# Mechanism of Hydrogenolysis. Part 1. Catalytic Hydrogenation of Vinyl and Aryltrifluoromethanesulphonates

**Antonio García Martínez,**[*a] **Roberto Martínez Alvarez,**[a] **Juan Arranz Aguirre,**[a] **and Lakshminarayanapuram R. Subramanian**[*b]

[a] *Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Complutense, Ciudad Universitaria, 28040-Madrid, Spain*
[b] *Institut für Organische Chemie der Universität Tübingen, Auf der Morgenstelle 18, D-7400 Tübingen 1, Germany*

A concerted cleavage of the C–O bond by the $MH_2$ species is proposed for the first step of the catalytic hydrogenation of vinyl and aryl trifluoromethanesulphonates. The alkene thus generated in the case of vinyl trifluoromethanesulphonates, is subsequently, reduced to an alkane. The stereochemistry of the reduction of vinyl trifluoromethanesulphonates is therefore identical to that observed in the reduction of the corresponding alkenes.

The catalytic hydrogenation of vinyl and aryl perfluoro-alkanesulphonates (2) and (5) has been shown[1-3] (Scheme 1) to take place smoothly (room temperature, atmospheric pressure) giving the corresponding hydrocarbons (3) and (6) in good

Tf = $CF_3SO_2$, Nf = $n-C_4F_9SO_2$, M = Ni,Pt,Pd
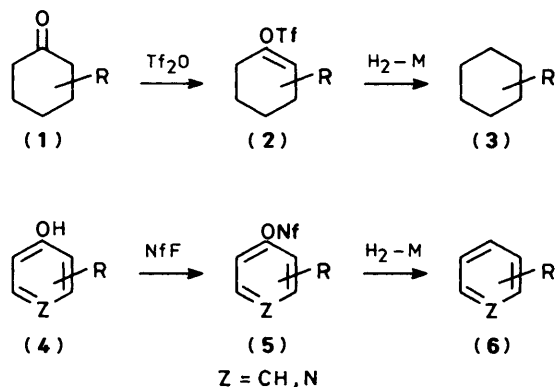
**Scheme 1.**

yields (>80%). This is a good alternative method for defunctionalising ketones and for reductive removal of phenolic groups. We now report on the mechanism and stereochemistry of hydrogenation of vinyl and aryl trifluoromethanesulphonates (triflates) using transition metal catalysts.

## Results and Discussion

Compounds (7)—(14) (Scheme 2) were hydrogenated in absolute ethanol using palladium, platinum, or ruthenium as the catalyst at room temperature and atmospheric pressure. The
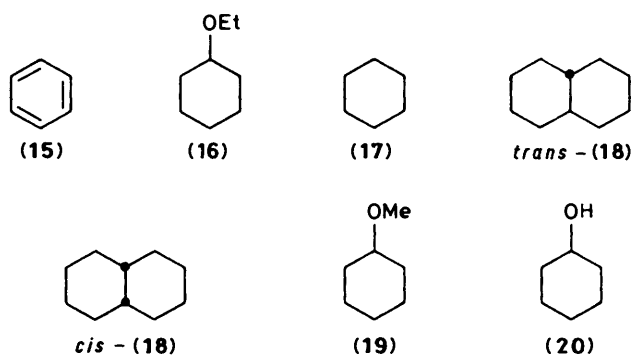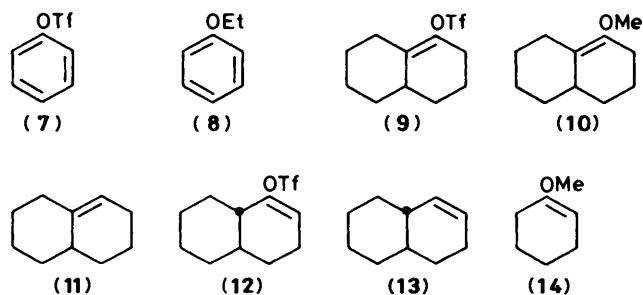
reaction time, conditions, and the products formed are listed in Table 1. The composition of the products obtained was estimated by g.c. The yield given in parenthesis refers to relative yield of the products in the mixture; the overall yield was higher than 90%. Compounds (16) and (19) were identified by mass spectrometry. All other products (Scheme 3) were identified by combined g.c.–m.s. technique using authentic samples.

The hydrogenolysis of vinyl and aryl triflates can be compared with the catalytic hydrogenation of vinyl and aryl ethers. Nishimura[4] has suggested an addition–elimination mechanism for the transition metal-catalysed hydrogenation of vinyl and aryl ethers. The major product of this reaction is the saturated ether [*e.g.* (26)] or the hydrogenolysis product [*e.g.* (24)].

This mechanism is not applicable in the case of the vinyl ether (10), whose hydrogenation is slow due to steric hindrance in the addition step as in the case of tetrasubstituted alkenes. However, the likewise hindered vinyl triflate (9) undergoes hydrogenolysis under the same conditions giving a good yield of the hydrocarbon product *cis/trans*-(18) indicating that the reduction is not taking place according to the Nishimura mechanism.[4]

The Nishimura mechanism explains the fact that the yield of the hydrogenolysis products from the aryl and vinyl triflates (7) and (12) are higher than the aryl and vinyl ethers (8) and (14) owing to the easy elimination of trifluoromethanesulphonic acid as compared to ethanol/methanol in the latter cases. However, the rate of hydrogenation of the aryl and vinyl triflates (7) and (12) using different catalysts cannot be correlated to the rate of hydrogenation of the aryl and vinyl ethers (8) and (14) (Table).

According to the addition–elimination mechanism, it is

**Table.** Hydrogenation of compounds (7)—(14)

| Substrate | Catalyst | Time (h)/% consumed | Products (%) |
|---|---|---|---|
| (7) | PtO$_2$[a] | 1/100 | (15)(100) |
|  | Pd–C[b] | 25/100 | (15)(100) |
|  | Ru–C[c] | 50/0 | (7)(100) |
| (8) | PtO$_2$ | 58/73 | (8)(27) + (15)(4) + (16)(36) + (17)(33) |
|  | Pd–C | 90/0 | (8)(100) |
|  | Ru–C | 22/5 | (8)(95) + (15)(5) |
| (9) | PtO$_2$ | 0.5/100 | trans-(18)(49) + cis-(18)(51) |
|  | Pd–C | 90/100 | trans-(18)(81) + cis-(18)(19) |
|  | Ru–C | 60/0 | (9)(100) |
| (10) | PtO$_2$ | 14/0 | (10)(100) |
|  | Pd–C | 24/0 | (10)(100) |
|  | Ru–C | 65/0 | (10)(100) |
| (11) | PtO$_2$ | 0.25/100 | trans-(18)(49) + cis-(18)(51) |
|  | Pd–C | 20/100 | trans-(18)(80) + cis-(18)(20) |
|  | Ru–C | 25/100 | trans-(18)(24) + cis-(18)(76) |
| (12) | PtO$_2$ | 0.1/100 | trans-(18)(100) |
|  | Pd–C | 40/100 | trans-(18)(100) |
|  | Ru–C | 60/0 | (12)(100) |
| (13) | PtO$_2$ | 0.1/100 | trans-(18)(100) |
|  | Pd–C | 1/100 | trans-(18)(100) |
|  | Ru–C | 3/100 | trans-(18)(100) |
| (14) | PtO$_2$ | 14/100 | (19)(98) + (20)(2) |
|  | Pd–C | 48/90 | (14)(10) + (19)(90) |
|  | Ru–C | 65/20 | (14)(80) + (19)(20) |

[a] Platinum dioxide prepared according to Adams and Shriner (Fluka AG). [b] Palladium-on-charcoal (Fluka AG). [c] 5% Ruthenium-on-charcoal (L. Light and Co.)

expected that the rate relation $k_A/k_B$ for the reaction paths A and B as illustrated for the vinyl and aryl ethers (21) and (27) in Scheme 2, should be larger for the reduction of phenyl triflate (7) than for the phenyl ether (8), because the ethoxy group should prefer path B due to its $+k$ effect.[4] Contrary to this only benzene (15) was obtained from the hydrogenation of compound (7).
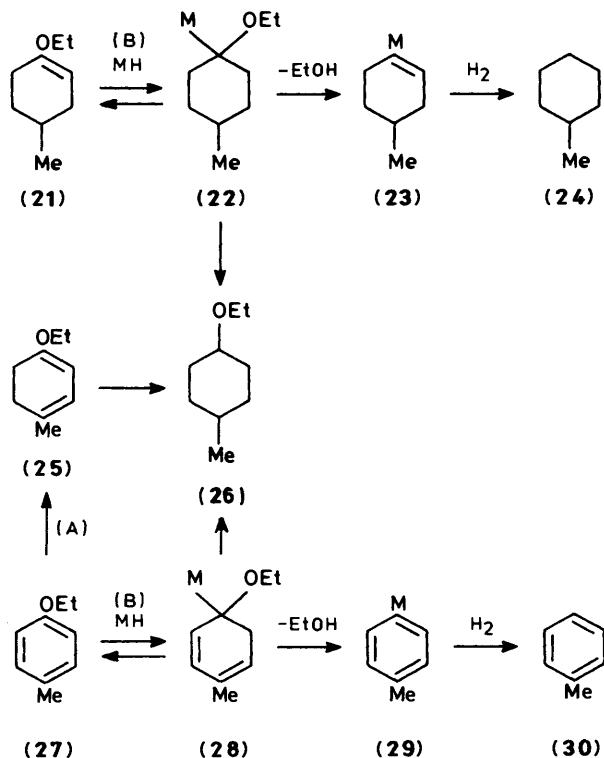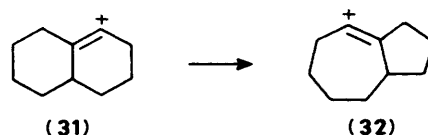


**Scheme 2.**

The hydrogenolysis of triflates (7), (9), and (12) show a similar dependency on the catalyst indicating a common mechanistic pathway involving the cleavage of C–OTf bond.

Under the present reaction conditions, the aryl and vinyl triflates do not undergo any $S_N1$ substitution reaction,[5] which could be seen as an alternative to the Nishimura mechanism. Moreover, it is known that the cation (31) formed from compound (9) rearranges to the cation (32) (Scheme 3).[6] No rearranged products were obtained from the hydrogenolysis of (9). An $S_N2$ mechanism can also be ruled out since no nucleophilic vinylic substitution is known.[5]

The homolytic cleavage of the C–OTf bond has not yet been observed.[7] Therefore it is not surprising that no reaction between the triflates (7), (9), and (12) and triphenyltin hydride, a radical reducing agent,[8] takes place.

The only remaining possibility is the concerted cleavage of the C–OTf bond by the reduction medium, which is commonly designated as MH$_2$.[9] This process can take place according to two different pathways, I and II (Scheme 4), where path I is a $[\sigma_S^4 + \sigma_S^2]$- reaction and path II corresponds to a chelotropical insertion. For the insertion to take place, the metal must be activated by hydrogen, as no reaction takes place between metal and substrate in the absence of hydrogen. To our knowledge, no reaction according to Path I has been reported. On the other hand insertion reactions are known to be common in the chemistry of transition metals. The formation of the reducing species MH$_2$ from the metal and hydrogen is a simple example of this. The homogeneous catalytic hydrogenation of alkenes appears to take place according to this mechanism.[10]

A concerted cleavage is expected when the substrate possesses a comparatively weak C–O bond as in the case of aryl and vinyl
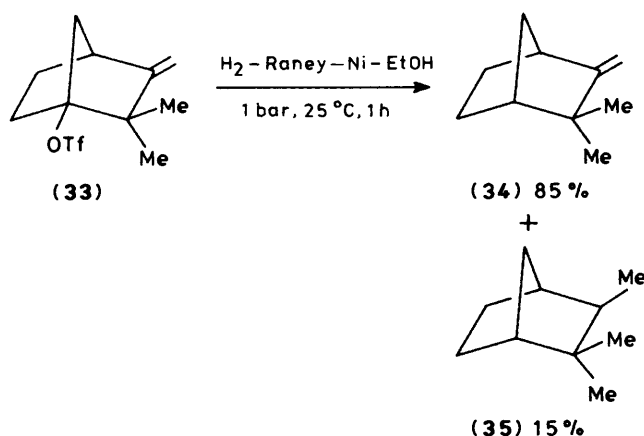


**Scheme 3.**
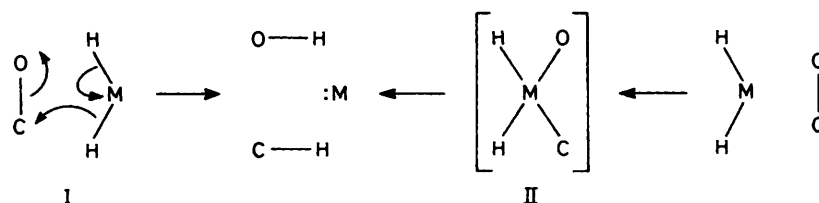
**Scheme 4.**

triflates. On the other hand the corresponding ethers should hydrogenolyse according to the Nishimura mechanism,[4] which is favourable because of the + $k$ effect of the EtO group. It should be noted that the hydrogenolysis of the bridgehead triflate (33) (Scheme 5) which has no tendency to react either via an $S_N1$ or $S_N2$ reaction occurs very easily,[11] while the corresponding ether can be cleaved only under vigorous conditions.[4]

The stereoselectivity of hydrogenation of vinyl triflate (9) corresponds to the alkene (11) under comparable conditions (see also lit.,[12]). This points out that the reduction of vinyl triflate (9) to the hydrocarbon cis/trans-(18) occurs via the alkene (11) in agreement with our proposed mechanism. While



**Scheme 5.**

no alkene was found in the reaction product from the vinyl triflates (9) and (12), the reduction of the corresponding alkene (11) first formed must be the fast reacting step. In fact the rate of reduction of compounds (11) and (13) are higher than that of (9) and (12) (Table).

## Experimental

Phenyl trifluoromethanesulphonate (7) was prepared according to a literature procedure,[13] 2,3,4,4a,5,6,7,8-octahydro-naphthalen-1-yl trifluoromethanesulphonate (9) and trans-3,4,4a,5,6,7,8,8a-octahydronaphthalen-1-yl trifluoromethane-sulphonate (12) were prepared by treating trans-decahydro-naphthalen-1-one with triflic anhydride.[14] The isomers (9) and (12) formed in a ratio of 66 : 34 were separated by preparative gas chromatography (10% Carbowax 20M, Chromosorb P-AW-DMCS, 60—80 mesh, 2 m × 1/4″; 130 °C).

1-Methoxy-2,3,4,4a,5,6,7,8-octahydronaphthalene (10).—To a solution trans-decahydronaphthalen-1-one (0.5 g, 3.2 mmol) and trimethyl orthoformate (0.38 g, 3.61 mmol) in absolute methanol (20 ml) was added one drop of concentrated hydrochloric acid and the mixture was kept at room temperature for 12 h. The methanol was then removed under reduced pressure and the residue was extracted three times with

ether. The combined ether layer was washed successively with saturated aqueous sodium hydrogen carbonate and water, and dried ($MgSO_4$). The residue obtained after removal of the solvent was mixed with 85% phosphoric acid (30 mg) and absolute pyridine (10 mg) and heated to 100 °C for 1 h in a distillation apparatus. After the reaction was over and methanol had been distilled off, the residue was extracted with ether. The ether phase was washed successively with saturated aqueous sodium hydrogen carbonate and water, and dried ($MgSO_4$). Removal of the solvent and chromatography of the residue on basic alumina using pentane as the eluant afforded the product (10) (0.32 g, 66%).

According to g.c. and [1]H n.m.r. data, the product contained 10% of the isomer, 1-methoxy-3,4,4a,5,6,7,8,8a-octahydro-naphthalene, $\nu_{max.}$(film) 1 660 (C=C) and 1 210 and 1 100 cm$^{-1}$ (CO); $\delta_H$(CDCl$_3$) 1.2—2.0 (15 H, m, ring CH$_2$,CH) and 3.40 (3 H, s, OMe); $m/z$ (100 eV) 166 ($M^+$, 75%), 137 ($M^+$ − Et, 45), 134 ($M^+$ − OMe, 36), 98(100), 31(OMe$^+$, 41) (Found: $M^+$, 166.1358. Calc. for $C_{11}H_8O$: 166.1358).

1-Methoxycyclohexene (14).—This was prepared from cyclo-hexanone and trimethyl orthoformate adapting the same procedure as that described for compound (10) (85%) b.p. 137—140 °C/760 Torr (lit.,[15] 140—145 °C/760 Torr); $\nu_{max.}$ 3 070 (C=CH), 1 670 (C=C), and 1 215 and 1 105 cm$^{-1}$ (CO); $m/z$ 112 ($M^+$, 69%), 111 ($M^+$ − H, 58), 97 ($M^+$ − Me, 60), and 84 ($M^+$ − C$_2$H$_4$, 100).

General Procedure for Hydrogenation.—To a solution of the substrate (5 mmol) in absolute ethanol (50 ml) contained in a hydrogenation flask, was added the catalyst (70 mg). After the flask had been evacuated and filled with hydrogen three times, the pressure was adjusted to 1 bar and the contents of the flask were hydrogenated at room temperature, with shaking. After the hydrogenation was complete, the catalyst was filtered off, the filtrate evaporated, and water (100 ml) was added to the residue. The product was extracted with dichloromethane (3 × 30 ml) and the combined organic phases were washed with water (2 × 50 ml), dried (Na$_2$SO$_4$), and evaporated under reduced pressure. The residue was analysed by g.c.–m.s. In the case of the substrate (8), no work-up was done and the crude product was analysed directly.

Ethoxycyclohexane (16): $m/z$ (100 eV) 128 ($M^+$, 20%), 99 ($M^+$ − Et, 20), 85 ($M^+$ − C$_3$H$_7$, 100), and 82 ($M^+$ − EtOH, 15).

Methoxycyclohexane (19): $m/z$ (100 eV) 114 ($M^+$, 31%), 86 ($M^+$ − C$_2$H$_4$, 23), 83 ($M^+$ − OMe, 31), and 72 (C$_4$H$_7$O$^+$, 100).

Attempted Reduction of Trifluoromethanesulphonates with Triphenyltin Hydride.—A solution of the trifluoromethane-sulphonate (0.7 mmol) and triphenyltin hydride[8] (0.7 mol) in absolute ether (15 ml) was allowed to stand at room temperature for 15 min. The solvent was then evaporated and the residue was taken up in pentane. The pentane phase was washed with water (2 × 50 ml), dried ($MgSO_4$) and the solvent was evaporated. An analysis of the residue revealed the presence of unchanged trifluoromethanesulphonate only.

## References

1 A. G. Martinez and R. M. Alvarez: preliminary work on the hydrogenolysis of triflates was presented at the 18th Annual Conference of the Spanish Chemical Society, 1980.
2 V. B. Jigajinni and R. H. Wightman, *Tetrahedon Lett.*, 1982, 117.
3 L. R. Subramanian, A. García Martínez, A. Herrera Fernández, and R. Martínez Alvarez, *Synthesis*, 1984, 481.
4 S. Nishimura, M. Katagiri, T. Watanabe, and M. Uramoto, *Bull. Chem. Soc. Jpn.*, 1971, 44, 166; S. Nishimura, M. Uramoto, and T. Watanabe, *ibid.*, 1972, 45, 216.
5 P. J. Stang, Z. Rappoport, M. Hanack, and L. R. Subramanian, 'Vinyl Cations,' Academic Press, San Francisco, 1979.
6 M. J. Chandy, L. R. Subramanian, and M. Hanack, *Chem. Ber.*, 1975, 108, 2212.
7 K. Laali, I. Szele, and K. Yoshida, *Helv. Chim. Acta*, 1983, 66, 1710.
8 E. J. Kupchik and R. J. Kiesel, *J. Org. Chem.*, 1964, 29, 764.
9 R. G. Pearsen, *Chem. Eng. News*, 1970, 48, 66; M. J. S. Dewar, *Angew. Chem.*, 1971, 83, 859; *Angew. Chem., Int. Ed. Engl.*, 1971, 10, 767.
10 S. Masamune, W. Choy, J. S. Patersen, and L. R. Sita, *Angew. Chem.*, 1985, 97, 1; *Angew. Chem., Int. Ed. Engl.*, 1985, 24, 1.
11 H. Bentz, L. R. Subramanian, M. Hanack, A. García Martínez, M. Gómez Marín, and R. Pérez-Ossorio, *Tetrahedron Lett.*, 1977, 9.
12 G. V. Smith and R. L. Burwell, *J. Am. Chem. Soc.*, 1962, 84, 925; A. W. Weitkamp, *J. Catal.*, 1966 6, 431.
13 L. R. Subramanian, M. Hanack, W. K. Chang, M. A. Imhoff, P.v.R. Schleyer, F. Effenberger, W. Kurtz, P. J. Stang, and T. E. Dueber, *J. Org. Chem.*, 1976, 41, 4099.
14 C. J. Collins, A. García Martínez, R. Martínez Alvarez, and J. Arranz Aguirre, *Chem. Ber.*, 1984, 117, 2815.
15 A. J. Birch, *J. Chem. Soc.*, 1947, 102.