# Experimental Evidence for a Phenyl Cation Intermediate in the Solvolysis Reactions of Dienynyl Trifluoromethanesulphonates

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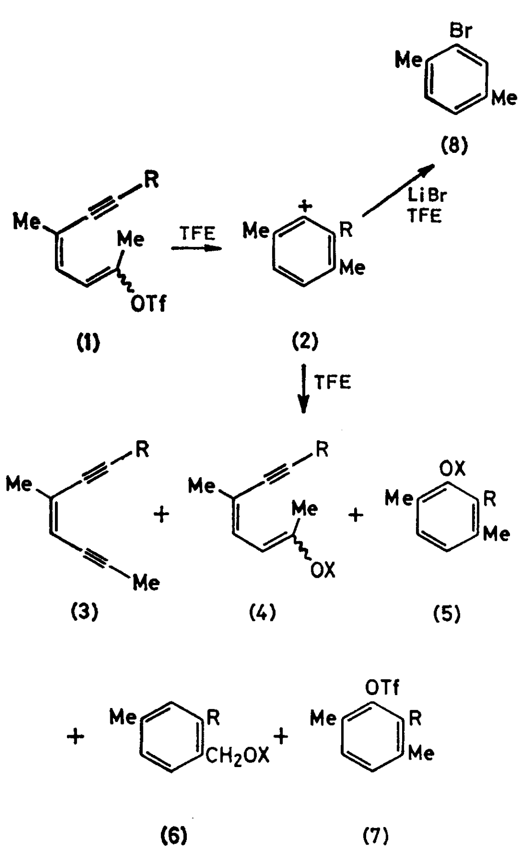
*Summary* The synthesis, separation, and solvolysis of the stereoisomeric dienynyl trifluoromethanesulphonates (**1**) are described, whereby the *E*-isomers, in contrast with the *Z*-isomers, rearrange to a remarkable extent to form the phenyl ethers (**5**) *via* the phenyl cations (**2**).

Recently we reported on the solvolysis of 1,4-dimethylhepta-1,3-diene-5-ynyl trifluoromethanesulphonate (**1b**) in acetone, 2,2,2-trifluoroethanol (TFE), and ethanol, in which small amounts (up to 9%) of the phenol (**5b**; X = H) and the ethers (**5b**; X = $CH_2CF_3$ or $CH_2CH_3$) respectively were formed.[1] In addition, the elimination and substitution products (**3b**) and (**4b**) (X = H, $CH_2CF_3$, or $CH_2CH_3$) as well as the benzyl ether (**6b**) have been found in ratios dependent upon the solvent used. The formation of the aromatic products (**5b**) may be explained as occurring *via* the phenyl cation (**2b**) as the intermediate, generated by participation of the triple bond in (**1b**) during the solvolytic removal of the $CF_3SO_3$ group (Scheme 1).

A condition for participation of the triple bond in (**1**) is that the $CF_3SO_3$ leaving group should be *anti* with respect to the triple bond, a geometry which was not determined for (**1b**) earlier.[1]

The trifluoromethanesulphonates (**1a**) and (**1b**) were synthesized from the ketones (**10a**) and (**10b**) respectively (Scheme 2). Compounds (**10a**) and (**10b**) were obtained stereospecifically as the *Z*-isomers by the pyridinium chlorochromate oxidation of the cyclopropylcarbinols (**9a**) and (**9b**).[2] The reaction of (**10a**) or (**10b**) with trifluoromethanesulphonic anhydride in dichloromethane carried out in the presence of triethylamine or 2,6-di-t-butyl-4-methylpyridine yields the trifluoromethanesulphonates (**1**) as *Z*- and *E*-isomers in a ratio of 3 : 1 respectively. The trifluoromethanesulphonates (**1**) were separated by column chromatography ($SiO_2$) using light petroleum (b.p. 30—50 °C)–dichloromethane (10 : 1) as eluant. The *Z*-isomers of (**1**) were eluted first ($R_F$ 0·31) followed by the *E*-isomers ($R_F$ 0·21).



Tf = $CF_3SO_2$; X = $CH_2CF_3$
**a**; R = H
**b**; R = Me

Scheme 1

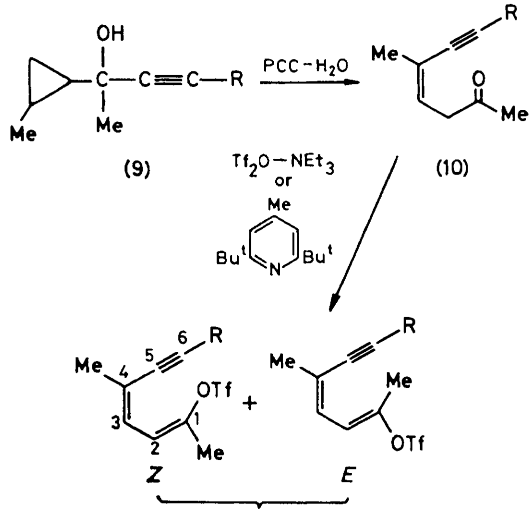
All spectroscopic and analytical data for (*E*)- and (*Z*)-(**1a**) and -(**1b**) are in accordance with their structures. The stereochemistry of (*Z*)- and (*E*)-(**1a**) was assigned from the ${}^3J_{C,H}$ coupling constants[3] between the 1-Me group (Scheme 2) and the vinylic proton at C-2: ${}^3J_{1Me2H}$ 4·4 Hz for *Z*-(**1a**) and 5·6 Hz for (*E*)-(**1a**).

The trifluoromethanesulphonates (*Z*)-(**1a**), (*E*)-(**1a**), and (*E*)-(**1b**) were solvolysed under the conditions given in the

TABLE. Solvolysis of the trifluoromethanesulphonates (*Z*)-(**1a**), (*E*)-(**1a**), and (*E*)-(**1b**) in various solvents with $Na_2CO_3$ as buffer at 100 °C for 5 days.

| Substrate (1) | Solvent | % Yield of products[a] | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | (1) | (3) | (4) | (5) | (6) | (7) | Unidentified | Polymer |
| (*Z*)-(**1a**)[b] | 100% TFE[c] | 1 | 29·4 | — | 1·4 | 19·5 | — | 9·7 | 40 |
| ” | 100% EtOH[d] | 1 | 70 | — | — | 1 | — | 5 | 24 |
| (*E*)-(**1a**)[b] | 100%TFE[c] | 1 | 19·5 | — | 26·4 | 7·8 | 2·1 | 5·5 | 38·7 |
| ” | 100% EtOH[d] | 52·4 | 18·7 | — | 6·1 | — | — | | |
| (*E*)-(**1a**)[b] | TFE–$H_2O$–dioxan[c] +LiBr (excess) | | —[f] | — | 14·4 | 41·2 | 1 | +16·6% of (**8**) | |
| (*E*)-(**1b**)[e] | 100% TFE[c] | | 21 | — | 24·6 | 15·6 | 9·3 | | |

[a] Determined by capillary g.l.c. with 1,3,5-tri-isopropylbenzene as internal standard. [b] R = H. [c] X = $CH_2CF_3$. [d] X = $CH_2CH_3$. [e] R = Me. [f] Yield could not be determined exactly because of overlap with the solvent g.l.c. peak.



PCC = pyridinium chlorochromate
**a**; R = H
**b**; R = Me

SCHEME 2

Table. The solvolysis products were identified by capillary-g.l.c., g.l.c.–mass spectroscopy, $^1H$ n.m.r. spectroscopy, and by comparison with authentic samples. The product composition (Table) clearly demonstrates that the aromatic products (**5a**) and (**5b**) (X = $CH_2CF_3$ or $CH_2CH_3$), (**7a**), (**7b**), and (**8**) are formed *via* the intermediate phenyl cations (**2a**) and (**2b**), which are generated by participation of the triple bond during vinyl cation formation from (**1a**) and (**1b**). This is consistent with the dependence of the formation of the aromatic products upon the stereochemistry of the trifluoromethanesulphonate; whereas from (*Z*)-(**1a**), in which the stereochemistry for participation of the triple bond is not favourable, only 1·4% of the substitution product (**5a**) arising from the intermediate phenyl cation (**2a**) is formed, (*E*)-(**1a**) with a favourable stereochemistry for participation of the triple bond yields the ether (**5a**) as the main solvolysis product. Solvolysis of (*E*)-(**1b**) in TFE also gives (**5b**; X = $CH_2CF_3$) as the main product; the corresponding *Z*-isomer of (**1b**), which was the originally reported example,[1] only yields 9% of (**5b**; X = $CH_2CF_3$). In absolute ethanol, a solvent of high nucleophilicity and low ionizing power, (*Z*)-(**1a**) reacts almost quantitatively with elimination to form the enediyne (**3a**), whereas from (*E*)-(**1a**) at least some (**5a**; X = $CH_2CH_3$) is formed. In the solvolysis of both (*E*)-(**1a**) and (*E*)-(**1b**) in TFE the phenyl trifluoromethanesulphonates (**7a**) and (**7b**) are formed, indicating an internal return process *via* the intermediate phenyl cations (**2a**) and (**2b**) respectively (Scheme 1).

To exclude other mechanisms for the formation of the aromatic products (**5a**), the solvolysis of (*E*)-(**1a**) in TFE was carried out with an added nucleophile, the bromide ion, to trap the intermediate phenyl cation (**2a**). 16·6% of the expected bromo-*p*-xylene (**8**) was formed (Scheme 1).

The other products listed in the Table are characteristic for the solvolysis of all the trifluoromethanesulphonates with formation of the corresponding vinyl cation; besides cyclization the vinyl cations can react *via* elimination to give the diynes (**3a**) and (**3b**) respectively. The substitution products (**4a**) and (**4b**) were not found. The composition of the products reflects typical solvent effects for solvolysis reactions. In TFE, a solvent of high ionizing power, the highest percentage of cyclization products are observed.

The mechanism for the formation of the benzylic derivatives (**6a**) and (**6b**) is under investigation.

We thank the Deutsche Forschungsgemeinschaft for financial support.

(*Received*, 10*th April* 1981; *Com.* 424.)

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