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PRELIMINARY NOTE

The Preparation of Partially Fluorinated Fused Ring Hydrocarbons

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SUMMARY

Diels-Alder reactions of fluorinated cyclobutenes and cyclopentenes with 1,3-butadiene and substituted 1,3-butadienes readily provide partially fluorinated fused ring systems. Hydrogenation, aromatization, acid hydrolysis and dehydrohalogenation of these adducts is easily accomplished and affords useful synthetic routes to partially fluorinated compounds.

The Diels-Alder reaction is one of the most widely utilized synthetic organic reactions for the construction of six-membered rings [1]. It's well documented that fluoroolefins can serve as useful dienophiles in this reaction scheme and can be employed in the synthesis of partially fluorinated systems [2,3].

Several years ago we became interested in the synthesis of partially fluorinated fused ring systems and elaboration or modification of these substrates as synthetic routes to other partially fluorinated compounds. A potentially useful one-step entry to these fused ring compounds is via the Diels-Alder reaction of cyclic fluorinated alkenes with conjugated dienes. The recent report by South and Liebeskind [4] prompts us to report our work with fluorinated cyclobutenes and cyclopentenes and some useful synthetic modifications of the Diels-Alder products.

When 2,3-dimethyl-1,3-butadiene (I), 2-methyl-1,3-butadiene (II), or 1,3-butadiene (III) are heated with fluorinated cyclobutenes or cyclopentenes at 170 ± 5°C in a sealed tube for 48 hours, good conversions of the fluorinated olefins to the respective fused ring systems is attained

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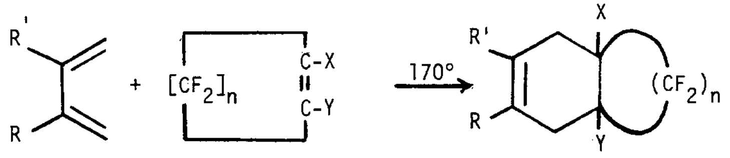
with (I) and (II). With diene (III) good conversion is only attained with 1-hydro-2-chlorotetrafluorocyclobutene. The results of these cycloaddition reactions are summarized in Scheme I.

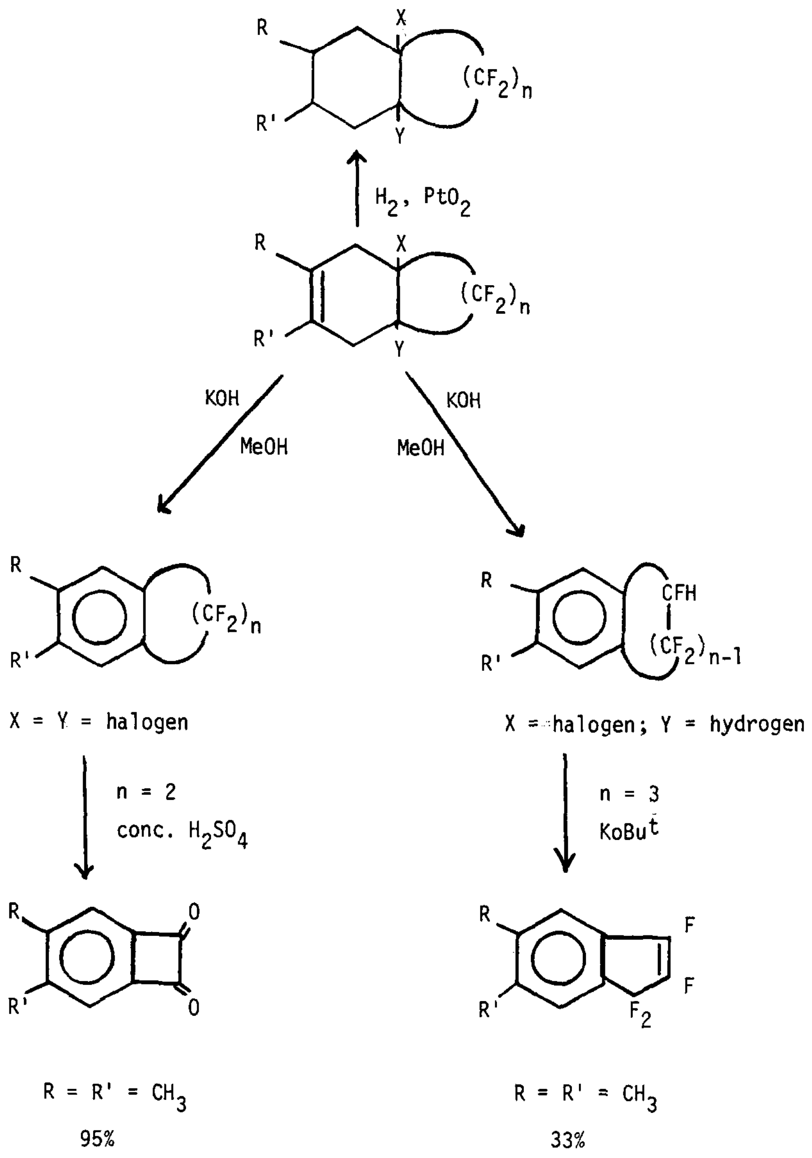


R	R'	X	Y	n	% Conversion*
CH_3	CH_3	F	F	3	60
CH_3	H	F	F	3	21
CH_3	CH_3	F	Cl	3	84
CH_3	H	F	Cl	3	16
CH_3	CH_3	F	H	3	88
CH_3	H	F	H	3	28
CH_3	CH_3	Cl	H	3	76
CH_3	H	Cl	H	3	35
CH_3	CH_3	F	F	2	77
CH_3	CH_3	F	Cl	2	89
CH_3	H	F	Cl	2	20
CH_3	CH_3	Cl	H	2	88
CH_3	H	Cl	H	2	84
H	H	Cl	H	2	28

*% conversion of fluoroolefin to adduct. All adducts gave satisfactory NMR, IR, and analytical data.

SCHEME I

Hydrogenation of the adducts outlined in Scheme I in 95% ethanol over PtO_2 at 50 psi readily gave the corresponding saturated adducts (Scheme II). Reaction with KOH/MeOH at reflux afforded the benzocyclobutane and benzocyclopentane derivatives (Scheme II). Best yields (50-90%) of the aromatized derivatives where obtained when R=R'=CH_3. When R=H, R'=CH_3, lower yields (5-15%) of the aromatic materials were obtained.


R
R'
X
Y
$(CF_2)_n$
H_2, PtO_2
KOH
MeOH
KOH
MeOH
CFH
$(CF_2)_{n-1}$
X = Y = halogen
X = halogen; Y = hydrogen
n = 2
conc. H_2SO_4
n = 3
$KoBu^t$
O
O
F
F
F_2
R = R' = CH_3
95%
R = R' = CH_3
33%

SCHEME II

The aromatic derivatives can be elaborated further via dehydrofluorination to an indene derivative or hydrolysis to benzocyclobutene diones (Scheme II). Preliminary oxidation experiments of the initial adducts also indicate that useful routes to substituted cyclobutanes and cyclopentanes are possible.

In conclusion, the Diels-Alder reaction of fluorinated cyclobutenes and cyclopentenes provide a useful route to fused ring systems which can be subsequently modified via conventional chemistry.

ACKNOWLEDGEMENT

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REFERENCES

1 A. Wasserman, Diels-Alder Reactions, Elsevier, London, 1965.
2 D.R.A. Perry, Fluorine Chemistry Reviews, 1, (1967), 253.
3 R.D. Chambers, Fluorine In Organic Chemistry, John Wiley, N.Y., 1973, pg 184.
4 M.S. South and L.S. Liebeskind, J. Org. Chem., 47 (1982) 3815.