Synthesis and Solvolysis of a Novel Cyclic Dienynyl Trifluoromethanesulphonate

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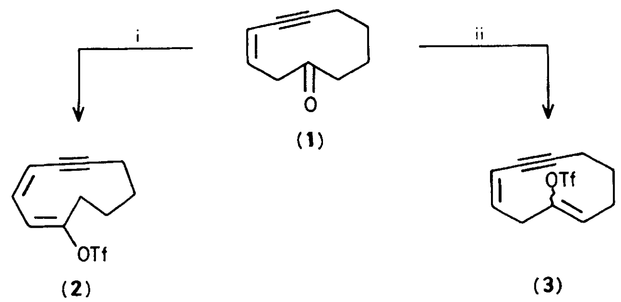
Cyclodeca-1,3-dien-5-yn-1-yl trifluoromethanesulphonate (**2**) has been synthesized and solvolysed in different solvent systems to give cyclized aromatic products exclusively, which are formed mainly *via* an aryl cation (**5**) intermediate.

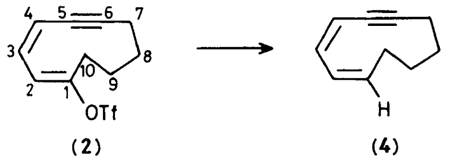
As a part of our work[1—3] on the solvolytic generation of phenyl cations *via* triple bond participation with vinyl cations, we have now studied for the first time the solvolyses of the cyclic dienynyl compound (**2**), with respect to the formation of a tetrahydronaphthyl cation (**5**). We expected that for (**2**), owing to its higher ground-state energy, the favourable conformation of the triple bond for participation, and the favourable stereochemistry of the triflate (SO_3CF_3) leaving group, in contrast to acyclic triflates,[1,2] practically quantitative rearrangement with formation of (**5**) should take place.

Approaches to the synthesis of the dienynyl triflate (**2**) are given in Scheme 1. Cyclodec-3-en-5-ynone (**1**)[4] was first



Tf = SO_2CF_3

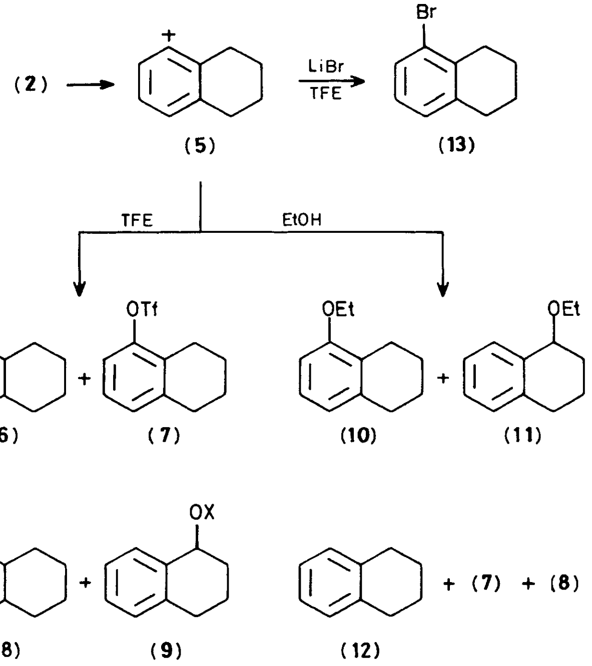
Scheme 1. *Reagents:* i, KH, $PhNTf_2$ or LDA, $PhNTf_2$; ii, triethylamine, Tf_2O, or 2,6-di-t-butyl-4-methylpyridine, Tf_2O, or pyridine, Tf_2O, or Na_2CO_3, Tf_2O.



Scheme 2. *Reagents:* $(Ph_3P)_4Pd$, LiCl, Bu_3SnH.

treated with trifluoromethanesulphonic anhydride (Tf_2O) in dichloromethane in the presence of various bases. By this method the ketone (**1**) undergoes *O*-acylation at the carbonyl group exclusively,[5] the oxonium ion formed is stabilized by elimination of a proton, and the triflate (**3**) with a non-conjugated double bond is formed. The triflate (**2**) is, however, obtained by reaction of the ketone (**1**) with potassium hydride or lithium di-isopropylamide (LDA) and *N,N*-bis(triflyl)anilide.[6] The enolate anion is formed with a conjugated double bond and attacks *N,N*-bis(triflyl)anilide at the sulphur atom with formation of (**2**). In all cases a small amount of tetrahydronaphthyl triflate (**7**) was also found. The triflate (**2**)† was purified by flash chromatography (silica gel, 3.5 bar) using light petroleum (b.p. 30—50 °C) as eluant. Compound (**2**) is a pale yellow liquid, which is stable in solution but decomposes in the pure state. All spectroscopic and analytical data, including ^1H n.m.r. double resonance experiments for (**2**) and (**3**) are in accordance with their structures.

Vinyl triflates undergo palladium-catalysed coupling reactions with organotin compounds to give alkene-substituted products.[7] We applied this reaction to determine the stereochemistry of the triflate (**2**), particularly the geometry of the CF_3SO_3 leaving group. Compound (**2**) was stereospecifically reduced by tetrakis(triphenylphosphine)palladium(0)–lithium chloride–tri-n-butyltin hydride to form cyclodeca-1,3-dien-5-yne (**4**) (Scheme 2). The configuration of the diene (**4**) was assigned from the $^3J_{H,H}$ coupling constants between the vinylic protons, which were determined by ^1H n.m.r. double resonance experiments, and established as the (*Z*)/(*Z*)-configuration shown ($^3J_{2H,1H}$ 12.4; $^3J_{3H,4H}$ 11.3 Hz).[4] As a result we conclude that the triflate (**2**) has the (*E*)-configuration shown at the C-1,C-2 double bond.



Tf = SO_2CF_3, X = CH_2CF_3

Scheme 3

The triflate (**2**) was solvolysed under the conditions given in Table 1. In contrast with acyclic triflates,[1,2] which required 100 °C for 5 days for solvolysis, the reaction of the triflate (**2**) in all solvents used was complete after 3 days at 50 °C. The products were identified by capillary g.l.c., using columns with different coatings (SE 30, SE 52, UCC), g.l.c.–mass spectroscopy, and comparison with authentic samples. The product composition (Table 1) clearly demonstrates that the aromatic compounds (**6**), (**7**), (**8**), (**10**), and (**13**) are formed *via* the intermediate tetrahydronaphthyl cation (**5**), which is generated by participation of the triple bond in (**2**) during the solvolytic removal of the triflate group.

In 2,2,2-trifluoroethanol (TFE) and aqueous TFE, solvents of high ionizing power and low nucleophilicity, but also in ethanol, a solvent of high nucleophilicity and low ionizing power, the cyclized aromatic products (**6**), (**7**), (**8**), and (**10**) are formed almost quantitatively by direct substitution of the intermediate (**5**) with nucleophiles. Elimination and substitution products from a first formed vinyl cation were not found. The intermediate tetrahydronaphthyl cation (**5**) was also trapped by an added nucleophile. In the solvolysis of (**2**) in TFE, carried out in the presence of an excess of lithium bromide, 16% of the expected tetrahydronaphthyl bromide (**13**) was obtained (Scheme 3). The formation of tetrahydronaphthyl triflate (**7**) in all TFE solvolyses by internal return of the triflate anion is additional proof for the intermediate tetrahydronaphthyl cation (**5**). In summary, the expected quantitative rearrangement of the cyclic dienynyl triflate (**2**) in the solvolyses, even in a solvent of high nucleophilicity, *via* an aryl cation intermediate (**5**) was fully confirmed by the products given in Table 1.

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† Spectroscopic data for (**2**): i.r.: ν (film) 2940m, 2870w, 2220w ($C{\equiv}C$), 1660m ($C{=}C$), 1445m, 1415vs (SO_3), 1250s, 1240s, 1215vs (CF_3), 1145s (SO_3), 1075m, 995s, and 930s cm^{-1}; ^1H n.m.r.: δ ($CDCl_3$, 400 MHz) 6.19—6.15 (dd, $^3J_{3H,4H}$ 11.2, $^3J_{3H,2H}$ 5.6 Hz, 1H, 3-H), 5.97 (d, $^3J_{2H,3H}$ 5.6 Hz, 1H, 2-H), 5.55—5.52 (dd, $^3J_{4H,3H}$ 11.2, $^4J_{4H,2H}$ 1.2 Hz, 1H, 4-H), 2.75 (m, 2H, $\equiv C{-}CH_2$), 2.39 (m, 2H, $={COTf}{-}CH_2$), and 1.96—1.73 (m, 4H, 2 × CH_2); ^{13}C n.m.r. ($CDCl_3$) 152.1 (C-1), 131.8 (C-2), 118.4 (C-3), 112.5 (C-4), 139.9, 125.6, 111.4, 97.5 (CF_3, J_{CF} 319.5 Hz), 104.7, 83.6 (C-5, C-6), 31.0, 26.5, 26.0, and 20.3 (C-7—C-10).

Table 1. Solvolysis of the trifluoromethanesulphonate (**2**) in various solvents with Na_2CO_3 as buffer at 50 °C for 3 days.

	% Yield of products[a]							
Solvent	(**6**)	(**7**)	(**8**)	(**9**)	(**10**)	(**11**)	(**12**)	(**13**)
100% TFE	72.9	13.9	—	0.4	—	—	—	—
75% aq. TFE	71.9	4.5	1.6	—	—	—	—	—
50% aq. TFE	61.6	2.8	12.1	—	—	—	—	—
100% EtOH	—	1.6	—	—	80.7	1.5	15.2	—
50% aq. EtOH	—	—	36.6	—	42.8	2.1	11.6	—
TFE–H_2O–dioxane + LiBr (excess)	40.8	5.3	15.5	—	—	—	—	15.7

[a] Determined by capillary g.l.c. with 2-bromotoluene as internal standard. Average values from 2—4 runs.

The formation of the ethers (**9**) and (**11**) as minor side products cannot be explained by the intermediacy of the aryl cation (**5**), however. They are formed by an addition–elimination mechanism as described recently.[2]

In the ethanolysis, up to 15% of tetrahydronaphthalene (**12**) was also formed (Table 1). As we have shown earlier,[8] strained cycloalkynes are reduced by ethanol to form the corresponding alkene. Assuming the same reaction to occur partly with the triflate (**2**), the cyclodecatrienyl triflate thus obtained after rearrangement and proton-elimination gives tetrahydronaphthalene (**12**).

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