Novel Cycloadducts from the Reactions of [α,α-Bis(3,3,3-trifluoropropynyl)]benzyl Benzoate and [1,1-Bis(3,3,3-trifluoropropynyl)]ethyl Ethanoate with Furan

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Reaction of furan with the dialkynyl ester $(CF_3C{\equiv}C)_2CPhOCOPh$ (**1a**) in dichloromethane at 50 °C affords a mixture of four 1 : 1 adducts, the (*Z*)-isomer of triene (**4a**) (major product), diketone (**5a**), and the benzopentacyclononenes (**3**) and (**6**), *via* the common intermediate 2-benzoyloxy-2-phenyl-4, 10-bis(trifluoromethyl)-7-oxapentacyclo[4.4.0.$0^{1,3}$.$0^{5,9}$.$0^{8,10}$]dec-3-ene (**9**) formed from the bis Diels–Alder adduct by intramolecular (${}_{\pi}2_s + {}_{\pi}2_s + {}_{\pi}2_s$) cycloaddition followed by retro-cleavage of furan; the corresponding reaction with the ester $(CF_3C{\equiv}C)_2CMeOCOMe$ (**1b**) gives analogously diketone (**5b**) (major product) and a mixture of the (*E*)- and (*Z*)-isomers of triene (**4b**), a rearranged furan–dialkyne 2 : 1 adduct (**7**) or (**8**) also being formed.

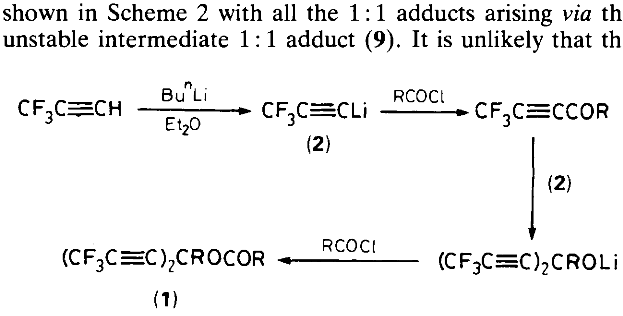
The Diels–Alder reaction of dienes with monoalkynes has been studied extensively,[1] but such cycloaddition has not been extended to 1,4-diynes. Having established a general route to 1,4-diynyl esters $(CF_3C{\equiv}C)_2CROCOR$ (**1**; R = alkyl or aryl) in near quantitative yield by treatment of 3,3,3-trifluoropropynyl-lithium (**2**) with an excess of the appropriate acid chloride[2] (Scheme 1), the reactions of the esters (**1a**, R = Ph) and (**1b**, R = Me) with furan (*ca.* 1 : 1 molar ratio) at 50 °C in dichloromethane were investigated.

The reaction with ester (**1a**) afforded a complex product mixture consisting of one major, three significant, and many minor components from which the major and two of the significant components were separated pure by repeated dry column flash chromatography [eluant light petroleum (b.p. 40—60 °C)/CH_2Cl_2]. These were identified (isolated yields given) in order of elution, as the novel 1 : 1 adducts benzopentacyclononene (**3**) (4.5%), triene (**4a**) (44.5%) as the (*Z*)-isomer, and diketone (**5a**) (6.5%), by elemental analysis and their NMR (^1H, ^{13}C, and ^{19}F) and mass spectra with the stereochemistry of compounds (**3**) and (**4a**) being established by *X*-ray crystallography.

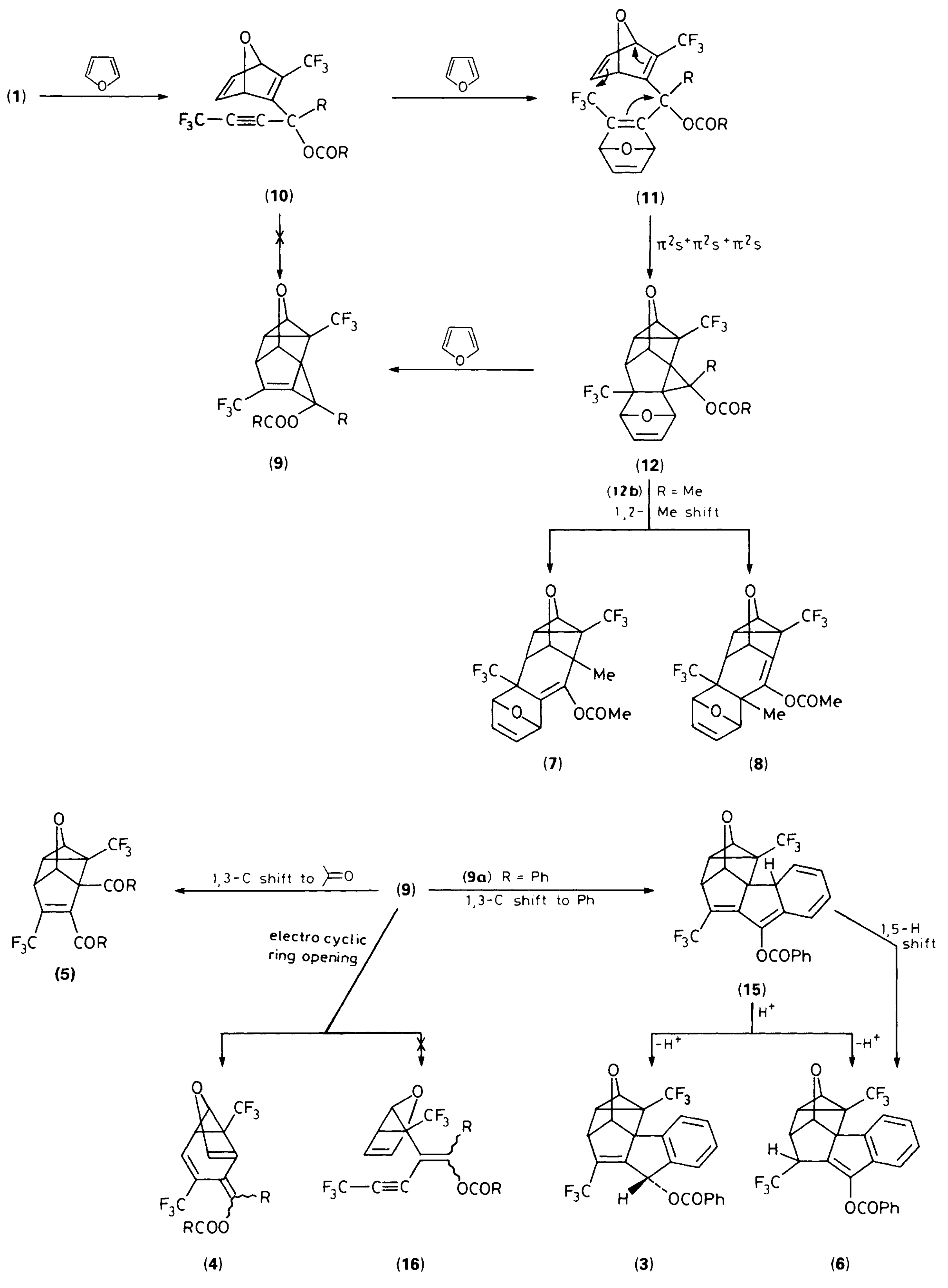
The remaining significant product could not be obtained pure owing to contamination by compounds formed by slow decomposition of triene (**4a**) on the silica column, but it was identified as the 3-ene isomer (**6**) (*ca.* 3%) of compound (**3**) by NMR (presence of CF_3CH, 2 bridgehead >CH–O hydrogens, 2 tertiary hydrogens, and 2 vinylic carbons).

From reaction with ester (**1b**) the products were unchanged ester (7.5% recovered), triene (**4b**) (20%) as a mixture of (*E*)- and (*Z*)-isomers (ratio *ca.* 2 : 1), diketone (**5b**) (26.5%), a furan–dialkyne 2 : 1 adduct (**7**) or (**8**) (10%) [as shown by elemental analysis, mass spectrometry, and NMR (2 $CF_3C\!<$, 4 bridgehead CH–O hydrogens, 2 vinylic hydrogens, 4 vinylic carbons, Me–C and OCOMe], an unidentified 1 : 1 adduct (*ca.* 3%), and various minor unidentified compounds.

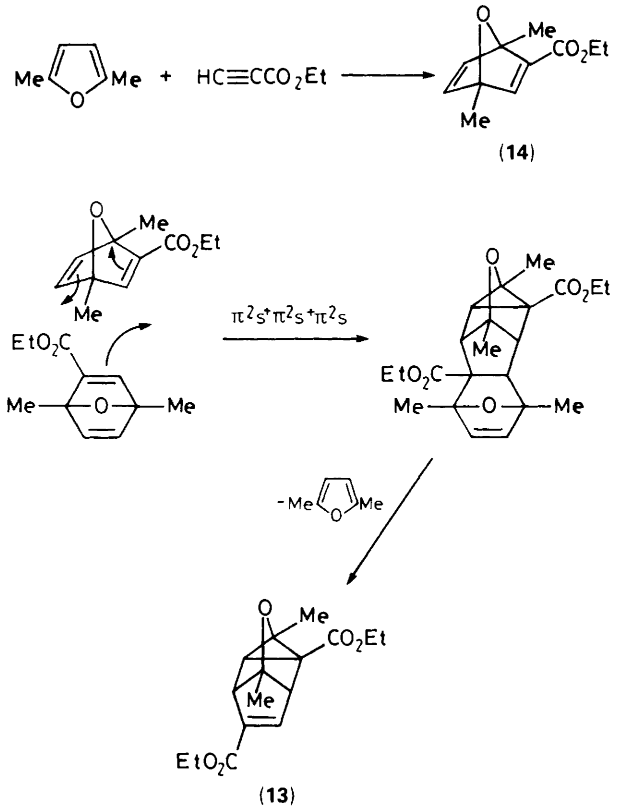
The identified products are considered to be formed as shown in Scheme 2 with all the 1 : 1 adducts arising *via* the unstable intermediate 1 : 1 adduct (**9**). It is unlikely that the



Scheme 1. **a**; R = Ph
b; R = Me


(1)
(10)
(11)
(9)
(12)
(12b)
1,2-
R = Me
Me shift
(7)
(8)
(5)
(4)
(16)
(3)
(6)
(15)
π2s+π2s+π2s
1,3-C shift to >=O
(9a) R = Ph
1,3-C shift to Ph
electro cyclic ring opening
1,5-H shift
H+
-H+
-H+
CF3
F3C
OCOR
RCOO
COR
OCOMe
Me
OCOPh
R

Scheme 2



Scheme 3

initial 1 : 1 Diels–Alder adduct (**10**) underwent cyclisation ($_{\pi}2_s$ + $_{\pi}2_s$ + $_{\pi}2_s$) to afford (**9**) directly because of the strain involved in bringing the acetylenic linkage within bonding distance of the oxanorbornadiene system. A more reasonable explanation is that intermediate (**9**) is formed *via* the 2 : 1 adduct (**11**) and this is supported by the isolation of the 2 : 1 adduct (**7**) or (**8**) from the ester (**1b**) reaction arising by rearrangement of 2 : 1 adduct (**12b**, R = Me) and by a report that the 2 : 1 adduct (**13**) from reaction of 2,5-dimethylfuran with ethyl propynoate is formed by dimerisation ($_{\pi}2_s$ + $_{\pi}2_s$ + $_{\pi}2_s$) of 1 : 1 adduct (**14**) followed by retrocleavage of 2,5-dimethylfuran[3] (Scheme 3).

The highly strained intermediate (**9**), containing a bridgehead double bond in fused 5- and 3-membered rings, rearranges to triene (**4**) and diketone (**5**). In the case where R = Ph, rearrangement involving an *ortho*-phenyl carbon also competes to yield adduct (**15**). Since suprafacial 1,7-hydrogen shifts are disallowed thermally it is probable that aromatisation of adduct (**15**) to the isolated 1 : 1 adduct (**3**) is catalysed by traces of protons available on the walls of the Pyrex reaction vessel. Rearrangement of (**15**) to 1 : 1 adduct (**6**) could occur by a thermally allowed suprafacial 1,5-hydrogen shift although it is equally possible that it is formed by an acid-catalysed reaction.

The monoalkyne (**16**) (or products derived from it) arising by the alternative electrocyclic ring opening of intermediate (**9**) was not detected.

The possibility that triene (**4a**) was the precursor to the 1 : 1 adducts (**3**), (**5a**), and (**6**) was discounted, because these products were not detected when the triene (**4a**) was heated in dichloromethane under the reaction conditions. Slow decomposition of the triene did occur and a considerable number of minor unidentified products were formed.

The structure of the 2 : 1 adduct (**7**) or (**8**) awaits an *X*-ray study and work is continuing on the reactions of the esters (**1**) with other dienes the results of which will be reported elsewhere in due course.

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References

1 For example see W. Carruthers, 'Some Modern Methods of Organic Synthesis,' 2nd edn., Cambridge University Press, 1978, p. 161.
2 S. Tajammal and A. E. Tipping, unpublished results; S. Tajammal, M.Sc. Thesis, University of Manchester, 1988.
3 A. W. McCulloch, D. G. Smith, and A. G. McInnes, *Can. J. Chem.*, 1974, **52**, 1013.