

Diels–Alder Reactions of Trichloro- and Trifluoro-1,2,4-triazine

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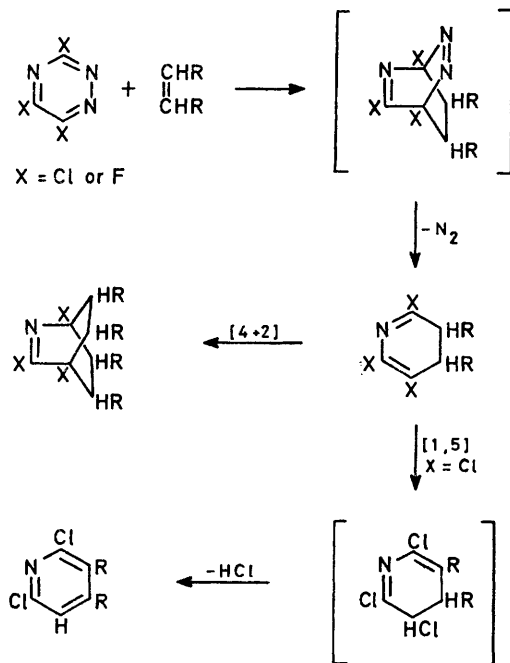
Summary Diels–Alder addition of olefins to trichloro- and trifluoro-1,2,4-triazines gives, *via* loss of nitrogen, intermediate dihydropyridines, which undergo a variety of further pericyclic reactions.

TRIFLUORO-1,2,4-TRIAZINE is conveniently obtained in 90% yield¹ by fluorination of trichloro-1,2,4-triazine² over potassium fluoride at 450 °C in a flow system. Both these electron-deficient systems undergo Diels–Alder addition of hydrocarbon olefins.

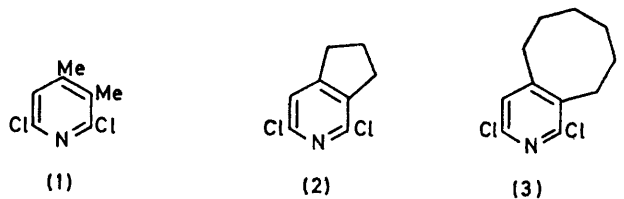
Trichloro-1,2,4-triazine undergoes reluctant reaction with ethylene, giving 2,6-dichloropyridine (1%), but reacts efficiently (at 70 °C over 1.5–6 days) with *cis*-but-2-ene, cyclopentene, and *cis*-cyclo-octene, giving the dichloropyridines (1),³ (2),⁴ and (3), respectively, in 75–80% yield. With cyclopentene, the bis-adduct (4) is also formed in low yield (3%), and the bis-adduct (5) is the sole product (95%) with bicyclo[2.2.1]hept-2-ene.

In contrast, trifluoro-1,2,4-triazine gives bis-adducts (6), (7), and (8) only with cyclopentene (55%), bicyclo[2.2.1]hept-2-ene (52%), and cyclo-octene (13%), respectively (at

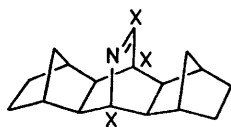
60–70 °C over 7 days). Bicyclo[2.2.1]hepta-2,5-diene gives 2,3,6-trifluoropyridine (9) (43%), and traces of bis-adducts containing bicycloheptadiene or cyclopentadiene residues (at 70 °C over 3 days). Bis(trimethylstannyl)acetylene gives the pyridine (10) (11%) (at 60 °C over 18 h in tetrahydrofuran).



SCHEME



(10); X = SnMe₃



It appears that the initial 3,4-dihydropyridine obtained from the olefins (see Scheme) may undergo (X = Cl) [1,5] sigmatropic shift of hydrogen and loss of hydrogen chloride, except for the addition of bicyclo[2.2.1]hept-2-ene and cyclopentene to a minor extent, where a second addition of olefin occurs; this [4 + 2] addition is obtained exclusively with the fluorinated systems. However, with bicyclo[2.2.1]hepta-1,5-diene, retro-Diels–Alder elimination of cyclopentadiene occurs from the intermediate dihydropyridine, and 2,3,6-trifluoropyridine is obtained.

The ¹³C n.m.r. spectra of adducts (5) and (7) indicate that they have the structure (11), since in particular, the chemical shifts of carbon nuclei of the CH₂CH₂ groups are characteristic of a bicycloheptane system with *exo*-substituents⁵ on the other two-carbon bridge [at 30.3 and 30.4 p.p.m. for (5), and 30.2 and 30.3 p.p.m. for (7), relative to SiMe₄]. The adducts (4)–(8) all appear to have a similar stereochemistry about the central bicyclo[2.2.2]oct-2-ene fragment.

There have been few studies of Diels–Alder reactions of 1,2,4-triazines,⁶ and the halogeno-derivatives have considerable synthetic promise, particularly since they react

with simple hydrocarbon olefins, which rarely undergo such addition.⁷ The intermediate 3,4-dihydropyridines are also active dienes. Annulated pyridines such as (2) and (3) are not readily synthesised, although similar pyridines have recently been obtained by intramolecular cycloaddition to a 4,6-dihydroxypyrimidine under vigorous conditions.⁸ The imidoyl halide function in adducts (4)—(8) offers a site for further chemical attack.

(Received, 4th April 1979; Com. 360.)

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