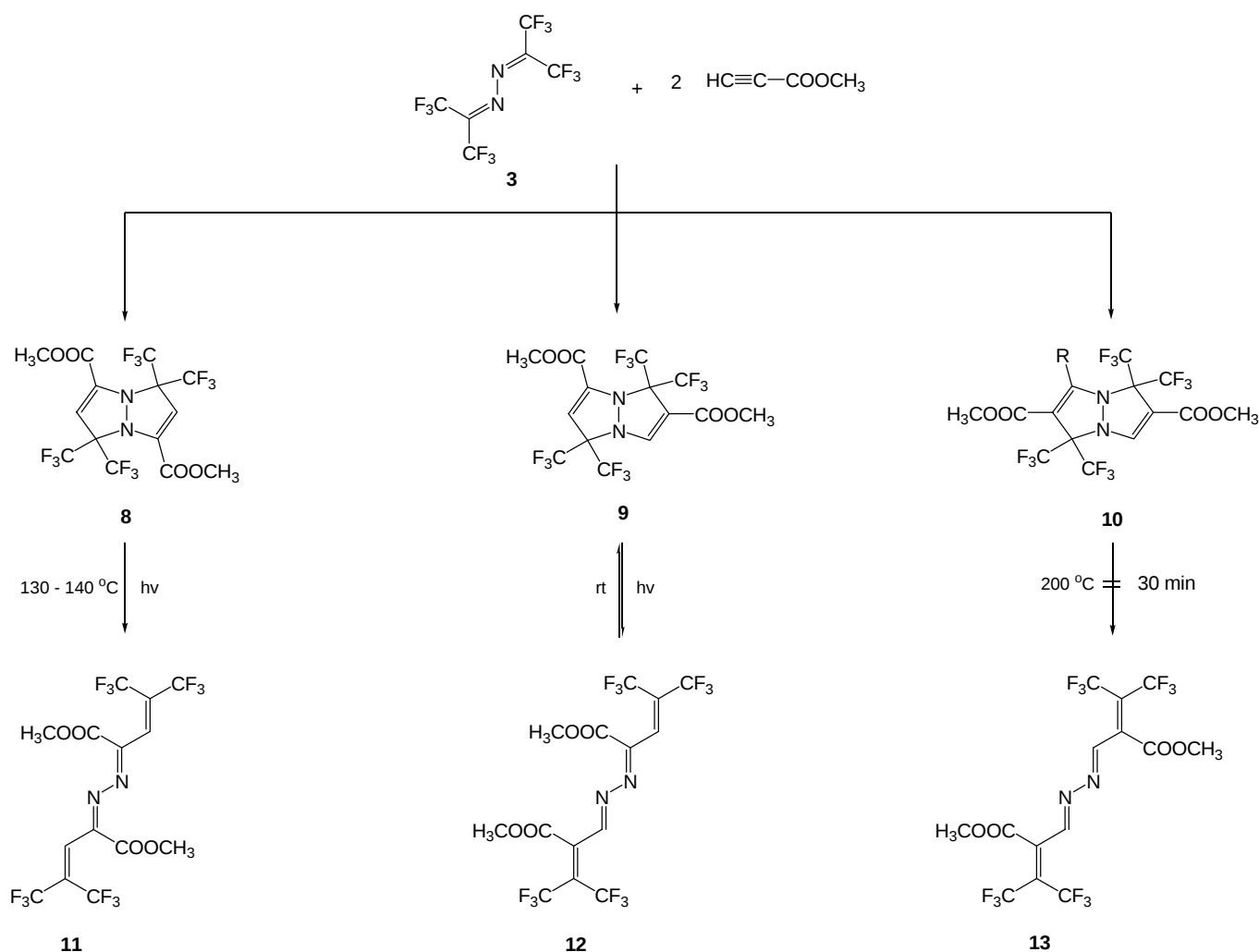
2.2. 1,5-Diazabicyclo[3.3.0]octa-2,6-dienes. Valence Isomerization

At room temperature hexafluoroacetone azine (**3**) readily adds two equivalents of alkynes to give the corresponding criss-cross cycloadducts (**6**),^{9a,14} which are thermolabile. The temperature necessary to start a tandem electrocyclic ring cleavage depends on the substitution pattern. While the valence isomerization of **6a** (R = H) is complete at 120 °C (bath temperature) within 2 h, the transformation of **6b** (R = phenyl) is quantitative after heating up to 150 °C (bath temperature) for 3 h. Therefore, [2:1] adducts obtained by Tipping *et al.* in a sealed tube reaction at 170 °C⁵ are open-chain valence isomers (**7**) and not [1.5]-diazabicyclo[3.3.0]octa-2,6-dienes (**6**) as they originally postulated.

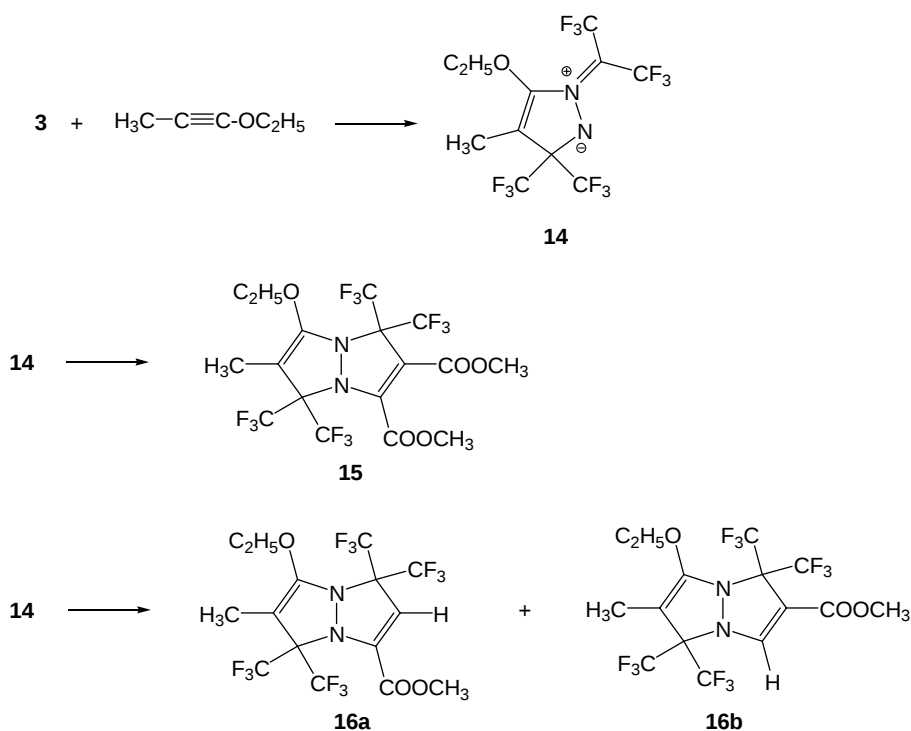


The reaction of **3** with methyl propiolate gave a mixture of three isomers (**8** – **10**)¹⁴ of different thermostability. While compound (**8**) undergoes ring opening (**8** → **11**) at 130 – 140 °C, **10** is stable even

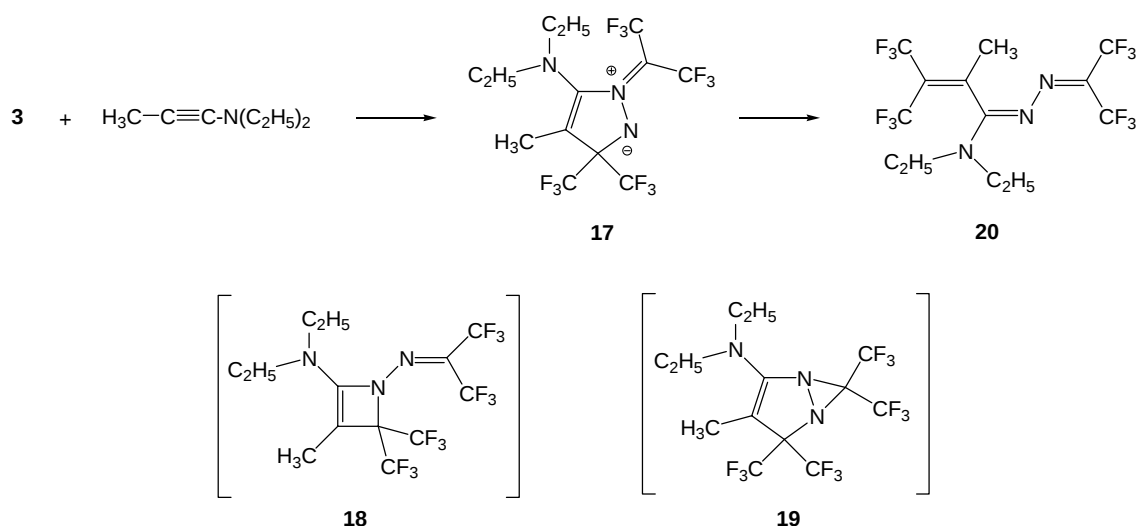
on heating to 200 °C for 30 min. Compound (**9**) was unchanged after heating to 170 °C for 15 h. However, photochemical ring opening (**9** → **12**) was achieved quantitatively within 3 h, indicating that the right location of the substituents is responsible for the stability of the bicyclic system. Surprisingly, the retro reaction (**12** → **9**) takes place on standing at room temperature within a few days (Scheme 4).



When **3** was reacted with two equivalents of ethoxypropyne, ^{19}F NMR spectroscopy reveals that after stirring the reaction mixture for 8 d at 0 °C and further 3 d at room temperature the azomethine imine (**14**) was formed in very good yields and can be trapped by various dipolarophiles to give mixed criss-cross cycloaddition products (**14** → **15**). Trapping reactions with propiolates occur regiospecifically (**14** → **16a,b**) (Scheme 5).¹⁵



In contrast, azomethine imine (**17**) formed from **3** and diethylaminopropyne at $-50\text{ }^{\circ}\text{C}$ to $-20\text{ }^{\circ}\text{C}$, without trapping reagent already at $0\text{ }^{\circ}\text{C}$ rearranges to give an open chain product (**20**).¹⁵ Two mechanistic alternatives *via* intermediates (**18**) and (**19**) have been discussed.

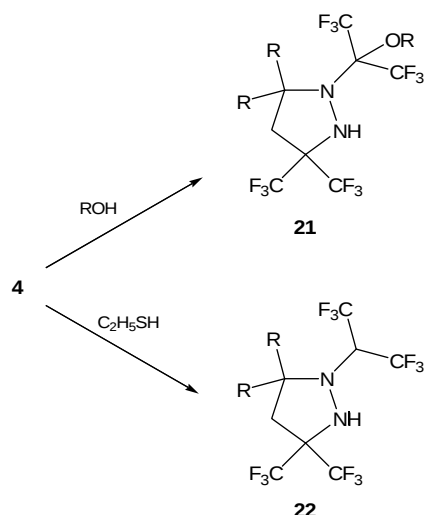


3. Structure and Reaction Behavior of the [1:1] Adducts (Azomethine Imines)

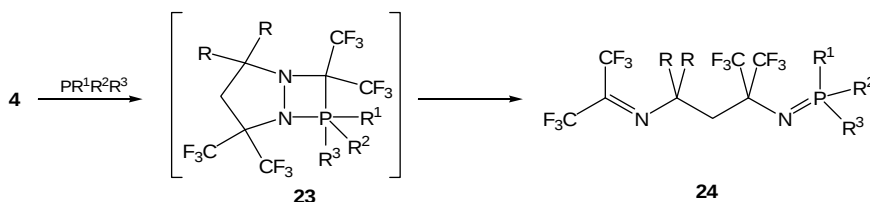
The trifluoromethyl substituted azomethine imines (**4**) are reactive species and show considerable synthetic potential, *i.e.* for the construction of partially fluorinated heterocycles.

3.1. Addition of Nucleophiles

Alcohols add to azomethine imines (**4**) to give 1,3-adducts (**21**).¹⁶ In contrast, treatment with ethane thiol results in a reduction of the 1,3-dipolar skeleton (**4** → **22**). Compounds (**22**) are also obtainable on treatment of (**4**) with LiAlH₄ or by catalytic hydrogenation.

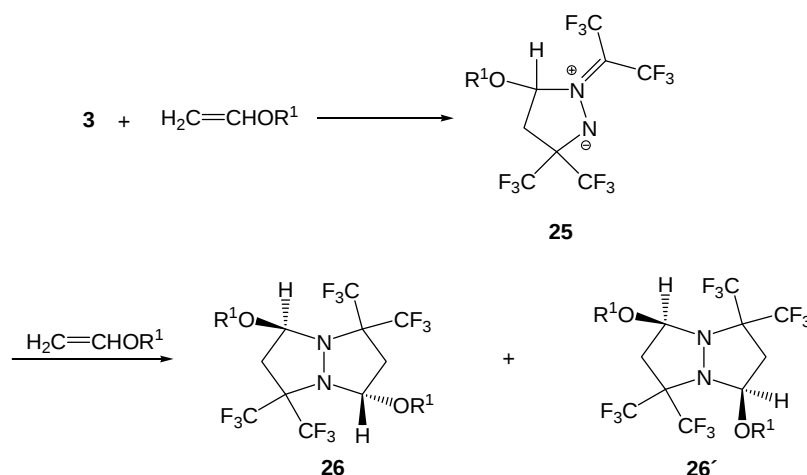


[1:1] Adducts from **4** and phosphites were assigned the structure of [7,7,7-trifluoro-2,2,6-tris(trifluoromethyl)-1,5-diaza-5-heptenyldiene]phosphoranes (**24**).¹⁷ A reaction sequence including a [3+1] cycloaddition to give a five-coordinated phosphorus species (**23**) followed by a [2+2] cycloreversion (**4** → **23** → **24**) plausibly explains the experimental facts.

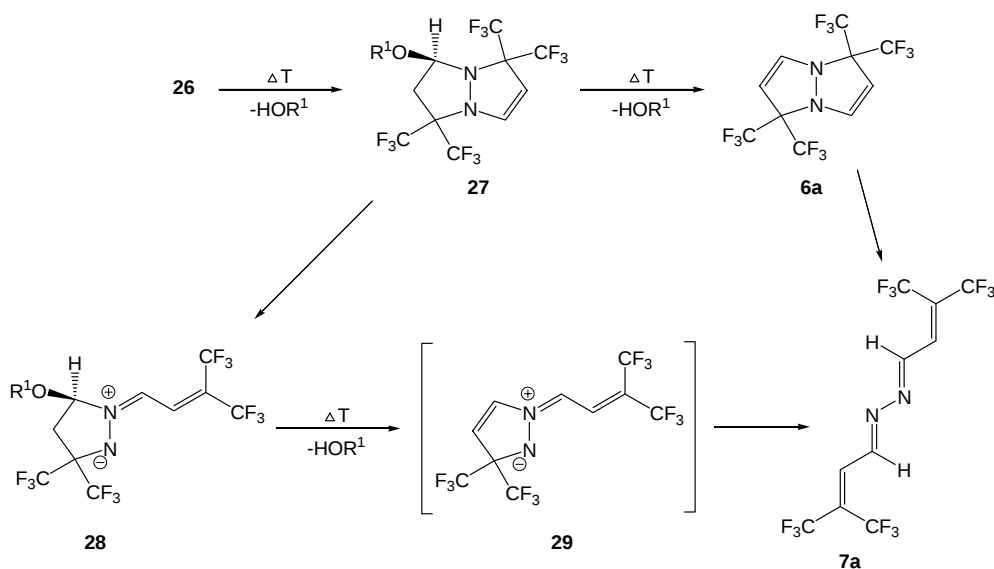


3.2. [3+2] Cycloaddition versus Heterolytic Cleavage¹⁸

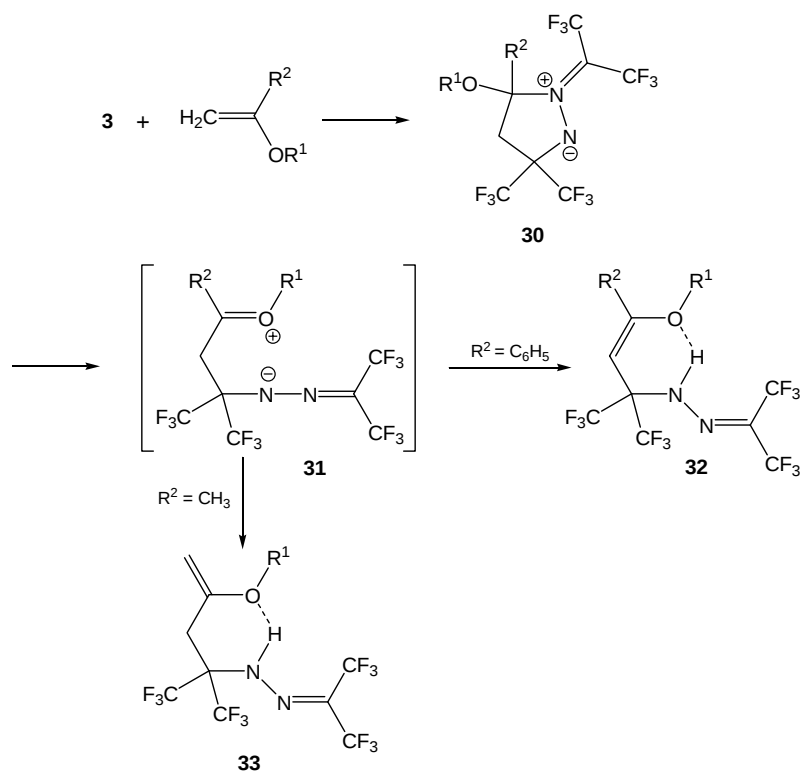
Hexafluoroacetone azine (**3**) readily reacts with open-chain and cyclic enol ethers to give azomethine imines (**25**, **30** and **34**). When 2 equivalents of vinyl ether CH₂=CHOR were added in a temperature range of -20 to -10 °C criss-cross cycloadducts (**26**) were formed. Both cycloaddition steps occur regiospecifically. The influence of solvent polarity on the diastereomeric ratio is negligible. However the diastereomeric ratio can be manipulated by varying the size of substituent R. Monitoring the progress of the reaction by ¹⁹F NMR spectroscopy we found that the diastereomeric ratio **26** : **26'** changed from 3:2 to 4:1 on substitution of R = C₂H₅ by n-C₄H₉ and i-C₄H₉, respectively.



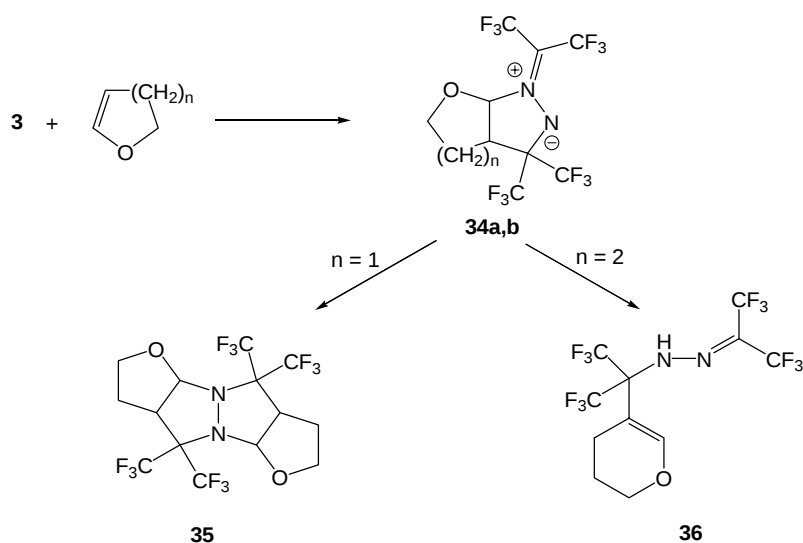
Compounds (**26**) ($\text{R} = \text{C}_2\text{H}_5$) start to eliminate ethanol already below room temperature, at 100°C (3 h) **26** was nearly completely transformed into 1,5-diazabicyclo[3.3.0]oct-2-enes (**27**). At about 140°C a second mol of ethanol was split off to give the 1,5-diazabicyclo[3.3.0]octa-2,6-diene (**6a**) which itself is thermolabile (*vide supra*) (**6a** $\rightarrow$ **7a**). However, a mechanistic alternative pathway to **7a** seems possible (**27** $\rightarrow$ **28** $\rightarrow$ **29** $\rightarrow$ **7a**).



Azine (**3**) and α -substituted enol ethers $\text{CH}_2=\text{CR}^2\text{-OR}^1$ even when the latter were added in excess react to give exclusively [1:1] adducts. ^{19}F NMR spectral analysis reveals that the adduct formed first is an azomethine imine (**30**), which rearranges to give hydrazones (**32**) and (**33**). The incorporation of a second substituent R^2 into skeleton position C-5 causes an elongation of the C(5)-N(1)-bond which now becomes sensitive to heterolytic cleavage especially in polar media at elevated temperatures. The zwitterionic species (**31**) formed stabilizes by proton transfer.



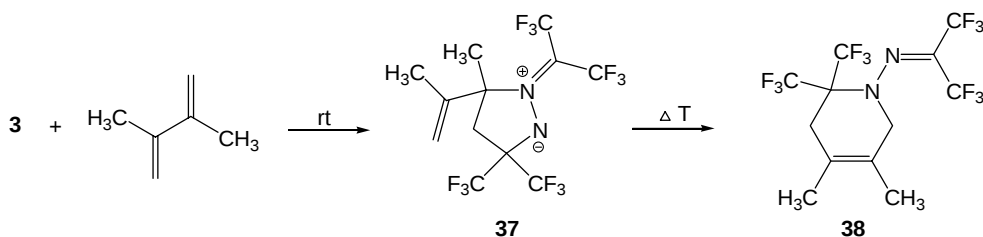
Cyclic enol ether like 2,3-dihydrofuran and 2,3-dihydro-4*H*-pyran studied so far add to **3** to give azomethine imines (**34**) which have been isolated and fully characterized. Compound (**34a**) ($n=1$) is susceptible to add a second molecule of the enol ether to give the criss-cross cycloadduct (**35**), while compound (**34b**) ($n=2$) in polar solvents or in the presence of proton and Lewis acids rearrange to give hydrazones (**36**).



Hexafluoroacetone azine (**3**) and enamines react analogously.¹⁸

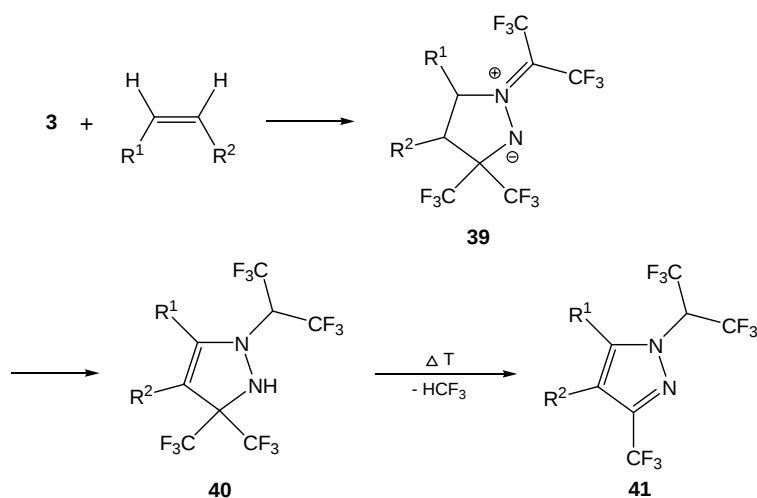
3.3. [2,3] Sigmatropic Rearrangements

Azomethine imines (**37**) generated from **3** and 2,3-dimethylbutadiene on heating undergo a [2,3] sigmatropic rearrangement (**37** $\rightarrow$ **38**) to give tetrahydropyridine derivatives.¹⁹



3.4. 3-Trifluoromethylpyrazoles from 1H-3-Pyrazolines

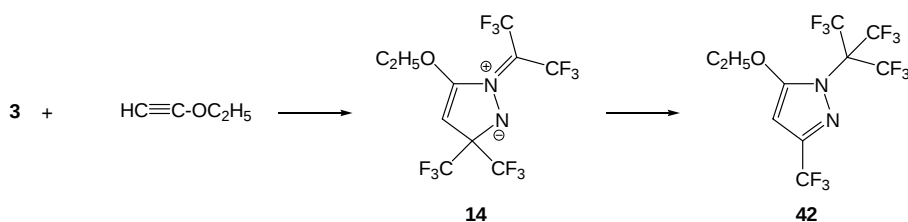
On treating **3** with olefins of type $R^1-CH=CH-R^2$ 2-[3,3-bis(trifluoromethyl)-1-pyrazolin-1-yl]-1,1,1,3,3,3-hexafluoro-2-propanides (**39**) are initially formed, which are capable to react further to give criss-cross cycloadducts or rearrange to give 1H-3-pyrazolines (**40**).^{20,21} The rate of the proton migrations depends on the substituent pattern of the olefins. Especially in the case of terminal olefins with bulky substituents the yields of 1H-3-pyrazolines (**40**) are high because the competing [3+2] cycloaddition to give criss-cross adducts is sterically unfavorable.



5,5-Bis(trifluoromethyl)-1H-3-pyrazolines (**40**) have been transformed into pyrazoles (**41**) by flow pyrolysis at 450 °C.^{3,22} We found that this heteroaromatization process already occurs below 200 °C. In certain cases the CHF₃-elimination already starts on prolonged standing at room temperature.²³

3.5. *N*-(Perfluoro-*t*-butyl)pyrazoles. [1,4]-Trifluoromethyl Group Migration

An efficient approach to *N*-(perfluoro-*t*-butyl)-3-trifluoromethylpyrazole (**42**) was achieved starting from **3** as fluorinated building block. Azomethine imines (**14**) obtained from **3** and ethoxyacetylenes are the key intermediates of the synthesis. Surprisingly, a [1,4]-trifluoromethyl group migration already occurs on prolonged standing of the 1,3-dipolar species (**14**) at room temperature.²⁴ Again heteroaromatization is the driving force of the rearrangement (**14** → **42**). To the best of our knowledge this is the first case of a construction of a perfluoro-*t*-butyl group *via* trifluoromethyl group [1,4]-migration.



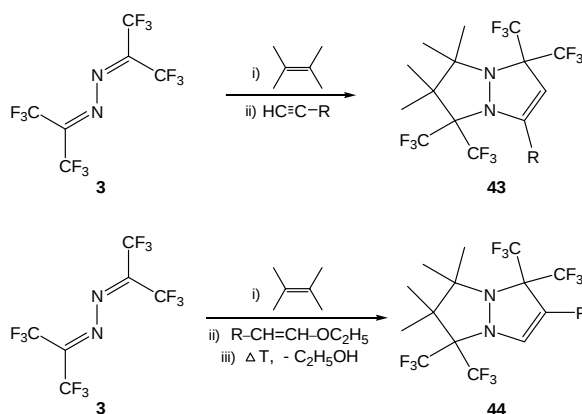
4. Mixed Criss-Cross Cycloaddition and Consecutive Reactions

4.1. 1,5-Diazabicyclo[3.3.0]octanes

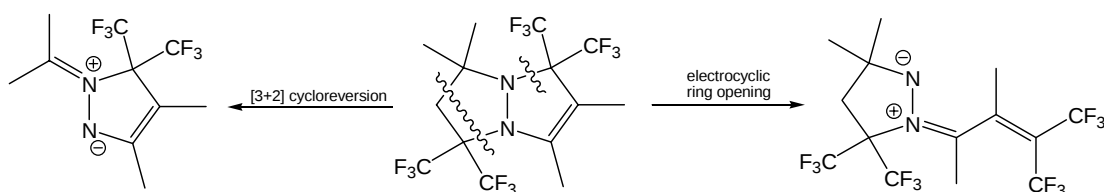
Bicyclic systems with highly variable substitution patterns are easily obtainable *via* mixed criss-cross cycloaddition using different 1,3-dipolarophiles for both cycloaddition steps.

4.2. 1,5-Diazabicyclo[3.3.0]oct-2-enes. Valence Isomerization

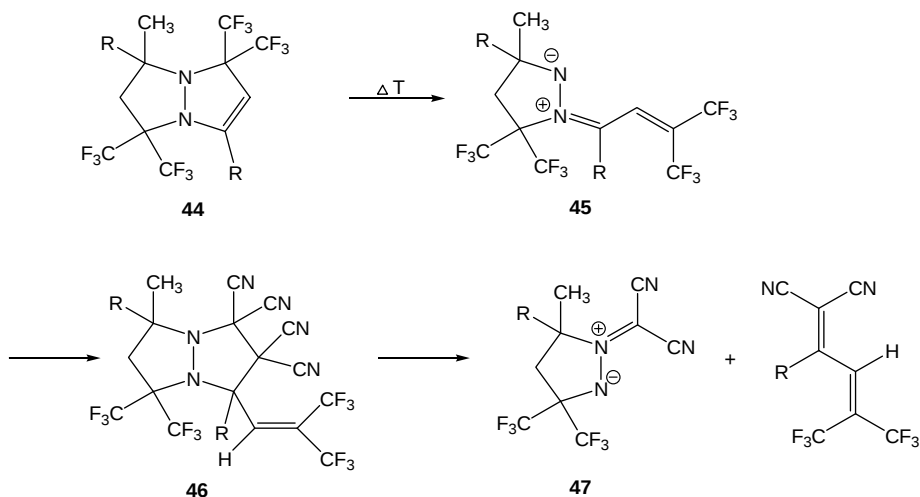
1,5-Diazabicyclo[3.3.0]oct-2-enes are readily available *via* different routes applying the concept of the mixed criss-cross cycloaddition. Consecutive addition of an olefin and an acetylene to the hexafluoroacetone azine skeleton (**3** → **4** → **43**) and consecutive addition of an olefin and an enoether followed by elimination of alcohol (**3** → **4** → **44**) are now standard strategies for the synthesis 1,5-diazabicyclo[3.3.0]oct-2-enes.



1,5-Diazabicyclo[3.3.0]oct-2-enes are interesting candidates for ring transformations. There are two options to start the reaction sequence, namely *via* electrocyclic ring opening or *via* [3+2] cycloreversion. Since both reactions are orbital symmetry controlled processes, therefore the reaction pathway which finally is observed very much depends on the substituent pattern.

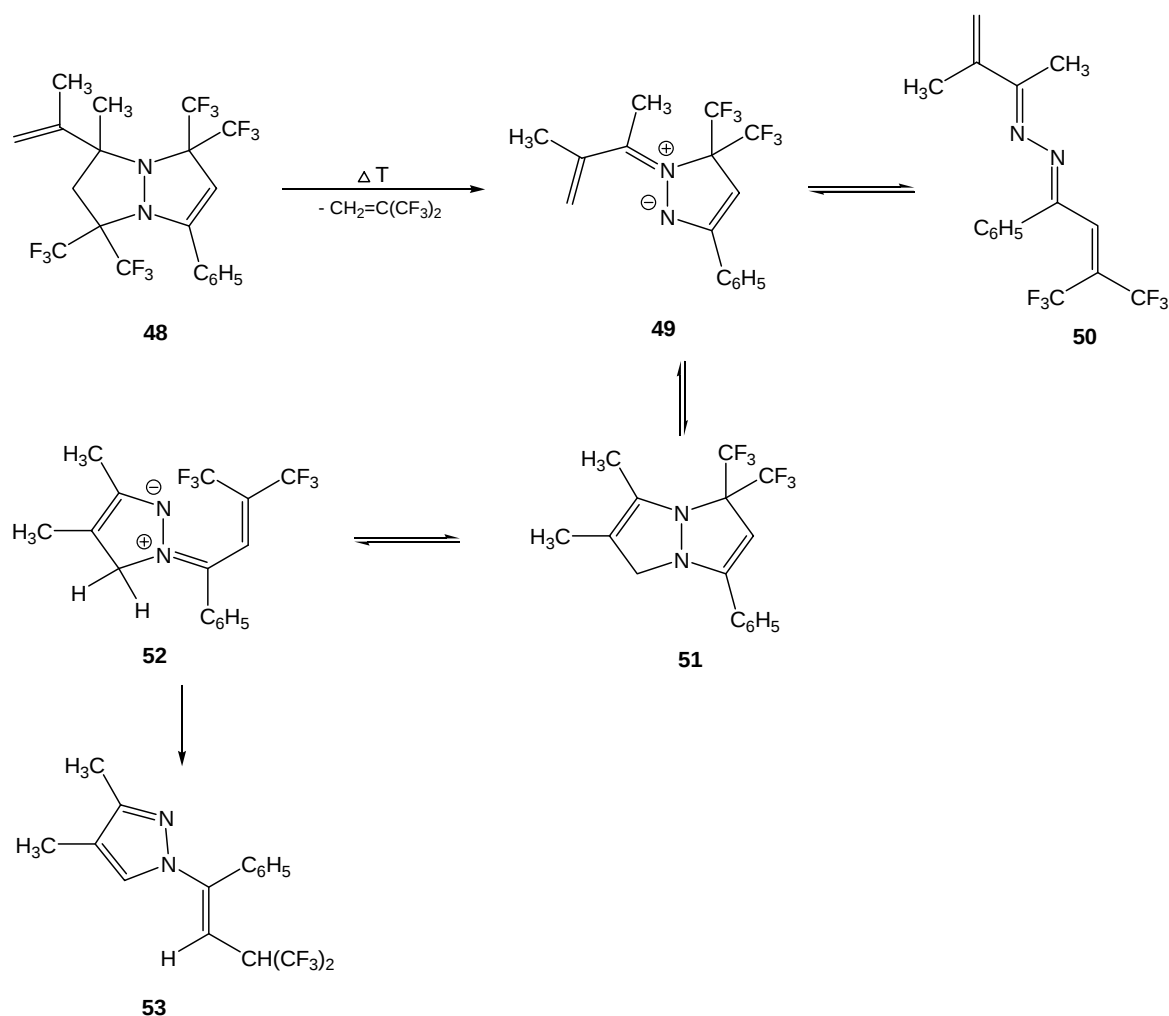


On heating compounds of type (**44**) undergo an electrocyclic ring opening to give 1,5-dipolar species (**45**).²⁵ The extended dipolar system reacts with dipolarophiles as 1,3-dipole to give thermally unstable [3+2] cycloadducts (**45** → **46**), e.g. tetracyanoethylene is added site selectively across the CC double bond. Already at room temperature a [3+2] cycloreversion process takes place. The over-all reaction represents a metathesis (**45** → **47**)²⁶ giving ready access to cyano-substituted azomethine imines and 1,3-dienes.



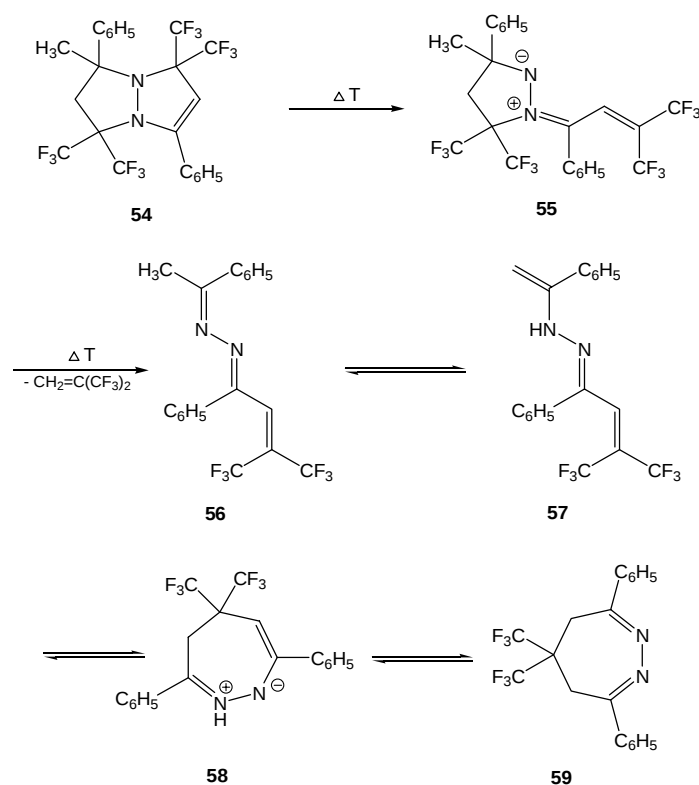
4.3. 1-Vinyl-1H-pyrazoles

When the mixed criss-cross cycloadduct (**48**) obtained from **3**, 2,3-dimethylbutadiene and phenylacetylene was submitted to thermolysis, 1-vinylpyrazole (**53**) was formed. The multistep procedure can be understood as a sequence of orbital symmetry controlled reactions, namely [3+2] cycloreversion (**48** → **49**),²⁷ electrocyclic ring closure (**49** → **51**), electrocyclic ring opening (**51** → **52**)²⁸ and finally [1,5] hydrogen shift (**52** → **53**).

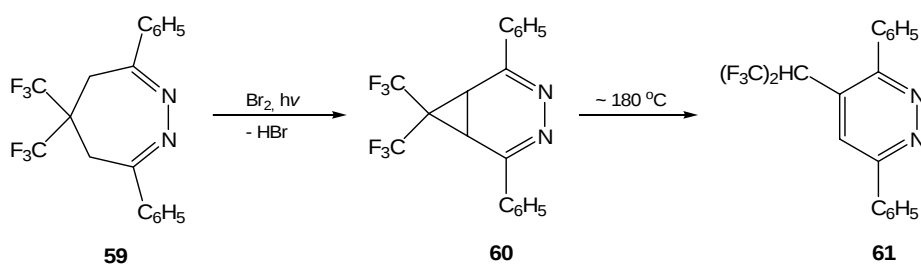


4.4. 4H-5,6-Dihydro-1,2-diazepines

When 2-phenyl-4,4,8,8-tetrakis(trifluoromethyl)-1,5-diazabicyclo[3.3.0]oct-2-enes (**54**) were heated (bath temperature: 200 °C), elimination of 1,1-bis(trifluoromethyl)ethylene occurs. The NMR spectra indicate that a symmetrical compound is formed. MS spectrometry shows a ring contraction $[\text{M} - \text{N}_2]^+$ indicating that a azine subunit is still present in the new compound which we ascribe structure (**59**) based on the spectroscopical data. Again a domino reaction²⁹ nicely explains the unexpected formation of 5,5-bis(trifluoromethyl)-4H-5,6-dihydro-1,2-diazepine (**59**).³⁰ The reaction sequence starts with an electrocyclic ring opening with formation of a 1,5-dipole (**54** $\rightarrow$ **55**) (*vide supra*). Further steps which are involved in this cascade are a [3+2] cycloreversion, proton migration, 7-endo trig ring closure³¹ and finally proton migration to give a cyclic azine system (**59**).

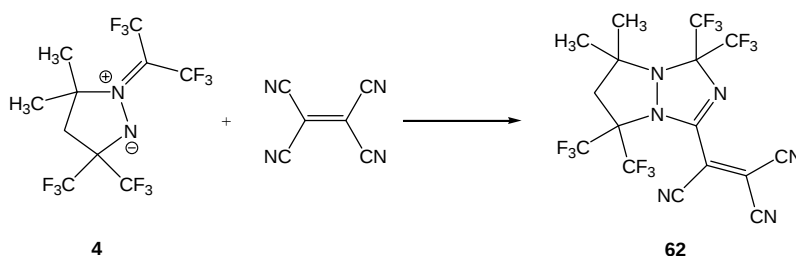


Structure (**59**) was proved by a ring transformation consisting of photobromination, dehydrobromination and finally thermally induced heteroaromatization (**59** → **61**).



4.5. Site Selective [3+2] Cycloaddition of Tetracyanoethylene

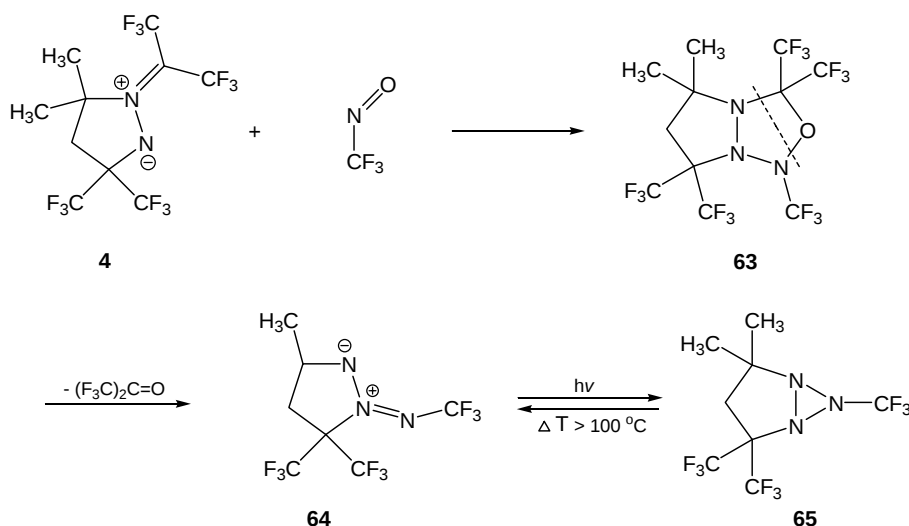
Cycloaddition reactions to tetracyanoethylene (TCNE) generally proceed with high site selectivity across the CC double bond. Examples where the nitrile group acts site selectively as dipolarophile or dienophile are rare.³²



Azomethine imines (**4**) react with tetracyanoethylene in refluxing benzene to give dark red crystalline adducts we ascribe structure (**62**).³³ The [3+2] cycloaddition process occurs site and regio specifically across one of nitrile groups.

4.6. Stable Triaziridines. Dipol Metathesis

Triaziridines³⁴ and pentazoles³⁵ are important members of the rare class of nitrogen homocycles. Azimines (**64**) are the result of a dipol metathesis consisting of a [3+2] cycloaddition of trifluoronitrosomethane to azomethine imine (**4**) and successive [3+2] cycloelimination of hexafluoroacetone.³⁶ Ring closure to give the valence isomer was achieved on irradiation with a photo lamp ($\lambda = 253.7$ nm) at room temperature.³⁷ The triaziridines (**65**) formed were purified by distillation *in vacuo* because they are thermally stable up to 80 °C.

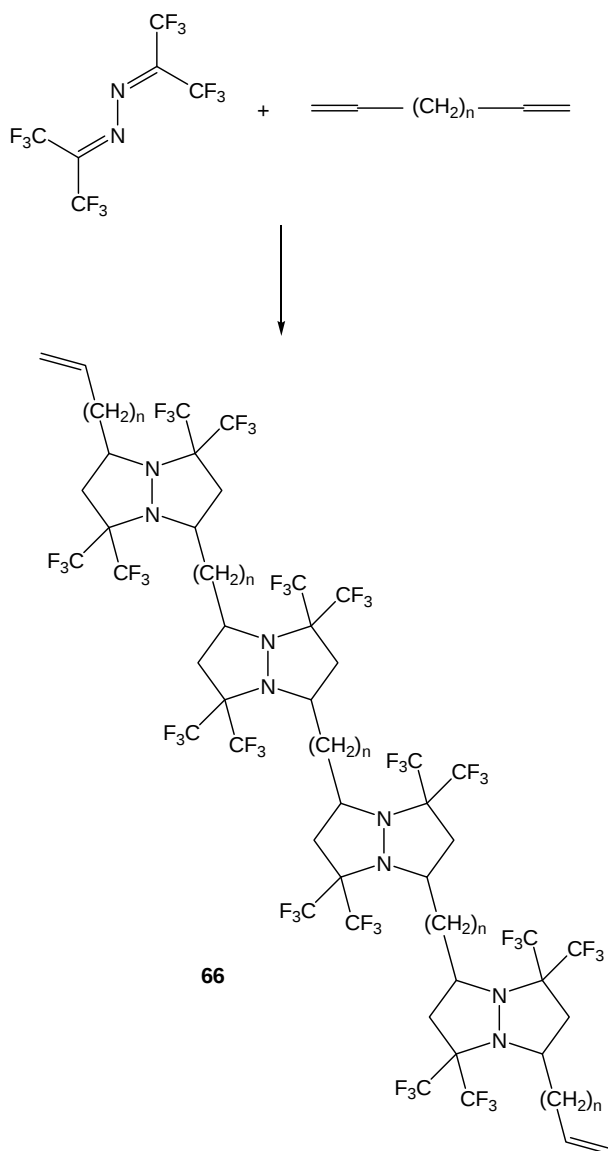


Since triaziridines (**65**) like other three-membered heterocycles are valence isomers of 1,3-dipoles (**64**), they can be transformed into azimines on heating above 100 °C.³⁷ The photochemical ring closure and the thermal ring cleavage can be repeated several times confirming the structural assignment.

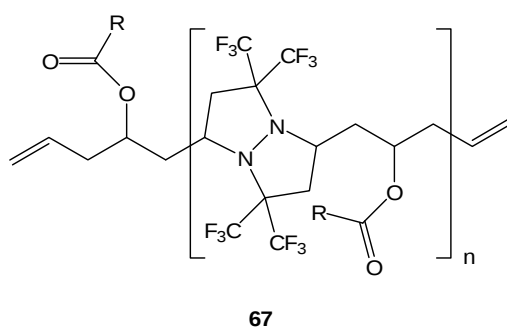
5. Polymerization via Criss-Cross Cycloaddition

The reaction of hexafluoroacetone azine with linear α,ω -diolefins was used to synthesize a new type of polymers (**66**) with diazabicyclo[3.3.3]octane-diyl subunits in the main chain.³⁸ The polymerization process represents a sequence of [3+2] cycloaddition reactions. The solubility of the polymers strongly depends upon the flexibility of the polymer chain which is a function of the chain length. In contrary,

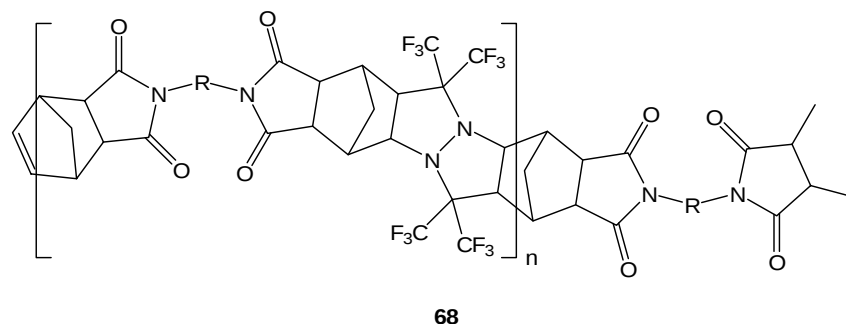
cyclic dienes like 1,4-cyclohexadiene and 1,5-cyclooctadiene do not react with hexafluoroacetone azine under identical reaction conditions (no solvent, room temperature).



Soluble polymers (**67**) have been obtained on reaction with substituted linear α,ω -diolefines, e.g. O-acylated 1,6-heptadien-4-ols.³⁹



The reaction between hexafluoroacetone azine and bis(bicyclo[2.2.1]hept-5-en)-2,3-dicarboximides (dinadimides) yields polymers (**68**) with number-average molar masses between 1700 and 5700 depending on the reactants.⁴⁰ In contrast to the above results, **3** and dimaleimides do not react to form polymers.^{41,42}



ACKNOWLEDGEMENTS

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